SYNTHESIS OF ARYL DENSE POLYSILOXANES

SYNTHESIS AND PROPERTY OPTIMIZATION OF ORDERED, ARYL DENSE POLYSILOXANES USING BORON CATALYSIS

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Lay Abstract

Silicone fluids and elastomers possess numerous desirable characteristics which leads to their use in a wide range of applications in the automotive, electronics and biomedical fields, among others. Developing techniques to create well defined, ordered, modified silicones with improved optical properties, mechanical strength and thermal stability was the main focus of this thesis. These objectives were accomplished by incorporating aromatic groups into silicones using boron catalysis. Following the initial (intended) Piers-Rubinsztajn reaction, atmospheric moisture was utilized to promote further polymerization. Statistically relevant libraries of silicone elastomers were prepared using both standard and combinatorial chemistry techniques. This library of elastomers permitted the analysis of trends associated with small changes in elastomer formulation, which could not be accomplished using traditional one-by-one reaction methods in a timely fashion. The modified silicone materials exhibited high refractive indices (up to 1.59), elevated stiffness and improved thermal stability (maintain structure up to 500 °C) when compared to previously synthesized polymers.

Abstract

Silicones are widely used polymeric materials due to their unique properties. The material properties of silicones may be altered by incorporating various organic groups. Traditional methods for linear silicone synthesis involve ring-opening polymerization, which leaves the growing chain susceptible to acid or base mediated chain redistribution and the formation of cyclic monomer byproducts. The Piers-Rubinsztajn (PR) reaction is an alternative siloxane synthetic route that avoids the use of tin- or platinum- based, or of Brønsted acid/base catalysts. Siloxane bond formation is catalyzed by tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) ($R'_3Si\text{-}H + RO\text{-}SiR''_3 \rightarrow R'_3Si\text{-}O\text{-}SiR''_3 + RH$); alkoxysilanes can be replaced with silanols or alkoxybenzenes.

The catalytic activity of $B(C_6F_5)_3$ was shown to be hindered by trace water in solution; water acts as a Lewis base coordinating to $B(C_6F_5)_3$. Since the hydrate-free form of $B(C_6F_5)_3$ is required to initiate a PR reaction, water can act as an inhibitor. In a somewhat contradictory fashion, water was also shown to react with hydrosilanes via a $B(C_6F_5)_3$ catalyzed hydrolysis reaction to give silanols, that themselves are reagents for the process. The reactivity of alkoxysilanes (or aryl ethers) in the PR reaction was found to be much quicker than water. This was exploited in the synthesis of $A_x(AB)_yA_x$ triblock copolymers. The aryl rich AB core was first synthesized using the PR reaction. Excess silicone condensed via hydrolysis forming the A blocks. This method of exploiting relative reactivity to tune structure was applied to elastomers made using a single linker (eugenol) with multiple functional groups – elastomer morphology was controlled by changing order of addition.

The development of aryl dense silicones is of interest for use in electronic devices. Phenylmethyl homopolymers and highly ordered phenyl pendant copolymers (Ph/Si ratio of 0.5-1.5) were synthesized from monomers to give polymers with high refractive indices (1.51-1.59) and M_w up to 170 kDa. Statistically relevant libraries of aryl functional silicones were developed using combinatorial chemistry in order to analyze their structure-property relationship. Incorporating aromatic groups into silicones worked to elevate thermal stability, refractive index and improve the mechanical strength of silicone rubbers.

Acknowledgments

First and foremost I would like to thank my supervisor Dr. Michael A Brook. His enthusiasm and passion for chemistry is truly inspiring and it motivated me to grow into the chemist I am today. He has been an amazing mentor and role model to me constantly offering advice, knowledge and endless ideas. I cherish all of his positive support and assistance I needed during those difficult times and I admire his uncanny ability to spin seemingly negative results in a positive way. I would also like to thank my committee members Dr. Adronov and Dr. Hoare for their helpful suggestions and for challenging me to approach my research in alternative ways.

Special thanks to all of the Brook group members, past and present for making my time at McMaster so memorable and for knowing how to laugh and enjoy life while still working hard. My thesis would not be where it is today without our whiteboard brainstorming sessions. A big thank you to Dan all his helpful suggestions and advice over the years and for his constant assistance with equipment (especially the Karl-Fischer). I am also grateful for the friendships I've made during my time at McMaster. Scott, Jen, Talena, Marlena, Nicole, Patricia, Greg (and more), its been a blast!

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Last (but definitely not least) thank you to my future husband Jonas for always supporting me and maintaining a positive attitude. This journey has been challenging but you were always there to listen to my presentations and my rants about research, even though you had no clue what I was talking about. You have been my rock, always there to believe in me and encourage me to reach my goals. One last thank you to baby Antanaitis for providing me with the final push I needed to conclude this amazing chapter of my life.

Table of Contents

List of Figures and Tables

Figures

Tables

List of Abbreviations and Symbols

$Đ_{\mathrm{M}}$	Dispersity
BCF	Tris(pentafluorophenyl)borane
$CDCl_3$	Deuterated chloroform
Cr(acac)3	Chromium (III) acetylacetonate
cSt	Centistokes
D_2D^{Ph}	1-Phenyl-1,3,3,5,5-pentamethylcyclotrisiloxane
D_3	Hexamethylcyclotrisiloxane
D_4	Octamethylcyclotetrasiloxane
D5	Decamethylcyclopentasiloxane
$D^{H}{}_{4}$	Tetramethylcyclotetrasiloxane
$D^{Ph}{}_{3}$	1,3,5-Triphenyl-1,3,5-trimethylcyclotrisiloxane
$D^{Ph}{}_{4}$	1,3,5,7-Tetraphenyl-1,3,5,7-tetramethylcyclotetrasiloxane
FTIR	Fourier-transform infrared spectroscopy
GC-MS	Gas chromatography/mass spectrometry
GPC	Gel permeation chromatography
HPLC	High performance liquid chromatography
HTV	High temperature vulcanization
IR	Infrared spectroscopy
kDa	Kilodaltons
KF	Karl Fischer
LED	Light emitting diode

M_3T^H	Tris(trimethylsiloxy)silane
MD^HM	Bis(trimethylsiloxy)methylsilane
M^HM^H	Tetramethyldisiloxane
MHz	Megahertz
MM^H	Pentamethyldisiloxane
M_n	Number average molecule weight
MW	Molecular weight
M_w	Weight average molecule weight
NMR	Nuclear magnetic resonance
P_3	Hexaphenylcyclotrisiloxane
P_4	Octaphenylcyclotetrasiloxane
PDI	Polydispersity index
Ph/Si	Ratio of phenyl groups to silicon atoms in a polymer
PDMS	Poly(dimethyl)siloxane
PMPS	Poly(methylphenyl)siloxane
PPMS	Poly(phenylmethyl)siloxane
ppm	Parts per million
PR	Piers-Rubinsztajn
RI	Refractive index
ROP	Ring opening Polymerization
RTV	Room Temperature Vulcanization
SEM	Scanning electron microscopy

TEOS	Tetraethylorthosilicate
T_g	Glass transition temperature
TGA	Thermogravimetric analysis
TMOS	Tetramethylorthosilicate
THF	Tetrahydrofuran
UV	Ultraviolet

Declaration of Academic Achievement

Published Manuscripts

1. A.F. Schneider, E. Laidey, and M.A. Brook. Facile Synthesis of $C_x(AB)_yC_x$ Triblock Silicone Copolymers Utilizing Moisture Mediated Living-End Chain Extension, *Macromolecular Chemistry and Physics*, **2019**, 1800575.

2. MC. Liao, A.F. Schneider, S.E. Laengert, C.B. Gale, Y. Chen and M.A. Brook. Living Synthesis of Silicone Polymers Controlled by Humidity, *European Polymer Journal*, **2018**, 107, 287-293.

3. S.E. Laengert, A.S. Schneider, E. Lovinger, Y. Chen and M.A. Brook. Sequential Functionalization of a Natural Crosslinker Leads to Designer Silicone Networks, *Chemistry – An Asian Journal*, **2017**, 12(11), 1208-1212.

Submitted Manuscripts

1. A.F. Schneider, Y. Chen, M.A. Brook. The Effects of Trace Water on Tris(pentafluorophenyl)borane Catalytic Activity in the Piers-Rubinsztajn Reaction: A Practical Comment, *RSC Dalton Transactions* **2019**.

Manuscripts in preparation

1. A.F. Schneider and M.A. Brook. High-Throughput Synthesis and Characterization of Aryl Silicones Using the Piers-Rubinsztajn Reaction, **2019**

2. A.F. Schneider, E. Lu, G. Lu and M.A. Brook. Facile Synthesis of Phenyl-rich Functional Siloxanes, **2019**

Preface

The first page of each chapter contains a footnote describing contributions of each author to the work contained in the chapter. The work for the 6 body chapters was completed between 2013 and 2019 (over the course of my graduate degree). For first authored chapters I performed a majority (or all) of the experimental work and was the lead author of the manuscript. Chapters in which I was the second author contain work where I contributed significant experimental data and assisted with manuscript writeups. Work done over the course of my PhD that was deemed not significant for publication was not included in this document.

Chapter 1: Introduction

1.1 Properties of Silicones

1.1.1 Utility of Silicones

Silicones represent a unique class of polymers possessing a silicon-oxygen backbone – based on a –SiRR'O– repeat unit.[1-2] Silicones were first discovered almost a century ago by Kipping in the 1900's and became industrialized in the 1940's.[3-4] The most common siloxanes used are poly(dimethyl)siloxanes (PDMS) (Figure 1.1), however, a variety of phenyl- and alkyl-pendant substituted siloxanes are also available commercially.[5] Various functional groups can be introduced either telechelic or pendant to the siloxane chain, allowing further modification of normally hydrophobic silicones.[3, 6-7]

In comparison to traditional organic polymers, silicones offer a host of exceptional and desirable properties, which justify the additional cost associated with silicone synthesis.[5, 8] Silicone materials exhibit high thermal stability, gas permeability, oxidative resistance, insulating properties, optical transparency, low toxicity, moldability, and maintenance of physical properties across a broad temperature range.[3, 7, 9-11] The thermal stability stems from the high strength Si-O bond – a higher temperature (more energy) is required to break these bonds compared to C-C bonds of traditional organic polymers; the bond energy of a Si-O bond is ~ 60 % higher than a C-C bond.[3] Although the Si-O bond is strong, it is also quite flexible. This flexibility results in high chain mobility allowing gases to easily permeate.[12] The high chain mobility allows alkyl regions to easily self-associate resulting in high hydrophobicity.[3, 12] Optical transparency is crucial for materials used in optical applications. Silicones are optically transparent because of their high transmittance of visible and UV light (absorb IR light) and exhibit little scattering due to the homogeneity of the material and absence of structural defects.[13-14] The moldability of silicones is a result of the polymer's low Tg (methylsilicones Tg ~ –120 °C).[12-14] Because of these many beneficial properties, siloxanes are used in a wide scope of applications from coatings, lubricants, sealants, adhesives and surfactants, to medical grade tubing, contact lenses and implantable devices, among others.[15-16]

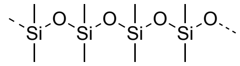

Figure 1.1 Poly(dimethyl)siloxane structure.

1.1.2 Low Basicity of Silyl Ethers

At first glance the oxygens in silyl ethers would be expected to be strong nucleophiles due to the highly polar Si-O bond. However, others have shown that siloxanes exhibit quite low basicity.[17-18] This was explained to be a result of π-type backbonding between an oxygen lone pair into a σ* orbital of silicon. Such backbonding between silicon and heteroatoms also explains the observed exceptionally short Si-O bond lengths – shorter than the sum of silicon and oxygen atomic radii.[3, 17-18]

1.1.3 Degradation of Silicones

Despite the widely accepted stability of silicones due to the strong Si-O bond, slow degradation of silicones does in fact occur in the environment. Acidic soil and microorganisms work to breakdown high molecular weight and cross-linked materials to oligomers and low molecular weight cyclic siloxanes. Atmospheric oxidative degradation eventually breaks these small molecules down to SiO_2, water and CO_2.[19]

1.2 Traditional Methods For Silicone Synthesis

1.2.1 Linear Silicone Synthesis

1.2.1.1 Condensation Polymerization

A general synthetic route to structured silicones involves hydrolysis of dialkyldichlorosilanes. In the presence of water or base, a chlorine on the chlorosilane is converted to a hydroxyl group (producing a dialkylchlorosilanol). The silanol functional group then condenses with another dialkyldichlorosilane molecules to produce a tetraalkyldichlorodisiloxane (Figure 1.2A). The process continues to chain extend the polymer, and excess water is added to eventually cap the linear silicone chain.[3, 16] It is challenging to grow the polymer chain to produce high molecular weight silicones using condensation methods and relatively large quantities of cyclic byproducts are unavoidable. Linear siloxane formation can be completely suppressed by diluting the reaction in organic solvents – the major cyclic products formed include hexamethylcyclotrisiloxane ($(Me_2SiO)_3$, D_3) and particularly octamethylcyclotetrasiloxane ($(Me_2SiO)_4$, D_4).[3, 20] The condensation method can also be used to make silicone block copolymers via condensation of a telechelic difunctional chloro-terminated polysiloxanes with a telechelic difunctional hydroxyl-terminated polysiloxanes (Figure 1.2B).[2]

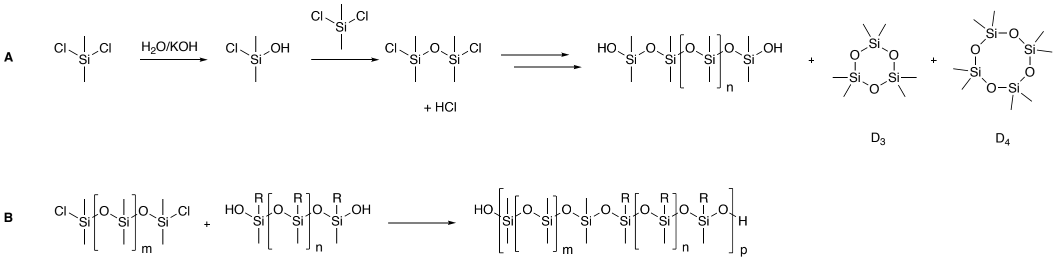

Figure 1.2 Hydrolysis process to produce A) linear silicones; B) block copolymers.

1.2.1.2 Ring Opening Polymerization

Higher molecular weight linear silicones (compared to those made using the condensation method) can be made by using acid or base-catalyzed ring opening polymerization (ROP) of cyclic siloxane starting materials (Figure 1.3).[1, 3, 16] D_3 is typically employed due to its ring strain (in comparison to D_4).[3, 21] The chain length of the linear polymer produced is controlled through starting material ratios of the initiator and the cyclic siloxane. In addition to the desired linear product, both large and small cyclic siloxanes are produced as a result of backbiting of the ionic chain.[3] At the appropriate level of conversion, chains are capped by the addition of chlorosilanes, and end group functionality can be selected at this point, and also through the selection of acid/base initiatior.[3] In Figure 1.3 trimethylsilyl end groups were selected as end groups. In the initiation step a $Me_3SiO^-M^+$ initiator was used. The other telechelic end group was also selected to be a trimethylsilyl group by using trimethylchlorosilane in the termination step. Acidic or basic conditions can also work to degrade siloxane bonds – the oxygen atoms are susceptible to protonation and electrophilic silicon is susceptible to basic attack, both processes result in cleavage of silicon-oxygen bonds (Figure 1.4). Therefore, it is important to quench the reaction while under kinetic control to avoid equilibration resulting in polymer products of broad polydispersities.[22] Pendant functional siloxanes can be synthesized if one (or more) of the methyl groups on the cyclosiloxane is substituted (with hydrogen or modified propyl groups, for example).[3]

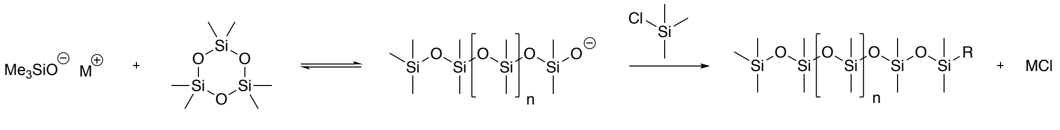

Figure 1.3 Anionic ring opening polymerization to produce high molecular weight linear silicones; M = K, Na, Cs.

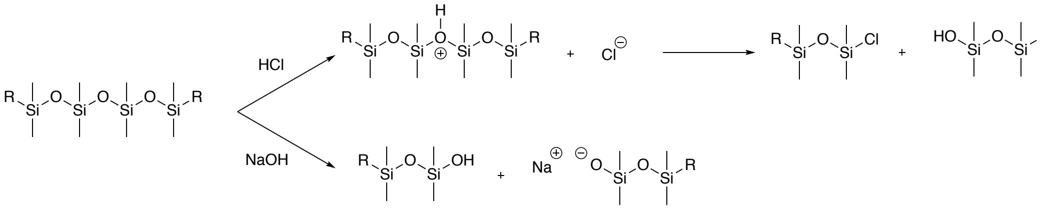

Figure 1.4 Acid and base-catalyzed degradation of silicones

1.2.2 (Cross-linked) Silicone Elastomer Synthesis

Room-temperature vulcanization (RTV) is a common siloxane curing process used on an industrial scale and describes a range of techniques that employ mixing of a 2-component system. The hydrolysis method utilizes tin catalysis in siloxane bond formation between silanols and alkoxy (or carboxyl) functional silanes. Dibutyltin dicarboxylates are activated by water and catalyze crosslinking of silanol-containing siloxanes (typically telechelic functional linear polymers) with tri- or tetra-functional silanes ($R'Si(OR)_3$ or $Si(OR)_4$), releasing, typically, an alcohol byproduct (Figure 1.5A).[3, 23-25] RTV cure may also refer to cure by platinum-catalyzed hydrosilylation, in which vinyl-functional silanes react with hydrosilanes (Figure 1.5B). This reaction yields no byproducts, and as a result, is commercially employed as an effective silicone cure system. Typically, one linear silicone is telechelic functional, while the other is pendant functional. The vinyl and hydride groups can exist on either polymer. Limitations of this method include the high cost of platinum, the inability to remove Pt from the cured system and the formation of a Si-C-C-Si crosslink rather than a pure siloxane bond.[26-28]

Peroxide cure is a high temperature vulcanization (HTV) radical cure method used in silicone synthesis. Heat is required to initiate the reaction by causing homolytic cleavage of the peroxides to form radical species. The resulting radicals work to abstract hydrogen from a methyl group on poly(dimethyl)siloxanes creating a $^{\bullet}CH_2Si$ radical that can couple with an adjacent chain and form an ethyl bridge between siloxane chains. Peroxides are more reactive towards vinyl substituents than methyl and therefore vinyl functional siloxanes are commonly also employed in HTV cure.[3, 29-30] Like the hydrosilylation method, HTV cure employs an ethyl bridge to crosslink siloxane chains.

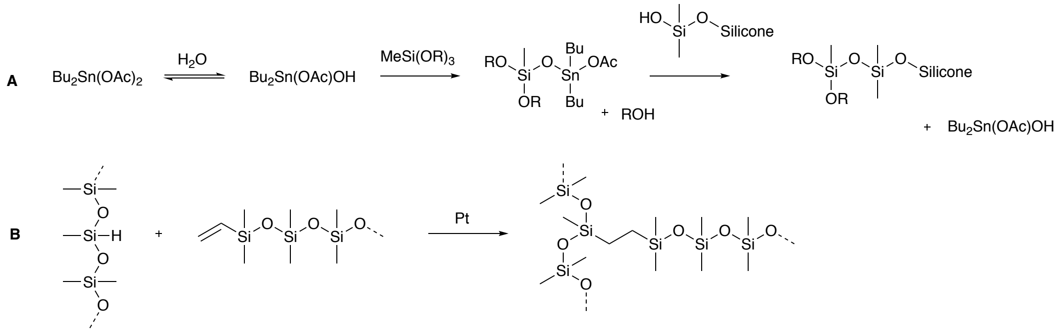

Figure 1.5 General siloxane crosslinking procedures; A) tin-catalyzed condensation; B) platinum-catalyzed hydrosilylation.

1.3 Siloxanes Possessing Aromatic Moieties

Modifications of PDMS are performed in order to tune the physical properties of silicones. The formation of silicone copolymers with organic polymers or the replacement of methyl groups by other organic groups on PDMS can work to alter the material properties of silicones. Specifically incorporating aryl groups into the PDMS backbone (e.g., silphenylenes) or substituting phenyl groups pendant on PDMS (e.g., poly(methylphenyl)siloxane, PMPS) can work to improve silicone thermal, optical and mechanical properties. For example PDMS, PMPS, silphenylene have T_g of -123 °C, -23 °C, and -61 °C respectively.[16]

1.3.1 Phenyl-Substituted Siloxanes

Pendant phenyl-substituted siloxanes exhibit superior optical properties to PDMS. The presence of aromatic groups on the silicon atoms works to decrease the angle of refraction of light (increasing the refractive index) and reduce birefringence (due to silicon-phenyl orbital interactions) making these materials optically clear. They are typically synthesized using analogous condensation and ROP techniques. In condensation polymerization, phenyl-substituted silanediols are reacted with dichlorosilanes (e.g., diphenylsilanediol with dichlorodimethylsilane).[31] ROP at elevated temperatures with cyclic phenyl-substituted monomers such as 1,3,5-trimethyl-1,3,5-triphenylcyclotrisiloxane (D^{Ph}_3), 1,3,5,7-tetramethyl-1,3,5,7-tetraphenylcyclotetrasiloxane (D^{Ph}_4), hexaphenylcyclotrisiloxane (D^{Ph2}_3, P_3), octaphenylcyclotetrasiloxane (D^{Ph2}_4, P_4), or combinations of phenyl-substituted cyclics with D_3 or D_4, can also be used to prepare phenylsilicones.[32-41] In addition to D^{Ph}_3, D^{Ph}_4, P_3 and P_4, other cyclic siloxanes containing different phenyl substitutions on each silicon are also employed (ex.1,1,3,3,5-pentamethyl-5-phenyl cyclotrisiloxane – D_2D^{Ph}). When mixtures of cyclic monomers possessing different substitution patterns are used (for example, a mixture of D_3 and P_4) the distribution of phenyl groups along the backbone in the linear polymer is random.

This is typically the case in the synthesis of polymers with low phenyl content.[32, 34-35] To ensure fidelity of repeating structure, a single, symmetrical monomer (Figure 1.6) must be used for the polymerization, or 2 monomers containing all the same substitutions on silicon (ex. P_3 with P_4, or $D^{Ph}{}_3$ with $D^{Ph}{}_4$). When a cyclic monomer with different substituents on each silicon is used, the electron withdrawing capabilities of phenyl groups make the phenyl-substituted silicon more electrophilic and more susceptible to attack by the propagating anionic chain, compared to dimethylsilyl units, ensuring a repeat structure with a phenyl group each third (Figure 1.6) or fourth monomer.[32] It should be noted that the level of control of placement of phenyl-containing monomers in a dimethylsilicone polymers is low. It is difficult, when using ROP, to obtain high yields of phenyl-rich silicones (phenyl-rich siloxanes contain a Ph/Si ratio >50 %), since the fraction of unreacted cyclic starting materials increases as phenyl content increases.[42]

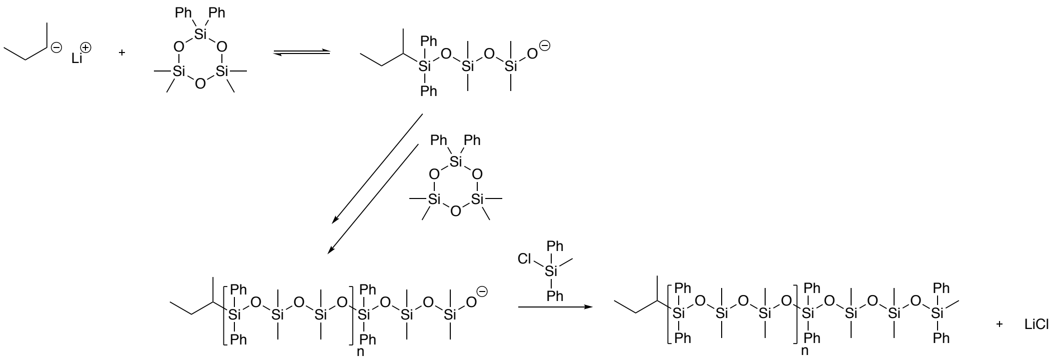

Figure 1.6 ROP of 1,1-diphenyl-3,3,5,5-tetramethylcyclotrisiloxane to produce phenyl substituted siloxane copolymer with ordered repeat unit.

1.3.2 Arylene-Substituted Siloxanes

Silphenylene-siloxane polymers represent a class of aryl silicone materials where aromatic groups are integrated in the PDMS backbone (as opposed to pendant to the backbone, as in PMPS).[43-46] Silphenylenes exhibit superior thermal and oxidative stability to PMPS and elastomeric materials containing silphenylenes possess greater mechanical strength than PMPS or PDMS counterparts – the aryl group adds rigidity to the siloxane chain.[45-47] Pure linear silphenylenes, exist as white solids that are difficult to dissolve in organic solvents (Figure 1.7A).[48] Silphenylene polymers that are diluted with dimethylsiloxane units are colourless liquids (Figure 1.7B); properties can be tuned by controlling silphenylene group concentration.[47, 49-50] Pure linear silphenylenes have been synthesized using palladium-catalyzed cross coupling between 1,4-bis(dimethylsilyl)benzene and water.[51] This synthesis was modified to develop linear silphenylene-containing polymers by coupling 1,4-bis(dimethylsilyl)benzene with a variety of organic and silicon-containing diols.[52-53] Catalyst free condensation polymerization techniques (under strict water-free conditions) have also been employed to synthesize analogues of the compounds shown in Figure 1.7B – 1,4-bis(dimethylhydroxysilyl)benzene can undergo condensation polymerization with dichlorosilanes, releasing HCl as a byproduct (Figure 1.8).[54] Silphenylene-containing resins have also been prepared using condensation polymerization by combining 1,4-bis(dimethylhydroxysilyl)benzene with a variety of di- and tri-chlorosilanes and silandiols and triols.

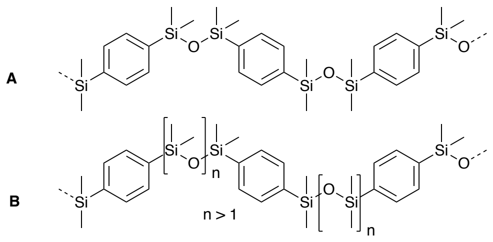

Figure 1.7 Silphenylene polymer structures (a) pure silphenylene; (b) silphenylene-siloxane.

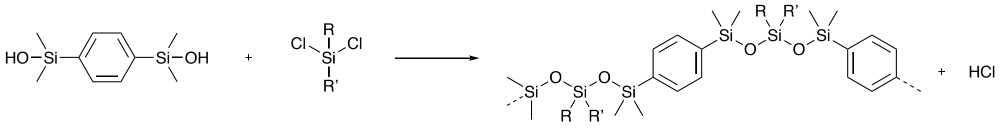

Figure 1.8 Silphenylene–siloxane synthesis via condensation polymerization.

1.3.3 Limitations of Current Methods in Phenyl and Arylene-Substituted Siloxane Synthesis

The current methods for production of silicones containing aromatic moieties are limited and possess a number of pitfalls/limitations. Condensation polymerization requires the use of chlorosilanes that are quite susceptible to hydrolysis by atmospheric moisture, and release gaseous HCl as a byproduct.[57] In addition to the potentially corrosive nature of the starting materials, condensation polymerization typically produces low molecular weight siloxanes, oligomers and appreciable amounts of cyclics that may be difficult to remove from the product.[3, 20] ROP requires the use of strong base (or acid) initiators and the resultant polymer products typically exhibit broad dispersities due to backbiting.[22] The use of ROP to create phenyl rich siloxanes specifically requires high reaction temperatures (> 100 °C).[32-33, 36]

When considering elastomers, crosslinking methods traditionally employ expensive or toxic catalysts (Pt and Sn, respectively) or high temperature curing (radical cure). All of these have issues. Hydrosilylation and radical cure crosslink the linear chains via an ethyl bridge – material is therefore not a pure siloxane; siloxane bonds are 40 % stronger than carbon-carbon sigma bonds.[3, 26-30] There is a need, therefore, to develop alternative cure strategies.

1.4 The Piers-Rubinsztajn Reaction

1.4.1 Catalytic Activity of $B(C_6F_5)_3$ in Silicone and Organosilicone Synthesis

Recent developments in silicone chemistry involve siloxane bond formation catalyzed by tris(pentafluorophenyl)borane, $B(C_6F_5)_3$ (BCF). The most common reaction of this type is the Piers-Rubinsztajn (PR) reaction, which involves the dehydrocarbonative condensation between a hydrosilane and an alkoxysilane (Figure 1.9). The reactive functional groups – SiH and SiOR – can be sourced from silicone monomers or polymers (pendant or telechelic functionality) or from small molecule silanes.[3, 58-61] The accepted mechanism proceeds first through SiH coordination to $B(C_6F_5)_3$. Following this, the nucleophilic alkoxysilane oxygen attacks the electrophilic silicon resulting in oxonium ion formation. The borohydride complex then cleaves the carbon-oxygen bond releasing the alkoxysilane.[59] Cella and Rubinsztajn have demonstrated that alkoxybenzenes can effectively replace alkoxysilanes in the PR reaction with SiH to form silyl aryl ether bonds.[62] Other tolerant nucleophilic functional groups that can work place of alkoxysilanes include carbonyls, epoxides and thiols (Figure 1.10).[58, 63-64] The versatility of the PR reaction provides endless possibilities for silicone functionalization and modification. Both simple and complex organic molecules, such as eugenol and lignin, respectively, have previously been functionalized with silicones via the PR reaction.[65-66] Vinyl-substituted poly(silphenylene-siloxane) copolymers have been previously synthesized using the PR reaction. The vinyl substituent provides a synthetic handle for further modification, for example, through hydrosilylation.[67]

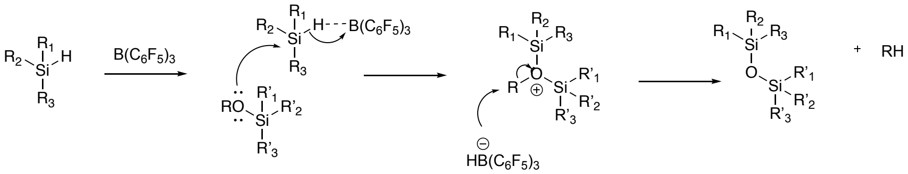

Figure 1.9 General mechanism for the PR reaction.

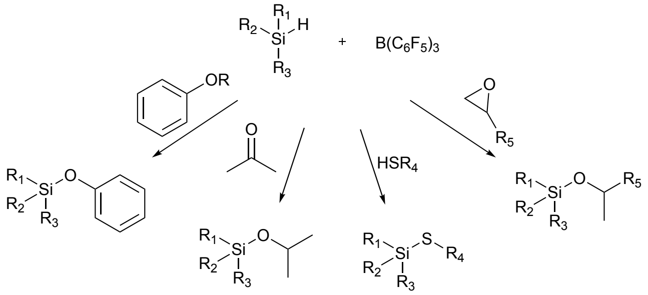

Figure 1.10 Hydrosilane + $B(C_6F_5)_3$: reactivity with various functional groups.

1.4.2 Tris(pentafluorophenyl)borane as a Lewis Acid

$B(C_6F_5)_3$ is a strong Lewis acid due to insufficient electrons on boron to form an octet and the inductive effects of the pentafluorophenyl substituents. Its Lewis acidity is predicted to fall between those of $TiCl_4$ and BF_3.[68-70] Lewis pairs form between $B(C_6F_5)_3$ and Lewis bases (heteroatom bearing), such as amines and alcohols. However, $B(C_6F_5)_3$ complexation is also heavily affected by sterics. A less obvious coordination (due to the lack of a lone pair) of $B(C_6F_5)_3$ with hydrosilanes also occurs.

Evidence for the proposed mechanism of hydrosilane activation in the PR reaction (Figure 1.9) was presented in a study performed by Piers *et al.* The reaction rates of $B(C_6F_5)_3$-catalyzed reductions of benzaldehydes and aryl ketones with triphenylsilane (Figure 1.11) were measured. They found that the reaction rate was inversely related to the strength of the Lewis base and as the concentration of the Lewis base increased, the

PR reaction rate decreased.[58, 63, 71] If an adduct formed between $B(C_6F_5)_3$ and the heteroatom-bearing Lewis base, its dissociation must occur prior to hydrosilane activation.[72-76] The stronger the Lewis basicity, the more difficult and slower the dissociation is, which explains why weaker Lewis bases reacted quicker with triphenylsilane Ph_3SiH via the PR reaction. Since free $B(C_6F_5)_3$ is required to initiate the PR reaction, increased Lewis base concentration works to retard the reaction rate by increasing adduct concentration.[58, 63, 76] Additionally, if a substantially strong (and small) Lewis base is present, the equilibrium lies towards the adduct, inhibiting $B(C_6F_5)_3$ catalytic activity in the PR reaction. This has been observed when small alcohols or amines are employed as nucleophiles in the PR reaction. Amines work to "poison" the catalyst by irreversibly binding to $B(C_6F_5)_3$. Notable exceptions include triarylamines, where bulky aromatic substituents work to restrict coordination[77-80]

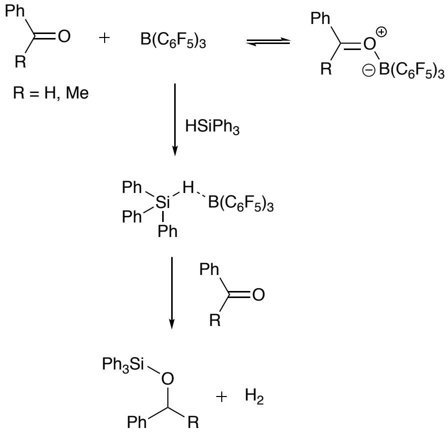

Figure 1.11 Coordination and dissociation of Lewis pair followed by subsequent PR reaction.

1.5 Thesis Objectives

1.5.1 Effects of Moisture on the PR Reaction

The Piers-Rubinsztajn reaction has been frequently used in the Brook group to develop a range of siloxane and organosiloxane-based materials. As effective as this process is in many cases, the catalytic activity is capricious; the origin in the change in catalytic activity was not clear. Some trends did emerge: reactions in the summer time were often more sluggish than the same reactions performed in the winter. Since one of the main attractions of the PR reaction is its ability to be performed at room temperature and in an open atmosphere, understanding this phenomenon and controlling the PR process was important in order to reproducibly produce well-defined polymers via this method.

It was suspected that atmospheric moisture played an inhibitory role in $B(C_6F_5)_3$ catalysis since water can act as a Lewis base, and free $B(C_6F_5)_3$ is required to catalyze the PR reaction. In fact, a molecule of $B(C_6F_5)_3$ has been shown to complex with up to 3 molecules of water ($[H_2O\bullet B(C_6F_5)_3]\bullet 2H_2O$) (Figure 1.12A).[61] Only one water molecule is directly bound to boron, while the other two are attached through hydrogen bonding with the boron bound water. The complexation of the first water molecule to boron causes the protons on that water to become very electron deficient. Therefore, they attract other water molecules to stabilize the polarization and a hydrate coordination sphere is formed.[81] The concentration of mono- di- and tri- hydrate forms of $B(C_6F_5)_3$ is directly related to the relative molar amounts of water to $B(C_6F_5)_3$ in solution (in toluene in this case).[82] The hydrates are in equilibrium with the unbound form of $B(C_6F_5)_3$, and dissociation of the hydrogen bound water molecules is much quicker than the boron bound water molecule.[82] Chapter 2 is a systematic study on how the PR reaction rate is effected by traces of water in both $B(C_6F_5)_3$ catalyst solution (in toluene) and in a model reagent mixture (hydrosilane and alkoxysilane mixture).

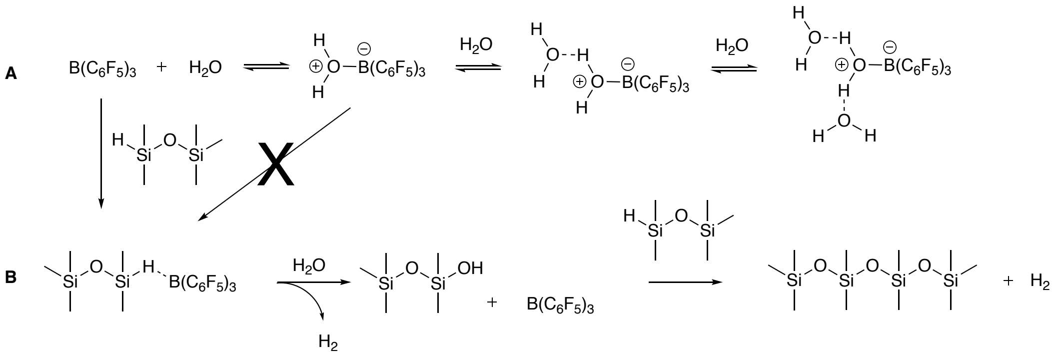

Figure 1.12 A) Inhibitory effects of water: mono-, di- and tri- hydrate forms of $B(C_6F_5)_3$; B) $B(C_6F_5)_3$ catalyzed hydrolysis reaction.

In a somewhat contradictory fashion, water is also able to participate in the PR reaction, acting as a nucleophile attacking the hydrosilane-boron complex (Figure 1.12B). That is, water that can inhibit catalysis by coordinating to $B(C_6F_5)_3$ can also dissociate and react with the hydrosilane to form a silanol. This process of $B(C_6F_5)_3$-catalyzed hydrolysis of SiH to SiOH then condensation of SiOH with another molecule of SiH, was studied in detail using both the small molecules and polymers, as described in Chapter 3. This author's contribution to the work covered the synthesis of high molecular weight linear PDMS from low molecular weight telechelic hydride-terminated poly(dimethyl)siloxanes (H-PDMS-H) via this hydrolysis method. The degree of chain extension as a result of water integration methods was studied : bulk water addition; polymerization in 'wet' toluene/diffusion of atmospheric moisture through toluene; and diffusion of atmospheric moisture into neat mixtures of starting material H-PDMS-H and $B(C_6F_5)_3$.

1.5.2 The Use of PR and Hydrolysis reactions in Linear Aryl Siloxane Synthesis

Organic polymers possessing aryl groups either integrated in the backbone (e.g., poly(*p*-phenylene oxide) or pendant to the backbone (ex. polystyrene) exhibit superior thermal and optical properties to their aryl-free counterparts.[16] Much interest surrounds high refractive index silicones due to their growing demand in a variety of electronic and optical applications such as flexible electronic displays, encapsulants for LEDs, antireflective coatings, optical and intraocular lenses, among others; in electronic devices, silicones are used as semiconductor encapsulants due to their high electrical resistivity.[83-84] In addition to having high refractive indices (RI > 1.50), these applications require materials that are flexible, permeable to oxygen (lenses), UV stable and thermally stable. Compared to organic polymers, silicone polymers are ideal candidates to satisfy all of these conditions.[84-88]

Chapter 4 describes the synthesis of linear $C_x(AB)_yC_x$ block copolymers containing aryl rich segments. Both arylene groups (aryl groups integrated into the PDMS backbone) and phenyl groups (pendant to the PDMS backbone) were incorporated into block copolymers. Sequential addition of monomer and the relative reactivity of the PR reaction and hydrolysis were exploited to control block structure and size in one-pot syntheses. This in turn provided tunability of the material's refractive index. The fast PR reaction proceeded first between hydride-terminated silicones and *p*-dimethoxybenzene to create the central block. Excess hydride-terminated silicone was sequentially added to the open vessel and atmospheric moisture facilitated hydrolysis chain extension (C blocks).

Chapter 5 describes the preparation of phenyl-rich siloxanes via $B(C_6F_5)_3$-catalyzed PR and hydrolysis reactions (alternatives to the previously described ROP and condensation polymerizations). A variety of linear homopolymers (Figure 1.13) and copolymers with high refractive indices (RI up to 1.59) and high molecular weights (M_w up to 300 kDa) were prepared; optical clarity was maintained, even at high Ph/Si ratios. In contrast to many of the ROP and condensation polymerization phenylsiloxanes described above, the linear phenyl rich siloxanes synthesized in Chapter 5 have telechelic hydride-terminated functionality. Hydrosilane end groups gives these polymers synthetic handles for further chemical modification.

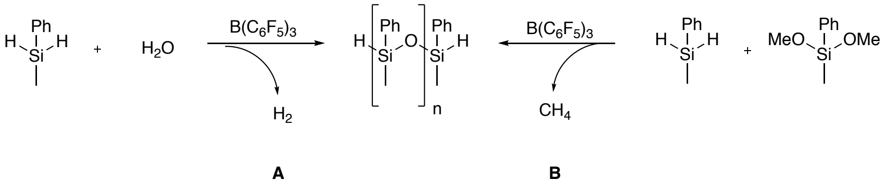

Figure 1.13 H-PMPS-H synthesis catalyzed by $B(C_6F_5)_3$; A) via hydrolysis; B) via the Piers-Rubinsztajn reaction.

1.5.3 Aryl Siloxane Elastomer Synthesis – Exploiting Relative Reactivities in the PR Reaction

The PR reaction is quite versatile. Under these conditions, hydrosilanes can react with various heteroatom-bearing organic and silicon-containing reagents (Figure 1.9 and Figure 1.10). The reactivity of these groups is diverse, for example, the reactivity of different oxygen nucleophiles towards a hydrosilane in the PR reaction follows the order:

alkoxysilanes, phenols > aryl ethers > silanols > water. Exploiting this relative reactivity allows us to control structure development in linear and crosslinked polymers. More specifically, sequential addition of defined equivalents of reagent allows reactivity selection at specific functional groups (for example, when multiple functional groups are present on different or the same polymer or linker).

The relative reactivity of methoxysilanes, ethoxysilanes, aryl ethers and water as nucleophiles in the PR reaction was exploited to develop aryl functional silicone elastomers in Chapter 6. Phenyl-substituted chain extenders were used to incorporate phenyl groups along PDMS and trifunctional aryl ether crosslinkers were incorporated to create rigidity in the three-dimensional structure (Figure 1.14). The effects small changes in aryl group concentration had on mechanical properties of the elastomers was analyzed using combinatorial chemistry. High-throughput synthesis and characterization methods were modified to facilitate the development of an aryl silicone library. The high-throughput synthesis methods used were limited by silicone viscosity (max. 100 cSt). Therefore, chain extenders were used to grow the molecular weight of linear silicones in situ prior to crosslinking; the relative reactivity of functional groups allowed these sequential reactions to proceed in the same pot. Elastomers were prepared in 96-well plates and recipes were repeated in 6+ wells to ensure statistically relevant elastomer characterization data. High-throughput Young's modulus characterization was adopted to manage the high volume of elastomer products. The work was solely done by the author.

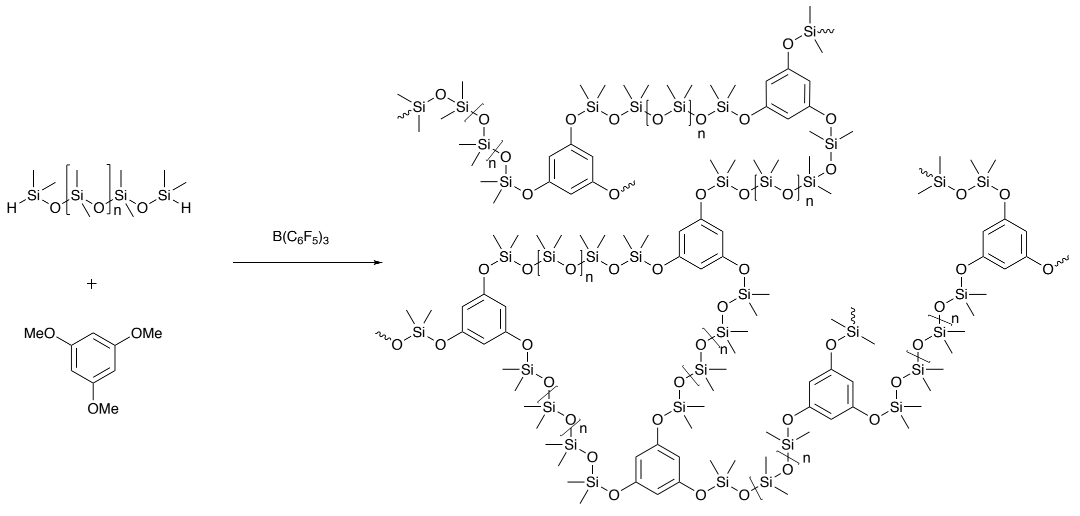

Figure 1.14 Trifunctional aryl ether crosslinked siloxane elastomer

Competition between different functional groups can occur both intermolecularly and intramolecularly. Chapter 7 exploits the relative reactivity of 3 different functional groups on a single organic linker – eugenol – to exhibit control over siloxane network architecture and resultant physical properties. Eugenol possess a phenol, methoxybenzene and vinyl group on a single aromatic ring, all of which can react with a hydrosilane via $B(C_6F_5)_3$ ($B(C_6F_5)_3$ catalyzed hydrosilylation requires much higher catalyst loadings than PR – ~ 5 % versus < 0.2 %).[89] This author's contribution to the work involved an analysis of the relative reactivities of aryl-substituted nucleophiles with hydrosilanes and preliminary examination of the relative reactivity of the functional groups on eugenol itself. The siloxane product obtained when a hydrosilane proceeds through the PR reaction with PhOH, PhOMe or PhOEt are all the same (Figure 1.15), however the rate and byproducts of each method differ.

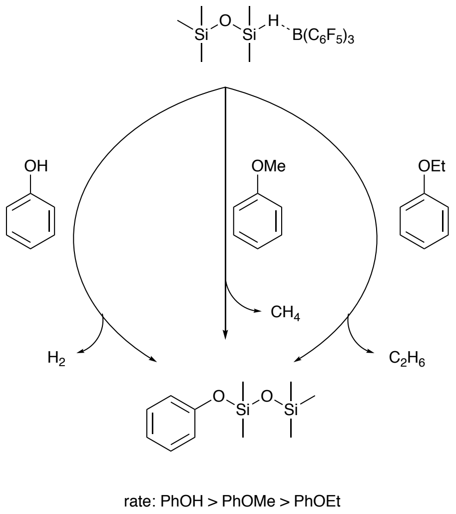

Figure 1.15 Siloxane bond formation using the Piers-Rubinsztajn reaction while varying the aromatic nucleophile.

Silicones are valued for their flexibility, thermal and oxidative stability, low toxicity and optical transparency. Dialing in different types and amounts of aromatic moieties into siloxane polymers allows for elevation and tuning of material optical and mechanical properties. These statements are supported by the research described in the following chapters.

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Chapter 2: Trace Water Affects Tris(pentafluorophenyl)borane Catalytic Activity in the Piers-Rubinsztajn Reaction: A Practical Comment[*]

2.1 Abstract

Improved methods to control silicone synthesis are required due to the sensitivity of siloxane bonds to acid/base-mediated chain redistribution/depolymerization. The Piers-Rubinsztajn reaction employs tris(pentafluorophenyl)borane as an efficient catalyst (≥ 0.07 mol%) for siloxane bond formation – typical reactions proceed in open flasks at room temperature within minutes. While advantageous under ideal conditions, the boron catalyst activity may be affected by age, storage conditions and various environmental factors, particularly humidity. Under conditions of high humidity it may be necessary to apply heat and/or use increased catalyst loading in the reactions; there is often an induction time. We examine induction times in the Piers-Rubinsztajn reaction as a function of rising trace water concentrations in the catalyst solution and show that water in the reagent solution or atmosphere is less problematic than water found in the catalyst stock solution. A relatively linear increase in induction time accompanied higher water concentrations in the catalyst solution – no such effect was observed when the water was in the reagent solution. Reaction rates in both scenarios were similar, i.e., not affected by the induction time. Improvement in the stability of catalyst solutions were observed when

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$B(C_6F_5)_3$ was stored in low molecular weight silicone oil, and precomplexed with $HSi(OSiMe_3)_3$. These outcomes are ascribed to the ability of HSi groups to outcompete water to initiate reaction, unless the boron is pre-complexed with water.

2.2 Introduction

Among its many uses,[1] tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (BCF) catalyzes siloxane bond formation in the Piers-Rubinsztajn (PR) reaction.[2] The PR reaction involves a dehydrocarbonative condensation between a hydrosilane and an alkoxysilane to produce a siloxane bond and an alkane by-product (Table 2.1ABC).[1, 3-6] The formation of a strong Si-O bond from a much weaker Si-H bond renders the process highly exothermic. The reaction begins with complexation of the hydrosilane (Si-H) with boron to form a Lewis complex (Figure 2.1A).[7] The alkoxysilane then acts as a nucleophile, attacking the electrophilic silicon and forming an oxonium ion intermediate (Figure 2.1B). Hydride transfer from the borohydride complex leads to carbon-oxygen bond cleavage and release of the siloxane product and alkane by-product (Figure 2.1C).[4, 8-10] Analogous reactions proceed with aryl ethers in place of alkoxysilanes, silanols or phenols (the latter two produce hydrogen gas as byproduct).[11-15] Relevant to this work is the fact that water may also participate as a nucleophile, but reactions occur much less rapidly than with alkoxysilanes.[16]

$B(C_6F_5)_3$ behaves as a Lewis acid; the Lewis acidity of boron is enhanced by the inductive effects of the pentafluorophenyl substituents. In that respect, $B(C_6F_5)_3$ would be expected to preferentially form an adduct with Lewis bases, including amines, carbonyl, alkoxy or hydroxyl groups. Although these adducts may form, they are labile and exchange between the bound Lewis complex and the unbound Lewis pair occurs quickly (Figure 2.1D).[1, 4, 10]

Rates of $B(C_6F_5)_3$-catalyzed reactions involve a delicate balance between complexation of heteroatoms by boron, which are non-productive (Figure 2.1G), and complexation with hydrosilanes to give an adduct that is able to facilitate reduction.[17-21] Mechanistic studies showed that the coordination pathway of hydrosilanes by $B(C_6F_5)_3$ (Figure 2.1A) had a lower free energy than the complexation pathway of heteroatoms with $B(C_6F_5)_3$ (Figure 2.1D).[1, 22, 23] The balance between Lewis acid/Lewis base complexes and free $B(C_6F_5)_3$ is affected both by the strength of the Lewis base/boron complex and the concentration of the Lewis base. Piers et al. measured reaction rates of $B(C_6F_5)_3$ catalyzed reductions of benzaldehydes and aryl ketones with triphenylsilane and found that the reaction rate was inversely related to the strength of the heteroatom-bearing Lewis base. [1, 21, 23] Furthermore, as the concentration of the heteroatom-bearing Lewis base was increased the reaction rate slowed.

One (of many) appealing characteristic of the PR reaction is that that it can be done in an open vessel at room temperature. However, our group and, anecdotally, others have observed fluctuating degrees of reactivity in the PR reaction between various batches of $B(C_6F_5)_3$ and inconsistency in the efficiency of the process. For example, in our hands dramatic differences in reactivity were noted in reactions with the same batch of catalyst in winter and summer. Slower reaction times and longer induction times for the PR reactions performed in open vessels were observed when the relative humidity was high (~80 % in summer) versus times of low humidity (~20 % in winter).

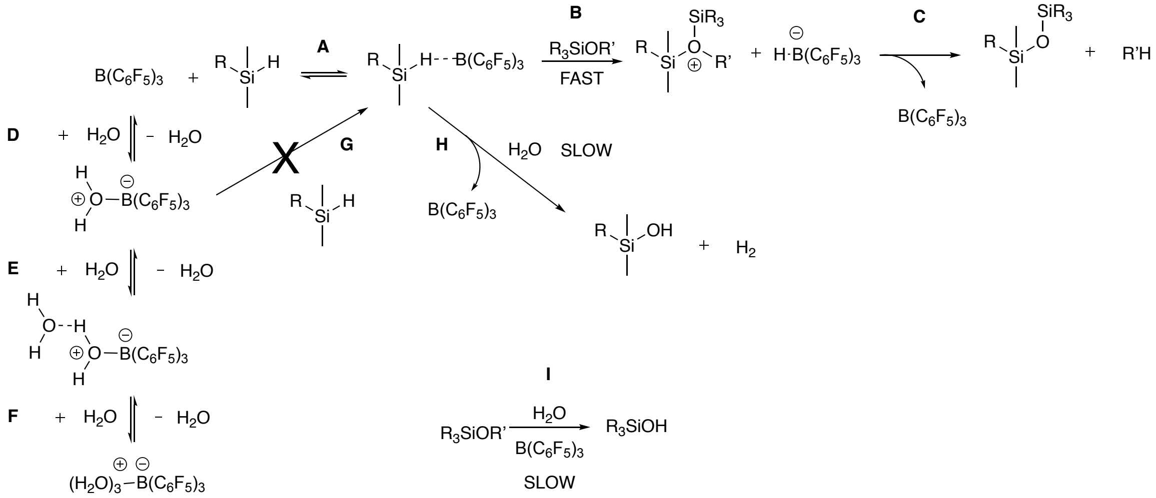

Figure 2.1 A) Coordination of hydrosilane to $B(C_6F_5)_3$; B) nucleophilic attack of alkoxysilane; C) borohydride cleavage of oxonium ion intermediate to release alkane byproduct; D) coordination of one water molecule to $B(C_6F_5)_3$; E) formation of $B(C_6F_5)_3$ dihydrate form; F) formation of $B(C_6F_5)_3$ trihydrate form; G) inhibitory effect of water on the PR reaction; H) $B(C_6F_5)_3$ catalyzed hydrolysis of SiH to SiOH; I) slow spontaneous hydrolysis of alkoxysilane to silanols

Danopoulos *et al.* described the complexation of $B(C_6F_5)_3$ with up to three water molecules ($[H_2O{\bullet}B(C_6F_5)_3]{\bullet}2H_2O$); the first water molecule binds directly to boron, while the others are hydrogen bound to the first water molecule (Figure 2.1DEF).[24] Beringhelli *et al.* used NMR spectroscopic analysis to examine the formation of these adducts in toluene. Hydrates with 1, 2 and 3 water molecules form sequentially as water is added to the solution of $B(C_6F_5)_3$ in toluene. The initial coordination of one molecule of water to one molecule of $B(C_6F_5)_3$ exists in a rapid exchange equilibrium; above 1 stoichiometric equivalent of water, free $B(C_6F_5)_3$ was no longer detectable. The complex was characterized by upfield shifts of the *meta* and *para* fluorine atoms in the ^{19}F NMR spectra, which is characteristic of the shift from tri- to tetracoordinate boron. When exactly two stoichiometric equivalents of water were added to a $B(C_6F_5)_3$ solution in toluene, the dihydrate form coexists with the presence of small equimolar amounts of the monohydrate and trihydrate. A further upfield shift in ^{19}F NMR spectroscopic chemical shifts of the *meta* and *para* fluorine atoms occurs following titration by three equivalents of water.[25]

It is always possible to perform synthetic transformations under an inert atmosphere or, even more stringently, in a glove box. One of the charms with the PR reaction, in our experience, is the ability to perform the reaction in an open vessel, normally at room temperature. To better understand, in a practical sense, the limits within which the reaction may be effectively performed, we have quantitatively examined the effects that trace amounts of the Lewis base water, in both catalyst and reagent solutions, have on the induction times of reactions and the overall rates of reactions. We report that water contamination in the catalyst solution is problematic, while water in the reagent solutions poses few problems. Although water can participate in the PR reaction to initially give silanols (Figure 2.1H), the reactivity of water as a nucleophile is significantly lower than that of alkoxysilanes or aryl ethers and thus hydrolysis was not observed in the reactions considered below.[16]

2.3 Experimental

2.3.1 Materials

Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, BCF) was obtained from two sources – Sigma-Aldrich and Alfa Aesar. Decamethylcyclopentasiloxane (D_5), monohydride-terminated polydimethylsiloxane (H-PDMS, 5-8 centiStokes (cSt), MCR-H07, MW 1006 g mol^{-1}; and 8-12 cSt, MCR-H11, MW 1477 g mol^{-1}), trimethylsiloxy-terminated polydimethylsiloxane (PDMS, 20 cSt, DMS-T12, MW 2478 g mol^{-1}), and tris(trimethylsiloxy)silane (M_3T^H, SIT8721.0) were purchased from Gelest; triethoxyoctylsilane was purchased from Sigma-Aldrich; HPLC grade toluene and reagent grade toluene were purchased from Caledon (the HPLC grade solvent was dried in an activated alumina column). All compounds were used as received.

2.3.2 Methods

^{1}H NMR spectra were recorded on a Bruker AV600 MHz spectrometer using deuterated chloroform ($CDCl_3$) as the solvent. Water concentrations were determined using Karl Fischer titrations (Mettler Toledo DL39 Coulometer) with a one-component system containing a Hydranal Composite solution (system parameters are described in detail in Table S2.4 of the Supporting Information). Sample sizes of 400-800 mg were injected into the Karl Fischer titrator.

Reaction times were determined by following gas evolution.[26] One end of a piece of Tygon tubing was inserted (~2.5 cm) into an inverted 50 mL burette filled with paraffin oil; the other end was tightly fitted onto a 1 mL syringe with an 18 G needle inserted through a septum into the reaction vessel (diagram of the apparatus is represented in Figure S2.5 of the Supporting Information). Induction time began at the time of injection of catalyst solution into the reaction vessel and ended when bubble formation was visible by eye. Reaction time was measured from the beginning of visible bubble formation and terminated when gas evolution in the burette ceased. Reaction times were measured in triplicate by timing three distinct reactions (using the same reagent stock solution) performed under identical conditions. Studies were undertaken where the water concentration in $B(C_6F_5)_3$ was fixed, while that in the reagent solutions were varied, or vice versa (a flow chart depicting the experiments undertaken is outlined in Figure S2.6 of the Supporting Information).

2.3.3 Hydrated Catalyst Solutions in Toluene

To an oven dried glass vial (20 mL) was added tris(pentafluorophenyl)borane (51.4 mg, 0.10 mmol) and HPLC grade toluene (5.14 mL) to produce a 19.5 mM solution. Other $B(C_6F_5)_3$-water solutions were prepared by diluting $B(C_6F_5)_3$ (from different sources) in toluene containing various $[H_2O]$ to give 19.5 mM (10 mg mL^{-1}) solutions of $B(C_6F_5)_3$ in toluene; the $[H_2O]$ in each $B(C_6F_5)_3$ solution was measured in triplicate using the Karl Fischer titrator (Table 2.1, Table 2.2 and Table 2.3). Wet $B(C_6F_5)_3$ solutions ($mol_{H2O}/mol_{BCF} > 2$) were prepared by adding 1-2 droplets of water to prepared 19.5 mM $B(C_6F_5)_3$ solutions (in toluene).

2.3.4 Stock Reagent Solutions

To an oven dried glass vial (20 mL) containing a stir bar was added H-PDMS (5-8 cSt, 8.72 g, 8.67 mmol) and triethoxyoctylsilane (0.80 g, 2.89 mmol). The vial was capped and the reagent solution (RS) mixture was allowed to stir for 15 min. A similar solution was prepared used H-PDMS (8-12 cSt, 11.94 g, 8.67 mmol).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 4.70 (sep, 3H, *J*=2.8 Hz), 3.82 (q, 6 H, *J*=7.0 Hz), 1.42-1.25 (m, 25 H), 1.23 (t, 9 H, *J*=7.0 Hz), 0.89-0.87 (m, 13 H), 0.64-0.62 (m, 2 H), 0.55-0.52 (m, 7 H), 0.19 (d, 19 H, *J*=2.7 Hz), 0.09-0.04 (m, 213 H); 4.70 (sep, 3H, *J*=2.8 Hz), 3.82 (q, 6 H, *J*=7.0 Hz), 1.42-1.26 (m, 27 H), 1.23 (t, 9 H, *J*=7.0 Hz), 0.89-0.87 (m, 14 H), 0.64-0.62 (m, 2 H), 0.55-0.52 (m, 6 H), 0.19 (d, 18 H, *J*=2.8 Hz), 0.09-0.04 (m, 252 H).

2.3.5 Control Experiment – Catalyst (wet) amount required for PR reaction

To each of two dried 10 mL round-bottomed flasks containing a stir bar was added 3 mL of reagent solution (monoH-PDMS, 8-12 cSt. 2.16 g, 1.89 mmol; triethoxyoctylsilane 0.18 g, 0.63 mmol). Each flask was attached to the apparatus described above (Figure S2.5) and a solution of $B(C_6F_5)_3$ in toluene (wet, BCF 2d Table 2.2, $[H_2O]_{BCF\ 2d}$ = 1480.2 ± 28.5 ppm, 3.7 equivalents to $B(C_6F_5)_3$) was added to each in an attempt to elicit a reaction. To the first flask was added $B(C_6F_5)_3$ (BCF 2d, 50 μL, 9.75×10^{-4} mmol, 5.16×10^{-4} equivalents to SiH); no reaction occurred (this was determined by a lack of change in the volume of oil in the burette – no gaseous by-product evolved). To the second flask ($[B(C_6F_5)_3]$ was doubled) was added $B(C_6F_5)_3$ (BCF 2d, 100 μL, 1.95×10^{-3} mmol, 1.03×10^{-3} equivalents to SiH); PR induction time = 11:52 and PR reaction time = 2:22. This sets an approximate limit of water above which no PR reaction will occur (when $[B(C_6F_5)_3]$ is set at 0.05 mol% to SiH) to 3.7 eq. H_2O to $B(C_6F_5)_3$ – reaction can be elicited by doubling the catalyst concentration.

First flask: no reaction; second flask: reaction complete – ^{1}H NMR ($CDCl_3$, 600 MHz, δ): 1.38-1.23 (m, 25 H), 0.89-0.86 (m, 12 H), 0.55-0.45 (m, 8 H), 0.07 (s, 284 H).

2.3.6 Constant $[H_2O]$ in a $B(C_6F_5)_3$, Varying $[H_2O]$ in the Reagent Solution

A $B(C_6F_5)_3$ solution (starting from solid $B(C_6F_5)_3$ purchased from Sigma-Aldrich) in toluene (19.5 mM) was prepared (BCF 1 Table 2.1); the water concentration in this $B(C_6F_5)_3$ solution ($[H_2O]_{BCF1}$) was 80.6 ± 2.6 ppm (0.20 eq. to $B(C_6F_5)_3$). This solution was used to catalyze PR reactions in which the $[H_2O]_{RS}$ in the reagent solution was varied systematically. To each of three oven-dried 10 mL round-bottomed flasks capped with septa and containing stir bars was added 0.50 mL of the reagent solution (monoH-PDMS, 5-8 cSt, 0.44 g, 0.43 mmol; triethoxyoctylsilane 0.04 g, 0.14 mmol). One flask was attached to the apparatus described above (Figure S2.5) via a needle to follow the reaction with gas evolution. Tris(pentafluorophenyl)borane solution (100 μL, 1.95×10^{-3} mmol, 4.53×10^{-3} equivalents to SiH) was then added via a needle and syringe and a timer was simultaneously started. The induction and reaction times were measured (see section 2.3.2 Methods). This process was repeated for the other two round-bottomed flasks to obtain three reaction times, after which an average reaction time, with error, for a single reagent solution with a constant $[H_2O]_{RS1a}$ was generated (Table 2.1).

The effect of aging reagent solutions in the presence of atmospheric moisture was determined. A second set of water content and rate measurements were taken after the reagent solution had been exposed to atmospheric moisture for a few hours (RS 1b, Table 2.1). Following this, the reagent solution was once again exposed to atmospheric moisture for a few hours and the triplicate rate measurement process was repeated (RS 1c, Table 2.1). To the reagent mixture was added DI H_2O (2 μL, 0.11 mmol) and mixture was allowed to stir, after which three sequential PR reactions were preformed (RS 1d, Table 2.1). To the same reagent mixture was added more DI H_2O (2 μL, 0.11 mmol) and mixture was allowed to stir, after which three sequential PR reactions were preformed (RS 1e, Table 2.1). Average $[H_2O]$ (Karl Fischer readings) and reaction time data, with error, are reported in Table 2.1 (full data and a plot representing the data may be found in Table S2.5 and Figure S2.7 of the Supporting Information, respectively). Note: each product was a colorless oil and each reaction went to completion as confirmed by ^{1}H NMR spectroscopy. Sample ^{1}H NMR spectra for two completed reactions is given:

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 1.38-1.24 (m, 18 H), 0.88 (t, 9 H *J*=6.8 Hz), 0.55-0.52 (m, 8 H), 0.07 (s, 213 H); 1.38-1.26 (m, 23 H), 0.89-0.86 (m, 12 H), 0.55-0.49 (m, 6 H), 0.07 (s, 160 H).

Table 2.1 Average PR reaction times (with error) when $[H_2O]_{BCF}$ in catalyst solution was held constant and $[H_2O]_{RS}$ in reagent solution was varied

Solution	BCF 1	RS 1a	RS 1b	RS 1c	RS 1d	RS 1e
$[H_2O]_{Av}$ (ppm) [a]	80.6 ± 2.6	55.7 ± 1.1	63.8 ± 4.9	85.1 ± 2.8	275.8 ± 6.2	288.5 ± 17.4
Average Reaction Time (s) [a]	N/A	30.0 ± 1.0	30.3 ± 0.5	31.2 ± 1.9	32.0 ± 1.3	33.1 ± 0.5

[a] Error expressed as standard error of the mean ($\sigma/\sqrt{3}$); where σ represents standard deviation

2.3.7 Constant $[H_2O]_{RS}$ in Reagent Solution, Varying $[H_2O]_{BCF}$ in $B(C_6F_5)_3$ Solution

Complementary experiments were performed to those above, but in which water content in the boron catalyst solution was varied (Table 2.2). To each of three oven-dried 10 mL round-bottomed flasks capped with septa and containing stir bars was added 0.5 mL of the reagent solution (monoH-PDMS, 5-8 cSt, 0.44 g, 0.43 mmol; triethoxyoctylsilane 0.04 g, 0.14 mmol) (RS 2 Table 2.2). One flask was attached to the apparatus (Figure S2.5) described above via a needle. Tris(pentafluorophenyl)borane solution in toluene (100 µL, 1.95×10^{-3} mmol, 4.53×10^{-3} equivalents to SiH) was then added via a needle and syringe and a timer was simultaneously started. Induction and reaction times were measured (see methods). This process was repeated for the other two round-bottomed flasks containing reagent mixture to obtain three reaction times, after which an average reaction time, with error, for a single $B(C_6F_5)_3$ solution was generated (BCF 2a Table

2.2). Each product was a colorless oil and each reaction went to completion as confirmed by ^{1}H NMR. Sample ^{1}H NMR spectra for two completed reactions is given:

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 1.37-1.24 (m, 18 H), 0.88 (t, 9 H *J*=6.8 Hz), 0.55-0.52 (m, 8 H), 0.07 (s, 213 H); 1.38-1.26 (m, 23 H), 0.89-0.86 (m, 12 H), 0.55-0.49 (m, 6 H), 0.07 (s, 161 H).

This process was repeated for the other $B(C_6F_5)_3$ solutions containing different $[H_2O]_{BCF}$ (BCF 2b, BCF 2c, BCF 2d, BCF 3a, BCF 3b, BCF 3c, BCF 3d, Table 2.2).

Stringent precautions were taken to minimize atmospheric moisture entering both the catalyst and reagent solutions during repeated measurements of reaction time and $[H_2O]$.

Average $[H_2O]$ (Karl Fischer readings) and reaction time data, with error, are reported in Table 2.2 (Full data may be found in Table S2.6 and Table S2.7 in the Supporting Information).

The experimental data obtained here (Table 2.2, Figure 2.3) was collected from PR reactions elicited using two analogous reagent solutions and two commercial sources of $B(C_6F_5)_3$. Two reagent stock solutions were prepared ($[H_2O]_{RS\ 2}$ = 87.8 ± 8.5 ppm and $[H_2O]_{RS\ 3}$ = 57.2 ± 6.6 ppm, Table 2.2) and two different sources of $B(C_6F_5)_3$ catalyst were used; RS 2 used Sigma-Aldrich $B(C_6F_5)_3$ and RS 3 used Alfa-Aesar $B(C_6F_5)_3$. Trace water in the reagent solution had no impact on the induction and reaction times of a model PR reaction, as was demonstrated above (Table 2.1, $[H_2O]_{RS\ 1}$ in reagent solution ranged 55-289 ppm, and the PR reaction times were the same within error, see Supporting Information Figure S2.7). As a result, the data represented in the split table below (Table 2.2) was displayed together in Figure 2.3.

Table 2.2 Average PR induction and reaction times when the $[H_2O]_{RS}$ in a model reagent solution was held constant and the $[H_2O]_{BCF}$ in the catalyst solution was varied

Solution	RS 2	BCF 2a	BCF 2b	BCF 2c	BCF 2d
Sigma-Aldrich BCF					
Average [H_2O] (ppm)[a]	87.8 ± 8.5	111.5 ± 5.1	567.8 ± 8.3	658.7 ± 14.1	1480.2 ± 8.5
Average Induction Time (s)[a]	N/A	0	10.5 ± 0.4	12.1 ± 0.2	40.7 ± 1.6
Average Reaction Time (s)[a]	N/A	18.2 ± 0.9	25.7 ± 1.7	25.7 ± 1.1	25.9 ± 1.2
Alfa-Aesar BCF	RS 3	BCF 3a	BCF 3b	BCF 3c	BCF 3d
Average [H_2O] (ppm)[a]	57.2 ± 4.6	211.3 ± 1.6	649.27 ± 13.6	793.8 ±7.0	884.8 ± 15.1
Average Induction Time (s)	N/A	8.6 ± 1.4	14.7 ± 2.2	26.4 ± 1.8	33.4 ± 3.1
Average Reaction Time (s)	N/A	22.5 ± 1.2	24.6 ± 1.9	23.4 ± 2.2	25.5 ± 1.4

[a] Error expressed as standard error of the mean ($\sigma/\sqrt{3}$); where σ represents standard deviation; full data may be found in Supporting Information

2.3.8 Use of Molecular Sieves in $B(C_6F_5)_3$ Solution to Adsorb Trace Water

To each of three oven-dried 10 mL round-bottomed flasks capped with septa and containing stir bars was added 0.5 mL of the RS2 (monoH-PDMS, 5-8 cSt, 0.44 g, 0.43 mmol; triethoxyoctylsilane 0.04 g, 0.14 mmol) ($[H_2O]_{RS2} = 87.8 \pm 8.5$ ppm). A $B(C_6F_5)_3$ solution was prepared and stored over molecular sieves for 24 hours; the resultant $[H_2O]_{BCF\text{-}sieves} = 88.90 \pm 4.53$ ppm). PR reactions were carried out on the reagent solution (RS2) in triplicate, as above – induction time = 57.5 ± 0.9 s, reaction time = 33.2 ± 1.2 s).

2.3.9 Use of Tris(trimethylsiloxy)silane to Stabilize $B(C_6F_5)_3$ in Various Solvents

To four different solutions of tris(pentafluorophenyl)borane (10 mg mL^{-1} in dry toluene, wet toluene, D_5 and PDMS) was added tris(trimethylsiloxy)silane (in a 1 molar eq. to $B(C_6F_5)_3$) and a dried stir bar. Solutions were allowed to stir for 24 h to allow adequate time for SiH to coordinate to $B(C_6F_5)_3$.[27] Coordination in solutions made with D_5 and PDMS was evident by transition of the heterogeneous solution (solid $B(C_6F_5)_3$ dispersed in silicone) to a homogenous solution (M_3T^H•$B(C_6F_5)_3$ complex soluble in silicones). Analogous experiments to those above were undertaken with the exception that 0.68 mL of reagent solution was used for each experiment (monoH-PDMS, 8-12 cSt. 0.59 g, 0.43 mmol; triethoxyoctylsilane 0.04 g, 0.14 mmol) – note that moles of SiH are the same as in the preceding experiments. ^1H NMR data of the reaction products are given below and average [H_2O] (Karl Fischer readings) and reaction time data, with error, are reported in Table 2.3 (full data in Table S2.6 of the Supporting Information).

In D_5: ^1H NMR ($CDCl_3$, 600 MHz, δ): 1.37-1.24 (m, 18 H), 0.88 (t, 9 H *J*=6.8 Hz), 0.55-0.52 (m, 8 H), 0.07 (s, 213 H); 1.38-1.26 (m, 23 H), 0.89-0.86 (m, 12 H), 0.55-0.49 (m, 6 H), 0.07 (s, 245 H).

In PDMS: ^1H NMR ($CDCl_3$, 600 MHz, δ): 1.37-1.24 (m, 18 H), 0.88 (t, 9 H *J*=6.8 Hz), 0.55-0.52 (m, 8 H), 0.07 (s, 213 H); 1.38-1.26 (m, 23 H), 0.89-0.86 (m, 12 H), 0.55-0.49 (m, 6 H), 0.07 (s, 245 H).

In wet and dry toluene (spectra were the same): ^1H NMR ($CDCl_3$, 600 MHz, δ): 1.37-1.24 (m, 18 H), 0.88 (t, 9 H *J*=6.8 Hz), 0.55-0.52 (m, 8 H), 0.07 (s, 213 H); 1.38-1.26 (m, 23 H), 0.89-0.86 (m, 12 H), 0.55-0.49 (m, 6 H), 0.07 (s, 225 H).

Table 2.3 PR induction and reaction times when $B(C_6F_5)_3$ solution contains tris(trimethylsiloxy)silane in various solvents

Solution	RS 4	$BCF_{Dry\ Tol}$	$BCF_{Wet\ Tol}$	BCF_{D5}	BCF_{PDMS}
Average [H_2O] (ppm)[a]	97.4 ± 12.0	47.1 ± 5.2	1210.2 ± 21.1	120.2 ± 5.0	71.69 ± 2.9
Average Induction Time (s)[a]	N/A	0	77.0 ± 0.4	0	0
Average Reaction Time (s)	N/A	35.7 ± 1.5	42.2 ±1.3	49.5 ± 1.7	56.6 ± 2.1

[a] Error expressed as standard error of the mean (σ/√3); where σ represents standard deviation.

2.4 Results

2.4.1 Reagent and Catalyst Selection

Triethoxyoctylsilane was chosen as a convenient model alkoxysilane for the PR reaction, as consumption of ethoxy groups can be easily tracked in the ^{1}H NMR spectra. The volatility of this alkoxysilane is low, which avoided loss by evaporation during the exothermic PR reaction. The steric bulk provided by both the octyl group and the ethyl groups (ethoxysilanes are known to react slower than methoxysilanes via the PR reaction at room temperature[8, 10, 28]) ensured that rates were conveniently rapid, but could be readily measured. The reaction partner, a mono-hydride functional polydimethylsiloxane (monoH-PDMS) (Figure 2.2) is non-volatile and miscible with triethoxyoctylsilane to allow adequate mixing for the neat reaction, and representative of hydrogen-terminal silicones, which are more commonly telechelic.

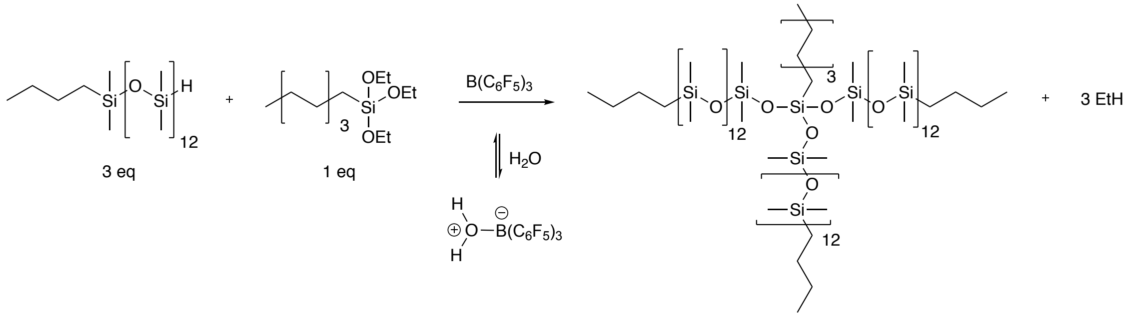

Figure 2.2 Model PR reaction used to measure reaction time in quantitative studies

The concentrations of catalyst typically required in PR reactions (< 0.1 mol%)[4] are relatively low. The amount of catalyst required can be directly affected by the presence of water; complete suppression of the reaction by water is possible. A reaction with 0.05 mol% of $B(C_6F_5)_3$ to SiH (a typical catalyst concentration used for PR)[5] was tested using a wet catalyst solution ($[H_2O]_{BCF}$ = 1480.2 ± 28.5 ppm, 3.7 eq. to $B(C_6F_5)_3$) – no reaction was observed within 24 hours. By doubling the catalyst concentration (0.1 mol% $B(C_6F_5)_3$ to SiH) a PR reaction was observed – the induction time was close to 12 minutes. In light of these observations, a larger amount of catalyst than is typically required for a PR reaction (0.45 mol% to SiH) was used in the experiments described here in order to ensure short induction times and quick reaction times. With this higher amount of catalyst, even moist catalyst (> 3 eq. H_2O to $B(C_6F_5)_3$) solutions were able to elicit PR reactions (Table 2.2, Figure 2.3) at convenient rates. Two types of experiments were undertaken: reactions in which a (low) concentration of water was added to the $B(C_6F_5)_3$ catalyst solution and the water content of the reagent mixture was varied, or vice versa.

2.4.2 Trace Water Concentration and Reaction Rate Measurements – General Methods

The $[H_2O]$ of each solution ($B(C_6F_5)_3$ and reagent mixture) was measured in triplicate using the Karl Fisher (KF) titrator to give an average $[H_2O]$. A small flask containing reagent mixture and stir bar was sealed with a septum that was connected, via a needle and syringe, to an oil filled burette (Figure S2.5 of the Supporting Information). Using a 1mL syringe and a 22G needle, 100 μL of the $B(C_6F_5)_3$ solution of known $[H_2O]$ was injected into the reaction vessel and a timer was simultaneously started. The induction time refers to difference between the time of injection and the onset of bubble formation in the reaction vessel. Gaseous by-products of the PR reaction travelled through the tubing and displaced paraffin oil in the burette – a change in oil level signified reaction. The timer was stopped and reaction time concluded once gas evolution ceased. The overall reaction time (induction time and reaction time) for each specific set of experiments (for example RS 2 with BCF 2b, Table 2.2) was measured in triplicate to produce an average induction time and average reaction time, with error.

2.4.3 Trace Water in PR Reagent Solution Does Not Significantly Affect Reaction Rate

In the first set of experiments, the trace water concentration in a $B(C_6F_5)_3$ solution was held constant ($[H_2O]_{BCF\ 1}$ = 80.60 ± 2.64 ppm, 0.20 eq. to $B(C_6F_5)_3$) while the $[H_2O]_{RS\ 1}$ in a reagent solution was varied from ~ 50 – 300 ppm (0.12 – 0.75 eq. to $B(C_6F_5)_3$, Table 2.1). Attempts to form solutions with higher concentrations of water (> 300 ppm) were unsuccessful, as the water formed a dispersed phase and, thus, KF measurements of trace water would be undependable. Induction times were not observed in any of these reactions; the PR reaction began immediately following catalyst addition and all reactions reached completion within ~ 30 – 33 seconds (Figure S2.7, Supporting Information).

2.4.4 Trace Water in the $B(C_6F_5)_3$ Solution Inhibits PR Reaction

The effect of water on the catalytic activity of $B(C_6F_5)_3$ in the PR reaction was analyzed by measuring changes in induction and reaction times as a result of higher water concentrations in the $B(C_6F_5)_3$ catalyst solution (10 mg/mL in toluene); solid $B(C_6F_5)_3$ was dissolved in toluene containing trace water and the solution was left overnight (16 hours). As the $[H_2O]_{BCF}$ in the $B(C_6F_5)_3$ solution increased, the induction time increased but the reaction time remained constant (Figure 2.3). An induction time was initially observed when the concentration of water surpassed 200 ppm (0.5 eq. to $B(C_6F_5)_3$), lower than in the case of water in the reagent solution.

2.4.5 Controlling the Introduction of Water

One of the attractive features of the PR reaction is the ability to run the reaction in an open system, rather than under an inert atmosphere or more stringent glove box techniques. The focus of these experiments became a determination of just how flexible the reaction could be. Once it was discovered that water in the catalyst was particularly problematic, rather than water present during reactions *per se*, $B(C_6F_5)_3$ solutions (in toluene) were stored in desiccators to reduce the quantity of atmospheric moisture entering the catalyst solution. However, it was soon discovered that this system was very inefficient. A initially 'low water' content solution of $B(C_6F_5)_3$ ($[H_2O]_{BCF} = 80.59 \pm 1.64$ ppm, 0.20 eq. to $B(C_6F_5)_3$) was prepared for long term experiments, where the catalyst was used once to twice a week and stored in a desiccator between uses; over a period of two months the $[H_2O]_{BCF}$ in solution of $B(C_6F_5)_3$ jumped to $[H_2O]_{BCF} = 922.59 \pm 11.37$ ppm (2.3 eq. to $B(C_6F_5)_3$)! While this says something about our own experimental habits, it is also a comment on just how hygroscopic the catalyst solution is – the spike in $[H_2O]$ was a direct result of an influx of atmospheric moisture during exposure of the catalyst solution during frequent aliquot removal.

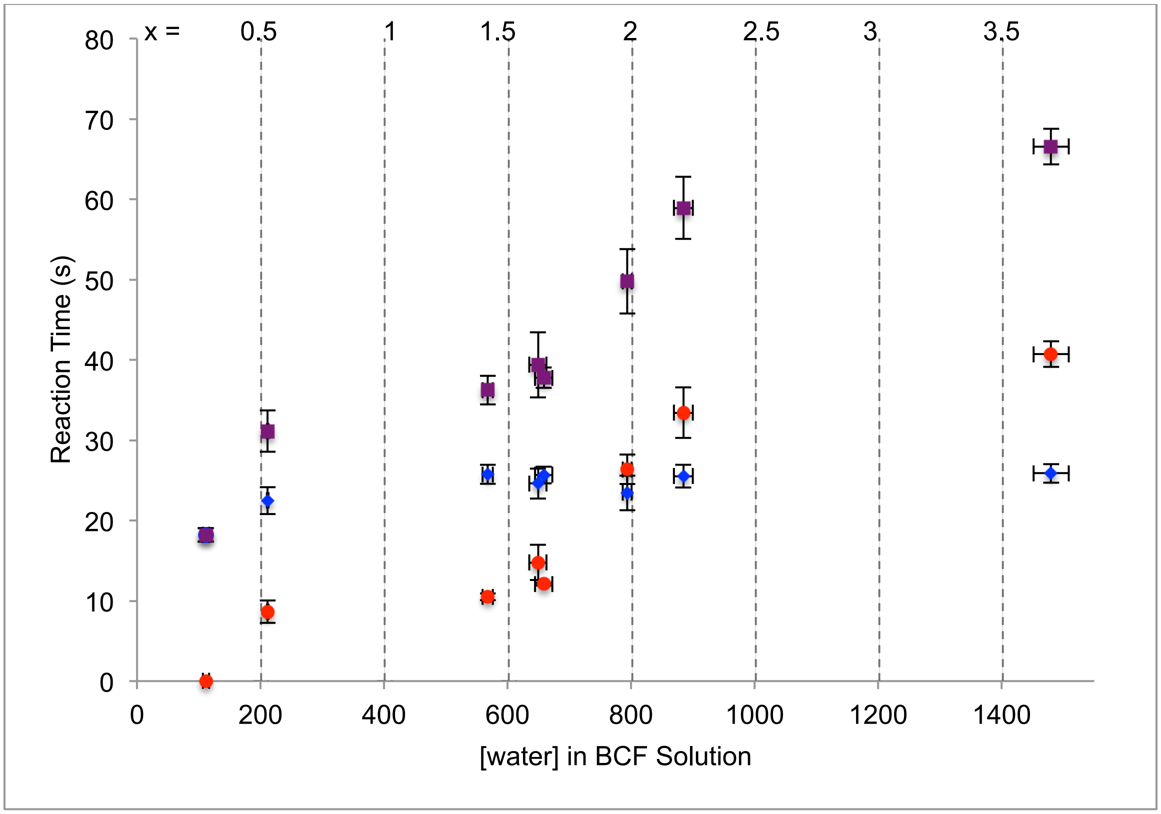

Figure 2.3 Average induction times (red ●), reaction times (blue ◆) and reaction completion times (induction + reaction, purple ■) of the model PR reaction ($[H_2O]_{RS} \approx 50 - 95$ ppm) as a function of the average $[H_2O]_{BCF}$ in the $B(C_6F_5)_3$ catalyst solution, with error; $xn_{BCF} = n_{water}$

A simple alternative to keeping samples dry – storage over molecule sieves – was not effective here. Longer induction times (induction time = 56.47 ± 0.97 s; reaction time = 31.17 ± 2.33 s) were observed for samples stored over 4Å molecule sieves, even though the trace water concentration in the $B(C_6F_5)_3$ solution was quite low (87.24 ± 3.21 ppm, 0.22 eq to $B(C_6F_5)_3$). Neutral alumina is commonly used to remove $B(C_6F_5)_3$ silicones after a PR reaction,[10] and the analogous loss of active $B(C_6F_5)_3$ in the presence of aluminosilicates is, in retrospect, not unexpected.

Water is rather insoluble in silicone oils (the solubility of the small cyclic silicone monomer D_4 $(Me_2SiO)_4$ in water is 56 parts per billion[29]). The use of silicone oils, which cannot absorb much moisture as a carrier solvent, as a replacement for toluene (solubility of water in toluene is 0.033 %) was examined in catalyst solutions. Decamethylcyclopentasiloxane (D_5) was selected as a carrier due to its lower volatility than D_4, and convenient viscosity, and trimethylsiloxy-terminated PDMS was also tested due to its much lower vapor pressure (compared to D_5); both are less soluble in water than D_4. $B(C_6F_5)_3$ proved not to be soluble in silicone polymer oils. It could be rendered soluble, however, by the addition of a tris(trimethylsiloxy)silane (M_3T^H) which, it was proposed, could coordinate to $B(C_6F_5)_3$ to give a complex $M_3T^H{\bullet}B(C_6F_5)_3$ that is soluble in silicones; the complex requires 24 hours to form. Note that M_3T^H is not very effective in the PR reaction – reaction of M_3T^H with a silanol surface required over 24 hours to form siloxane bonds via the PR reaction.[27] Therefore, any reaction between M_3T^H and the ethoxysilane (in the reagent mixture) will not be able to compete with the model reaction. Regardless of the nature of the interaction of M_3T^H with $B(C_6F_5)_3$ that leads to solubilization, M_3T^H did not work to effectively protective against water. After aging a mixture of $B(C_6F_5)_3$ with M_3T^H in wet toluene ($[H_2O]_{BCF} = 1210.25 \pm 21.06$ ppm, 3 eq. to $B(C_6F_5)_3$) for 24 hours, induction times in the PR reactions were still long (42.18 ± 1.31 s) when compared with the mixture of $B(C_6F_5)_3$ with M_3T^H in dry toluene ($[H_2O]_{BCF} = 47.10 \pm 5.12$ ppm, 0.12 eq. to $B(C_6F_5)_3$, no induction time)(Table 2.3).

2.5 Discussion

Water played different roles on the outcome of the PR reaction depending on whether it was found in the catalyst solution (over time, vide infra) or in the reagent solution. Most importantly, in catalyst solution water can form an adduct with $B(C_6F_5)_3$ leading to slower reaction times, since dissociation must occur prior to catalysis of the PR reaction (Figure 2.1ADG).[1, 22, 23] (We note that a strong Brønsted acidity has been reported for H_2O-$B(C_6F_5)_3$ adducts,[4, 30] however, this has not been observed by us to be problematic with silicones). Other potential problems, for example, hydrolysis of alkoxysilanes (Figure 2.1I),[31] or competitive attack by water on the borohydride complex to give silanols (Figure 2.**1**H) were not observed; alkoxysilanes have been shown to react more rapidly than water in the PR reaction.[1, 16, 22, 23] In all the experiments undertaken, if a PR reaction took place, it did so at essentially the same velocity, regardless of water concentration (Figure 2.3, Figure S2.6, Supporting Information). However, water played a strong role in changing the induction time, but only of the water found in the catalyst solution.

2.5.1 Trace Water in $B(C_6F_5)_3$ Catalyst Solution Slows the PR Reaction

Two regimes were observed in the experiments undertaken: reactions with catalyst solutions containing < 0.5 eq. of water (< 200 ppm H_2O), where there was no induction time; and reactions containing 0.5 – 3.75 eq. of water (201 – 1500 ppm H_2O) in the catalyst solution, where the induction time was tracked with water content, but there was no difference in reaction time (Figure 2.3).

Beringhelli *et al.* reported that there is no detectable free $B(C_6F_5)_3$ in solutions in toluene containing > 1eq H_2O (Figure 2.1D).[25] At higher levels of water, the boron forms first the dihydrate (Figure 2.1E), combined with smaller amounts of the mono- and trihydrate, and at yet higher concentrations, the trihydrate is favoured (Figure 2.1F). Somewhat surprisingly, the binding energies of the second and third equivalent of water are higher than for the first,[1] while the SiH-$B(C_6F_5)_3$ complex is energetically favoured over complexes formed between heteroatoms and $B(C_6F_5)_3$.[1, 22, 23]

Below 0.5 eq. of water (200 ppm H_2O) in the $B(C_6F_5)_3$ catalyst solution there exists more free $B(C_6F_5)_3$ than water bound $B(C_6F_5)_3$. In these cases, sufficient free catalyst is present such that no induction time was observed (Figure 2.3). At higher water concentrations, the equilibria lie away from free $B(C_6F_5)_3$ catalyst; water-boron complexes must decompose before the active B-H complex can be formed (Figure 2.3, Figure 2.1 ADG). The induction time is attributed to decomposition of water-$B(C_6F_5)_3$ complexes.

2.5.2 Trace Water in PR Reagent Solution Does Not Significantly Affect Reaction Rate

There was no discernible difference in reaction rates as the water concentration was increased in the reagent solution from ~55 to 290 ppm ($H_2O/B(C_6F_5)_3$ = 0.14 – 0.72; $[H_2O]_{BCF}$ =80.59 ± 2.64 ppm, 0.20 eq. to $B(C_6F_5)_3$, Table 2.1). That is, the effect of water on the reaction outcome depends on whether it was found in the reagent or catalyst while, as noted above, water in the catalyst solution is inhibitory. These differences can explain, in part, the origins of inconsistency in the outcomes of PR reactions.

These data suggest that the rates of water complexation to $B(C_6F_5)_3$ in the mixed reaction (catalyst+reagent) solutions are not very high, when compared to complexation of HSi compounds by boron. For example, during reactions using RS 1e (Table 2.1) the total water content is about 1 eq. (400 ppm, 300 from the reagent solution, and 80 in the $B(C_6F_5)_3$ solution) – no induction time was observed. Contrast that with RS 3 with BCF 3a (Table 2.2) – the total concentration of water was approximately the same once the catalyst was added to the reagent, but there was an induction time in these cases. We infer that, on mixing, the catalyst/reagent solutions hydrosilanes are able to outcompete water for free catalyst and, once the PR reaction commences, it is rapid. By contrast, if the water is pre-complexed with boron, the induction time is affiliated with first decomposing the water complex to generate free $B(C_6F_5)_3$ (Figure 2.1D).

2.5.3 Reducing the Amount of H_2O Entering the Catalytic System

These experiments are a cautionary tale. The PR reaction is practical in open flasks but one must take care about water ingress, particularly into the catalyst solution (and the pure catalyst from which the solution is made). Fresh preparation of solvent solutions from the starting material without the use of a nitrogen blanket is acceptable provided that exposure to the atmosphere is short lived. We were surprised at the efficiency with which water is absorbed by toluene solutions; frequent catalyst use (4-5 times per week, with storage in a desiccator) resulted in an increase in the amount of trace water in the catalyst solution from 0.20 to 2.3 eq. ($nH_2O/nB(C_6F_5)_3$) over a period of two months. Influx of atmospheric moisture was most significant in the summer months (up to 80% relative humidity).

A simple strategy to increase the lifetime of $B(C_6F_5)_3$ catalyst solutions without taking extensive precautions involves the use of solvents that solubilize water less readily than toluene, such as D_5 and PDMS. However, $B(C_6F_5)_3$ is not soluble in silicones. Addition of

M_3T^H to the dispersion leads to a transparent solution within 24 hours. Attempted PR reactions between this silane and methoxysilanes, for example, do not occur at appreciable rates (Figure 2.4).[16, 27] However, addition of a different hydrosilane to the mixture leads to efficient reactions, but note that the reactions occur more slowly (Table 2.3), presumably because the M_3T^H•$B(C_6F_5)_3$ complex must dissociate prior to catalytic activity involving the added silane. Solutions of M_3T^H•$B(C_6F_5)_3$ complexes in D_5 and PDMS were prepared (Table 2.3) and catalyst solutions were used frequently (4-5 times per week) for 3 months; in contrast to solutions in toluene, these solutions were stored on benchtop, not in a desiccator. The solutions absorbed less water than solutions in toluene with a final $[H_2O]$ = 691.89 ± 23.13 ppm (1.72 eq. to $B(C_6F_5)_3$) and 349.13 ± 16.23 ppm (0.87 eq. to $B(C_6F_5)_3$), respectively. Thus, storing $B(C_6F_5)_3$ (in low viscosity) PDMS with an equimolar quantity of M_3T^H acts to reduce water absorption into the catalyst solution and in turn stabilize catalytic activity over extended periods of time, much longer than in toluene (or D_5).

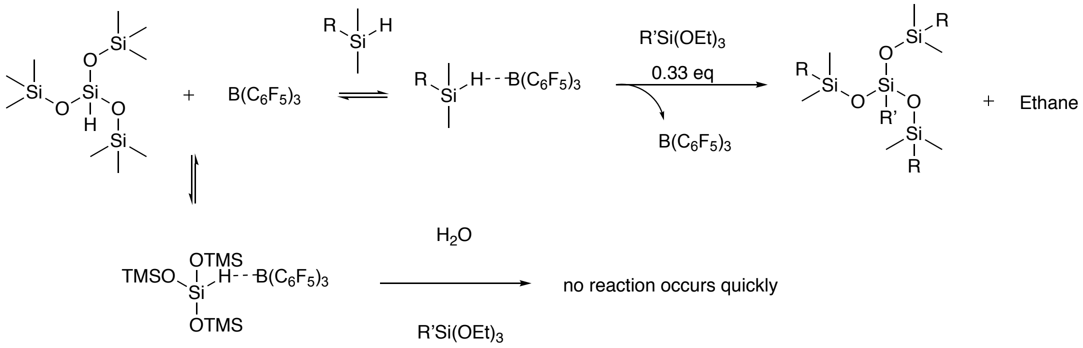

Figure 2.4 Complex formation and dissociation of M_3T^H•$B(C_6F_5)_3$ prior to catalytic activity

2.6 Conclusion

Trace water in the $B(C_6F_5)_3$ catalyst solution in particular works to retard the rate of the PR reaction. Storing $B(C_6F_5)_3$ in a solvent in which water has very low solubility, such as D_5 improves the longevity of the catalyst solution. The use of M_3T^H as a solubilization agent and catalyst stabilizer further improves stability of $B(C_6F_5)_3$ catalyst solutions.

2.7 Acknowledgements

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S2.9 Appendix 1 – Supporting Information

Table S2.4 System Parameters used on the Karl-Fischer Titrator – measure trace water in $B(C_6F_5)_3$ solutions and PR reagent mixtures

	BCF	**RS**
Sample Parameters		
Minimum (g)	0	0
Maximum (g)	2.000	5.000
Entry	during	before
Mixing Parameters		
Speed (%)	40	40
Mix Time (s)	10	15
Auto Start	No	No
Control Parameters		
Current (µA)	2	2
End Point (mV)	100	100
Generation Speed	fast	Normal
Termination Parameters		
Max Time (s)	300	300
Drift Stop	Relative	Relative
Drift (µg min^{-1})	3	3

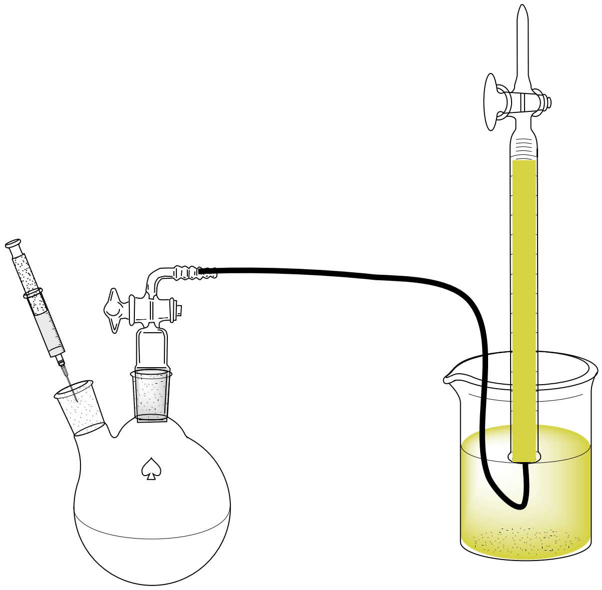

Figure S2.5 Apparatus to measure rate of gas evolution

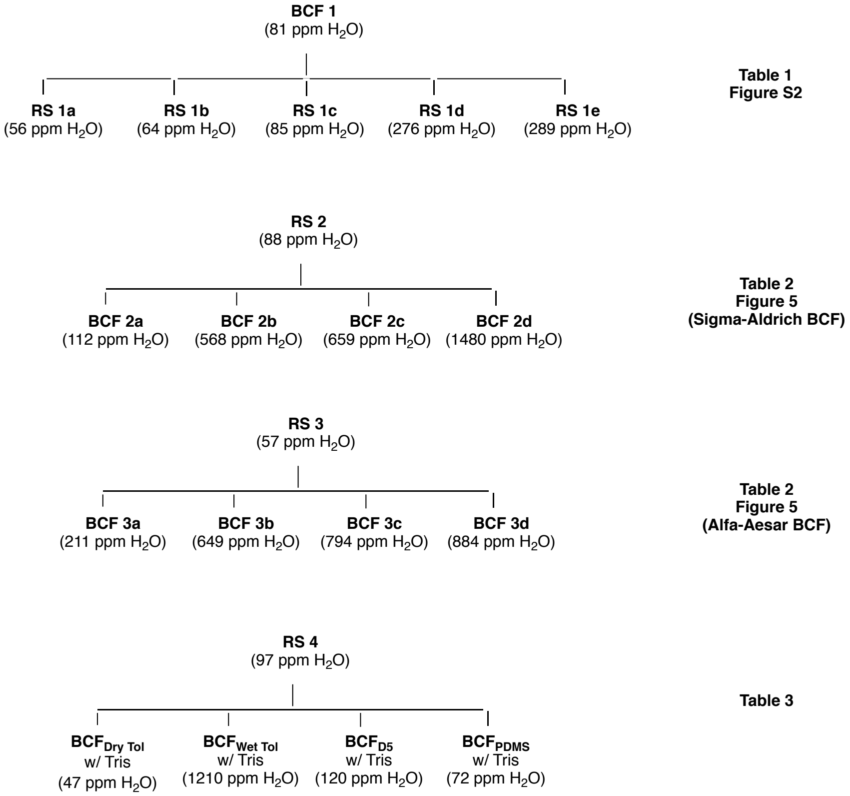

Figure S2.6 PR Reaction Flow Chart – different numbers represent different stock solutions where different letters designate different water concentrations of the same (numbered) solution

Table S2.5 PR reaction times (with error) when $[H_2O]_{BCF}$ in catalyst solution is held constant and $[H_2O]_{RS}$ in reagent solution is varied (Table 2.1 expanded)

Solution	**BCF1**	**RS1a**	**RS1b**	**RS1c**	**RS1d**	**RS1e**
$[H_2O]$ (ppm)	80.75	53.65	54.07	80.44	279.84	315.93
KF	75.95	57.07	69.19	84.68	263.53	293.23
	85.08	56.50	68.21	90.04	283.92	256.38
Average $[H_2O]$ (ppm)	80.6 ± 2.6	55.7 ± 1.1	63.8 ± 4.9	85.1 ±2.8	275.7 ± 6.2	288.5 ± 17.4
PR Reaction	N/A	28.36	29.52	28.23	31.27	32.7
Time (s)	N/A	31.73	30.22	30.8	30.18	32.39
	N/A	29.93	31.22	34.59	34.55	34.11
Average Reaction Time (s)	N/A	30.0 ± 1.0	30.3 ± 0.5	31.2 ± 1.9	32.0 ± 1.3	33.1 ± 0.5

Table S2.6 PR induction and reaction times when the $[H_2O]_{RS}$ in a model reagent solution is held constant and the $[H_2O]_{BCF}$ in the catalyst solution (Sigma-Aldrich $B(C_6F_5)_3$) varies (Table 2.2 expanded)

Solution	**RS2**	**BCF2a**	**BCF2b**	**BCF 2c**	**BCF 2d**
$[H_2O]$ (ppm)	78.88	111.69	567.11	686.73	1426.13
KF readings	104.79	102.55	553.8	647.63	1523.02
	79.83	120.34	582.42	641.81	1491.39
Average $[H_2O]$ (ppm)	87.8 ± 8.5	111.5 ± 5.1	567.8 ± 8.3	658.7 ± 14.1	1480.2 ± 28.5
PR Induction Time (s)	N/A	0	9.67	11.91	43.79
	N/A	0	10.82	11.87	38.48
	N/A	0	10.98	12.5	39.8
Average Induction Time (s)	N/A	0	10.5 ± 0.4	12.1 ± 0.2	40.7 ± 1.6
PR Reaction Time (s)	N/A	19.39	25.73	24.06	26.98
	N/A	16.56	22.83	25.29	27.11
	N/A	18.64	28.65	27.67	23.51
Average Reaction Time (s)	N/A	18.2 ± 0.9	25.7 ± 1.7	25.7 ± 1.1	25.9 ± 1.2

Table S2.7 PR induction and reaction times when the $[H_2O]_{RS}$ in a model reagent solution is held constant and the $[H_2O]_{BCF}$ in the catalyst solution (Alfa-Aesar $B(C_6F_5)_3$) varies (Table 2.2 expanded)

Solution	**RS3**	**BCF3a**	**BCF3b**	**BCF 3c**	**BCF 3d**
$[H_2O]$ (ppm)	48.95	209.23	642.69	797.02	855.07
	64.88	210.19	629.6	780.38	904.46
	57.74	214.41	675.51	804.02	894.91
Average $[H_2O]$ (ppm)	57.2 ± 4.6	211.3 ± 1.6	649.3 ± 13.6	793.8 ± 7.0	884.8 ± 15.1
PR Induction Time (s)	N/A	5.87	17.1	24.71	34.04
	N/A	10.34	10.38	30.02	27.68
	N/A	9.71	16.86	24.31	38.5
Average Induction Time (s)	N/A	8.6 ± 1.4	14.8 ± 2.2	26.4 ± 1.8	33.4 ± 3.1
PR Reaction Time (s)	N/A	20.17	27.16	21.61	23.00
	N/A	23.91	20.94	27.74	25.66
	N/A	23.36	25.73	20.94	27.86
Average time (s)	N/A	22.5 ± 1.2	24.6 ± 1.9	23.4 ± 2.2	25.5 ± 1.4

Table S2.8 PR induction and reaction times when $B(C_6F_5)_3$ solution contains tris(trimethylsiloxy)silane in various solvents (Table 2.3 expanded)

Solution/ BCF Solvent	**Reagent**	**Dry Toluene**	**Wet Toluene**	**D_5**	**PDMS**
$[H_2O]$ (ppm)	110.48	28.95	1252.08	121.77	66.13
	73.53	25.6	1184.99	110.85	75.99
	108.28	56.74	1193.69	128.04	72.94
Average $[H_2O]$ (ppm)	97.4 ± 12.0	47.1 ± 5.2	1210.2 ± 21.1	120.2 ± 5.0	71.7 ± 2.9
PR Induction Time (s)	N/A	0	77.69	0	0
	N/A	0	76.55	0	0
	N/A	0	76.60	0	0
Average Induction Time (s)	N/A	0	77.0 ± 0.4	0	0
PR Reaction Time (s)	N/A	38.78	39.99	46.04	51.32
	N/A	34.44	44.51	51.29	56.75
	N/A	34.02	42.04	51.08	49.74
Average Reaction Time (s)	N/A	35.7 ± 1.5	42.2 ± 1.3	49.5 ± 1.7	56.6 ± 2.1

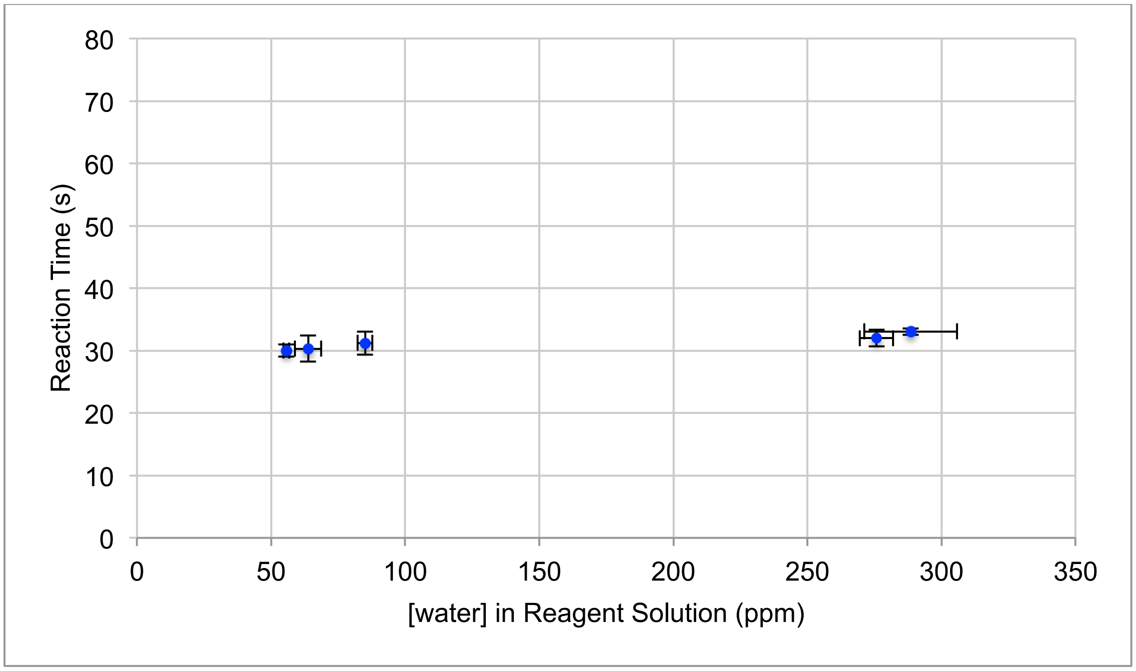

Figure S2.7 PR overall reaction time as a function of $[H_2O]$ in reagent solution; $[H_2O]$ in BCF solution = 80.59 + 2.64 ppm. Note: no induction time, reactions began immediately following catalyst addition (Table S2.4)

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 0.01-0.5 mol% $B(C_6F_5)_3$, 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 hydrophobic silicone and hydrophilic water plays a role in reaction rates. In the case of (accidental) introduction of excess water, SiH groups are quickly converted to SiOH, halting polymer growth. 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 homo or 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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† Chapter reproduced from MC. Liao, A.F. Schneider, S.E. Laengert, C.B. Gale, Y. Chen and M.A. Brook, European Polymer Journal, 2018, 107, 287-293 with permission from Elsevier Sciences Ltd, copyright 2018. Schneider performed hydrolysis reactions on DMS-H03 using different water sources and assisted with write-up of the manuscript. Liao performed all small molecule hydrolysis reactions, hydrolysis of DMS-H31, and was the lead author 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 linear 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.[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 becomes more challenging with increasing molecular weight. Additionally, it can be difficult 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 ($(Me_2SiO)_3$). The end groups in the product may be identical or different; monofunctional polymers are prepared this way.[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[8] and alternating block copolymers of silicones and polycarbonate exhibit excellent toughness while remaining highly transparent, owing to the strong interaction between polycarbonate blocks.[9] ABA triblock silicone copolymers can be prepared by initiating anionic polymerization with difunctional initiators.[10] Silicone-silicone alternating block terpolymers (e.g., ($A_mC_jB_nBBB_nC_jA_m$) 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.[11-14] 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 or 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 co-monomer sequence[17]; dendrimers[18]; elastomers[19]; foams[20]; and resins[21-22]. Analogous processes operate between HSi compounds and borates[23], phenols and alkoxybenzene derivatives[24-25] including lignin[26-27] and silanols[28] (Figure 3.1A). The catalyst most commonly used for these processes is tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), including a photoactivated version[29]; Oestreich *et al.* have reviewed the catalysts that can be used for these processes.[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 ($ArOH > ArOMe > Ar\text{-}CH_2H{=}CH_2$) could be used to create block copolymers or precise networks just by varying the order of addition of different SiH-telechelic silicones (Figure 3.1B).

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 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 3.2). The reaction was efficient at room temperature, with isolated yields after distillation of 85-95 % using 0.1 mol% $B(C_6F_5)_3$ and water droplets as the source of water. *Note: hydrogen gas is a by-product of* *these reactions and appropriate caution must be exercised with respect to both flammability and buildup of pressure.*

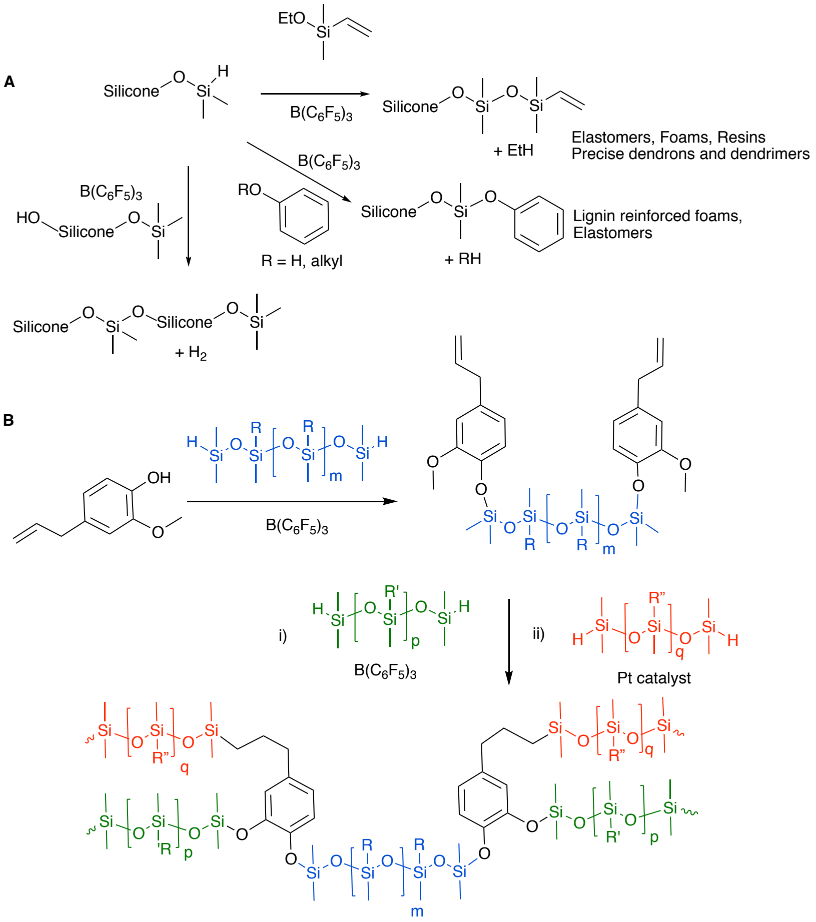


Figure 3.1 A) Selected Piers-Rubinsztajn type reactions; B) sequential use of such reactions to assemble precise silicone networks

Steric effects influenced the outcome of the reaction. Using water droplets (bulk water) as the water source, 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 gas 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 3.2A-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 3.2E).[32-33]

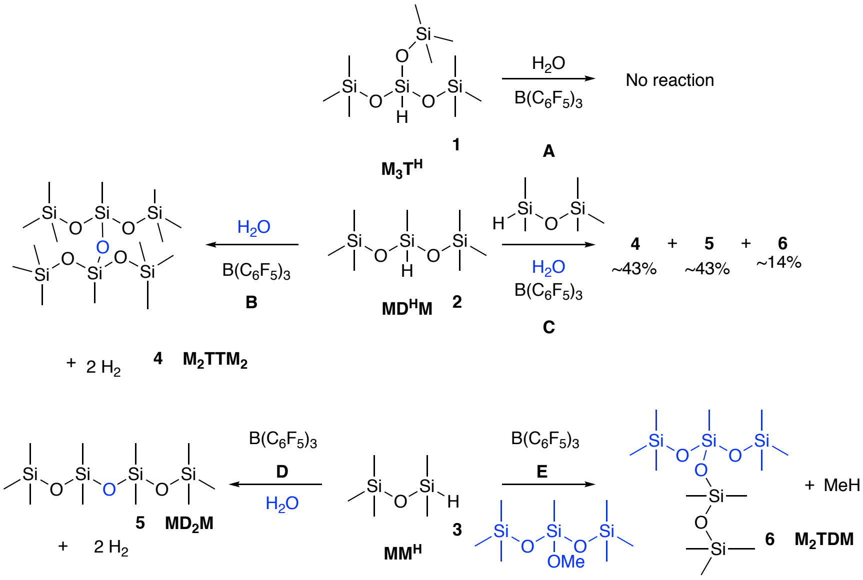


Figure 3.2 Dimerization reactions of monofunctional siloxanes (water is present in stoichiometric excess)

HSi-telechelic silicone polymers are commercially available in many different molecular weights ranging from the disiloxane 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 0.02 mol% $B(C_6F_5)_3$ (200 ppm) led to chain extension (Figure 3.3ABC). 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 3.1 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 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 of HSi groups (Figure 3.3A), followed by the faster condensation process between HOSi and HSi leading to siloxane bond formation (Figure 3.3B). The ideal, stoichiometrically matched, polymerization by iteration of these two steps leads to higher MW polymers (Figure 3.3C). These processes are not associated with significant increases in cyclic monomer concentration and, for a condensation process, excellent dispersities were observed.

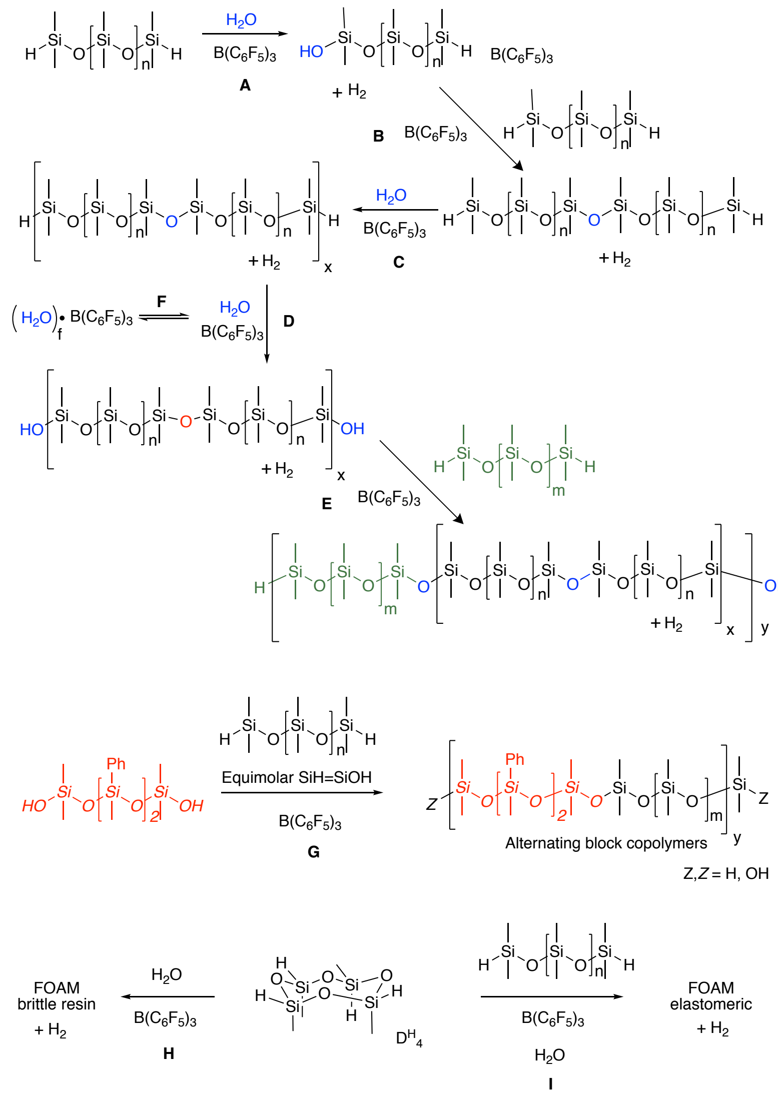


Figure 3.3 Hydrolysis and condensation reactions of: A-G) telechelic siloxanes; H,I) crosslinked siloxane polymers

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, although it has a smaller rate constant than that for condensation, the concentration of water will be significantly higher than that of residual SiH groups. In addition, as MW and viscosity of the product polymers increase, there will be an attendant reduction in the polymer condensation reaction rate. On the day of the reaction (winter, low humidity), the concentration of water arising from room humidity only won the battle to give HO-telechelic polymers at M_n ~35,000 (starting from a disiloxane) (Figure 3.3D); 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 $B(C_6F_5)_3$. 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 into a mixture of HSi-terminated silicone starting material and $B(C_6F_5)_3$, such that hydrolysis did not consume all the SiH groups (Figure 3.3ABC); atmospheric moisture led to slower polymer 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 3.1 entries 5-6, Supporting Information Table S3.6). 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-terminated ‘dead polymer’ forms (Figure 3.3D). 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 in the same flask until the desired molecular weight is realized (Figure 3.3E, or if water is in deficit, by opening the flask to permit ingress of atmospheric moisture). 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 $B(C_6F_5)_3$. Additional water drags the equilibrium towards the hydrate (Figure 3.3F); 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 $B(C_6F_5)_3$ 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 of cyclic trisiloxanes, followed by acid-catalyzed polymerization, in a process that they labeled "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. The relative reactivity is a consequence of both the 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}, respectively),[38] immiscibility may well be the key factor controlling reactivity with this oxygen nucleophile.

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. In particular, 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 require hydrolysis of HSi, giving polymers up to M_n = 251,000 g mol^{-1} with dispersities below 2 (R=Me, Figure 3.3G, Table 3.1 entry 10, Supporting Information Table S3.6).

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 3.3G, Table 3.1 entry 11, Supporting Information Table S3.6); 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 alternating silicone block copolymers by traditional routes requires the use of organic links.

Resins[22], elastomers[20] and foams[19] are readily prepared using the Piers-Rubinsztajn reaction. When exposed to water under the same simple process conditions starting materials containing multifunctional SiH groups could be utilized to prepare highly reticulated materials whose properties depended on the M_c (that is, n in Figure 3.3I). 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 (Figure 3.4). The addition of a telechelic short spacer (MW 1600) to this formulation 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[40-42], and Gevorgyan[43-45] established the general reactivities of different organic groups towards reduction by hydrosilanes in the presence of $B(C_6F_5)_3$. To these we can begin to add rules for the relative reactivity of various oxygen nucleophiles towards the creation of siloxane bonds 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 (performed mostly at room temperature and atmospheric pressure), facile and forgiving. Several advantages accrue from the PR by hydrolysis: a broad range of appropriately functional (telechelic SiOH or 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 redistribution methods, dispersity values of the products are < 2; unlike most AA + BB condensation polymerizations, it is facile to overcome initial mismatches of stoichiometry; alternating or random block copolymers of different block length and functionality are readily synthesized with excellent control over final MW and dispersity; and additionally, 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.

3.4 Experimental Section

3.4.1 Materials

Pentamethyldisiloxane (MM^H), bis(trimethylsiloxy)methyl-silane (MD^HM), tris(trimethylsiloxy)silane (M_3T^H) and tetramethyldisiloxane (M^HM^H) were purchased from Gelest and dried over molecular sieves before use. α,ω-Hydride-terminated poly(dimethyl)siloxanes (H-PDMS-H, DMS-H03 (450 g mol^{-1}, 2-3 cSt), DMS-H25 (16,000 g mol^{-1}, 500 cSt), DMS-H31 (27,600 g mol^{-1}, 1,000 cSt), DMS-H41 (62,700 g mol^{-1}, 10,000 cSt)), α,ω-hydroxyl-terminated poly(dimethylsiloxane) (HO-PDMS-OH, DMS-S14 (1,270 g mol^{-1}, 35-45 cSt), DMS-S31 (21,600 g mol^{-1}, 1,000 cSt)) and α,ω-hydride-terminated polyphenylmethylsiloxane (PMS-H03 (340 g mol^{-1}, 2-5 cSt)) were purchased from Gelest and were purified using kugelrohr distillation before use. Tetramethylcyclotetrasiloxane (D^{H}_{4}) was purchased from Sigma Aldrich and used as received. Ultrapure water (18 MΩ-cm) was obtained using 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.

3.4.2 Methods

^{1}H and ^{29}Si NMR spectra were recorded on a Bruker Avance 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 mm 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 a 5 min delay during solvent elution. 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.

3.4.3 Monofunctional Hydrosiloxane Dimerization

3.4.3.1 Hydrolysis reaction with pentamethyldisiloxane $MM^H + H_2O$ ($[OH]/[SiH]=4$; $[B(C_6F_5)_3]/[SiH]=0.1$ 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 to which was added $B(C_6F_5)_3$ (0.1 M, 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 and the product was collected by filtration through Celite under reduced pressure. The mass balance of the reaction was 86 %, 10.76 g due to volatility of some of the ingredients (Table 3.2).

Pentamethyldisiloxane: ^{1}H 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*, trace $Cr(acac)_3$, δ): 9.71 (s, 1Si), -6.76 (s, 1Si) ppm. GC-MS: $C_5H_{16}OSi_2$, MW: 148.07: MI [M-15]=133.1 (100).

Hydrolysis products of pentamethyldisiloxane: ^{1}H 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*, trace $Cr(acac)_3$*,* δ): 9.24 (s, 1Si), -21.49 (s, 1Si) ppm. GC-MS: $C_{10}H_{30}O_3Si_4$, MW: 310.13: [M-15]=295.1 (40), 207.1(100), 73.1 (30). $C_{12}H_{36}O_4Si_5$, MW: 384.15: [M-15]=369.2 (40), 281.1 (100), 147.1 (55), 73.2 (25). $C_{14}H_{42}O_5Si_6$, MW: 458.16: [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). $C_{16}H_{48}O_6Si_7$, MNW: 533.18: [M-15]=517.2 (5), 341.0 (20), 207.1 (80), 91.2 (100).

Table 3.1 Polymerization of HSi-telechelic silicones using water or HOSi-telechelic silicones

xe	n[a]	[OH]/[SiH]	$[B(C_6F_5)_3]/[SiH]$[b]	t (h)	H_2O[c]	M_n (kDa)	M_w (kDa)	$Đ_M$	Copolymer
1	0	3	200	3	L	50	76	1.52	
2	5	3	200	3	L	28	523	1.89	
3	370	3	200	3	L	33	51	1.53	
4	5	3	200	24	L	46	86	1.88	
5	5	NA	500	24	O	20	30	1.50	
6	5	0.08	500	24	S	183	349	1.91	
7	0	1	80	20	L	21	33	1.57	
8	0	3	200	3	L	50	76	1.52	
9	0	0.6	400	22	L	77	141	1.83	
10	370	1	500	24	NA	251	472	1.88	$HOSiMe_2O(SiMe_2O)_{371}H$
11	MePh[d]	1	200	24	NA	15	24	1.55	$HOSiMe_2O(SiMe_2O)_{16}H$

[a] n in $HSiMe_2O(SiMe_2O)_nSiMe_2H$; [b] ppm: $[B(C_6F_5)_3]/[SiH] \times 10^6$; [c] L = bulk liquid water (closed system), O open system 56 % relative humidity, S = 230 ppm water in toluene and the flask was open to the atmosphere; [d] $HSiMe_2O(SiMePhO)_3SiMe_2H$, at 50 °C

3.4.3.2 Hydrolysis products of bis(trimethylsiloxy)methylsilane - $MD^HM + H_2O$ ($[OH]/[SiH]=4$; $[B(C_6F_5)_3]/[SiH]=0.1$ 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 $B(C_6F_5)_3$ (0.1 M, 0.72 mL, 0.072 mmol) diluted in toluene at room temperature. After 3 h the reaction was quenched by alumina. Yield: 95% (17.44 g, Table 3.2).

Bis(trimethylsiloxy)methylsilane: ^{1}H 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*, trace Cr(acac)$_3$, δ): 9.36 (s, 2Si), -36.40 (s, 1Si) ppm. GC-MS: $C_7H_{22}O_2Si_3$, MW: 222.09: [M-15]=207.2 (100), 73.1 (50)

Hydrolysis products of bis(trimethylsiloxy)methylsilane: ^{1}H 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*, trace Cr(acac)$_3$, δ): 7.59 (s, 4Si), -54.51 (s, 0.17Si), -65.93 (s, 2Si) ppm. GC-MS: [M-15]=355.0 (5), 207.1 (100), 106.1 (100), 77.1 (80), 51.1 (30). $C_{14}H_{42}O_5Si_6$, MW: 458.16: [M-15]=443.2 (50), 355.1 (50), 281.1 (55), 221.1 (100), 147.1 (70), 73.1 (75).

3.4.3.3 Hydrolysis reaction using a mixture of pentamethyldisiloxane (MM^H) and bis(trimethylsiloxy)methylsilane (MD^HM)-MM^H + H_2O ([OH]/[SiH]=4; [$B(C_6F_5)_3$]/[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 $B(C_6F_5)_3$ (0.1 M, 0.18mL, 0.018 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.

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*, 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: $C_{10}H_{30}O_3Si_4$, MW: 310.13: [M-15]=295.1 (50), 207.1(100), 73.1 (50). $C_{12}H_{36}O_4Si_5$, MW: 384.15: [M-15]=369.1 (30), 281.1 (100), 207.0 (90), 147.1 (40), 91.1 (25). $C_{14}H_{42}O_5Si_6$, MW: 458.16: [M-15]=443.2 (60), 355.1 (60), 281.1 (70), 221.1 (100),147.1 (70), 73.1 (75).

3.4.3.4 Hydrolysis reaction using tris(trimethylsiloxy)silane - M_3T^H + H_2O ([OH]/[SiH]=4; [B(C_6F_5)_3]/[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 and to which was added $B(C_6F_5)_3$ (0.1 M, 0.72 mL, 0.072 mmol) diluted in toluene at room temperature. After 3 h the reaction was quenched by alumina and the product was collected by filtration through Celite under reduced pressure. No reaction products were observed.

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*, trace Cr(acac)$_3$, δ): 9.41 (s, 3Si), -82.74 (s, 1Si) ppm.

3.4.4 Chain Extension of Telechelic H-terminated Silicones

3.4.4.1 General procedure for chain extension using hydrolysis - water droplets (Table 3.1, 1-4, 7-9, Table S3.6 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 $B(C_6F_5)_3$ diluted in toluene (0.1 M, 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.

Hydrolysis products of pentamethyldisiloxane: ^{1}H 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*, trace Cr(acac)$_3$, δ): 9.24 (s, 1Si), -21.49 (s, 1Si) ppm. GC-MS: $C_{10}H_{30}O_3Si_4$, MW: 310.13: [M-15]=295.1 (40), 207.1(100), 73.1 (30). $C_{12}H_{36}O_4Si_5$, MW: 384.15: [M-15]=369.2 (40), 281.1 (100), 147.1 (55), 73.2 (25). $C_{14}H_{42}O_5Si_6$, MW: 458.16: [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). $C_{16}H_{48}O_6Si_7$, MW: 533.18: [M-15]=517.2 (5), 341.0 (20), 207.1 (80), 91.2 (100).

Table 3.1 entry 4.

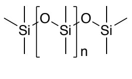
Note: ^{1}H NMR and ^{29}Si NMR are diagnostic for loss of SiH groups but are otherwise not helpful. Representative NMR spectroscopic data is provided; the other samples differ only in the relative magnitude of the $SiMe_2$ peak.

Entry 4, Table 3.1: ^{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*, trace Cr(acac)$_3$*,* δ): -21.94 (s, 1Si) ppm.

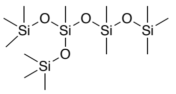
Table 3.2 GC-MS results for low cyclic-containing silicone oils by hydrolysis of monofunctional hydrosiloxanes

MM^H +H_2O ([OH]/[SiH]=4)			
Structure[a]	Nomenclature	Relative ratio (%) GC	Product ratio by ^{29}Si NMR (% ± 5%)
A n=2	MD_2M	93	-
A n=3	MD_3M	5	-
A n=4	MD_4M	1	-
A n=5	MD_5M	1	-
MD^HM +H_2O ([OH]/[SiH]=4)			
Unknown low boiling compound[b]	-	3	-
C	M_2TTM_2	97	-
MM^H + MD^HM + H_2O ([OH]/[SiH]=4)			
A n=2	MD_2M	30	40
B	M_2TDM	9	14
C	M_2TTM_2	61	46

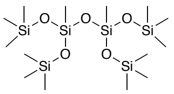
[a]



A MD_nM



B M_2TDM



C M_2TTM_2

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

3.4.4.2 General procedure for chain extension using hydrolysis by moisture in an open flask (Table 3.1, entry 5, Table S3.6, entry 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 (0.1 M, 0.040 mL, 4 mmol) ($[B(C_6F_5)_3]/[SiH]$=0.05 mol%, humidity: 15 %). The mixture was stirred at room temperature open to atmosphere and, after 10 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.

3.4.4.3 General procedure for chain extension using hydrolysis by moisture in an open flask augmented with wet toluene (Table 3.1, Table S3.6, 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. To the mixture was added $B(C_6F_5)_3$ diluted in toluene (0.04 M, 0.020 mL, 0.77 μmol) ($[B(C_6F_5)_3]/[SiH]$=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.

3.4.4.4 Copolymerization of $HMe_2Si(OSiMe_2)_nSiMe_2H$ + $HOMe_2Si(OSiMe_2)_nSiMe_2OH$ (Table 3.1, entry 10, Table S3.6 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 hydroxy-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 connected to a condenser under a nitrogen blanket, was added $B(C_6F_5)_3$ diluted in toluene (0.01 M, 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.

3.4.4.5 Copolymerization of $HMe_2Si(OSiMePh)_3SiMe_2H$ + $HOMe_2Si(OSiMe_2)_nSiMe_2OH$ (Table 3.1, entry 11, Table S3.6 Entries 18-23)

To an oven-dried 100.0 ml round-bottomed flask under a 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 g mol^{-1}, 0.500, 1.25 mmol). To this stirring mixture was added $B(C_6F_5)_3$ (10 µl 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, an additional 5-10 ml of dry toluene was added to allow stirring to continue. After 24 h, 0.50 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.

3.4.5 Silicone Resin Preparation using Hydrolysis

3.4.5.1 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-bottomed flask with $B(C_6F_5)_3$ (0.078 M, 0.625 mL, 0.049 mmol) diluted in toluene. The mixture was stirred at room temperature open to the atmosphere. An image 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 3.4A).

^{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.

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

3.4.5.2.1 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}).

3.4.5.2.2 Preparation of silicone foam using D^H_4 + DMS-H11 ([B(C_6F_5)$_3$]/[SiH]=0.02 mol%)

An oven dried round-bottomed 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), and 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 3 h. The resulting foam was removed from the flask and extracted using a Soxhlet extraction device.

3.4.5.3 Preparation of silicone foam using H-PDMS-H and D^H_4 with hexane ([B(C_6F_5)$_3$]/[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 well plate with B(C_6F_5)$_3$ (0.078 M, 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 3.4BC).

3.4.5.4 Preparation of silicone elastomer ($[B(C_6F_5)_3]/[SiH]=0.3$ 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 height, 35 mm diameter) was added $B(C_6F_5)_3$ (0.078 M, 15 μl, 1.17 mmol). 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 3.4D).

A B C D

Figure 3.4 A) Silicone resin prepared using D^H_4 and water; B) Bubble-free silicone elastomer prepared using D^H_4 and H-PDMS-H ($[B(C_6F_5)_3]/[SiH]=0.3$ mol%); C) Silicone foam prepared using D^H_4 and H-PDMS-H ($[B(C_6F_5)_3]/[SiH]=0.9$ mol%); D) The SEM image of the silicone foam

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 the preparation of large silicones with low dispersity of molecular weights up to 250,000 g mol^{-1}. Alternating block copolymers are readily accessed from the condensation reaction, in the absence of water, between 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 dihydro-silanes or -silicones 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 by-products.

3.6 Acknowledgments

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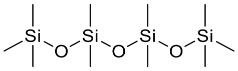
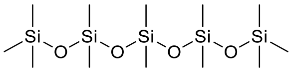
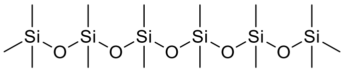
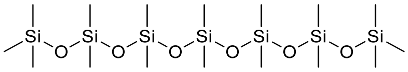
S3.8 Appendix 2 – Supporting Information

S3.8.1 Hydrolysis products of pentamethyldisiloxane

Table S3.3 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

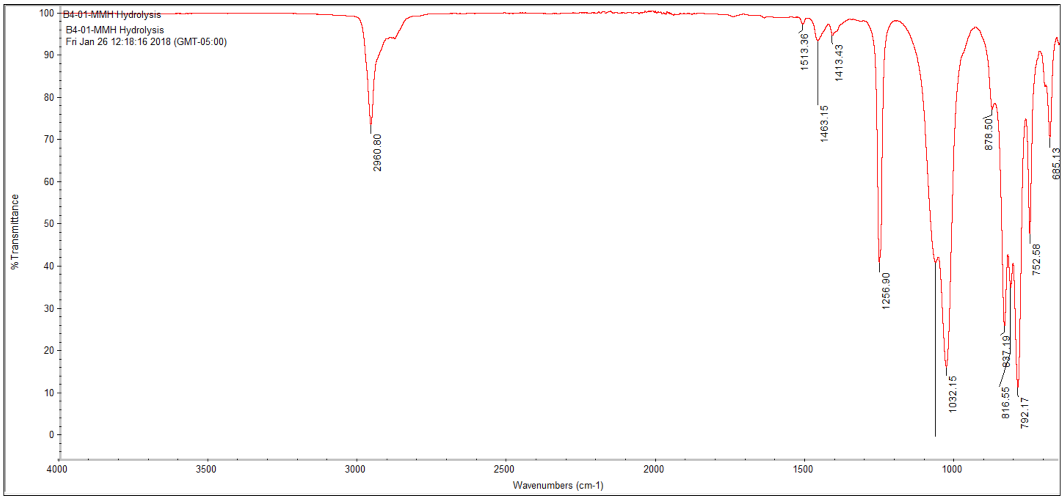
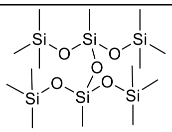


Figure S3.5 IR spectrum for hydrolysis reaction using pentamethyldisiloxane (MM^H)

S3.8.2 Hydrolysis products of bis(trimethylsiloxy)methylsilane

Table S3.4 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

[a]Insufficient sensitivity to characterize the peak

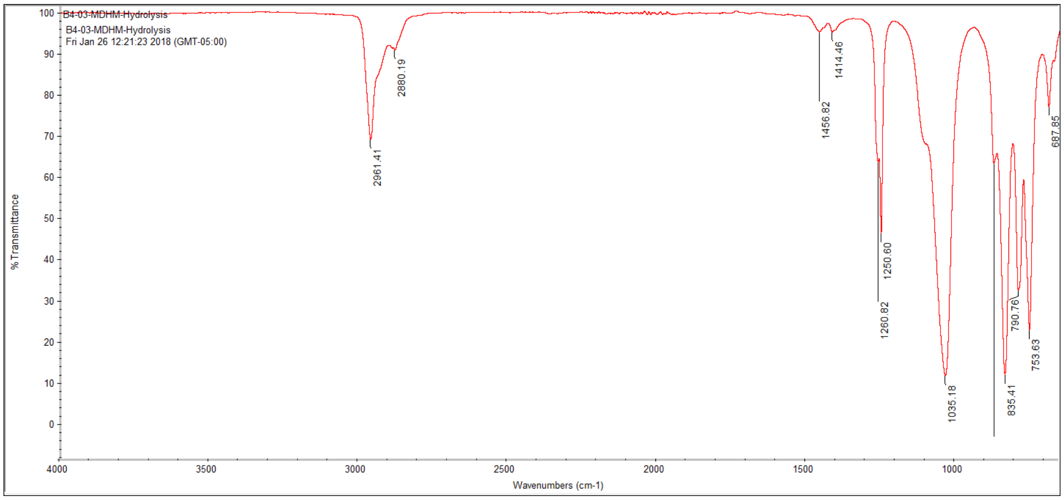
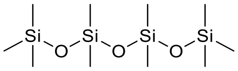
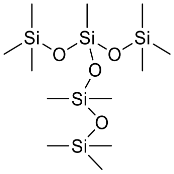
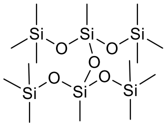


Figure S3.6 IR spectrum for hydrolysis reaction using bis(trimethylsiloxy)methylsilane (MD^HM)

S3.8.3 Hydrolysis products using a mixture of pentamethyldisiloxane (MM^H) and bis(trimethylsiloxy)methylsilane

Table S3.5 GC-MS results for hydrolysis reaction of 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

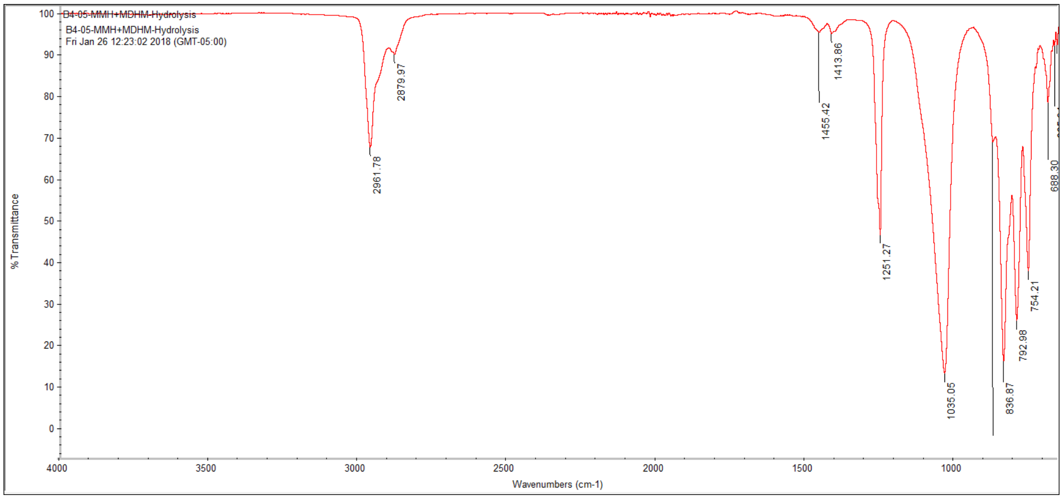
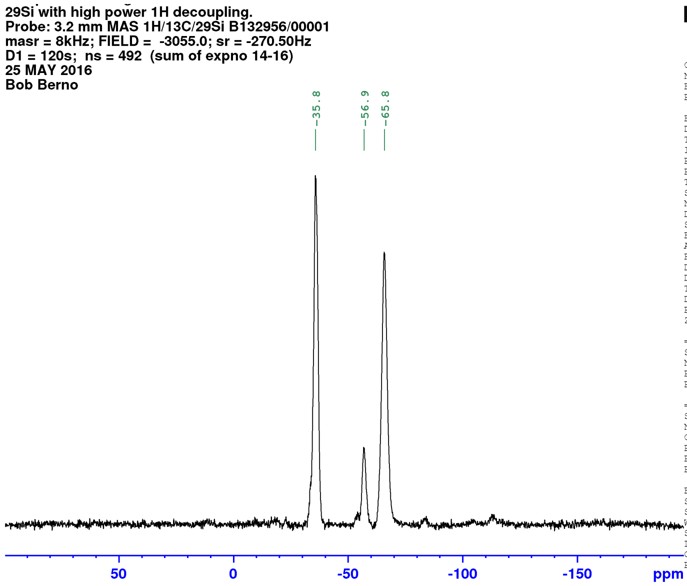


Figure S3.7 IR spectrum for hydrolysis reaction using pentamethyldisiloxane (MM^H) and bis(trimethylsiloxy)methylsilane (MD^HM)

S3.8.4 Silicone resin preparation from D^H_4 and water - solid state ^{29}Si NMR spectra for silicone resin



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PROCNO                 1

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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
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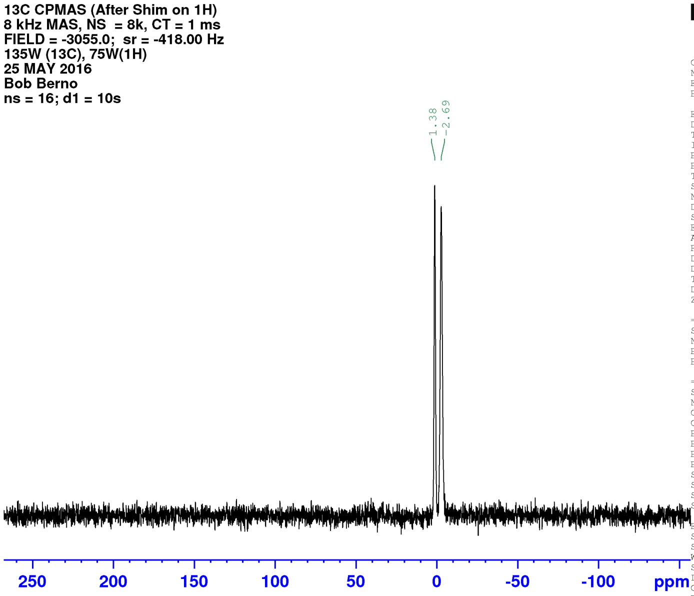
Figure S3.8 ^{29}Si solid state NMR spectrum for silicone resin preparation using D^H_4 and water



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EXPNO                 27
PROCNO                 1

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PULPROG               cp
TD                  4188
SOLVENT              D2O
NS                    16
DS                     0
SWH         100000.000 Hz
FIDRES       23.877747 Hz
AQ           0.0209400 sec
RG              181.89
DW               5.000 usec
DE                6.50 usec
TE               298.0 K
D1         10.00000000 sec
ZGOPTNS

======== CHANNEL f1 ========
SFO1       213.7898011 MHz
NUC1                 13C
P15            1000.00 usec
PLW1      135.00000000 W

======== CHANNEL f2 ========
SFO2       850.2017004 MHz
NUC2                  1H
CNST21    0
CPDPRG[2        spinal64
P3                4.00 usec
PCPD2             8.40 usec
PLW2      0 W
PLW12      75.00000000 W
SPNAM[0]  ramp70100.100
SPOAL0             0.500
SPOFFS0   0 Hz
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 S3.9 ^{13}C solid state NMR spectrum for silicone resin preparation using D^H_4 and water

Table S3.6 Examples of copolymers, elastomers and resins

Starting Materials		n	Mn	Mw	Đ$_M$
$HSiMe_2O(SiMe_2O)_nSiMe_2H$	DMS-H31	370	26,600	39,300	1.48
	DMS-H03	5	540	780	1.44
	M^HM^H	0	134	134	1.00
$HOSiMe_2O(SiMe_2O)_{12}SiMe_2OH$	DMS-S14	12	1300	1800	1.38
$HSiMe_2O(SiMePhO)_3SiMe_2H$	PMS-H03	3	370	400	1.08

Effect of		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 (Đ$_M$)	
	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	
[B(C$_6$F$_5$)$_3$] and chain 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	0.23	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	0.02	51.2	0.0014	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	2.06	H_2O	0.072	N	1	0.02	51.2	0.016	NA	NA	1	2700	3100	1.15	
Water source	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	
	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	25.6	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	25.6	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	25.6	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	25.6	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	25.6	0.01	toluene	5+5	3	14,400	21,200	1.47	1.5
	23	3	0.5	NA	NA	N	1	0.02	25.6	0.01	toluene	5+5	24	15,500	24,000	1.55	1.5

Chapter 4: Facile Synthesis of $C_x(AB)_yC_x$ Triblock Silicone Copolymers Utilizing Moisture Mediated Living-End Chain Extension[‡]

4.1 Abstract

The physical and chemical properties of silicone block copolymers depend upon the block size and chemical characteristics. Silicone block co-polymer synthetic procedures typically involve chain-growth polymerization techniques that are difficult to control, require low temperatures, inert atmospheres, etc., and which are subject to polymer chain redistribution; the latter process broadens dispersity and leads to the formation of cyclic monomers that must be removed. Once formed, tuning the size of the individual blocks is challenging. We demonstrate the controlled one pot synthesis of organosilicone $C_x(AB)_yC_x$ triblock co-polymers with aryl rich cores by exploiting the Piers-Rubinsztajn reaction and a hydrolysis/condensation polymerization, both using $B(C_6F_5)_3$ catalysis. A fast Piers-Rubinsztajn reaction between HSi-terminated silicones and aryl phenyl ethers leads preferentially to the formation of the aryl-rich core. Subsequent addition of HSi-terminated silicones permits controlled chain extension of the flanking homosilicone blocks via a slower hydrolysis/condensation facilitated by atmospheric moisture and leads in one pot, two steps to clean $C_x(AB)_yC_x$ triblocks. The products are surprisingly resilient to hydrolysis.

[‡] Chapter reproduced from A.F. Schneider, E. Laidey, and M.A. Brook, Macromolecular Chemistry and Physics, 2019, 220, 1800575 with permission from Wiley-VCH, copyright 2019. Schneider performed all experiments outlined in this publication and was the lead author of the manuscript with additions, edits and guidance provided by Dr. Brook. Laidley performed preliminary experiments which laid groundwork for the project.

4.2 Introduction

Block copolymers inhabit an important and unique niche in polymer chemistry, since each segment can contribute distinct properties to the overall material. Additionally, they spontaneously assemble into interesting and useful nanostructures.[1-3] Block copolymers containing silicones provide the many attractive properties of siloxanes including low Tg, oxygen permeability, biocompatibility, resistance to thermal and oxidative degradation, among others.[4-6]

Well-defined silicone-containing block copolymers are typically synthesized using a variety of living polymerization techniques. Ring-opening polymerization employs a highly reactive initiator (typically BuLi) combined with a strained cyclic siloxane (most commonly D_3, D = Me_2SiO) at low temperatures, in solvents, and under an inert atmosphere; the use of difunctional initiators has also been reported.[7] Blocks are formed by the sequential addition of different types of cyclic siloxanes that are added to the reactive chain end of the growing polymer.[4, 8-13] Chains are typically terminated with reactive silicone species such as chlorosilanes. Although high molecular weight poly(dimethyl)siloxanes can be easily prepared by this method, copolymers with silicones bearing bulky side chains (e.g., Ph) are less readily available.[4-5, 14-17] The use of both alkyl lithium and chlorosilane reagents are disadvantageous, as both can react with atmospheric moisture, in some cases violently. Backbiting of the growing chain at higher conversion to form cyclic monomers, typically D_4, can also occur in the presence of living anionic ends resulting in polymer products of broader dispersity.[5, 18]

The Piers-Rubinsztajn reaction (PR) involves the condensation between a hydrosilane and an alkoxysilane catalyzed by tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) (BCF), which leads to new siloxanes and concomitant alkane formation (Figure 4.1A).[19] Functional silicone precursors bearing SiH and SiOR groups can be sourced from silicone polymers (pendant or telechelic functionality) or from small silanes.[5, 20-22] In addition to alkoxysilanes, analogous reactions occur with silanols (including mineral surfaces), borates, phenols and alkyl aryl ethers (Figure 4.1B[23]).[24] Recently, the use of water as a chain extender for α,ω-hydride-terminated poly(dimethyl)siloxanes (H-PDMS-H) was described. Water slowly reacts with hydrosilanes, in the presence of $B(C_6F_5)_3$, to generate silanols (Figure 4.1C) that can then undergo a typical PR-type condensation reaction with SiH (Figure 4.1D).[25]

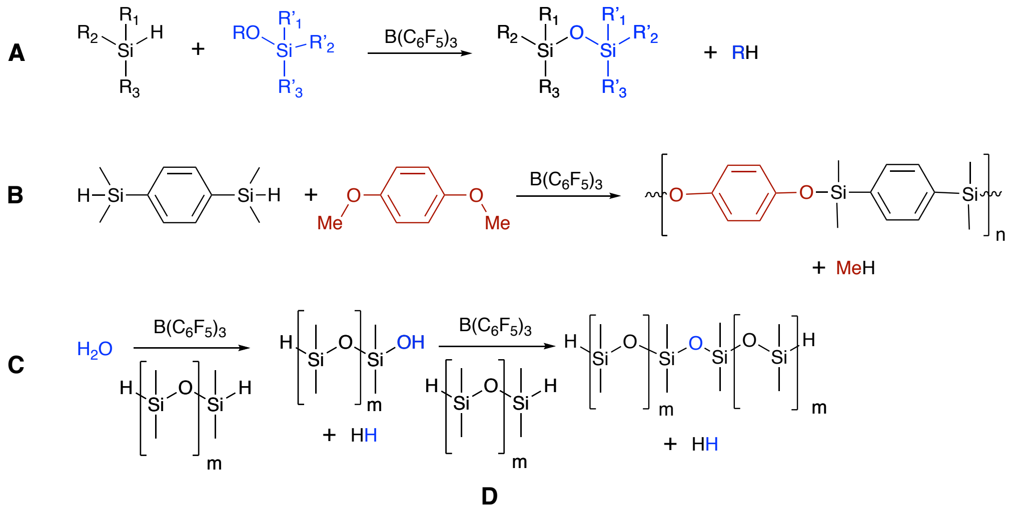

Figure 4.1 A) Standard PR reaction; B) PR with aryl ethers; C) $B(C_6F_5)_3$-catalyzed hydrolysis of SiH, then D) condensation of silanol with SiH

For most AA + BB condensation copolymerization reactions, the product molecular weight is highly dependent on the stoichiometry between [AA] and [BB]. Mismatched stoichiometries typically lead to lower molecular weight products.[26] During experiments designed to create aryl-rich, alternating silicone copolymers using the PR reaction, we unexpectedly found very high molecular weight products that, on further examination, were the result of both the expected PR reaction between SiH and MeOAr (Figure 4.1B) and the unexpected PR reaction between SiH and silanols (Figure 4.1D) formed from hydrolysis (Figure 4.1C); water was inadvertently provided through atmospheric moisture. We describe below our strategy to exploit these processes to reliably produce $C_x(AB)_yC_x$ triblock copolymers, where the constitution and molecular weight of each block is controlled (Figure 4.2).

4.3 Experimental Section

4.3.1 Reagents

Tris(pentafluorophenyl)borane and 1,1-diphenylethylene were purchased from Sigma-Aldrich; 1,1,3,3-tetramethyldisiloxane (M^HM^H), α,ω-hydride-terminated poly(dimethyl)siloxanes (H-PDMS-H, 2-3 centiStokes (cSt) MW 730 g mol^{-1}, 7-10 cSt MW 1170 g mol^{-1}, RI = 1.395 & 1.399, respectively), α,ω-hydride-terminated poly(phenylmethyl)siloxane (H-PPMS-H, 2-5 cSt MW 410 g mol^{-1}) and α,ω-hydroxy-terminated poly(dimethyl)siloxane (HO-PDMS-OH, 50,000 cSt MW 110,000 g mol^{-1}) were purchased from Gelest; reagent grade and HPLC grade toluene were purchased from Caledon (the HPLC grade solvent was dried in an activated alumina column); *p*-

dimethoxybenzene (RI=1.533) was purchased from Eastman. All compounds were used as received.

4.3.2 Catalyst Stock Solution

Tris(pentafluorophenyl)borane catalyst stock solution was prepared by dissolving $B(C_6F_5)_3$ (20.0 mg, 0.04 mmol), in dry HPLC grade toluene (2.00 mL) to give a 19.5 mM stock solution.

4.3.3 Methods

^1H NMR spectra were recorded on a Bruker AV600 MHz spectrometer using deuterated solvents ($CDCl_3$, toluene-d_8). Gel permeation chromatography was carried out using one of two different systems. For low molecular weight materials (M_n < 10 kDa), a Waters Alliance GPC System 2695 calibrated with a polystyrene calibration kit S-M-10 (Lot 85) from Polymer Laboratories was used. The system was equipped with a Waters 2414 refractive index detector, a Waters 2996 photodiode array detector, and three Jordi Fluorinated polydivinylbenzene mixed bed columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. For high molecular weight materials (M_n > 10 kDa), 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 (8mm x 30cm) 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. Water content was determined by Karl Fischer titration (Mettler Toledo DL32/DL39 Coulometer) with a one-component system using Hydranal Composite. FTIR data was collected on a Nicolet 6700 FTIR using Thermo Electron's OMNIC software.

Thermal stability was measured using a TGA Q50 thermogravimetric analyzer (TA Instruments) under argon with a flow rate of 20 $mLmin^{-1}$.

4.3.4 General Procedure for Polymerization

To an oven-dried 100 mL round-bottomed flask (moles silicone ≤ 1.5) or a 250 mL round-bottomed flask (moles silicone > 1.5) equipped with a magnetic stir bar were added the starting materials diluted in HPLC grade toluene (47 ppm H_2O) or reagent grade toluene (230 ppm H_2O). The reaction mixture was allowed to stir at room temperature (under N_2 if diluted in HPLC grade toluene, and open to the atmosphere if diluted in reagent grade toluene). Following a 15 min mixing time, $B(C_6F_5)_3$ catalyst stock solution was added to the reaction mixture; precise amounts added are reported in the reagent section of each specific experiment. At the chosen reaction time, neutral alumina (~ 0.5 g) was added to complex/quench the catalyst. The mixtures were gravity filtered and concentrated under reduced pressure. Product GPC data is reported in Table 4.5.

4.3.5 ^1H NMR Chemical Shift Assignments (related to subsequent experimental data)

6.83 (d, $\mathrm{MeOC_3}\mathit{H_2}\mathrm{C_3H_2OSiMe_2}$, J=9.1 Hz), 6.77 (d, $\mathrm{MeOC_3H_2C_3}\mathit{H_2}\mathrm{OSiMe_2}$, J=9.1 Hz), 6.75 (s, $\mathrm{SiOC_6}\mathit{H_4}\mathrm{OSi}$), 4.70 (sep, $\mathit{H}\mathrm{SiMe_2}$, J=2.8 Hz), 3.76 (s, $\mathrm{OC}\mathit{H_3}$) 0.20 (s, $\mathrm{ArOSi(C}\mathit{H_3}\mathrm{)_2}$), 0.18 (d, $\mathrm{HSi(C}\mathit{H_3}\mathrm{)_2}$, J=2.4 Hz), 0.07 (s, $\mathrm{SiC}\mathit{H_3}$).

4.3.6 Control Experiments

4.3.6.1 Hydrolysis/condensation of H-PDMS-H using atmospheric moisture – HO(Me_2SiO)$_n$H synthesis (Figure 4.2AB)

Reagents: H-PDMS-H (2-3 cSt, 0.54 g, 0.74 mmol), reagent grade toluene (10 mL), $B(C_6F_5)_3$ catalyst solution (100 µL, 1.95×10^{-3} mmol, 1.32×10^{-3} equivalents to SiH); reaction time: 24 h. The polymer product was a viscous colorless oil (0.32 g, 99 % recovered from crude). An analogous reaction was carried out using 7-10 cSt H-PDMS-H (entries 1-2 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 0.07 (s, SiMe).

4.3.6.2 H-PDMS-H with a molar excess of p-dimethoxybenzene – MeOAr-PDMS-ArOMe synthesis (Figure 4.2C)

Reagents: H-PDMS-H (7-10 cSt, 1.00 g, 0.85 mmol), *p*-dimethoxybenzene (0.38 g, 2.74 mmol), reagent grade toluene (10 mL), $B(C_6F_5)_3$ catalyst solution (100 µL, 1.95×10^{-3} mmol, 1.15×10^{-3} equivalents to SiH); reaction time: 30 min. The crude mixture was purified under reduced pressure using Kugelrohr distillation at 90 °C for 30 minutes to remove residual *p*-dimethoxybenzene. The polymer product was a colorless oil (0.71 g, 63 % recovered from crude). The product molecular weight was only marginally larger than the starting material, reflecting a mixture of ~ 63 % MeOAr-PDMS-ArOMe and ~ 37 % MeOAr-PDMS-OArO-PDMS-ArOMe (entry 3 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 6.83 (d, 4 H, J=9.1 Hz), 6.77 (d, 4 H, J=9.1 Hz), 6.75 (s, 1.5 H), 3.76 (s, 6H), 0.20 (s, 18 H), 0.07 (s, 118 H).

^{1}H NMR spectrum available in the Supporting Information (Figure S4.4).

4.3.6.3 Alternating Copolymer Synthesis using matched stoichiometry – a central block (AB)$_y$ (Figure 4.2D)

Reagents: H-PDMS-H, *p*-dimethoxybenzene, HPLC grade toluene (10 mL), $B(C_6F_5)_3$ catalyst solution (reagent amounts in Table 4.1); reaction time: 1 h. The polymer products were viscous colorless oils (entries 4-9 Table 4.5).

Table 4.1 Reagent amounts for above synthetic procedure to produce alternating copolymers.

Table 4.5 entry	H-PDMS-H MW (g mol^{-1})	g (mmol)	*p*-MeOArOMe g (mmol)	$B(C_6F_5)_3$ (mol % to SiH)	^{1}H NMR[a] (*δ*)
4	134	1.16 (8.64)	1.20 (8.64)	0.02	6.77-6.73 (m, 34 H), 4.71 (sept, 2 H, J=2.8 Hz), 0.26 (s, 12 H), 0.18 (s, 135 H)
5	730	0.34 (0.47)	0.07 (0.47)	0.10	6.83 (d, 4 H, J=9.0 Hz) 6.77 (d, 4 H, J=9.5 Hz), 6.75 (s, 16 H), 3.76 (s, 6 H), 0.20 (s, 58 H), 0.07 (s, 314 H)
6	730	0.50 (0.62)	0.09 (0.62)	0.08	6.84 (d, 4 H, J=9.1 Hz) 6.78-6.76 (m, 54 H), 3.76 (s, 6 H), 0.21 (s, 164 H), 0.07 (s, 755 H)
7	730	0.50 (0.62)	0.09 (0.62)	0.08	6.75 (s, 108 H), 4.71-4.69 (m, 2 H), 0.20 (s, 348 H), 0.07 (s, 1540 H)
8	1170	0.47 (0.40)	0.06 (0.40)	0.10	6.75 (s, 4H), 0.20 (s, 12 H), 0.07 (s, 100 H)
9	410	1.27 (3.11)	0.43 (3.11)	0.03	7.67-7.27 (m, 10 H), 6.68-6.60 (m, 4 H), 0.31-0.10 (m, 19 H)

[a] $CDCl_3$, 600 MHz, *δ*.

Sample GPC spectrum (for entry 7) available in Supporting Information (Figure S4.*7*).

4.3.7 C$_x$(AB)$_y$C$_x$ Block Copolymer Synthesis – two step synthesis (Figure 4.2DE)

4.3.7.1 Methylsilicone core

Central block (Alternating Copolymer): H-PDMS-H (A, 2-3 cSt, 2.00 g, 2.74 mmol), *p*-dimethoxybenzene (B, 0.38 g, 2.74 mmol), HPLC grade toluene (18 mL), $B(C_6F_5)_3$

catalyst solution (200 μL, 3.9×10^{-3} mmol); reaction time: 1 h; the reaction likely went to completion within the first 5 min based on the cessation of bubbles.

Flanking blocks: the above reaction mixture (5.0 mL) was added to each of 4 flasks, respectively. To 3 of those flasks was added H-PDMS-H diluted in toluene (C = A in this case, entries 10-12 Table 4.2); reaction time: 24 h. To the 4th flask was added H-PPMS-H (entry 13 Table 4.2). Polymer products were viscous colorless oils (entries 10-13 Table 4.5, respectively).

Table 4.2 Additional H-terminated silicones added to alternating copolymer solution above containing catalyst to obtain the desired overall mole ratio of silicone to arylenes – ^{1}H NMR data.

Table 4.5	H-PDMS-H		Reagent Grade Toluene	Silicone: Aryl	^{1}H NMR[a] (δ)
entry	MW (g mol^{-1})	g (mmol)	mL	Mole Ratio	
10	730	1.00 (1.37)	10	3:1	6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 267 H)
11	730	2.00 (2.74)	20	5:1	6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 371 H)
12	730	4.50 (6.19)	45	10:1	6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 595 H)
13	407	1.11 (2.73)	10	5:1	7.67 (d, 5 H, *J*=6.4 Hz), 7.65-7.30 (m, 38 H), 6.93-6.68 (m, 4 H), 0.49 (s, 6 H), 0.41 (s, 12 H), 0.33-0.12 (m, 54 H), 0.08 (s, 72 H)

[a] $CDCl_3$, 600 MHz, δ.

Sample ^{1}H NMR and GPC spectra (for entry 10) available in the Supporting Information (Figure S4.5 and Figure S4.8 respectively).

4.3.7.2 Phenylsilicone core

Central block (Alternating Copolymer): H-PPMS-H (2-5 cSt, 1.26 g, 3.11 mmol), *p*-dimethoxybenzene (0.43 g, 3.11 mmol), reagent grade toluene (50 mL), $B(C_6F_5)_3$ catalyst solution (100 μL, $1.95x10^{-3}$ mmol); reaction time: 1 h (entry 9 Table 4.1 & Table 4.5).

Flanking block: H-PDMS-H (2-3 cSt, 7.82 g, 10.75 mmol); reaction time: 24 h. The polymer product was a viscous colorless oil (entry 14 Table 4.5).

^1H NMR ($CDCl_3$, 600 MHz, δ): 7.60-7.22 (m, 10 H), 6.68-6.53 (m, 4 H), 0.26-0.07 (m, 26 H), 0.07 (s, 268 H).

4.3.8 Effect of Relative Humidity

These experiments were performed in the summer. A comparison of the effect of humidity was undertaken in a dryer season. Summer (~ 60% relative humidity entry 15 Table 4.5) vs winter (~ 20% relative humidity entry 16 Table 4.5) showed that greater humidity led to shorter flanking chains (hygrometry measurements obtained in lab).

Reagents: H-PDMS-H (2-3 cSt, 0.45 g, 0.62 mmol), *p*-dimethoxybenzene (0.09 g, 0.62 mmol), reagent grade toluene (10 mL), $B(C_6F_5)_3$ catalyst solution (50 μL, $9.75x10^{-4}$ mmol, $1.57x10^{-3}$ equivalents to SiH); reaction time: 1 h. Additional reagents: H-PDMS-H (2-3 cSt, 2 mL, 2.48 mmol); reaction time: 24 h. The polymer product was a colorless oil (entry 16 Table 4.5).

^1H NMR ($CDCl_3$, 600 MHz, δ): 6.75 (s, 4H), 0.02 (s, 13 H), 0.07 (s, 327 H).

4.3.9 $C_x(AB)_yC_x$ Block Copolymer Synthesis – one pot, initially dry, then open to atmosphere (sequential addition of moisture)

Reagents: H-PDMS-H (2-3 cSt, 3.92 g, 5.39 mmol), *p*-dimethoxybenzene (0.15 g, 1.07 mmol), HPLC grade toluene (20 mL), $B(C_6F_5)_3$ catalyst solution (50 μL, 9.77x10^{-4} mmol, 7.88x10^{-4} equivalents to SiH); reaction time: 24 h. The polymer product was a colorless oil (entry 22 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 6.75 (s, 2 H), 4.70 (sept, 2 H, *J*=2.8 Hz), 0.20 (s, 5 H), 0.18 (d, 13 H, *J*=2.4 Hz), 0.07 (s, 100 H).

The cap was removed and atmospheric moisture was allowed to enter the system, reaction time: 24 hours. The polymer product was a viscous colorless oil (entry 23 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 306 H).

4.3.10 $C_x(AB)_yC_x$ Block Copolymer Synthesis – sequential addition of H-PDMS-H monomers for the flanking C_x block

Reagents: H-PDMS-H (2-3 cSt, 2.30 g, 3.15 mmol), *p*-dimethoxybenzene (0.44 g, 3.15 mmol), reagent grade toluene (15 mL), $B(C_6F_5)_3$ catalyst solution (100 μL, 1.95x10^{-3} mmol); reaction time: 1 h. Additional H-PDMS-H (2-3 cSt, 1 mL); reaction time: 12 h. Additional H-PDMS-H (2-3 cSt, 1 mL); reaction time: 12 h. Additional H-PDMS-H (2-3 cSt, 1 mL); additional reaction time: 24 h (entries 17-21 Table 4.3, respectively).

Table 4.3 Growth of $C_x(AB)_yC_x$ living system by sequential H-PDMS-H addition & examination of the relative peak growths in GPCs – ^{1}H NMR data.

Table 4.5 entry	Molar excess of H-PDMS-H	Peaks in GPC #	Silicone: Aryl Mole Ratio	Major product/ peak[a] %	^{1}H NMR[b] (δ)
17	0	1	1:1	100	6.75 (s, 7 H), 4.70 (sept, 2 H, *J*=2.8 Hz), 0.19 (d, 36 H, *J*=9.3 Hz), 0.07 (s, 165 H)
18	1	2	2:1	78	6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 130 H)
19	2	2	3:1	74	6.75 (s, 15 H), 4.70 (sept, 2 H, *J*=2.7 Hz), 0.20 (s, 49 H), 0.18 (d, 36 H, *J*=2.7 Hz), 0.07 (s, 568 H)
20	3	2	4:1	65	6.75 (s, 6 H), 4.70 (sept, 2 H, *J*=2.8 Hz), 0.20 (s, 10 H), 0.18 (d, 15 H, *J*=2.7 Hz), 0.07 (s, 283 H);
21	3	2	4:1	83	6.75 (s, 4 H), 0.20 (s, 14 H), 0.07 (s, 209 H).

[a] Percentage composition calculated using methods outlined by Hawley[27]
[b] ^{1}H NMR ($CDCl_3$, 600 MHz, δ)

4.3.11 One Step One Pot Copolymer Synthesis – varying the molar excess of H-PDMS-H

Reagents: *p*-dimethoxybenzene (0.05 g, 0.36 mmol), H-PDMS-H (2-3 cSt, Table 4.4), reagent grade toluene, $B(C_6F_5)_3$ catalyst solution (Table 4.4); reaction time: 24 h. The polymer products were viscous colorless oils (entries 24-26 Table 4.5)

Table 4.4 Amount of H-PDMS-H (2-3 cSt) added to 0.05 g *p*-dimethoxybenzene in above synthetic procedures.

Table 4.5 entry	H-PDMS-H (730 g mol^{-1}) g (mmol)	Reagent Grade Toluene mL	$B(C_6F_5)_3$ µL (µmol)	Silicone: Aryl Mole Ratio	^{1}H NMR[a] (δ)
24	0.79 (1.08)	12	80 (1.56)	3:1	6.75 (s, 4 H), 0.20 (s, 15 H), 0.07 (s, 218 H)
25	1.38 (1.90)	16	100 (1.95)	5:1	6.75 (s, 4 H), 0.20 (s, 15 H), 0.07 (s, 357 H)
26	2.75 (3.77)	24	150 (2.93)	10:1	6.75 (s, 4 H), 0.20 (s, 15 H), 0.07 (s, 716 H)

[a] $CDCl_3$, 600 MHz, δ.

An analogous experiment to entry 25 Table 4.4 was performed using H-PPMS-H:

Reagents: H-PPMS-H (2-5 cSt, 1.06 g, 2.61 mmol), *p*-dimethoxybenzene (0.07 g, 0.51 mmol), reagent grade toluene (15 mL), $B(C_6F_5)_3$ catalyst solution (100 μL, 1.95×10^{-3} mmol, 7.47×10^{-4} equivalents to SiH); reaction time: 24 h. The polymer product was a colorless oil (entry 27 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.67 (d, 4 H, J = 6.4 Hz), 7.54 (d, 6 H, J = 6.7 Hz), 7.44-7.30 (m, 22 H), 6.68-6.63 (m, 4 H), 0.49 (s, 5 H), 0.41 (s, 7 H), 0.31-0.01 (m, 50 H).

4.3.12 Monitoring Random Copolymer Development Over Time

Relative functional group consumption (Figure 4.3A): Reagents: H-PDMS-H (2-3 cSt, 0.57 g, 0.78 mmol), *p*-dimethoxybenzene (0.04 g, 0.26 mmol), 1,1-diphenylethylene (46.25 μL, 0.26 mmol), reagent toluene, $B(C_6F_5)_3$ catalyst solution (80 μL, 1.56×10^{-3} mmol, 1.00×10^{-3} equivalents to SiH); reaction time: 12 hr. Aliquots: 0s, 10s, 30s, 60s, 5m, 10m, 30m, 12h. ^{1}H NMR data for each aliquot is available in Supporting Information (Table S4.6).

Monitoring polymer molecular weight growth over time (Figure 4.3B): Reagents: H-PDMS-H (2-3 cSt, 2.36 g, 3.24 mmol), *p*-dimethoxybenzene (0.09 g, 0.65 mmol), reagent toluene, $B(C_6F_5)_3$ catalyst solution (200 μL, 3.91×10^{-3} mmol, 6.03×10^{-4} equivalents to SiH); reaction time: 24 h. Aliquots: 1h, 3h, 5h, 8h, 14h, 19h, and 24h. ^{1}H NMR and GPC data for each aliquot is available in the Supporting Information (Table S4.7 and Table S4.8, respectively).

4.3.13 Testing Hydrolytic Stability of the Random Copolymer

Reagents: H-PDMS-H (2-3 cSt, 0.50 g, 0.69 mmol), *p*-dimethoxybenzene (0.01 g, 0.07 mmol), reagent toluene, $B(C_6F_5)_3$ catalyst solution (50 μL, 9.77×10^{-4} mmol, 7.08×10^{-4} equivalents to SiH); reaction time: 6 h. The polymer product was a colorless oil (0.19 g, 58% recovered from crude, significant mass loss due to removal of unreacted H-PDMS-H starting material; entry 28 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 6.75 (s, 8 H), 4.70 (sept, 2 H, $J = 2.8$ Hz), 0.20 (s, 24 H), 0.18 (d, 13 H, $J = 2.8$ Hz), 0.07 (s, 1243 H).

The polymer (23.8 mg) was dissolved in 5 mL THF. The resulting solution was boiled in 100 °C DI for water (20 mL) under reflux for 24 hours. The product was extracted using hexanes and concentrated under reduced pressure. The polymer product remained a colorless oil with no change in molecular weight (entry 29 Table 4.5).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 6.75 (s, 8 H), 4.71-4.69 (m, 2 H, $J = 2.8$ Hz), 0.20 (s, 24 H), 0.18 (d, 13 H, $J = 2.8$ Hz), 0.07 (s, 1269 H).

4.4 Results

4.4.1 Chain Extension by Hydrolysis/Condensation of H-PDMS-H

Two processes occur during triblock formation: the PR reaction, and hydrolysis/condensation, both of which lead to chain extension via siloxane formation. The latter reaction was initially examined by exposing a telechelic, hydrogen-terminated silicone (H-PDMS-H) to atmospheric moisture in the presence of $B(C_6F_5)_3$. Over time, monomer was consumed in a classic condensation process via slow growth in polymer molecular weight. High molecular weight products (> 100,000 g mol^{-1}) terminated by

SiOH were formed irrespective of the starting molecular weight of H-PDMS-H. Higher molecular weight materials result if the water is allowed to more slowly enter the reaction vessel such that not all SiH groups become competitively converted to SiOH groups (Figure 4.2AB, entries 1,2 Table 4.5). Our group has previously analyzed this hydrolysis process by varying the source water – allowing atmospheric moisture to enter the reaction vessel, facilitated by toluene, produced hydrolysis polymers of higher molecular weight when compared to hydrolysis polymers produced by combining H-PDMS-H with bulk water under a N_2 environment.[25] *Note: care must be taken with these* $B(C_6F_5)_3$*-catalyzed reactions that release flammable gases methane and/or hydrogen.*

4.4.2 The Core Block (AB)$_y$

The use of excess *p*-dimethoxybenzene with H-PDMS-H led to the rapid formation of aryl-capped silicones (Figure 4.2C, entry 3 Table 4.5) in a fast PR reaction. Alternating copolymers (aryl rich silicones, $(AB)_y$) arose by performing the PR reaction on stoichiometric mixtures of hydrogen-terminated silicones and *p*-dimethoxybenzene in the presence of small quantities of $B(C_6F_5)_3$. The concentration of the aryl groups in the product central block was readily tuned by selection of different molecular weight H-PDMS-H starting materials ($HMe_2Si(OSiMe_2)_nOSiMe_2H$ n = 0-14, entries 4-8 Table 4.5, Figure 4.2D). Very small errors in matching the A:B stoichiometry (due to dispersity in commercial H- terminated silicones) led, as expected, to large differences in product molecular weight (entries 5 v 6 v 7 Table 4.5). It was possible to use dimethyl- or phenylmethyl- silicones when creating the core block (entries 4-8 v 9 Table 4.5).

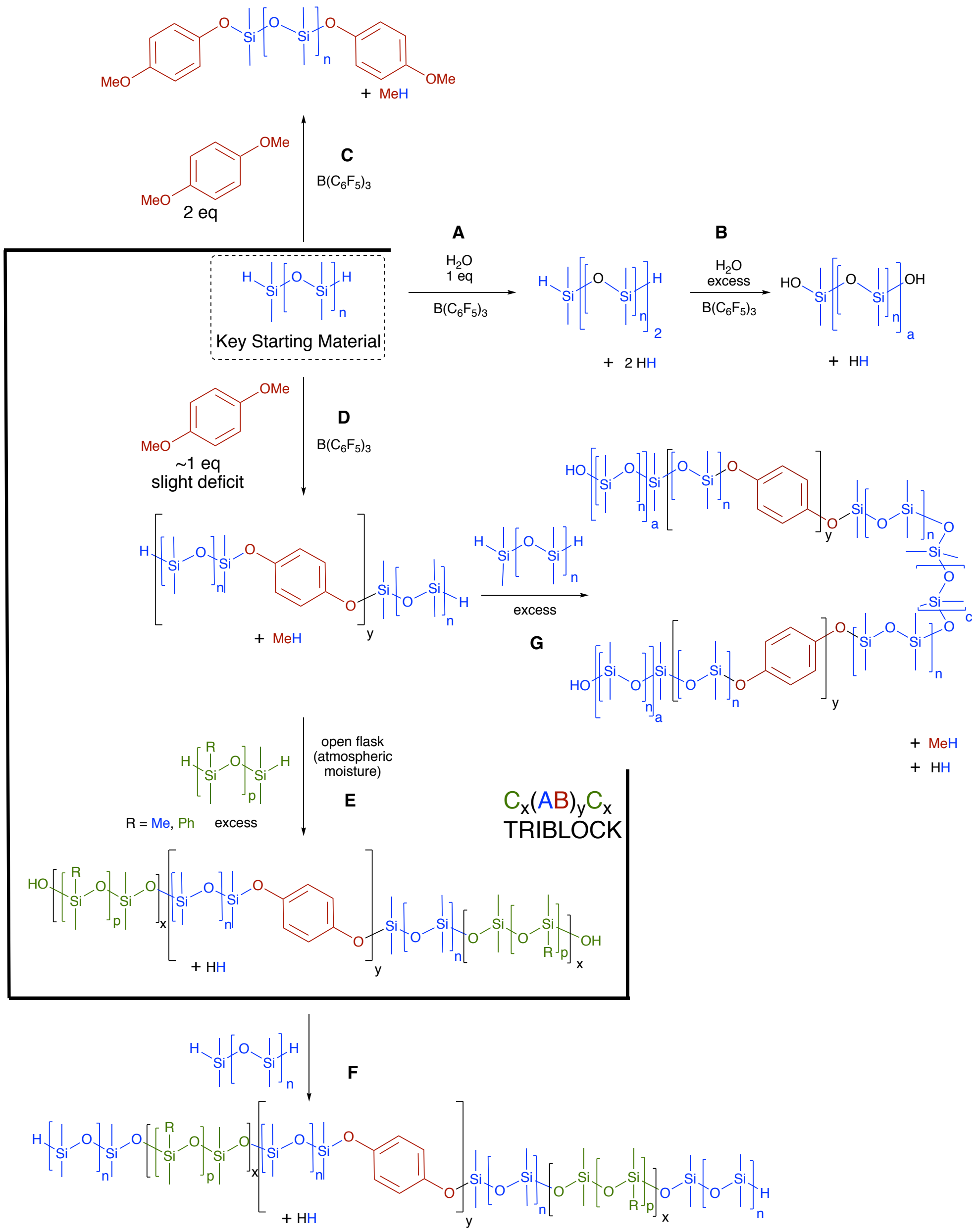

Figure 4.2 Various $B(C_6F_5)_3$-catalyzed reactions: A) Chain extension by hydrolysis and condensation of H-PDMS-H. B) Hydrolysis of SiH to SiOH. C) Capping the polymer with excess aromatic ether. D) Core block produced using an equimolar ratio of starting materials. E) Chain growth of flanking blocks via hydrolysis/condensation of excess H-terminated silicone (reaction performed open to the air). F) Restarting block growth after terminal hydrolysis to SiOH. G) Chain extension and condensation of $C_x(AB)_yC_x$ polymers – combination of processes A and E.

4.4.3 Growing the Flanking Blocks C_x

Flanking blocks were grown onto the core block simply by adding excess H-PDMS-H (3, 5, 10 fold, entries 10-12 Table 4.5, respectively) to the reaction mixture. Each reaction was left for 24 hours in an open vessel to allow complete chain extension (C_x block formation, Figure 4.2E). The elevation in polymer molecular weight occurred while retaining low dispersities. At early stages of the processes, self-condensation of H-PDMS-H also led the formation of low molecular weight silicones (Figure 4.2AB), as shown by GPC. Initially both the large central blocks and H-PDMS-H homopolymer blocks were observed to grow, but over time the PDMS homopolymer chains were mostly captured by the flanking blocks (Figure 4.2E); about 15% homopolymer remained. Chain growth of the flanking blocks terminated once consumption of SiH groups was complete and all termini were SiOH groups (Figure 4.2BE), a process that can be accelerated at higher levels of humidity (e.g., Canadian summer entry 15 Table 4.5 vs Canadian winter, entry 16, Table 4.5); a more complete discussion of effects of humidity in these reactions has been reported.[25]

Table 4.5. GPC and RI of control experiments and $C_x(AB)_yC_x$ polymers

Entry	H-terminated silicone		Mole ratio[a]	Product			
		MW ($g\ mol^{-1}$)		M_n (kDa)	M_w (kDa)	$Đ_M$	RI
	Control Experiments						
	Chain extension by hydrolysis of H-PDMS-H:						
1	H-PDMS-H	730	1:0	183	349	1.91	1.401
2	H-PDMS-H	1170	1:0	126	182	1.45	1.401
	Capping H-PDMS-H with MeOArOMe						
3	H-PDMS-H	1170	1:3	1.5	3	1.95	1.422
	Alternating copolymerization of silicone:arylenes – the central block						
4	M^HM^H	134	1:1	4	6	1.34	1.484
5	H-PDMS-H	730	1:1	2	4	1.84	1.431
6	H-PDMS-H	730	1:1	11	17	1.72	1.428
7	H-PDMS-H	730	1:1	40	46	1.19	1.427
8	H-PDMS-H	1170	1:1	68	99	1.46	1.419
9	H-PPMS-H	410	1:1	33	53	1.68	1.513
	Two Step Block Copolymer Syntheses						
	Central block H-PDMS-H; flanking block H-PDMS-H						
10	H-PDMS-H	730	3:1	57	80	1.42	1.411
11	H-PDMS-H	730	5:1	67	119	1.79	1.408
12	H-PDMS-H	730	10:1	101	151	1.49	1.404
	Central block H-PDMS-H; flanking block H-PPMS-H						
13	H-PDMS-H, H-PPMS-H	730 410	5:1	12	15	1.22	1.464
	Central block H-PPMS-H; flanking block H-PDMS-H						
14	H-PPMS-H, H-PDMS-H	730, 410	5:1	64	119	1.86	1.426
	Effects of humidity						
15	H-PDMS-H (summer)	730	5:1	67	119	1.79	1.411
16	H-PDMS-H (winter)	730	5:1	119	214	1.80	1.411
	Living termini block copolymer growth by sequential addition of H-PDMS-H						
17	H-PDMS-H	730	1:1	5	7	1.40	-[b]
18	H-PDMS-H	730	2:1	20	26	1.81	1.416
19	H-PDMS-H	730	3:1	24	37	1.55	1.414
20	H-PDMS-H	730	4:1	27	46	1.71	1.409
21	H-PDMS-H	730	4:1	107	239	2.236	1.409

	Single-step reagent addition (water starved then water added)						
22	H-PDMS-H (dry)	730	5:1	2	3	1.32	1.409
23	(open flask)			122	221	1.82	1.410
	One Step Copolymer Syntheses						
	Different H-PDMS-H ratio, fixed [MeOArOMe]						
24	H-PDMS-H	730	3:1	42	71	1.68	1.415
25	H-PDMS-H	730	5:1	93	157	1.69	1.410
26	H-PDMS-H	730	10:1	138	261	1.89	1.410
27	H-PPMS-H	410	5:1	10	12	1.29	1.510
	Hydrolytic stability of copolymer						
28	H-PDMS-H (before reflux)	730	10:1	14	16	1.16	1.404
29	H-PDMS-H (after reflux)	730	10:1	15	16	1.13	1.404

[a] Telechelic hydride terminated silicone/MeOArOMe. [b] Not measured.

The C_x block formation was living, in the sense that additional aliquots of H-PDMS-H led to higher molecular weight triblocks (entries 17-21 Table 4.5). That is, instead of adding all the monomer for the flanking blocks at once, it is possible to dial in additional monomer on demand. This was particularly easily seen when the central block was different from the silicone in the flanking blocks (Figure 4.2E, entries 13-14 Table 4.5). For example, higher RI polymers were prepared by use of a phenylsilicone ($(HMe_2SiOSiPh_2)_2O$) in lieu of H-PDMS-H (entries 9, 13, 14, 27 Table 4.5). Even in the case where the reaction has prematurely been quenched by water, addition of fresh H-PDMS-H can restart the process (Figure 4.2F).[25]

The alternative two step process, where all reagents except water were mixed initially and the second step involved exposing the reaction to moisture, did not lead to the same triblock polymers. For example, when H-PDMS-H and *p*-dimethoxybenzene were combined in a 5:1 molar ratio, catalyst was added, and the reaction was performed under dry conditions (entry 22 Table 4.5), GPC data demonstrated the formation of very low molecular weight copolymers $(AB)_y$ in a PR process. It is most likely that these are mixtures of unreacted H-PDMS-H and H-PDMS-OArO-PDMS-H. Once the reaction vessel was opened to the environment, however, extensive growth in polymer molecular weight occurred over 24 hours as a result of atmospheric moisture reacting with SiH, leading to chain extension (entry 23 Table 4.5). These polymers were made using a 3-fold, 5-fold and 10-fold molar excess of H-PDMS-H to *p*-dimethoxybenzene (entries 24-26 Table 4.5, the reaction was also performed with the phenylmethylsiloxanes, entry 27). Although these products exhibited similar molecular weights, refractive indices and thermal stability, based on TGA data (products exhibited superior thermal stability when compared to typical HO-PDMS-OH of similar molecular weight) to polymers formed by sequential addition of H-PDMS-H, the processes will be random (Figure 4.2G) and perfect alternating copolymer blocks will not form. TGA curves available in Supporting Information (Figure S4.10).

4.4.4 Examining the Relative Reaction Rates

The ability to cleanly prepare $C_x(AB)_yC_x$ triblock polymers hinges on large differences in the relative rates of the two reactions while creating the central block: PR vs hydrolysis/condensation. ^{1}H NMR was used to track the functional group consumption of SiH versus OMe when a 4:1 molar ratio of H-PDMS-H: *p*-dimethoxybenzene was mixed in d_8-toluene and left open to the atmosphere. Following catalyst addition, fractions were removed and immediately quenched and the residual concentration of each functional group (SiH vs OMe) was plotted (Figure 4.3A; growth in MW of a 5:1 H-PDMS-H : *p*-dimethoxybenzene solution is shown in Figure 4.3B). Completely sequential reactions would have seen 25% SiH consumed at the point at which all the OMe groups had reacted. Instead, all the OMe groups had reacted when ~ 37% SiH remained, indicating contamination of the faster PR process by some slower SiH hydrolysis and condensation leading to polymers with a less controlled block structure (Figure 4.2G). As a consequence, well-defined triblock polymers can only be accessed using a one pot, two step process in which the core block is first prepared using stoichiometrically matched quantities of the two monomers. ^{1}H NMR data of each fraction is available in Supporting Information (Table S4.6).

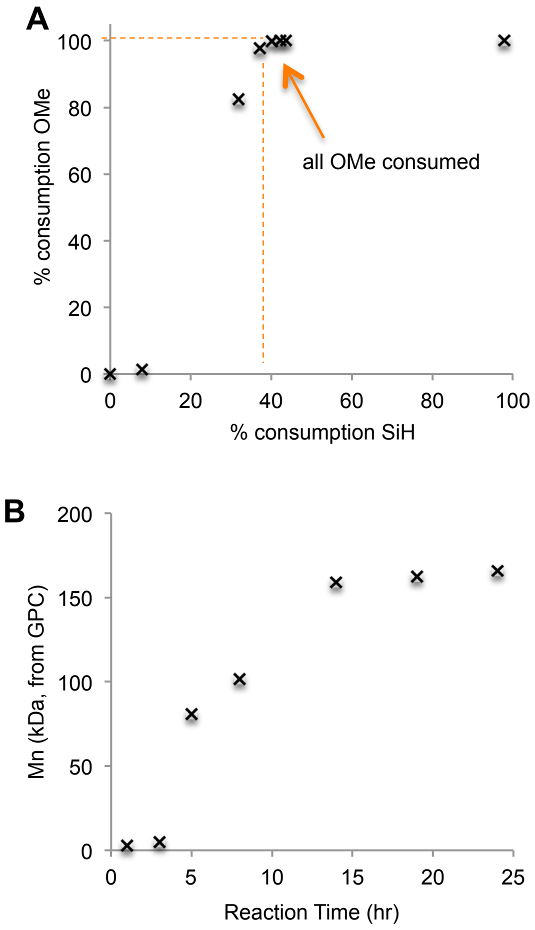

Figure 4.3 A) Relative functional group consumption of SiH vs OMe in a 4:1 starting material ratio reaction. PR reactions dominate until all OMe is consumed, after which only SiH hydrolysis and condensation occur. B) Growth was monitored via GPC of the random copolymer synthesis over time – from a 5:1 H-PDMS-H: *p*-dimethoxybenzene starting material molar ratio mixture in an open vessel.

4.4.5 Product stability

Alkoxysilanes are known to undergo ready hydrolysis; such reactions form the basis of room temperature vulcanization elastomer formation.[28] A copolymer synthesized using the one-pot one shot system was refluxed in 100 °C water for 24 hours. No significant changes in polymer molecular weight were observed after reflux in boiling water (entries

28-29 Table 4.5). Thus, both the silicone and SiOC linkages (at least for arylsiloxanes) in the polymer were hydrolytically stable under these vigorous conditions.

4.5 Discussion

The PR reaction between SiH groups and a variety of oxygen nucleophiles is known to occur at different rates: alkoxysilanes, phenols > aryl ethers > silanols > water.[24-25, 29] The utilization of two reactions with SiH groups simultaneously, catalyzed by the same $B(C_6F_5)_3$ catalyst, allows the controlled synthesis of triblock copolymers. With aryl methyl ethers as the nucleophile it was necessary, if undesirable, to include toluene in the reactions to solvate the aryl ether. For related alternating copolymer reactions that use alkoxysilane monomers that are more soluble in silicones, this solvent may not be necessary.[30-31]

The difference in rates between the PR reaction of SiH groups with ArOMe and H_2O is large. Given the choice between reacting with adventitious or added water in a one pot, one step process, the reaction of SiH with Ar-OMe groups was favored leading to the formation of the central block comprised mostly of alternating co-monomers (Figure 4.2D). However, the difference in rates between the two reactions is insufficiently high to guarantee the perfect fidelity of the central block when there is an excess of H-PDMS-H, as shown by the consumption of the ArOMe groups (Figure 4.3A); some higher order block polymers form (Figure 4.2G). In a similar vein, a one pot, two step process in which all reagents are initially combined with catalyst (excess of H-terminated silicone with *p*-dimethoxybenzene) and water is introduced in the second step led to polymers of comparable molecular weight to proper triblocks, but without structural control (Figure

4.2G). In this case low molecular weight oligomers are first formed via the PR reaction, followed by condensation of oligomers once water is introduced (entries 22-23 Table 4.5).

Perfect fidelity of the central block is achieved in a first step using the PR reaction which occurs rapidly, in under an hour (Figure 4.2D). The central block length is controlled by the ability to match the stoichiometry of the two monomers (H-PDMS-H and *p*-dimethoxybenzene). Due to the dispersity in commercial H-PDMS-H, this is not always straightforward.

Once the central block is formed from a reaction mixture of matched stoichiometry, in the same open flask, addition of H-PDMS-H allows the flanking blocks to grow at will, in our case, in up to at least a 10 fold molar excess with respect to the content in the core block (entries 10-21 Table 4.5, Figure 4.2E); contamination of the triblock by homopolymer was about 15%. The desired block length may be achieved by one shot addition of the excess H-PDMS-H, or by titrating the material in (entries 10-12 vs 17-21 Table 4.5). In these processes, it is necessary to ensure that the water content is low enough to prevent premature termination by conversion of SiH to SiOH groups (Figure 4.2B). Even in that case, the process can be restarted by adding more SiH functional monomer (Figure 4.2F).

Within the silicone community, the hydrolytic instability of SiOC linkages (alkoxysilanes) is widely exploited, particularly in moisture cured, room temperature vulcanization systems. Compounds such as TEOS ($Si(OEt)_4$), TMOS ($Si(OMe)_4$), $MeSi(OEt)_3$, $MeSi(OMe)_3$, and silicones terminated with such groups, e.g., $(MeO)_2MeSi(OSiMe_2)_nOSiMe(OMe)_2$, readily react in the presence of water with HO-terminated silicones. Legitimate concern, therefore, could be raised about the utility of ArOSi compounds over time. However, organic chemists broadly use silyl ethers ($R^1R^2R^3SiOR$) as protecting groups for alcohols in organic synthesis.[32-33] In such applications, the steric bulk of R^1, R^2 and R^3 controls the rate of the hydrolysis reaction, which can vary over several orders of magnitude. The phenoxysilyl groups present in the $C_x(AB)_yC_x$ polymers produced here exhibited surprising stability towards hydrolysis – no change in molecular weight was observed after boiling for 24 hours in water (entry 28-29 Table 4.5); these are very vigorous conditions to which silicones will be exposed only in exceptional cases.

Multiblock polymers hold an increasingly important place in polymer chemistry, because of their ability to stabilize a wide variety of interfaces, and to segregate into structures at the nanoscale. The process described to create triblock copolymers has, as its primary advantage, simplicity. The conditions are extremely mild and forgiving and even at room temperature the reactions can be complete in a few hours. The central block is prepared by a PR reaction that involves formation of an alternating copolymer at room temperature. The flanking blocks are constructed in a living process, such that their size is readily controlled by the quantity of the same or a different H-terminated silicone added.

4.6 Conclusions

$C_x(AB)_yC_x$ triblock silicone polymers (e.g., A,C = silicone; B = 1,4-substituted benzene) were readily prepared in a simple, one pot reaction, using a two step process and low catalyst loadings (≤ 0.07 mol%) under mild reaction conditions; small amounts of toluene facilitate the reaction, possibly by acting as a co-solvent for water, silicone and the evolving polymer. An alternating copolymer $(AB)_y$ was first produced by a rapid PR reaction between a hydride-terminated silicone and *p*-dimethoxybenzene. Flanking blocks were added to the core block in a second, slower step by allowing hydride-terminated silicones to polymerize onto the termini of the central block using atmospheric moisture as a chain extender. The silicones in the core and flanking blocks may be the same or different.

4.7 Acknowledgments

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4.8 References

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S4.9 Appendix 3 – Supporting Information

Table S4.6 Examining the relative reaction rates (Figure 3A) – ^{1}H NMR data

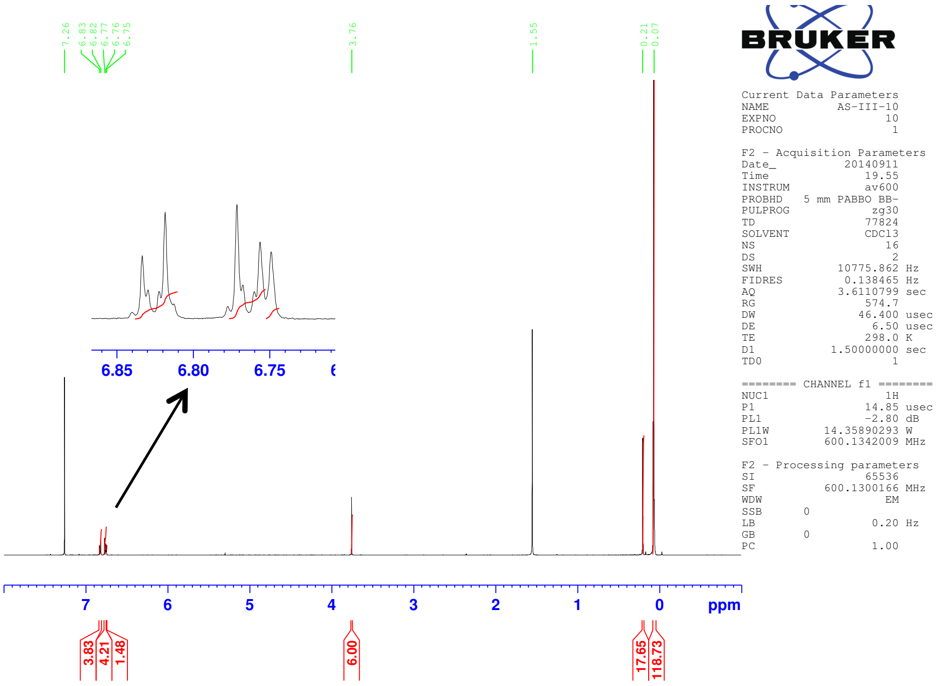
Fraction	^{1}H NMR (toluene-d_8, 600 MHz, δ)
Initial mixture	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 8 H), 6.68 (s, 4 H), 5.33 (s, 2 H), 4.99-4.91 (m, 7.3 H), 3.35 (s, 5.6 H), 0.25-0.12 (m, 226 H)
1	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 14 H), 6.68 (s, 4 H), 5.33 (s, 2 H), 4.99-4.91 (m, 6.7 H), 3.35 (s, 5.5 H), 0.25-0.12 (m, 218 H)
2	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 23 H), 6.71-6.69 (m, 1 H), 5.33 (s, 2 H), 4.99-4.91 (m, 5 H), 3.35 (s, 1 H), 0.27-0.13 (m, 226 H)
3	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 15 H) 5.33 (s, 2 H), 4.99-4.91 (m, 4.6 H), 3.35 (s, 0.1 H), 0.28-0.12 (m, 216 H)
4	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 14 H), 5.33 (s, 2 H), 4.99-4.91 (m, 4.4 H), 3.35 (s, 0.01 H), 0.28-0.11 (m, 220 H)
5	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 15 H), 5.33 (s, 2 H), 4.99-4.91 (m, 4.2 H), 0.28-0.11 (m, 218 H)
6	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 16 H), 5.33 (s, 2 H), 4.99-4.91 (m, 4.13 H), 0.28-0.11 (m, 222 H)
7	7.26 (d, 4 H, *J* = 7.7 Hz), 7.11-7.08 (m, 15 H), 5.33 (s, 2 H), 4.99-4.91 (m, 0.2 H), 0.25-0.12 (m, 225 H)

Table S4.7 Monitoring chain growth of random copolymer (Figure 4.3B) – ^{1}H NMR data

Reaction time (h)	^{1}H NMR ($CDCl_3$, 600 MHz, δ)
1	6.75 (s, 2 H), 4.70 (sep, 2 H, *J* = 2.8 Hz), 0.20 (s, 5 H), 0.18 (d, 14 H *J* = 2.5 Hz), 0.07 (s, 121 H)
3	6.75 (s, 3 H), 4.72-4.69 (sep, 2 H, *J* = 2.8 Hz), 0.20 (s, 10 H), 0.18 (d, 12 H, *J* = 2.6 Hz), 0.07 (s, 234 H)
5	6.75 (s, 4 H), 0.20 (s, 15 H), 0.07 (s, 334 H)
8	6.75 (s, 4 H), 0.20 (s, 15 H), 0.07 (s, 364 H)
14	6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 365 H)
19	6.75 (s, 4 H), 0.20 (s, 14 H), 0.07 (s, 372 H)
24	6.75 (s, 4 H), 0.20 (s, 13 H), 0.07 (s, 363 H)

Table S4.8 Monitoring chain growth of random copolymer (Figure 4.3B) – GPC data

Rxn time (h)	**Mn**	**Mw**	***Đ*$_M$**	**SiH in IR**
1	2996	3673	1.206	Yes
3	5007	6109	1.220	Yes
5	80,943	220,055	2.719	Yes (faint)
8	101,851	231,230	2.270	No
14	159,072	323,670	2.035	No
19	162,438	250,001	1.539	No
24	166,483	275,798	1.657	No



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Current Data Parameters
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EXPNO                   10
PROCNO                   1

F2 - Acquisition Parameters
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Time                 19.55
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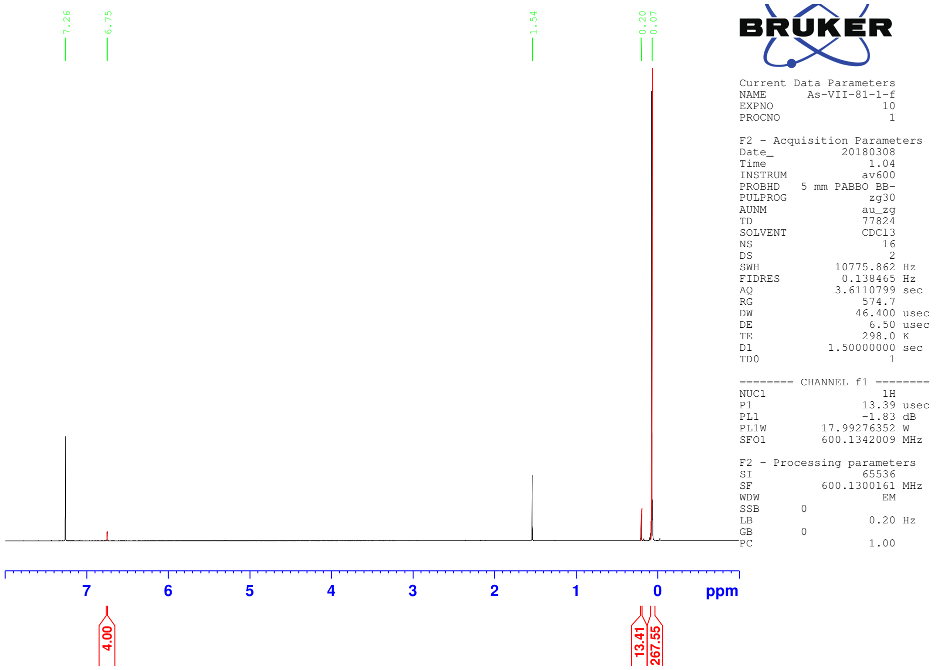
PROBHD   5 mm PABBO BB-
PULPROG               zg30
TD                   77824
SOLVENT              CDCl3
NS                      16
DS                       2
SWH              10775.862 Hz
FIDRES            0.138465 Hz
AQ               3.6110799 sec
RG                   574.7
DW                  46.400 usec
DE                    6.50 usec
TE                   298.0 K
D1              1.50000000 sec
TD0                      1

======== CHANNEL f1 ========
NUC1                    1H
P1                   14.85 usec
PL1                  -2.80 dB
PL1W           14.35890293 W
SFO1           600.1342009 MHz

F2 - Processing parameters
SI                   65536
SF             600.1300166 MHz
WDW                     EM
SSB      0
LB                    0.20 Hz
GB       0
PC                    1.00
```

Figure S4.4 Sample ^{1}H NMR spectrum: 63 % MeOAr-PDMS-ArOMe, 37 % MeOAr-PDMS-OArO-PDMS-ArOMe mixture



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Current Data Parameters
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EXPNO                10
PROCNO                1

F2 - Acquisition Parameters
Date_          20180308
Time               1.04
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PROBHD   5 mm PABBO BB-
PULPROG            zg30
AUNM              au_zg
TD                77824
SOLVENT           CDCl3
NS                   16
DS                    2
SWH           10775.862 Hz
FIDRES         0.138465 Hz
AQ            3.6110799 sec
RG                574.7
DW               46.400 usec
DE                 6.50 usec
TE                298.0 K
D1           1.50000000 sec
TD0                   1

======== CHANNEL f1 ========
NUC1                 1H
P1                13.39 usec
PL1               -1.83 dB
PL1W        17.99276352 W
SFO1        600.1342009 MHz

F2 - Processing parameters
SI                65536
SF          600.1300161 MHz
WDW                  EM
SSB      0
LB                 0.20 Hz
GB       0
PC                 1.00
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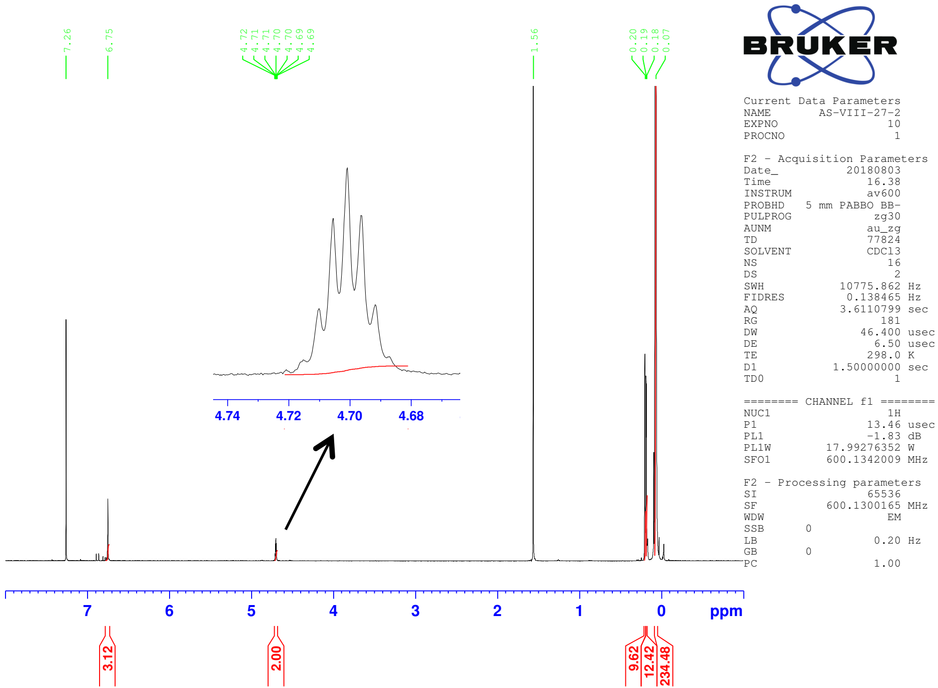
Figure S4.5 Sample ^{1}H NMR spectrum: $C_x(AB)_yC_x$ Block Copolymer entry 10 Table 4.5



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PROCNO                 1

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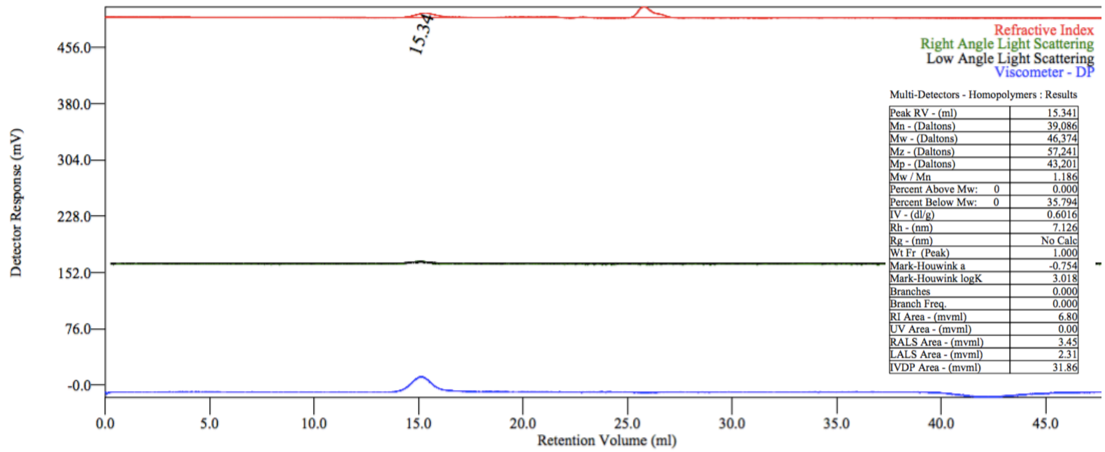
PULPROG             zg30
AUNM               au_zg
TD                 77824
SOLVENT            CDCl3
NS                    16
DS                     2
SWH            10775.862 Hz
FIDRES          0.138465 Hz
AQ             3.6110799 sec
RG                   181
DW                46.400 usec
DE                  6.50 usec
TE                 298.0 K
D1            1.50000000 sec
TD0                    1

======== CHANNEL f1 ========
NUC1                  1H
P1                 13.46 usec
PL1                -1.83 dB
PL1W         17.99276352 W
SFO1         600.1342009 MHz

F2 - Processing parameters
SI                 65536
SF           600.1300165 MHz
WDW                   EM
SSB      0
LB                  0.20 Hz
GB       0
PC                  1.00
```

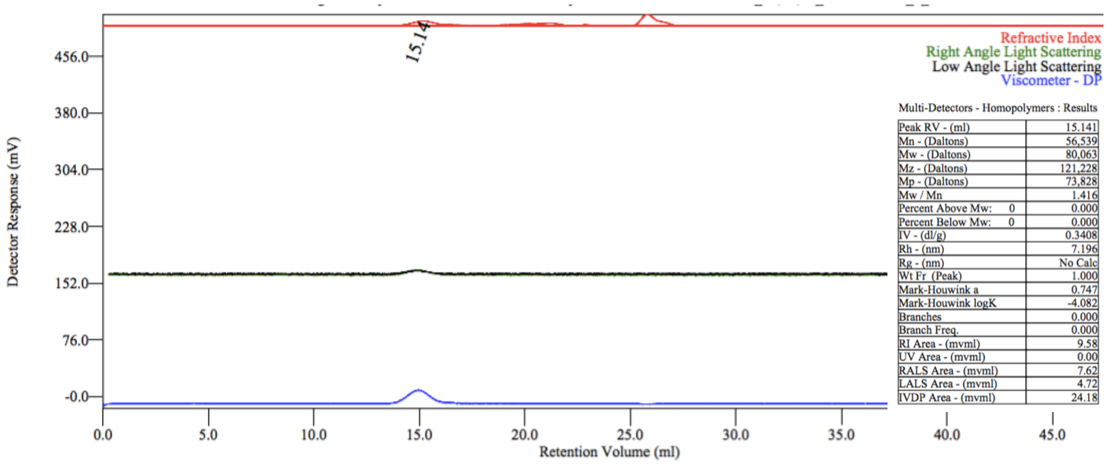
Figure S4.6 Sample ^{1}H NMR spectrum: random copolymer synthesis following 3 hr reaction time (Table S4.7)



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	15.341
Mn - (Daltons)	39,086
Mw - (Daltons)	46,374
Mz - (Daltons)	57,241
Mp - (Daltons)	43,201
Mw / Mn	1.186
Percent Above Mw: 0	0.000
Percent Below Mw: 0	35.794
IV - (dl/g)	0.6016
Rh - (nm)	7.126
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	-0.754
Mark-Houwink logK	3.018
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	6.80
UV Area - (mvml)	0.00
RALS Area - (mvml)	3.45
LALS Area - (mvml)	2.31
IVDP Area - (mvml)	31.86

Figure S4.7 Sample GPC of alternating copolymer, Entry 7 Table 4.5



Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	15.141
Mn - (Daltons)	56,539
Mw - (Daltons)	80,063
Mz - (Daltons)	121,228
Mp - (Daltons)	73,828
Mw / Mn	1.416
Percent Above Mw: 0	0.000
Percent Below Mw: 0	0.000
IV - (dl/g)	0.3408
Rh - (nm)	7.196
Rg - (nm)	No Calc
Wt Fr (Peak)	1.000
Mark-Houwink a	0.747
Mark-Houwink logK	-4.082
Branches	0.000
Branch Freq.	0.000
RI Area - (mvml)	9.58
UV Area - (mvml)	0.00
RALS Area - (mvml)	7.62
LALS Area - (mvml)	4.72
IVDP Area - (mvml)	24.18

Figure S4.8 Sample GPC of $C_x(AB)_yC_x$ Block Copolymer, Entry 10 Table 5 (^{1}H NMR spectrum Figure S4.5).

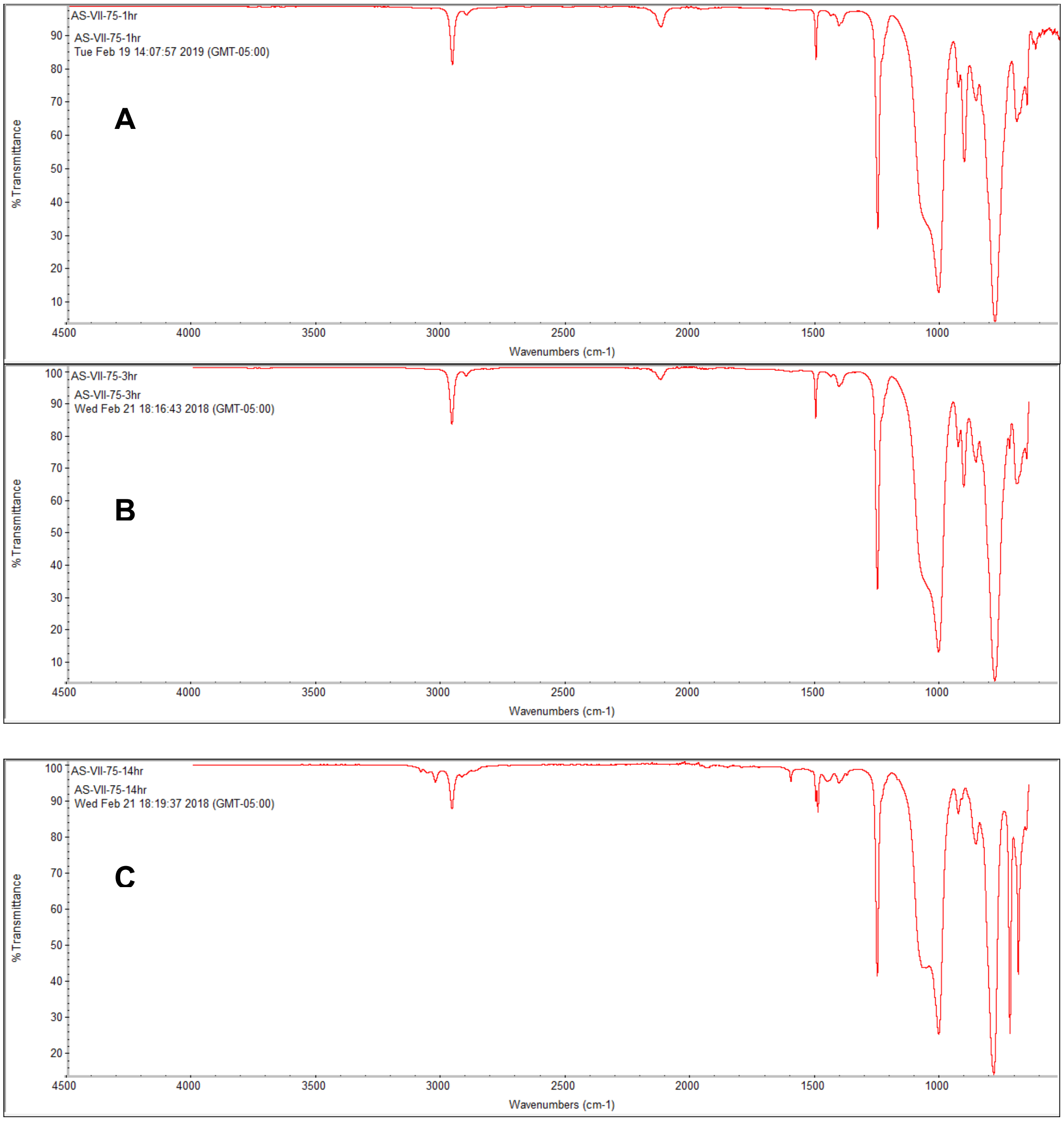


Figure S4.9 Sample FT-IR spectra for samples taken while monitoring chain growth of random copolymer (Figure 4.3B, Table S4.8) – monitoring disappearance of SiH peak around 2100 cm^{-1} after a reaction time of A: 1 hr; B: 3 hr; C: 14 hr.

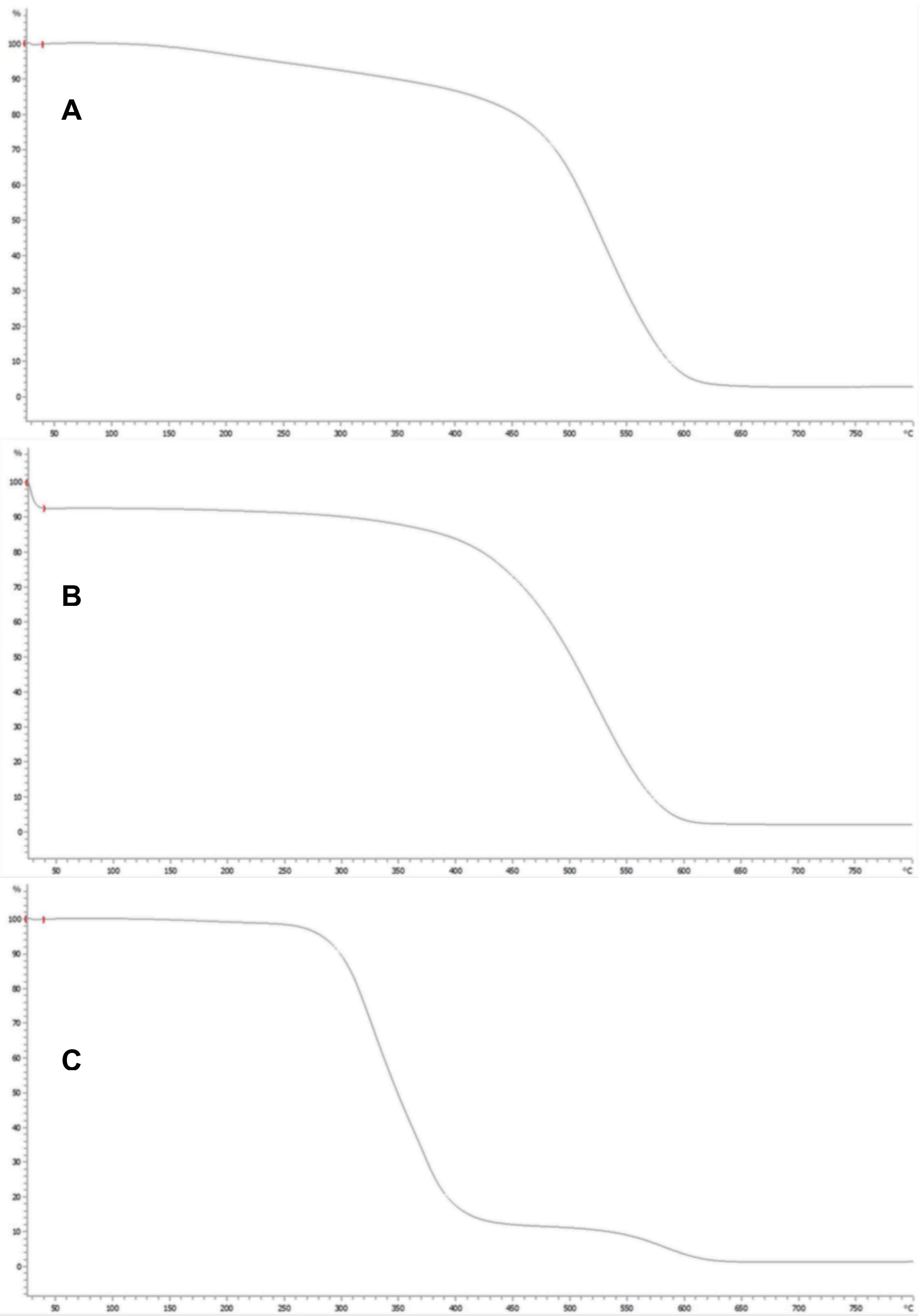


Figure S4.10 TGA data of polymers made from two step versus one step processes compared to aryl free hydroxy-terminated PDMS. A: 2-step $C_x(AB)_yC_x$ triblock copoylmer (entry 16 Table 4.5); B: 1-step random copolymer (entry 25 Table 4.5); C: hydroxy-terminated PDMS (MW 110 kDa).

Chapter 5: Facile Synthesis of Phenyl-Rich Functional Siloxanes[§]

5.1 Abstract

Phenyl-rich silicone polymers have excellent thermal properties and high refractive indices. Traditional methods for the synthesis of phenyl-rich silicone polymers utilize cationic or anionic equilibration, which limits the molecular weights that can be achieved due, in part, to the coproduction of cyclic monomers. Kinetically controlled processes may avoid, in part, these limitations, but require high temperatures, alkyllithium initiators and an inert atmosphere and generally form random copolymers. We report that the Piers-Rubinsztajn reaction allows the formation of ordered, Si-H terminated, phenyl-rich silicone polymers comprised of phenylmethyl, diphenyl and, optionally, dimethylsilicone monomers. The process occurs under very mild conditions and permits a high level of structural control through the formation of alternating copolymers with different levels of phenyl content (Ph/Si = 0.3-1.5) with molecular weights (M_n) up to 88 kDa. Even higher molecular weights were achieved – up to 300 kDa – when phenyl rich siloxanes were incorporated into block copolymers with dimethylsilicones (Ph/Si = 0.4). The refractive index of the most phenyl rich silicone was 1.58, which had a molecular weight of 4 kDa. Unlike most ring-opening polymerizations, where cyclic monomers form at higher

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[§] To be submitted once additional experiments are completed, A.F. Schneider, E. Lu, G. Lu and M.A. Brook (2019). Schneider performed all hydrolysis experiments, various copolymer syntheses and was the lead author of the manuscript. E. Lu performed numerous copolymer syntheses and G. Lu performed copolymer syntheses involving PMS-H03.

conversions, cyclics are formed in these processes near the outset of reaction. Their impact can be reduced by judicious choice of monomers.

5.2 Introduction

Silicones are found in a wide range of applications due to their interesting properties, which include flexibility, thermal stability, electrical resistance, hydrophobicity and biocompatibility, among others. While methylsilicones are the workhorse polymers – almost all silicones are derived from D (Me_2SiO) units – a few functional groups are also found in silicone polymers, including Si-H and Si-vinyl to permit crosslinking by hydrosilylation, and organofunctional alkyl groups ($Si(CH_2)_nX$, n is normally 1, 3 and X = F, Cl, NH_2, OH, polyether…).[1]

Phenylsiloxanes, containing non-methyl substituents, are a special class of silicones derived from phenylsilanes, often starting from D^{Ph} (MePhSiO) and/or P (Ph_2SiO)-containing cyclic monomers.[2] The aromatic group conveys higher thermal stability (and higher T_g) to the already stable silicone chain, although they can suffer from yellowing upon heating. As a consequence of their thermal stability, these types of polymers are often used (in elastomeric form) in LEDs.[3-5] The aromatic groups also convey much higher refractive indices to the polymers, typically 1.5 or higher.[6-9] In describing these polymers below, we will focus on two parameters: M_n and the fraction of phenyl groups to silicon atoms that are present in the polymer, expressed as Ph/Si. For example, Ph/Si = 1 could be achieved with $(PhMeSiO)_n$, or $(Ph_2SiOMe_2SiO)_n$.

Phenylsilicones are traditionally produced using ring-opening polymerization (ROP) of cyclic tri- or tetrasiloxane monomers, catalyzed by a strong base (Figure 5.1) under strictly dry conditions (inert atmosphere). Common monomers include 1,3,5-trimethyl-1,3,5-triphenyl cyclotrisiloxane (D^{Ph}_3), 1,3,5,7-tetramethyl-1,3,5,7-tetraphenyl cyclotetrasiloxane (D^{Ph}_4), or combinations of D^{Ph}_3 or D^{Ph}_4 with hexamethyltrisiloxane (D_3) or octamethyltetrasiloxane (D_4).[2, 10-18] ROP has also been be performed on various combinations of D_3, D_2D^{Ph}, D_4, D_3D^{Ph}, D_4D^{Ph} and/or DD^{Ph}_2 to give random methylphenyl-co-dimethyl siloxane polymers.[2] One restriction associated with ROP is the difficulty in obtaining narrow dispersities due to the issue of back-biting in the chain, a process that is particularly facile in the ROP of P_3.[16] Backbiting shortens the propagating chain and produces cyclic oligomers (Figure 5.1D). That is, while cyclics are the starting monomers, at high conversion new cyclics are generated by backbiting of the living chain end. The equilibrium between linear and cyclic polymers favours the cyclic monomers.[9] Thus, care must be taken to try to maintain kinetic control and reduce backbiting of the living chain to the highest degree possible to limit cyclic formation at the expense of polymer (Figure 5.1D). A variety of ROP syntheses have been reported in the literature and some relevant examples are summarized in Table 5.1. All required strong base initiators and high reaction temperatures. The yields quoted were obtained from the purification methods used to remove cyclics and low MW polymers; large cyclics, which may have remained in the polymer population, were not accounted for.

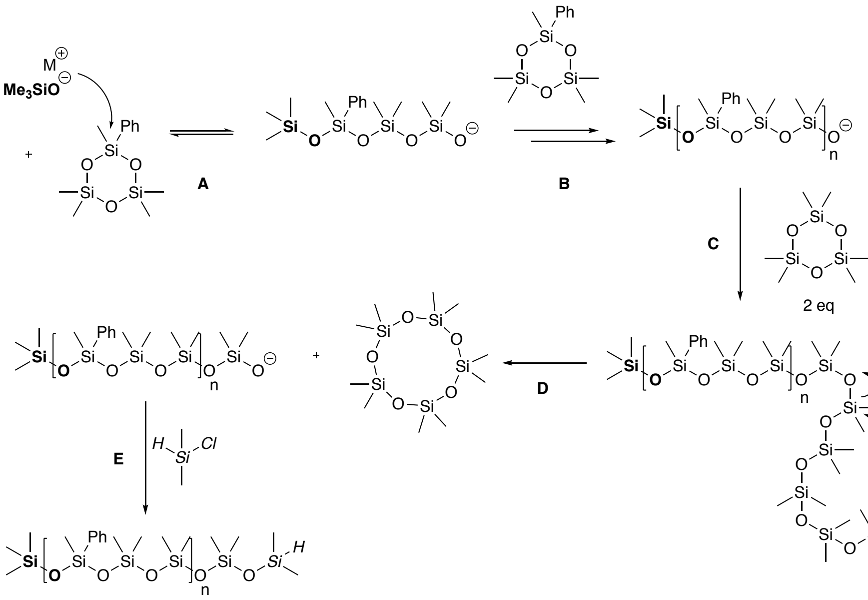

Figure 5.1 ROP of phenyl containing siloxane block copolymers; A) initiation of ring opening polymerization of 1-phenyl-1,3,3,5,5-pentamethylcyclotrisiloxane (D_3^{1Ph}); B) propagation of chain to produce polymer with phenylmethylsiloxy-co-tetramethyldisiloxy polysiloxane block; C) propagation of two equivalents of D_3 to create poly(dimethylsiloxane) block; D) backbiting to release D_5 and shorten the propagating chain; E) termination of the propagating chain

Table 5.1 Summary of ROP methods and results

Initiator (type)	**Purification**	**Reaction Temp (°C)**	**Ph/Si**	**M_n (kDa)**	**Đ_M**	**Yield**	**Reference**
Ring Opening Polymerization							
RMe_2SiO^- $^+NMe_4$	Vacuum at 80 °C then precipitation in MeOH[a]	110	< 0.07	75	~ 3	~80	11
RMe_2SiO^- $^+NMe_4$	Vacuum at 150 °C	80	0.14	20	-[c]	93	12
HO^- $^+NMe_4$	Precipitation in MeOH	85	0.65	10	~3	-	2
			0.38	32	~3	-	
RMe_2SiO^- ^+Li	Precipitation in MeOH	170/190	1.67	48	-	50	10
			1.33	30	-	83	
			0.67	15	-	30	
$(CH_3)_2HC^-$ ^+Na[b]	-	70	1	70	1.7	~80[d]	9
Condensation Polymerization							
[e]	Precipitation in MeOH	60	1	2.4	1.7	23	19
-	Recrystallization with MeOH	RT	1	62	1.4	75	20

[a] Distillation was performed prior to precipitation, % lost from distillation was not reported

[b] 12-crown-4 ethers used to solvate the cation

[c] '–' indicates value was not reported

[d] 20 % cyclics formed

[e] $[RhCl(cod)]_2$ catalysis

Polymer synthesis using mixtures of different monomers lead to randomly distributed phenyl and diphenyl groups along the siloxane backbone.[11-12] A strategy to improve control over the location of phenyl groups along the silicone backbone involved the use of a single type of monomer (e.g., D_2D^{Ph}). The phenyl group is more electron withdrawing than the methyl group on the silicon atom. Therefore, an incoming anion will preferentially attack a phenyl-bearing silicon atom leading, in the case of the monomer D_2D^{Ph}, to polymers in which the phenylsilicon group (generally) appears at every third monomer along the chain (Figure 5.1AB).[2] Perfectly alternating diphenyl-co-dimethyl siloxane copolymers were made using a condensation polymerization[19-21] between diphenylsilandiol and dichlorodimethylsilane in the presence of a secondary amine,[20] or $[RhCl(cod)]_2$ catalyst (Table 5.1).

Although ROP processes are effective for the creation of phenyl rich, high molecular weight siloxanes, they require strong base (or acid) initiators, inert atmospheres, elevated reaction temperatures (> 100 °C) and chlorosilanes as quenching agents.[2, 10, 13] Reactions must be kept dry in particular to avoid the hydrolysis of chlorosilanes (generating HCl).[22] ROP also produces appreciable amounts of cyclic by-products as a result of backbiting and formation of ordered polymers is difficult.[23]

The Piers-Rubinsztajn (PR) reaction is a dehydrocarbonative condensation reaction between a hydrosilane and an alkoxysilane catalyzed by $B(C_6F_5)_3$ to form a siloxane bond and release an alkane byproduct (Figure 5.2A).[24-26] An analogous hydrolysis reaction occurs with water (where water acts in place of the alkoxysilane) to form a silanol (Figure 5.2B) that, in the presence of additional hydrosilanes, will further condense to form a siloxane bond (Figure 5.2C).[27] These processes have been used to make high molecular weight silicones including those containing -PhMeSiO- blocks,[27-28] and alternating copolymers with silphenylene monomers.[29]

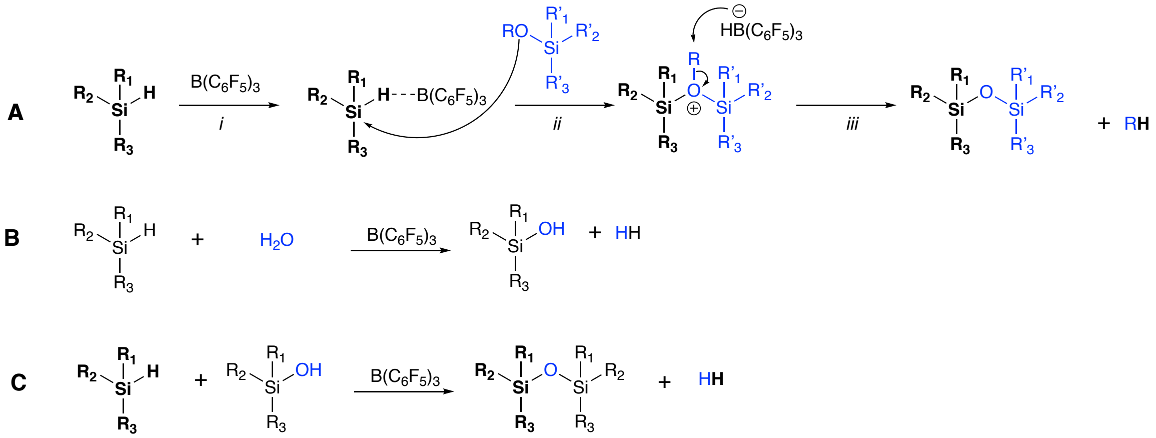

Figure 5.2 $B(C_6F_5)_3$ catalyzed condensation reactions; A) Piers-Rubinsztajn reaction; B) hydrolysis; C) condensation.

We report the facile synthesis of a variety of phenylsiloxane polymers containing high concentrations of phenyl groups in an ordered structure starting directly from silane monomers rather than cyclic siloxane monomers (Figure 5.3). The combination of PR and hydrolysis reactions allowed for selectivity over the precise polymer structure formed and over end group functionality. The process occurs under mild conditions – in some cases open to the atmosphere – and does not require an initiator. The siloxane polymers made were hydride-terminated, which provides synthetic handles for further modification, including the production of block copolymers or elastomers via further hydrolysis, PR or hydrosilylation reactions.

5.3 Experimental

5.3.1 Materials

Tris(pentafluorophenyl)borane was purchased from Sigma-Aldrich; phenylmethylsilane, diphenylsilane, dimethyldimethoxysilane, phenylmethyldimethoxysilane, diphenyldimethoxysilane, 1,1,3,3-tetramethyldisiloxane (M^HM^H), α,ω-hydride-terminated poly(phenylmethyl)siloxane (PMS-H03, $(HMe_2SiOSiPhMe)_2O$, 2-5 centiStokes (cSt.), MW 407 g mol^{-1}), α,ω-hydride-terminated poly(dimethyl)siloxane (H-PDMS-H, 100 cSt, MW 4000 g mol^{-1}) and α,ω-hydroxy-terminated poly(dimethyl)siloxane (HO-PDMS-OH, 35-45 cSt, MW 1328 g mol^{-1}) were purchased from Gelest; reagent grade and HPLC grade toluene were purchased from Caledon (the HPLC grade solvent was dried in an activated alumina column). All compounds were used as received.

5.3.2 Methods

^1H NMR spectra were recorded on a Bruker AV600 MHz spectrometer using deuterated chloroform ($CDCl_3$). Gel permeation chromatography was carried out using one of two different systems. For low molecular weight materials (M_n < 20 kDa), a Waters Alliance GPC System 2695 calibrated with a polystyrene calibration kit S-M-10 (Lot 85) from Polymer Laboratories was used. The system was equipped with a Waters 2414 refractive index detector, a Waters 2996 photodiode array detector, and three Jordi Fluorinated polydivinylbenzene mixed bed columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min. For high molecular weight materials (M_n > 10 kDa), 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 (8mm x 30cm) 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. Fourier Transform Infrared Spectroscopy (FTIR) was carried out on a Nicolet 6700 FTIR in ATR mode using a Smart™ iTX accessory and spectra were processed using Thermo Electron's OMNIC software. Thermogravimetric analysis (TGA) was performed on a

Mettler Toledo TGA 2 thermogravimetric analyzer. Data was collected on samples of < 5 mg, heated in alumina crucibles to 1000 °C under an argon atmosphere (heating rate of 20 °C min^{-1}).

5.3.3 Nomenclature (Figure 5.3)

HOMO: Homopolymers: **PhMe**) poly(phenylmethyl)siloxane and **Ph$_2$**) poly(diphenyl)siloxane.

Co: Alternating copolymers: **1**) poly((bis(phenylmethyldisilox))-*alt*-dimethyldisilox)ane; **2-Me**) poly(methylphenyl-*alt*-dimethyl)siloxane; **2-Ph**) poly(methylphenyl-*alt*-diphenyl)siloxane; **3-Me**) poly(diphenyl-*alt*-dimethyl)siloxane; **3-Ph**) poly(diphenyl-*alt*-methylphenyl)siloxane; **4-Me**) polysiloxane with a 1,1,3,3,5-pentamethyl-5-phenyltrisiloxane repeat unit; **4-Ph**) polysiloxane with a 1,1,3,3-tetramethyl-5,5-diphenyltrisiloxane repeat unit; **5-Me**) polysiloxane with a 1,1,3,5,7,7,9-heptamethyl-3,5,9-triphenylpentasiloxane repeat unit; **5-Ph**) polysiloxane with a 1,1,3,5,7,7-hexamethyl-3,5,9,9-tetraphenylpentasiloxane repeat unit.

5.3.4 Catalyst Stock Solution

Tris(pentafluorophenyl)borane catalyst stock solution was prepared by dissolving $B(C_6F_5)_3$ (20.0 mg, 0.04 mmol), in dry HPLC grade toluene (2.00 mL) to give a 19.5 mM stock solution.

5.3.5 General Polymerization

5.3.5.1 Hydrolysis Reaction General Procedure – reagent amounts in Table 5.2

To a 10 mL round-bottomed flask containing magnetic stir bar was added a silane and, in certain cases, reagent grade toluene. The reaction mixture was allowed to stir at room temperature open to the atmosphere. Following a 15 min mixing time, $B(C_6F_5)_3$ catalyst stock solution and DI H_2O were added to the reaction mixture. After 3 d an additional aliquot of $B(C_6F_5)_3$ catalyst stock solution was added to the reaction mixture. The reaction was left for an additional 4 d, following which a septum was placed on the reaction vessel and a needle inlet was used to supply a N_2 environment. Additional silane (excess) was added to cap the polymer with SiH functionality. Following a 1 h reaction time ^{1}H NMR was taken to ensure SiH end group functionality. Neutral alumina (~ 0.5 g) was added to complex/quench the catalyst. The mixtures were gravity filtered, concentrated under reduced pressure, and purified using kugelrohr distillation at 200 °C for 40 min. Polymer products were viscous oils (with the exception of **HOMO-Ph$_2$**, which was a white solid). Mass loss occurred during kugelrohr distillation as a consequence of loss of cyclic by-products and excess capping agent. GPC (Table 5.4), ^{1}H NMR (Supporting Information, Table S5.7) and TGA (spectra for select samples given in Supporting Information, Figure S5.8 – Figure S5.10) characterization was performed.

Prior to kugelrohr distillation, GC/MS analysis of the polymer mixture showed D^{Ph}_3, D^{Ph}_4, and D^{Ph}_5 present in the sample. After distillation, the concentration of D^{Ph}_3 decreased to almost 0%, the concentration of D^{Ph}_4 decreased slightly while the concentration of D^{Ph}_5 did not appreciably change (see Supporting Information Table S5.5). GC/MS of the distillate showed it to contain mostly D^{Ph}_3 and phenylmethylsilane (capping agent). Therefore, higher MW cyclics could not be removed via kugelrohr distillation and are therefore present in the pure polymer sample and visible in GPC spectra – a GPC spectra of commercial D_5 was compared to the spectra of the polymer mixtures (sample spectra displayed in Supporting Information Figure S5.5 –Figure S5.7, Table S5.6).

Table 5.2 Reagent amounts used in hydrolysis/condensation polymerizations

Entry Table 5.4	Hydrosilane		H_2O	Toluene (mL)	BCF soln (x2)	Capping hydrosilane (total)	Yield[b]
	Type	g (mmol)	µL (mmol)		µL	µL	%
HOMO-PhMe	$MePhSiH_2$	2.00 (16.4)	49 (2.72)	N/A	60	30	62
HOMO-PhMe	$MePhSiH_2$	1.09 (8.93)	20 (1.11)	4 mL	100	20	87
HOMO-Ph$_2$[a]	H_2SiPh_2	0.43 (2.34)	10 (0.55)	3 mL	30	20	66
Co1	PMS-H03	1.00 (2.46)	5 (0.28)	N/A	70	100	37
Co1	PMS-H03	1.47 (3.63)	10 (0.55)	5 mL	80	200	25

[a] Polymer was HOSi-terminated and was a white solid

[b] Recovered from crude during kugelrohr distillation

5.3.5.2 PR Reaction General Procedure – reagent amounts in Table 5.3

To a 100 mL round-bottomed flask containing a magnetic stir bar was added silane and alkoxysilane reagents. The reaction mixture was allowed to stir at room temperature under a N_2 environment. Following a 15 min mixing time, $B(C_6F_5)_3$ catalyst stock solution was added (in 20 µL increments to give a total volume expressed in Table 5.3, ≤ 0.02 mol% to SiH) to the reaction mixture. The reaction was left for 12 h (although reactions were completed within 2 hours) after which ^1H NMR was used to determine end group functionality. In the absence of SiH peak (δ ~ 4.71) and presence of SiOMe peak (δ ~ 3.5) additional (excess) hydrosilane starting material was added to ensure telechelic SiH functional polymer; if SiH was present and SiOMe was absent, no capping step was required/performed. The capping was left for 2 h after which, SiH end group functionality was confirmed by ^{1}H NMR (in the absence of a SiH peak in the ^{1}H NMR, the capping step was repeated). Neutral alumina (~ 0.5 g) was added to complex/quench the catalyst. The mixtures were gravity filtered, concentrated under reduced pressure, and purified using Kugelrohr distillation at 200 °C for 40 min. Low molecular weight capping agent (excess) was removed during rotoevaporation or kugelrohr distillation ($MePhSiH_2$, Ph_2SiH_2, M^HM^H, PMS-H03) and low molecular weight products (including cyclic siloxanes) were removed during the kugelrohr distillation step (expressed as yield). Polymer products were viscous oils. GPC (Table 5.4), ^{1}H NMR (Supporting Information, Table S5.7), IR (spectra for select samples given in Supporting Information, Figure S5.12, Figure S5.13) and TGA (spectra for select samples given in Supporting Information, Figure S5.8, Figure S5.9 and Figure S5.11) characterization was performed.

Table 5.3 Reagent amounts used in PR reaction polymerizations

Entry Table 5.4	Hydrosilane		Alkoxysilane		BCF soln	Capping hydrosilane	Yield[a]
	Type	g (mmol)	Type	g (mmol)	µL	µL	%
HOMO-PhMe	$MePhSiH_2$	2.00 (16.4)	$MePhSi(OMe)_2$	2.98 (16.4)	180	350	99
HOMO-Ph$_2$	Ph_2SiH_2	1.72 (9.44)	$Ph_2Si(OMe)_2$	2.31 (9.44)	300	100	82
Co2-Me	$MePhSiH_2$	2.00 (16.4)	$Me_2Si(OMe)_2$	1.97 (16.4)	100	270	74
Co2-Ph	$MePhSiH_2$	1.18 (9.55)	$Ph_2Si(OMe)_2$	2.33 (9.55)	100	200	90
Co3-Me	Ph_2SiH_2	1.78 (9.66)	$Me_2Si(OMe)_2$	1.16 (9.67)	100	100	89
Co3-Ph	Ph_2SiH_2	1.15 (6.27)	$MePhSi(OMe)_2$	1.14 (6.26)	100	200	88
Co4-Me	M^HM^H	2.00 (14.9)	$MePhSi(OMe)_2$	2.72 (14.9)	160	300	96
Co4-Ph	M^HM^H	1.18 (9.55)	$Ph_2Si(OMe)_2$	2.33 (9.55)	100	100	74
Co5-Me	PMS-H03	2.02 (4.97)	$MePhSi(OMe)_2$	0.90 (4.95)	100	-	59
Co5-Ph	PMS-H03	2.00 (4.93)	$Ph_2Si(OMe)_2$	1.21 (4.95)	100	100	83

[a] Recovered from crude during kugelrohr distillation

5.3.6 PR Synthesis in Toluene – preparation of polymer ***Co5-Me***

To a 20 mL oven-dried vial containing a stir bar was added PMS-H03 (3.02 g, 7.41 mmol) and phenylmethyldimethoxysilane (1.35 g, 7.41 mmol) and HPLC grade toluene (10 mL); the mixture was stirred. To an oven dried 100 mL round-bottomed flask equipped with a magnetic stir bar was added 5 mL of reactant mixture (above) and tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) catalyst solution (100 µL, $1.95x10^{-3}$ mmol). Reaction began immediately, as was evident by visible bubble formation (methane gas evolution). Following a 5 min reaction time, the remaining reagent mixture was added to the round-bottomed flask and vigorous bubbling was observed. After 5 minutes, the bubbling ceased and another aliquot of $B(C_6F_5)_3$ catalyst (100 µL, $1.95x10^{-3}$ mmol) was added to the reaction mixture, no visible change was observed. The reaction was left overnight (~12 h) after which ^{1}H-NMR showed no SiH functional groups. PMS-H03 (200 µL, 0.46 mmol) was added, and mixture was left to react for 3 hours, ^{1}H-NMR still showed no end groups. Another aliquot of PMS-H03 (400 µL, 0.92 mmol) was added and reaction was left for 2 hours, ^{1}H-NMR showed SiH functional groups. Neutral alumina (~0.5 g) was added to the mixture to quench the catalyst and it was allowed to stir for 30 min. The mixture was gravity filtered and concentrated under reduced pressure. The polymer oil was purified by removal of low molecular weight silicones using kugelrohr distillation at 200 °C under vacuum (0.1 mmHg) for 2 h. The final polymer product was a transparent oil. Yield: 0.81g, 38% recovered from crude.

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.67-7.49 (m, 841 H), 7.46-7.30 (m, 878 H), 0.48-(-)0.07 (m, 3347 H); GPC: M_n = 37,268, M_w = 51,921, $Đ_M$ = 1.393; 31% cyclics remaining in polymer sample (by GPC); RI: 1.50.

*5.3.7 Synthesis of α,ω-silanol-terminated poly(phenylmethyl)siloxane (**HOMO-PhMe$_{OH}$**)*

To a 20 mL vial containing a stir bar was added phenylmethylsilane (3 g, 24.54 mmol), phenylmethyldimethoxysilane (4.47 g, 24.54 mmol) and dry toluene (15 mL); the mixture was stirred. To a 100 mL round-bottomed flask equipped with a magnetic stir bar was added the reagent mixture (5 mL) and tris(pentafluorophenyl)borane catalyst solution (100 µL, 1.95x10^{-3} mmol). The reaction vessel was briefly heated with a heat gun (~ 50 °C) to initiate the reaction – visibly indicated by bubble formation. Following a 5 min reaction time more reagent mixture (5 mL) and tris(pentafluorophenyl)borane catalyst solution (100 µL, 1.95x10^{-3} mmol) were added to the round-bottomed flask. Following a

5 min reaction time the remaining regent solution was added to the round-bottomed flask. After 1 h reaction time, ^{1}H-NMR revealed both SiH and SiOMe end groups remained. Additional tris(pentafluorophenyl)borane catalyst solution (40 µL, 7.81x10^{-4} mmol) was added to the reaction vessel and the reaction was left for 2 h. ^{1}H-NMR showed only SiOMe end groups. Therefore, methylphenylsilane (500 µL, 2.91 mmol) was added and reaction was left for 2 h. ^{1}H-NMR showed SiH end groups still remained. The reaction was left for an additional 48 h open to the atmosphere, at which point the ^{1}H-NMR showed no SiH end groups. The reaction mixture was quenched with neutral alumina (~0.5 g), gravity filtered, and concentrated under reduced pressure. The polymer oil was purified by removal of low molecular weight silicones using kugelrohr distillation at 200 °C under vacuum (0.1 mmHg) for 40 minutes. The polymer product was a translucent oil. FTIR analysis showed no SiH peaks (spectrum available in the Supporting Information, Figure S5.14).

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.65-7.27 (m, 15 H), 7.25-7.08 (m, 5 H), 0.58-0.06 (m, 13 H); GPC: $M_n = 4815$, $M_w = 6903$, $Đ_M = 1.434$; RI 1.55.

*5.3.8 PR Synthesis of Polymer **Co4-Ph** for Block Copolymer Synthesis*

To an oven dried 100 mL round-bottomed flask equipped with a magnetic stir bar was added M^HM^H (1.55 g, 11.5 mmol) and phenylmethyldimethoxysilane (1.35 g, 7.41 mmol); the mixture was allowed to stir for 5 min. To the flask was added tris(pentafluorophenyl)borane ($B(C_6F_5)_3$) catalyst solution (100 µL, 1.95x10^{-3} mmol). Reaction began immediately, evident by visible bubble formation (*note: M^HM^H is quite volatile and due to the exothermic nature of the reaction, unreacted starting material can* *easily be boiled off during polymerization*). The reaction was left overnight (~12 h) after which ^{1}H-NMR showed SiOEt functional groups. To the flask was added M^HM^H (200 µL, 1.13 mmol) and reaction was left for 2 h, ^{1}H-NMR still showed the presence of SiOEt functional groups. This process was repeated once more, following which ^{1}H-NMR showed only SiH groups (no SiOEt). Neutral alumina (~0.5 g) was added to mixture to quench the catalyst and mixture was allowed to stir for 30 min. The mixture was gravity filtered and concentrated under reduced pressure. The polymer oil was purified by removal of low molecular weight silicones using kugelrohr distillation at 200 °C under vacuum (0.1 mmHg) for 1 hour. The final polymer product was a transparent oil. Yield: 1.78 g, 78% recovered from crude.

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.59-7.55 (m, 228 H), 7.33-7.31 (m, 125 H), 7.25-7.23 (m, 132 H), 4.74-4.62 (m, 2H), 0.43 (s, 7 H), 0.08-(-)0.09 (m, 850 H); GPC: M_n = 18,744, M_w = 41,947, $Đ_M$ = 2.239; RI: 1.51.

*5.3.9 Hydrolysis of **Co3-Ph***

To a 100 mL round-bottomed flask equipped with a magnetic stir bar was added **Co3-Ph** (synthesized above, 0.30 g, M_n = 1003) and toluene (5 mL); the mixture was allowed to stir for 15 min in 60 °C oil bath. To the reaction mixture was added tris(pentafluorophenyl)borane catalyst solution (50 µL, 9.75×10^{-4} mmol) and DI H_2O (2 µL, 0.11 mmol). The mixture was allowed to stir open to the atmosphere for 3 d (*note: hydrolysis proceeds more quickly when bulk water is added to the reaction mixture*). Neutral alumina (~0.5 g) was added to mixture to quench the catalyst and mixture was allowed to stir for 30 min. The mixture was gravity filtered and concentrated under reduced pressure. The polymer oil was purified by removal of low molecular weight silicones using kugelrohr distillation at 200 °C under vacuum (0.1 mmHg) for 1 hour. The polymer product was a colourless viscous oil.

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.69-7.55 (m, 5 H), 7.52-7.28 (m, 32 H), 7.24-7.11 (m, 16 H), 7.10-6.91 (m, 14 H), 0.50-(-)0.16 (m, 14 H); GPC: M_n = 1069, M_w = 2188, $Đ_M$ = 2.046; IR showed no SiH peak.

5.3.10 Synthesis of Block Copolymers

BLOCK-1: To a 100 mL round-bottomed flask equipped with a magnetic stir bar was added α,ω-silanol terminated poly(phenylmethyl)siloxane (synthesized above, 1.57 g, M_n = 4815), H-PDMS-H (1.30 g, 0.33 mmol) and dry toluene (5 mL); the mixture was allowed to stir for 15 min. To the reaction mixture was added tris(pentafluorophenyl)borane catalyst solution (75 µL, $1.47x10^{-3}$ mmol); it was left for 12 h. The reaction mixture was quenched with neutral alumina (~0.5 g), gravity filtered, and concentrated under reduced pressure. The polymer oil was purified by removal of low molecular weight silicones using kugelrohr distillation at 200 °C under vacuum (0.1 mmHg) for 40 minutes. The polymer product was a very viscous colourless oil. Yield: 1.53 g, 66% recovered from crude.

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.73-7.27 (m, 15 H), 7.25-7.05 (m, 6 H), 0.56-(-)0.04 (m, 64 H); GPC: M_n = 200,635, M_w = 300,435, $Đ_M$ = 1.50; RI: 1.47.

BLOCK-2: To a 100 mL round-bottomed flask equipped with a magnetic stir bar was added **Co4-Ph** (synthesized above, 0.75 g, M_n = 18,744), HO-PDMS-OH (0.54 g, 0.03 mmol) and dry toluene (5 mL); the mixture allowed to stir for 15 min. To the reaction mixture was added tris(pentafluorophenyl)borane catalyst solution (70 µL, 1.37x10^{-3} mmol); it was left for 12 h. IR showed no SiH; therefore, to the reaction mixture was added M^HM^H (200 µL, 1.13 mmol). The reaction mixture was quenched with neutral alumina (~0.5 g), gravity filtered, and concentrated under reduced pressure. The polymer oil was purified by removal of low molecular weight silicones using Kugelrohr distillation at 200 °C under vacuum (0.1 mmHg) for 40 minutes. Polymer product was a viscous translucent oil. Yield: 0.50 g, 91 % recovered from crude.

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.58-7.55 (m, 107 H), 7.33-7.31 (m, 60 H), 7.25-7.23 (m, 80 H), 4.72-4.69 (m, 2 H), 0.07 (s, 2118 H), (-)0.03 (s, 283 H); GPC: M_n = 108,454, M_w = 124,580, $Đ_M$ = 1.149, 2% cyclics; RI: 1.46.

5.4 Results

A variety of phenyl-containing silicone homopolymers and copolymers were synthesized from hydrosilane starting materials using both the PR reaction (with alkoxysilanes) and hydrolysis/condensation (and/or condensation with pre-hydrolyzed silicones); in all cases catalyzed by $B(C_6F_5)_3$ (Figure 5.3). Hydrolysis was performed either neat or in toluene (Table 5.2, Figure 5.3 **HOMO-PhMe, HOMO-Ph$_2$** and **Co1**). Both methods involved combining hydrosilane starting material, catalyst and a molar deficit of bulk water (<25 mol%). SiH functional groups are able to react with available water to give SiOH + H_2 (Figure 5.2B). However, since a deficit of water was present, as silanols formed they competitively condensed with remaining SiH – a faster process than hydrolysis – to form a chain-extending siloxane bond, releasing H_2 in the process (Figure 5.2C). *Note: these processes typically involve the formation of flammable gases and* *appropriate care must be taken both to avoid pressure buildup, and to manage the flammable products, especially when reaction scaled is increased*. The reaction vessel was left open to allow atmospheric moisture to enter the system at a (low) rate that allows slow growth of the polymer rather than induce premature termination of the polymerization, which occurs when all SiH groups are converted to SiOH groups; this method was previously demonstrated to promote more efficient chain extension when compared to just adding a molar equivalent (to SiH) of bulk water at the outset of the reaction (a quicker, but less efficient, hydrolysis/condensation method, data not shown) .[27] In order to ensure the presence of SiH end groups in the product polymers, the silanol terminated polymers were capped with dihydrosilane starting material in the same vessel at the end of the process (Figure 5.2B). For the most part, no additional catalyst was required to elicit the capping step. GPC and RI data is given in Table 5.4.

This hydrolysis/condensation process was used to make poly(phenylmethyl)siloxane homopolymer, **HOMO-PhMe**. Attempts to make the analogous poly(diphenyl)siloxane, **HOMO-Ph$_2$,** led instead to very small oligomers (the PR synthesis of this polymer was similarly inefficient, Figure 5.3). Note that synthesis of the oligo(diphenyl)siloxanes using the hydrolysis method required use of toluene solvent – diphenylsilicones of even low molecular weight readily precipitate (Table 5.4). Copolymers with a Ph/Si of 0.5 were prepared in reasonable molecular weight through hydrolysis/condensation of a single polymeric monomer containing both dimethylsilyl and phenylmethylsilyl units (**Co1**). The major benefit of this reaction is simplicity, only one silicone monomer was used and the reaction can be left open to the atmosphere; the downfall is long polymerization times – preparation of high MW polymers via the hydrolysis/condensation method take approximately one week.

Homopolymers or alternating phenylsilicone copolymers could also be prepared using the PR process (Figure 5.3, Table 5.4). The phenyl rich regions of the copolymers were sourced both from the hydrosilane and from the alkoxysilane monomers. Reactions typically proceeded effectively at room temperature, however, in some cases heat was required to initiate a reaction (50 °C). Reactions were typically performed neat, with the exception of two PR reactions which were performed in toluene (a second polymer **Co5-Me** and **HOMO-PhMe$_{\mathbf{OH}}$**, see experimental). Reactions diluted in toluene were performed to confirm the hypothesis that reaction solvation would result in greater cyclic formation – GPC analysis confirmed this. For example, synthesis of **Co5-Me** neat produced 22% cyclics where the same polymerization in toluene produced 31% cyclics. The benefit of the PR reaction is that it proceeds quickly (within hours or less) and a variety of polymers with ordered structures can be easily created. In contrast to typical PR methods, these PR reactions were performed under dry conditions – in a N_2 environment and the reagents were stored over sieves – to avoid any secondary hydrolysis processes, which would disrupt the ordered alternating copolymer structure.

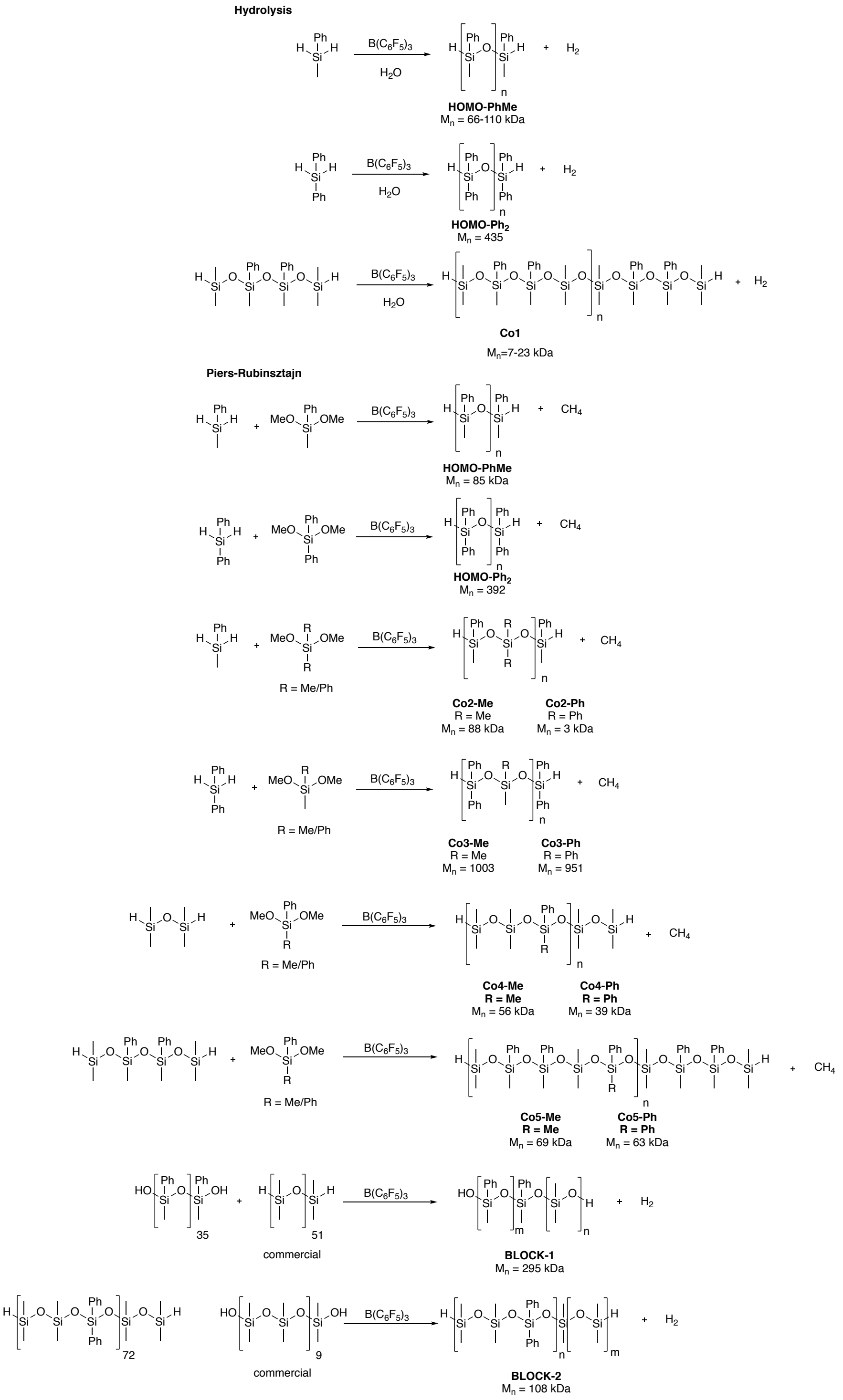

Figure 5.3 Phenylsiloxane synthesis reactions via hydrolysis/condensation reaction and the PR reaction – homopolymers (HOMO series), alternating copolymers (Co series) and block copolymers (BLOCK series)

Table 5.4 GPC data and RI for all phenylsiloxane polymers synthesized (Figure 5.3)

Polymer, (R in Figure 5.3)	Method[a]	Solvent	Ph/Si	n value[b]	M_n (kDa)	M_w (kDa)	$Đ_M$	RI	cyclic (%)[c]
	Hydrolysis								
HOMO-PhMe	H	Neat	1	482	66	76	1.17	1.55	24
HOMO-PhMe	H	Toluene	1	811	110	114	1.03	1.55	29
HOMO-Ph_2	H	Toluene	2	2	0.4	0.5	1.49	-	-
Co1	H	Neat	0.5	56	23	38	1.66	1.49	29
Co1	H	Toluene	0.5	18	7	9	1.28	1.49	46
	Piers-Rubinsztajn								
HOMO-PhMe	PR	Neat	1	622	85	92	1.08	1.55	24
HOMO-Ph_2	PR	Toluene	2	2	0.4	0.5	1.35	-	-
Co2-Me	PR	Neat	0.5	419	88	170	1.93	1.51	19
Co2-Ph	PR	Neat	1.5	8	3	4	1.38	1.58	-
Co3-Me	PR	Neat	1	3	1	2	1.72	1.57	-
Co3-Ph	PR	Neat	1.5	3	1	2	1.99	1.59	-
Co4-Me	PR	Neat	0.33	207	56	235	4.18	1.47	25
Co4-Ph	PR	Neat	0.67	116	39	165	4.24	1.52	6
Co5-Me	PR	Neat	0.6	128	69	147	2.12	1.50	22
Co5-Ph	PR	Neat	0.8	104	63	297	4.72	1.53	19
	PR – Block Copolymers								
BLOCK-1	PR	Toluene	0.41	-	295	322	1.09	1.47	0[d]
BLOCK-2	PR	Toluene	0.41	-	108	125	1.15	1.46	2

[a] H – hydrolysis; PR – Piers Rubinsztajn

[b] n value calculated using M_n from GPC data

[c] percent of 4 and 5 membered cyclics (phenyl analogs of D_4 and D_5) and low MW polymers unable to be removed (using kugelrohr distillation) in polymer sample; values not reported in low MW samples due to overlap between cyclic peak and polymer peak

[d] no cyclic peak was observed in GPC.

Block copolymers were prepared using the PR reaction between phenyl rich siloxanes synthesized here and commercially available poly(dimethyl)siloxanes. Silanol-terminated poly(phenylmethyl)siloxane **HOMO-PhMe$_{OH}$** (M_n = 4815) readily copolymerized with commercial H-PDMS-H (MW=4000) to give a block copolymer of M_n = 295 kDa. A phenyl rich hydride-terminated polysiloxane (**Co4-Ph**, M_n = 18,744) was copolymerized with commercial HO-PDMS-OH (MW=1328) to give a block copolymer of M_n = 108 kDa. Note that, in these cases, no cyclics were created confirming that the backbiting which typically occurs in traditional ROP reactions or equilibration reactions is not occurring here.

5.5 Discussion

PR and hydrolysis/condensation polymerizations catalyzed by $B(C_6F_5)_3$ allow the formation of a broad range of architectures and highly ordered alternating structures; such polymers are impossible to make using either the traditional hydrolysis or ring-opening polymerization processes of commercial monomers. Both produced phenyl rich polysiloxanes under milder conditions than ROP or condensation polymerization and both allowed selection of end group functionality on the polymer chain (H or OH in hydrolysis, and H or OMe in the PR reaction). We focussed on the preparation of hydride-terminated polymers because of the broad utility of this functional group for further elaboration.

*5.5.1 Hydrolysis/Condensation vs PR Reaction for Synthesis of Homopolymers (**HOMO**-series)*

$B(C_6F_5)_3$-catalyzed reactions (PR and hydrolysis) were both successfully used to synthesize hydride-terminated poly(phenylmethyl)siloxane homopolymers (**HOMO-PhMe**, Figure 5.3). Both methods produced polymers of similar molecular weights and low dispersities. While the origins of the low dispersity are currently unclear, they signal reaction processes that are not pure step growth, which would normally lead to dispersities of 2 in the best case.[30]

The hydrolysis method is simple, but time consuming. The PR reaction is much faster; polymer products can be recovered from starting materials in under a day (compared to hydrolysis which could take up to a week). Polymers produced using the PR method had higher yields and led to products that contained lower concentrations of cyclics than the hydrolysis method (higher yields indicated a smaller fraction containing monomers and small cyclics, that was removed by distillation, Table 5.2 and Table 5.3).

In typical ROP reaction, the reactions start with cyclics and, in addition to polymerization, cyclic formation occurs later in the polymerization due both to backbiting and chain redistribution.[1] In the $B(C_6F_5)_3$ catalyzed reactions described here, cyclic formation is a result of condensation between monomers and/or oligomers in early stages of the polymerization before the chain length gets to $\sim(SiO)_5$ – dilution enhances the cyclization process. During hydrolysis, cyclics can be formed via numerous routes. For example, a cyclotetrasiloxane can be prepared through condensation of a monomer and trimer, or two dimers, or 4 monomers, etc., and the SiH and SiOH can be sourced from any material; a variety of other sized cyclics can be easily formed – D^{Ph}_3, D^{Ph}_5 (Figure 5.4). As a consequence, higher fractions of cyclics accompanied the hydrolysis method (vs PR).

In literature syntheses of phenylsilicones, cyclic byproducts were "removed" during polymer precipitation[2, 10-11, 19-20] or during distillation, but the quantities of cyclics were not reported.[11-12] Our purification method involved removal of unreacted monomer, low

MW polymers and (some) cyclic byproducts by kugelrohr distillation at 200 °C. GC/MS analysis of the distillate obtained from purification of HOMO-PhMe confirmed the presence of monomer and D^{Ph}_3, and some other low MW byproducts. Comparison of the crude and purified polymer samples confirmed that D^{Ph}_4 and D^{Ph}_5 were also present in both samples (Table S5.5). The removal of higher MW cyclics by distillation was unsuccessful. In the GPC spectra a small peak appeared at much higher retention volumes (~21.9 mL) than the majority polymer population – this was inferred to be larger cyclics that remained after distillation (Figure S5.5, Figure S5.6). Evidence to support this came from the GC/MS analysis of purified polymers (Table S5.5) and comparison of GPC high retention volume peak to GPC spectrum of D_5 (Figure S5.7). The cyclic concentrations reported (Table 5.4) correspond to relative integration of the small GPC peaks (~ 21.9 mL retention time) to the majority polymer population peak (Table S5.6).

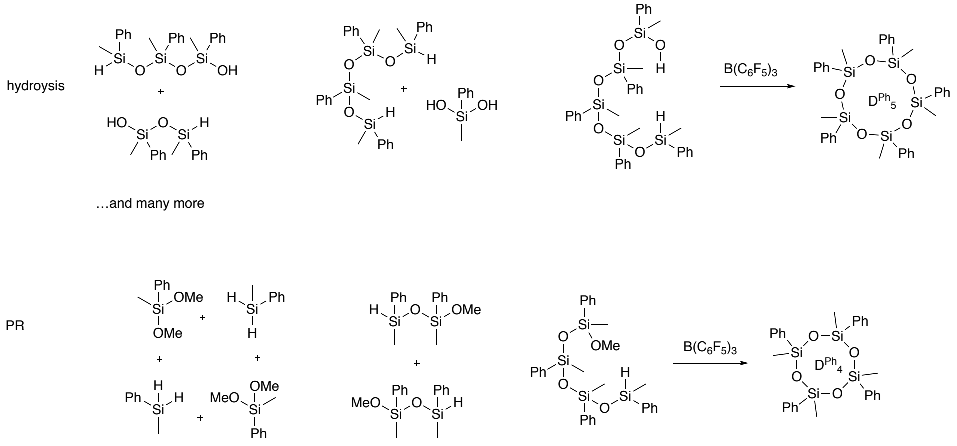

Figure 5.4 Putative evolution of cyclics during hydrolysis/condensation and the PR reaction

A major benefit of the hydrolysis reaction is simplicity; no stringently dry conditions are required - the reaction is left open to the atmosphere. The hydrolysis reaction is relatively slow. This can be beneficial as, in the case of the PR reaction, exothermic gas evolution can (too) quickly occur following catalyst addition. Sudden pressure increases are possible and, for safety reasons, *it is suggested to add the catalyst in small increments*.

5.5.2 Hydrosilane Starting Material Sterics and Ph Concentration Influence Polymer Molecular Weight

Two factors were most important in maximizing the overall molecular weight of polymers that could be obtained: steric bulk about the hydrosilane; and the use of high concentrations, preferably neat. The less bulky the hydrosilane starting material, the higher was the molecular weight of the obtained polymers. Synthesis of diphenylsiloxane monomers via hydrolysis or the PR reaction did not proceed to very high chain lengths – only dimers and trimers were formed. At the onset of polymerization, SiH must first coordinate to $B(C_6F_5)_3$. The 3 fluorinated aromatic rings in $B(C_6F_5)_3$ constrain access to boron. Once the Ph_2SiH_2-$B(C_6F_5)_3$ complex can form, its decomposition by nucleophilic attack of water should be facile because of water's small size, but decomposition of the complex by nucleophilic attack by Ph_2SiHOH will be sterically disfavoured (Figure 5.2C). Thus, polymerization will be slow. More importantly, intramolecular cyclization of an activated D^{Ph2}_3 species will outcompete intermolecular chain extension leading to cyclics.

Polymers **Co3-Me** and **Co3-Ph** also used bulky diphenylsilane as the hydrosilane starting material – chain extension here was not impressive (M_n = 1 kDa). It is suspected that same steric restrains that hinder poly(diphenyl)siloxane production (above) were also at work here.

Further reducing the steric bulk about the hydrosilane worked to produce polymers of higher molecular weight, as seen by comparing polymers **Co2-Ph** and **Co3-Ph**. Both polymers have the same repeat unit but the syntheses utilized were different – $PhMeSiH_2$ vs Ph_2SiH_2 were used as starting material hydrosilanes, respectively. The combination of $PhMeSiH_2$ + $Ph_2Si(OMe)_2$ led to polymers of slightly higher molecular weight (M_n = 3 kDa) than that of Ph_2SiH_2 + $PhMeSi(OMe)_2$ (M_n = 1 kDa).

Series **Co4** and **Co5** were prepared from unhindered hydrosilane starting materials – M^HM^H, and PMS-H03. Polymers produced using the PR reaction between these hydrosilanes and either $PhMeSi(OMe)_2$ or $Ph_2Si(OMe)_2$ had M_n of 40-70 kDa; molecular weights can be controlled by stoichiometric matching of monomer starting materials. Steric pressure of phenyl substituted silicon atoms in the growing silicone chains could also restrict chain extension.

5.5.3 Further Modification of Prepared Phenylsiloxanes

The silicones prepared using these methods can be further elaborated. The terminal SiOH, SiH, SiOR groups can be capped to give unreactive polymers, for example, by use of monofunctional compounds like $HSiMe_2OSiMe_3$ (+ polymerOH → polymer$SiOSiMe_2OSiMe_3$). Otherwise, the groups can be used for additional chain extension by the PR reaction. For example, a block copolymer containing phenylmethylsiloxane and dimethylsiloxane units was prepared by polycondensation of polymer **HOMO-PhMe$_{OH}$** (silanol-terminated poly(phenylmethyl)siloxane) and commercial H-PDMS-H. Both starting materials were of fairly low M_n (6 kDa and 4 kDa, respectively), but a block copolymer of M_n = 295 kDa was readily prepared. Note that in these latter processes there is no viable mechanism for cyclic formation from small molecules, and no viable mechanism for degradation by backbiting – these are not equilibration reactions.

Previous methods to synthesize phenyl-rich polysiloxanes utilized ROP of mixtures of cyclic monomers. Despite the commercial availability of certain phenyl containing cyclic monomers ($D^{Ph}{}_3$, D_3D^{Ph}, $D_2D^{Ph}{}_2$, $D^{Ph}{}_4$, and P_4 and $D^{Ph}{}_5$), most groups reported synthesis of cyclic monomers using a condensation process of chlorosilanes.[2, 10-11, 14, 16] The PR reaction avoids use of any chlorosilanes (condensation polymerization) or strong base initiators (ROP). Although the PR reaction does require a boron catalyst, the amount used is extremely low (<0.02 mol%). Also the hydrolysis and PR methods ensure strict order structure in the polymer product, unlike some of the previous synthetic methods discussed above.[2, 11]

Although water can participate in PR reactions, alkoxysilanes are much more reactive and therefore stringently dry conditions are not always necessary when using the PR reaction (in contrast to ROP). Furthermore, the PR reaction allows simple capping of the polymer end groups with hydrosilanes to ensure SiH terminated polymers. Polymers synthesized using hydrolysis naturally possessed SiOH end groups – PR capping with hydrosilane was used to produce SiH terminated polymers. SiH end groups allows the PR reaction or hydrosilylation to be performed on the polymers to produce block copolymers (**BLOCK-2**) or elastomers.

5.6 Conclusion

$B(C_6F_5)_3$-catalyzed PR and hydrolysis reactions are effective methods to produce phenyl-substituted polymethylsiloxanes with high phenyl content and Mw = 2-300 kDa (polymers contained up to 811 repeat units). The ready availability of a variety of silane monomers and silicone macromonomers lead to the ready synthesis of structurally ordered polymers with high phenyl content (Ph/Si up to 1.5) and RI up to 1.58 The PR reaction proved to be superior to the hydrolysis method in avoiding cyclic phenyl siloxane formation. As is commonly observed, Ph_2SiO monomers were difficult to incorporate because they lead to increased melting points.

5.7 Acknowledgments

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S5.9 Appendix 4 – Supporting Information

Table S5.5 Cyclic concentration (from GC/MS) analysis in polymer **HOMO-PhMe**

	Before Kugelrohr (mg mL^{-1})	After Kugelrohr (mg mL^{-1})
D^{Ph}_3	1.36	0.19
D^{Ph}_4	3.64	2.47
D^{Ph}_5	2.59	2.35
%[a] D^{Ph}_3 - D^{Ph}_5	28 %	12 %

[a] This is a very rough estimate

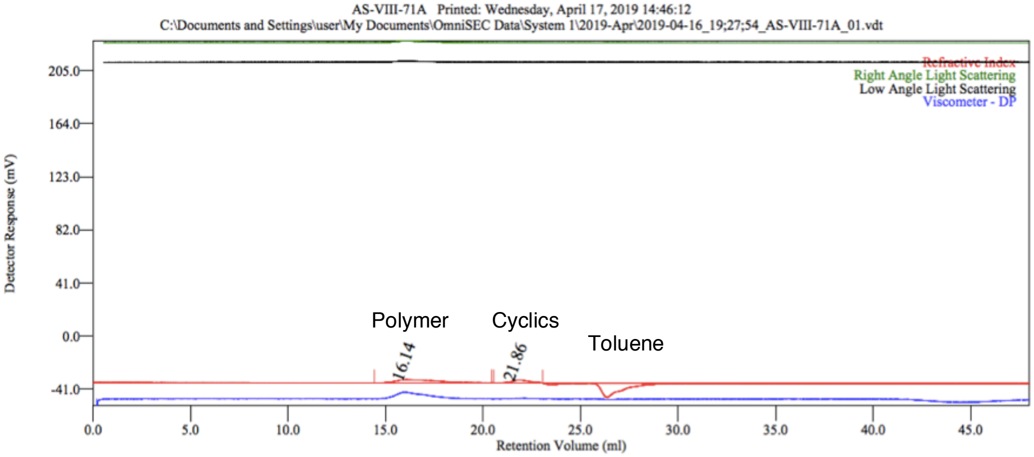

Figure S5.5 GPC spectrum of polymer **HOMO-PhMe**

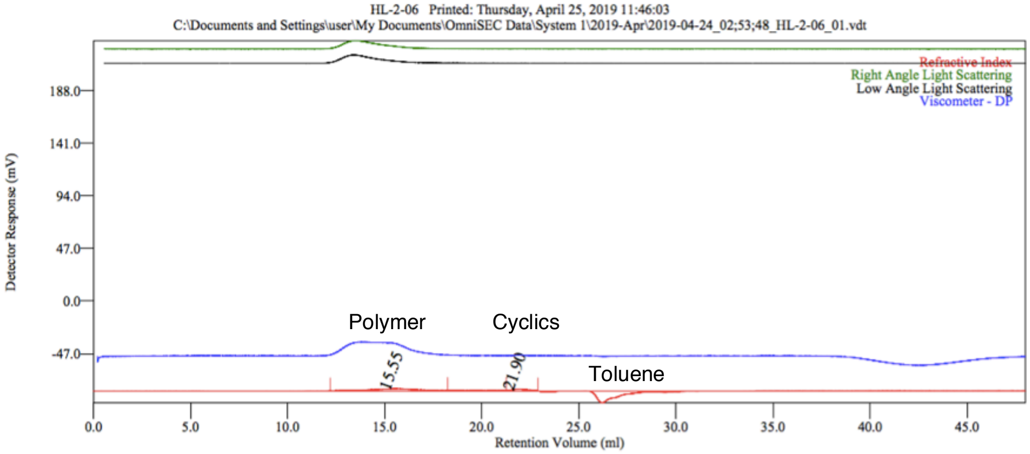

Figure S5.6 GPC spectrum of polymer **Co5-Ph**

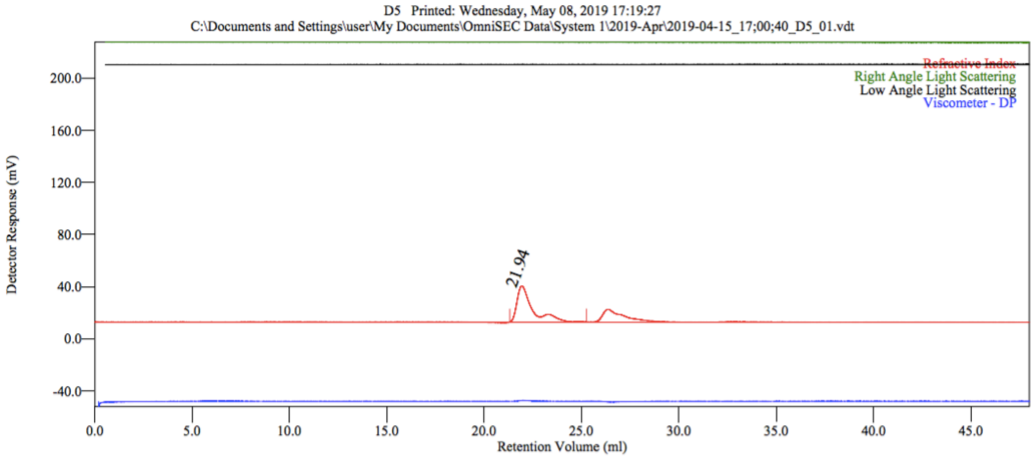

Figure S5.7 GPC spectrum of D_5

Table S5.6 Sample GPC data showing weight percent cyclics for polymer **HOMO-PhMe** (Figure S5.5)

Multi-Detectors - Homopolymers : Results

Peak RV - (ml)	16.141	21.859
Mn - (Daltons)	110,479	1
Mw - (Daltons)	114,101	1
Mz - (Daltons)	117,930	1
Mp - (Daltons)	142,514	1
Mw / Mn	1.033	1.000
Percent Above Mw: 0	0.000	0.000
Percent Below Mw: 0	21.392	100.000
IV - (dl/g)	0.1507	1.0000
Rh - (nm)	6.223	1.000
Rg - (nm)	80.148	No Calc
Wt Fr (Peak)	0.714	0.286
Mark-Houwink a	0.852	0.000
Mark-Houwink logK	-5.131	0.000
Branches	0.000	0.000
Branch Freq.	0.000	0.000
RI Area - (mvml)	6.63	2.65
UV Area - (mvml)	0.00	0.00
RALS Area - (mvml)	2.66	0.08
LALS Area - (mvml)	2.55	0.36
IVDP Area - (mvml)	13.49	2.09

Table S5.7 ^{1}H NMR data for siloxane polymers

Entry Table 5.4	^{1}H NMR ($CDCl_3$, 600 MHz, δ)	SiH in IR
HOMO-PhMe	7.63-7.27 (m, 804 H), 7.25-7.06 (m, 591 H), 4.34 (q, 2 H, *J*=4.3 Hz), 0.50-(-)0.06 (m, 847 H)	Yes
HOMO-Ph$_2$	7.52 (d, 2 H, *J*=7.1 Hz), 7.52 (d, 2 H, *J*=6.0 Hz), 7.33-7.16 (m, 12 H).	No
Co1	7.74-7.28 (m, 898 H), 4.79-4.64 (m, 2 H), 0.57-(-)0.08 (m, 1718 H)	Yes
Co1	7.57-7.47 (m, 192 H), 7.36-7.27 (s, 189 H), 4.78-4.70 (m, 2 H), 0.31-0.21 (m, 250 H), 0.08-(-)0.08 (m, 610 H)	Yes
Co2-Me	7.60-7.37 (m, 250 H), 7.35-7.28 (m, 155 H), 7.25-7.09 (m, 155 H), 5.16-5.12 (m, 2 H), 0.51-0.11 (m, 368 H), 0.10-(-)0.15 (m, 511 H)	Yes
Co2-Ph	7.67-7.29 (m, 218 H), 7.24-6.93 (m, 181 H), 5.11-5.04 (m, 2 H), 0.52-(-)0.11 (m, 91 H)	Yes
Co3-Me	7.64-7.27 (m, 42 H), 7.25-7.15 (m, 10 H), 5.52-5.32 (m, 2 H), 0.11-(-)0.03 (m, 22 H)	Yes
Co3-Ph	7.68-7.27 (m, 85 H), 7.22-7.07 (m, 34 H), 5.60-5.41 (m, 2H), 0.55-(-)0.03 (m, 39 H)	Yes
Co4-Me	7.66-7.29 (m, 131 H), 4.72-4.67 (m, 2 H), 0.50-(-)0.02 (m, 470 H); transparent (top) layer had one signal: 0.07 (s, $SiMe_2$)	Yes
Co4-Ph	7.61-7.56 (m, 1228 H), 7.36-7.34 (m, 652 H), 7.30-7.25 (m, 1228 H), 4.69-4.66 (m, 2H), 0.09-(-)0.12 (m, 3958 H)	Yes
Co5-Me	7.56-7.28 (m, 1545 H), 7.25-7.18 (m, 450 H), 4.63 (m, 2H), 0.49-(-)0.06 (m, 3892 H)	Yes
Co5-Ph	7.67-7.37 (m, 10 H), 7.35-7.28 (m, 5H), 7.24-7.15 (m, 6 H), 0.35-(-)0.08 (m, 21 H)	No[a]

[a] The polymer was translucent and no SiH groups were observed

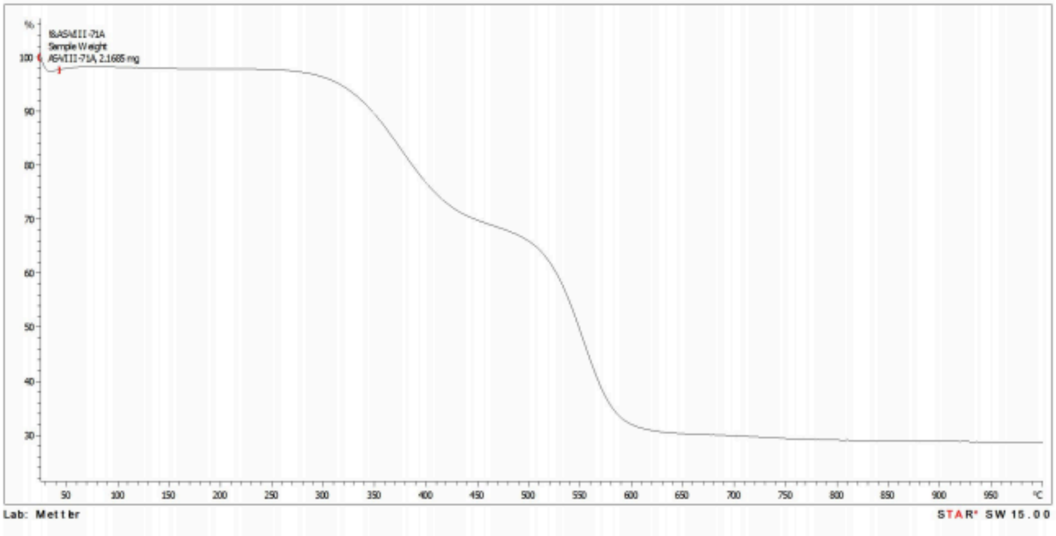

Figure S5.8 TGA for polymer **HOMO-PhMe** (Figure 5.3, Table 5.4)

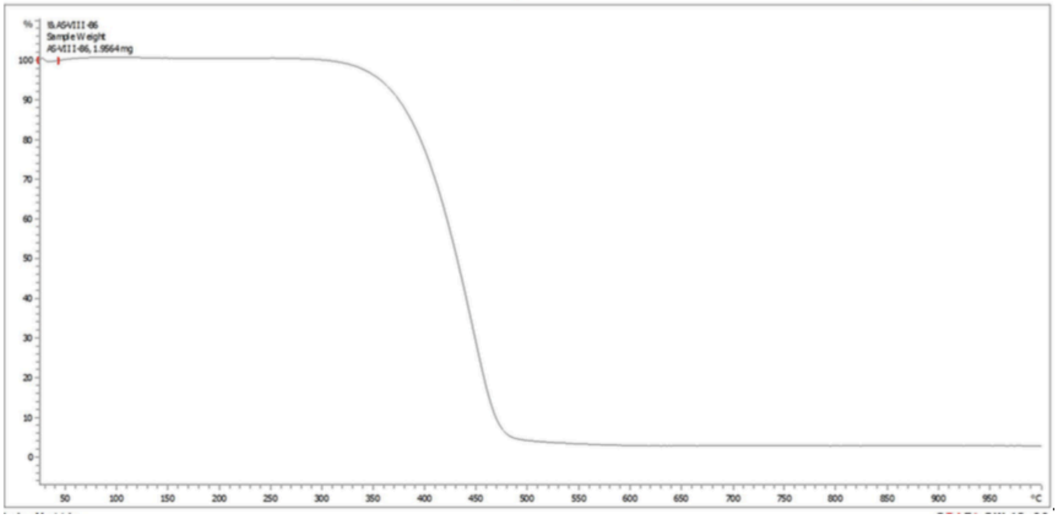

Figure S5.9 TGA data for polymer **HOMO-Ph$_2$** (Figure 5.3, Table 5.4)

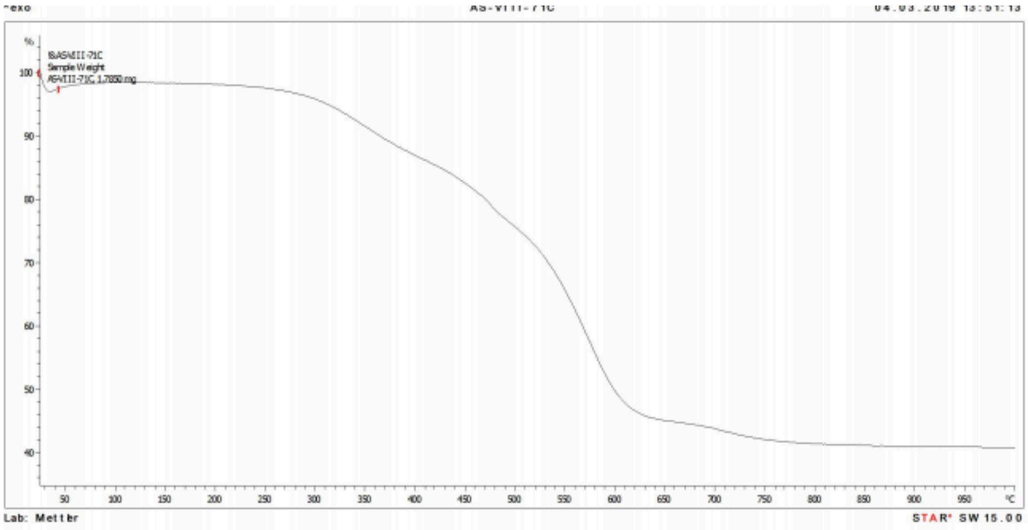

Figure S5.10 TGA for polymer **Co1** (Figure 5.3,Table 5.4)

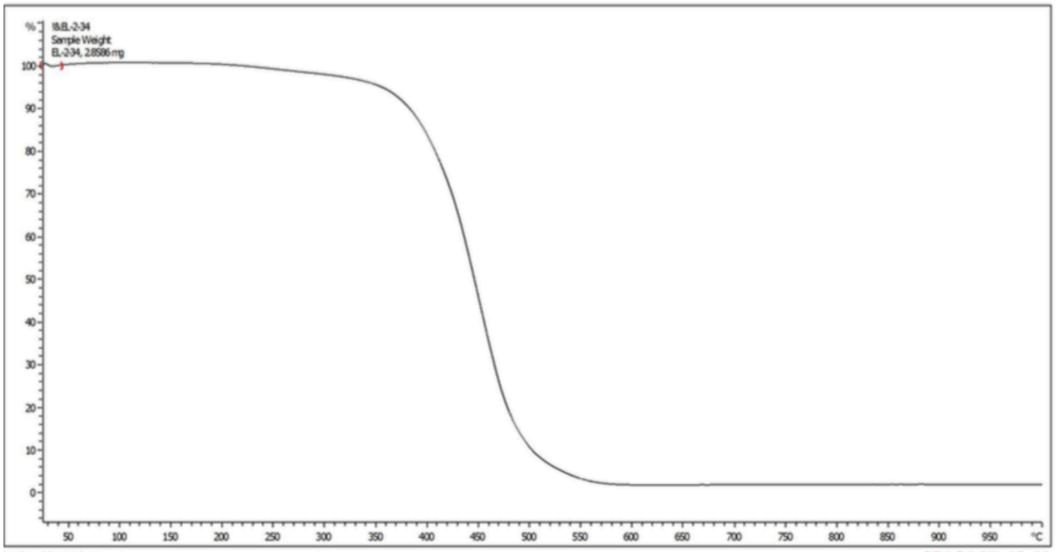

Figure S5.11 TGA for polymer **Co4-Ph** (Figure 5.3,Table 5.4)

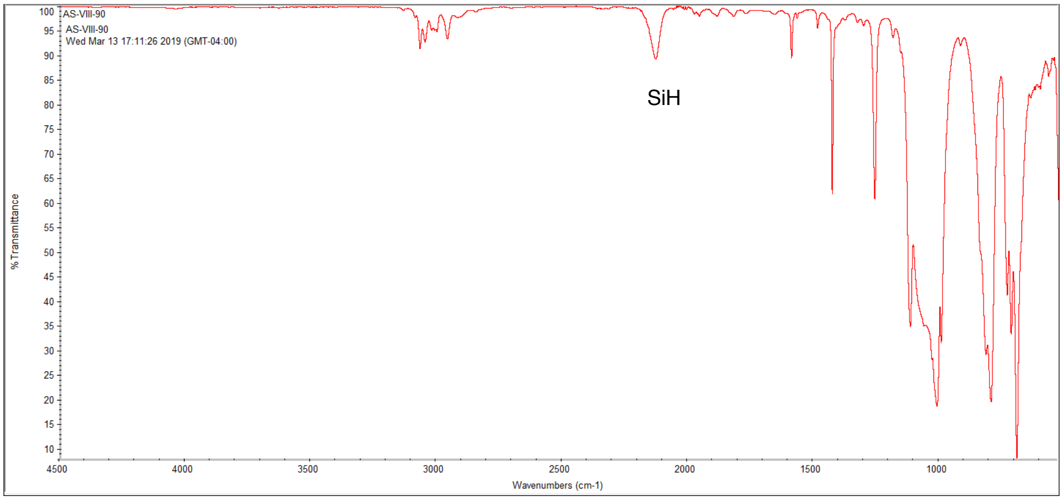

Figure S5.12 Sample IR spectrum for polymer **Co3-Me** (Figure 5.3,Table 5.4)

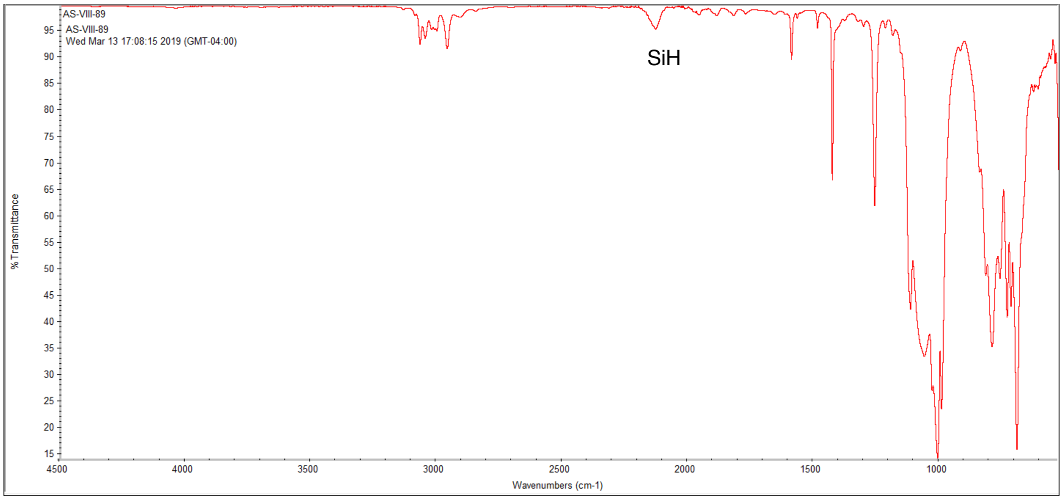

Figure S5.13 Sample IR spectrum for polymer **Co3-Ph** (Figure 5.3,Table 5.4)

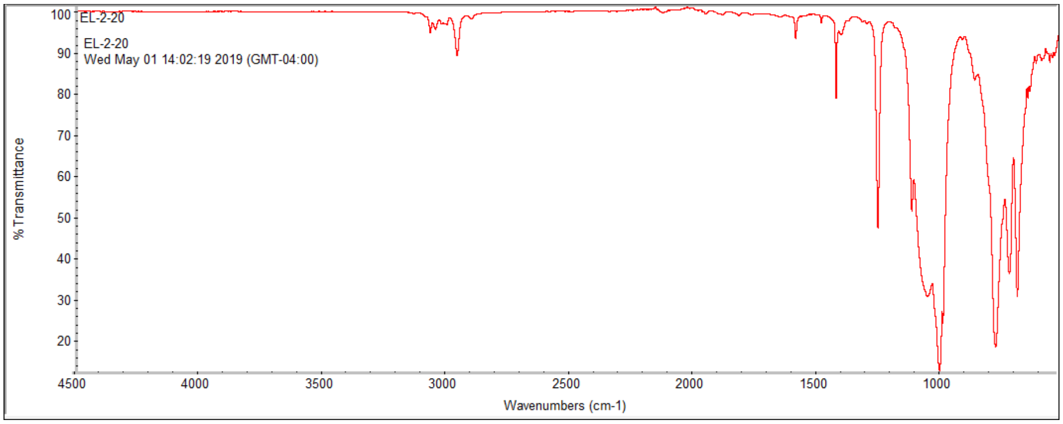

Figure S5.14 IR spectrum for **HOMO-PhMe$_{\mathbf{OH}}$** (hydroxyl-terminated poly(methylphenyl)siloxane)

Chapter 6: High-Throughput Synthesis and Characterization of Aryl Silicones Using the Piers-Rubinsztajn Reaction[**]

6.1 Abstract

Incorporating aromatic moieties into PDMS elastomers works to elevate the refractive index and thermal stability of silicones. Aromatic groups were incorporated into PDMS elastomers by exploiting the relative reactivity of different functional groups in the Piers-Rubinsztajn reaction to produce well-defined elastomeric networks. Crosslinker functional groups and concentrations were selected to avoid excessive bubble formation in the elastomers. In order to analyze trends in silicone mechanical properties as a result of increasing aryl concentration, libraries of silicone elastomers were quickly synthesized and characterized using high-throughput suites. The Tecan Evo 200 Material Screening System was used to formulate and cure up to 96 distinct elastomers in a 96-welled plate within 30 minutes. Liquid handling parameters were optimized to effectively work with silicones – these specifications are described in detail. Only lower viscosity silicones (< ~100 centiStokes) could be reliably dispensed by the robot synthesizer. High-throughput characterization of elastomer mechanical properties was also performed. Incorporating aryl crosslinkers into the PDMS backbone increased silicone elastomer modulus by ~50 % (at a crosslink density of 6% the Young's modulus of a pure silicone

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[**] To be submitted to Chemistry - A European Journal, A.F. Schneider and M.A. Brook. Schneider developed scripts for the Tecan Evo 200, performed all syntheses and was the lead author of the manuscript.

elastomer was 0.09 MPa and the Young's modulus of silicone crosslinked with an aromatic linker was 0.17 MPa).

6.2 Introduction

Silicone elastomers are sold based upon their physical properties post cure, including modulus (typically as Shore A or Shore OO durometer), extension at break, transparency, etc. The ability to attain those parameters depends both the pre-elastomer materials and the curing processes used.[1-2] Most commercial silicone elastomers are prepared from fluid pre-elastomers that are cured by radical chemistry at high temperatures,[3] moisture cure (room temperature vulcanization - RTV) of small carboxy, oxime or alkoxysilanes with silanol-terminated silicones,[2] and platinum-catalyzed hydrosilylation cure;[4-5] the latter process requires mixing two parts before cure (RTV cure may be one-part or two-part).[6]

It is well known that elastomer properties can be affected to some degree by curing conditions. For example, the rate of temperature increase in radical cure, ambient humidity during RTV-1 cure, or the ratio of Parts A and B in hydrosilylation cure can all affect the resulting network structure. In choosing pre-elastomers, the (commercial) developer of silicone elastomers has somewhat more flexibility than the user, as they can control the molecular structure of the pre-elastomer compounds, which then translate to elastomer properties. Even then, the traditional road to development involves use of a limited palette of (commercially available) higher molecular weight precursors that are painstakingly cured under a variety of conditions. While the approach has stood the test of time, the inefficiency of the process does not always lend itself to systematic studies and, therefore, capturing trends in structure/property relationships.

Many areas of science and engineering have taken their lead from the pharmaceutical industry, which developed and extensively exploits high throughput protocols to synthesize drug candidates.[7] The approach is more broadly utilized for biological assays.[8] High throughput processes often rely on robots to create statistically large numbers of compounds and/or large numbers of assays. The large number of compounds/assays allows one to tease out trends that are unlikely to be discovered in the one-by-one approach.[9-10]

High throughout approaches are almost absent from silicone chemistry. Ekin et al. described using a high-throughput method to produce a variety of organosilicones, however, this method required an inert atmosphere and had to be performed in a glove box.[11-13] Work on 3D printing of silicones showed that crosslinking and physical properties can be readily tuned simply by mixing ingredients in different ratios.[14-15] The approach has been used to make surface gradients by chemically modifying preexisting silicone surfaces.[16-18] There should be much broader opportunity to exploit high-throughput approaches in silicone chemistry; what are the limitations?

Typical silicone materials are made up of polydimethylsiloxanes (PDMS). Pure PDMS elastomers exhibit low mechanical strength and refractive index. The former challenge is addressed, in part, by the use of reinforcing fillers. Refractive index is important for silicones destined for optical applications. Incorporating aromatic moieties along the backbone, or pendant to the backbone, work to elevate the modulus of silicone elastomers,[13, 19] and increase refractive index.[20-21] Although silicones already exhibit high thermal resistance, the incorporation of aromatic groups can further improve this property.[22-24]

Aromatic groups can be easily incorporated into silicone polymers using the Piers-Rubinsztajn (PR) reaction, a siloxane bond forming dehydrocarbonative condensation reaction between a hydrosilane and an alkoxysilane (or aryl ether or silanol) releasing an alkane byproduct, catalyzed by tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)(Figure 6.1). This reaction assembles silicone polymers quickly at room temperature and in open vessels.[25-29] Silicones with pendant phenyl groups can be synthesized using a typical PR reaction (R_1 = Ph Figure 6.1A), or aryl groups can be incorporated into a PDMS backbone by using an alternative PR reaction with alkoxybenzenes or silphenylenes (Figure 6.1B).[29-30] These linear phenyl silicones can also be crosslinked using an analogous PR reaction to form the desired elastomer (Figure 6.2). $B(C_6F_5)_3$ also catalyzes a hydrolysis reaction between SiH and water (Figure 6.1C) to form a silanol. The silanol then condenses with another molecule of SiH to form a siloxane bond.[31]

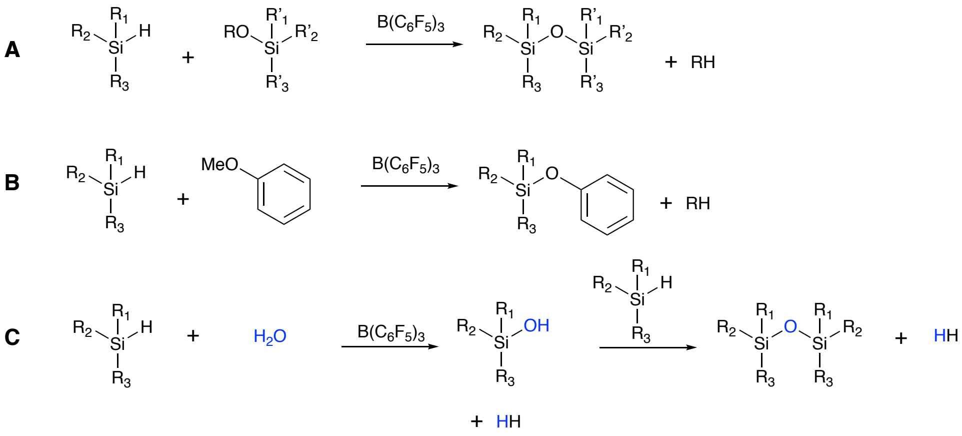

Figure 6.1 $B(C_6F_5)_3$-catalyzed siloxane bond formations A) typical PR reaction between a hydrosilane and an alkoxysilane; B) alternative PR reaction with aryl ethers; C) hydrolysis/condensation of hydrosilanes

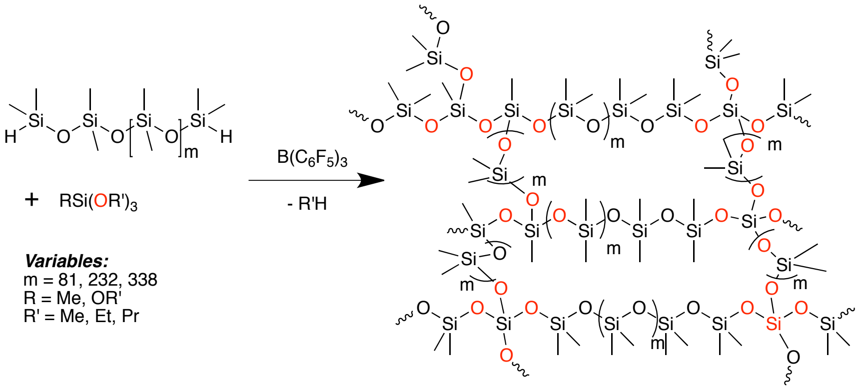

Figure 6.2 Elastomer synthesis using the PR reaction[32]

We elected to test the capacity of high-throughout methods to systematically prepare silicone polymers, focusing on aryl rich materials. While there are several metrics for physical properties that can be easily measured, RI and modulus were selected as they can, in part, also be measured in high-throughput mode. The PR reaction was employed in these syntheses in a system open to the atmosphere, which is feasible because $B(C_6F_5)_3$ is rather air tolerant.[28] Using this system, up to 96 distinct elastomers could be synthesized in just 30 minutes.

6.3 Experimental

6.3.1 Materials

Tris(pentafluorophenyl)borane, triethoxy(*n*-propyl)silane and triethoxy(octyl)silane were purchased from Sigma-Aldrich; α,ω-hydride-terminated poly(dimethyl)siloxane (H-PDMS-H, 2-3 centiStokes (cSt) MW 730 g mol^{-1}), phenylmethyldimethoxysilane, diphenyldimethoxysilane and phenyltriethoxysilane were purchased from Gelest; 1,3,5-

trimethoxybenzene and 1,1-diphenylethylene were purchased from Alfa Aesar; *p*-dimethoxybenzene was purchased from Eastman; HPLC grade toluene was purchased from Caledon (solvent was dried in an activated alumina column). All reagents were used as received.

6.3.1.1 Catalyst Stock Solution

Tris(pentafluorophenyl)borane catalyst stock solution was prepared by dissolving $B(C_6F_5)_3$ (20.0 mg, 0.04 mmol) in dry HPLC grade toluene (2.00 mL) to give a 19.5 mM solution.

6.3.1.2 Reagent Stock Solutions

1,3,5-Trimethoxybenzene (2.85 g, 16.9 mmol) was diluted with dry HPLC grade toluene (13.03 mL) to give a 1.3 M stock solution. Analogous procedures were followed to obtain 1.3 M stock solutions of all other crosslinkers and chain extenders used.

6.3.2 High-Throughout Methods

The robotic arms of a Tecan Evo 200 Assays Material Screening System were used to add specified amounts of H-PDMS-H, chain extender, crosslinker and catalyst solutions, into 60 wells of a 96-welled plate. The Tecan Evo 200 was also used to mix the contents of each well by aspiration followed by dispensing, prior to catalyst addition. Freedom EVOware software was used to develop scripts and program commands on the Tecan Evo 200 Assays Material Screening System. The parameters were optimized for silicones; specifications for the liquid handling, aspiration and dispensing of silicones for the Tecan Evo 200 are described in the Supporting Information Table S6.3).

6.3.3 Elastomer Synthesis

The requisite volumes of each reagent were input into the EVOware software based on the relative mole ratios desired. Calculations were based on a total reagent volume of 250 μL. The equation derivation is provided and an example sample calculation is given in the Supporting Information. Using the Tecan Evo 200 Materials Screen System, to 60 wells of a 96-welled plate were added (via robotic arms) H-PDMS-H (neat), crosslinkers (1.3 M solution in toluene) and (in selected cases) chain extender (1.3 M solution in toluene). Reagent amounts added for each plate are available in Table S6.2 of the Supporting Information. The contents of each well were mixed (via robotic arms) and to each well was added $B(C_6F_5)_3$ solution (10 μL, 1.95×10^{-4} mmol, 0.06-0.07 mol% to SiH). Each well was briefly mixed manually following catalyst addition. The robotic mixing function was not used in this case since cure occurred simultaneously – cure on a pipette tip could create a blockage causing pressure buildup in the robot arms. The plates were placed on a room temperature bench (open to the atmosphere) for 3 hours then transferred to a 50 °C oven and left overnight. In a single plate, the same amounts of materials were added to 12 wells in an attempt to make a set of 12 identical elastomers and obtain statistically relevant characterization data. Dispensing and curing errors were unavoidable; on occasion not all 12 elastomers were successfully synthesized. Following cure, an average Young's modulus with error was calculated for each formulation from the successfully cured materials.

The Young's modulus of each elastomer was characterized using the Biomomentum MACH 1 mechanical tester – a high-throughput compression-testing suite. The location of the desired wells which contained elastomers to be characterized were input into the Biomomentum software and the mechanical arm performed continuous uniaxial elastic indentation measurements for each well using a hemispherical indenter (0.3 mm). Young's modulus was calculated using the Biomomentum software using a Poisson's ratio of 0.5.

6.4 Results

6.4.1 High-Throughput Synthesis and Characterization

The Tecan Evo 200 Materials Screen System is an automated liquid handling system that was used to synthesize silicone elastomers in 96-welled plates. Freedom Evoware software was used to program the robot to dispense and mix specified volumes of reagent and catalyst into each well. The Tecan Evo 200 system was developed for handling aqueous materials and since silicones exhibit higher viscosity and hydrophobicity, the liquid handling specifications had to be optimized to aspirate and dispense silicones through the plastic LiHa tips (Supporting Information, Table S6.3).

Using the Tecan Evo 200 Materials Screen System, robotic arms dispensed and mixed H-PDMS-H (2-3 cSt MW = 730 g mol^{-1}), crosslinker solution and (sometimes) chain extender solution into 60 wells of a 96-welled plate. The robot was programmed to aspirate and dispense reagent mixtures from and back into the wells in order effectively mix the materials. The robot then dispensed catalyst solution into each well containing reagent mixtures (0.06-0.07 mol% to SiH). Each plate took under 30 minutes to prepare. Following manual mixing (the solutions were now to viscous to be aspirated by the robot), the plates were placed on a room temperature bench (open to the atmosphere) for

3 hours then transferred to a 50 °C oven over night to promote cure, toluene evaporation and subsequent hydrolysis reactions utilizing atmospheric moisture.

Two practical factors now became apparent during these experiments. First, the viscosity of the fluids to be dispensed needed to be below ~ 100 cSt (~ 6000 g mol^{-1} for dimethylsiloxane polymers). Otherwise, the time required to dispense/aspirate reagents was impractically slow and/or mixing was ineffective. When – as is the usual case – higher molecular weight spacers were required, low viscosity chain extenders were added to the recipe to convert low MW polymers to higher MW polymers on the fly, during cure. Second, the gaseous byproducts could be problematic. If the rate of release of gas was competitive with cure, foams formed, particularly if only PR reactions were used for cure; the small molecule alkane gas becomes trapped in the network (Supporting Information, Figure S6.8). Therefore, low catalyst loadings and dilution with toluene worked to slow the reaction and reduce foaming.

Two processes were therefore utilized sequentially for silicone elastomer formation – the PR reaction (Figure 6.1AB) and hydrolysis/condensation (Figure 6.1C) – in the reaction wells (a fast PR reaction followed by slow hydrolysis/condensation was used to avoid foam formation). The degree to which each reaction occurred was controlled simply by stoichiometry of starting materials. A molar deficit of alkoxy reagents (to SiH) first underwent the PR reaction with H-PDMS-H (2-3 cSt. MW 730 g mol^{-1}) (Figure 6.3A) leading to HSi-terminated silicones.[29] Following this, atmospheric moisture and/or trace water dissolved in toluene worked to hydrolyze and condense SiH chain ends (Figure 6.1C, Figure 6.3B) to form the final polymer network without entrained bubbles, in most cases.[31] For the PR reaction, H-PDMS-H was combined with methoxy/ethoxy functional chain extenders and crosslinkers.

It should be possible to encourage higher levels of structural control using kinetics. It has been previously demonstrated that methoxy groups react more quickly via the PR reaction than ethoxy groups do, which is a consequence of steric bulk at the nucleophilic oxygen.[33] Therefore, methoxy functional chain extenders and ethoxy functional crosslinkers were used for the most part (Figure 6.5) – chain extenders preferentially react with H-PDMS-H growing the molecular weight of the siloxane chains, followed by crosslinking with ethoxy functional silanes at higher conversions. We wished to keep to the 'ethoxy crosslinker and methoxy chain extender motif.' However, triethoxybenzene is not commercially available. 1,3,5-Trimethoxybenzene was therefore used in its place as a functional aromatic crosslinker (Figure 6.3). The relative reactivities of ArOMe and $ArMe_2SiOMe$ with a hydrosilane were tested (Supporting Information Figure S6.6, Table S6.4); methoxysilanes were observed to react faster than methoxybenzenes. These synthetic strategies allow the rapid and systematic formation of silicone elastomers.

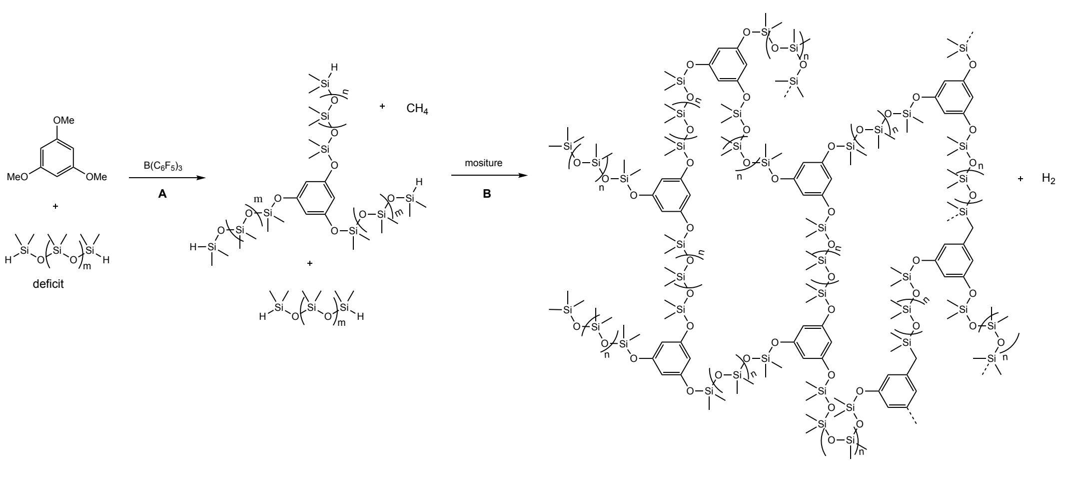

Figure 6.3 H-PDMS-H crosslinked with trimethoxybenzene via the PR reaction

The Biomomentum Mach-1 mechanical tester was used to measure the Young's modulus of elastomers in each well (Figure 6.4A). The software was programmed to sequentially measure mechanical properties of materials in selected well locations on a 96-welled plate. Although this process was automated it took approximately 3 hours to obtain Young's modulus data for 60 elastomers. Small bubbles were present in a number of elastomer samples, due to gas evolution upon curing (Figure 6.4B) and data from these samples were rejected.

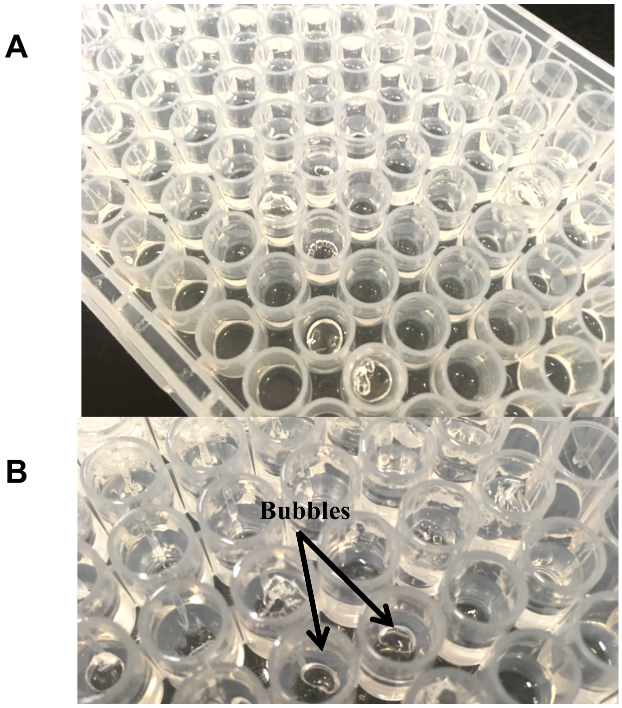

Figure 6.4 A) Elastomers made in a 96-welled plate; B) close up showing small amounts of bubbles trapped in elastomer in some cases

6.4.2 Aromatic Moieties in Silicone Elastomers – the Effect on Young's Modulus

Incorporating aromatic groups into the backbone (via a crosslinker) would give a structure analogous to that depicted in Figure 6.3. Having a phenyl pendant or aryl-free silane crosslinker would produce elastomers with structure analogous to those in Figure

6.2. We examined the relative effect that aromatic moieties have on siloxane mechanical properties, when they are placed in backbone or pendant to the PDMS backbone (R_1=Ph Figure 6.1A).

6.4.2.1 The Effect of Pendant Phenyl Groups

The role of pendant phenyl groups was examined by incorporating -PhMeSiO- or -Ph_2SiO- chain extenders with triethoxy(*n*-propyl)silane as the crosslinker. Diphenylsilicones normally have higher melting points than the methylphenylsilicone analogues due to enhanced association of the aryl groups in the former case. A library of elastomers was prepared using 20% diphenyldimethoxysilane as a chain extender and 6-10 % triethoxy(*n*-propyl)silane as the crosslinker. The average modulus data obtained (with error) was compared to analogous formulations using phenylmethyldimethoxysilane and data is displayed in Figure 6.5A. Adding an additional phenyl group onto the chain extender (diphenyldimethoxysilane) led to a modest decrease of the modulus by 20-40%.

6.4.2.2 The Effect of an Aromatic Crosslinker

Using the high-throughput synthesis methods described above, H-PDMS-H (MW = 730 g/mol, 2-3 cSt) was combined with ~5-10 mol% 1,3,5-trimethoxybenzene (1.3 M in toluene) in a single plate. In a second plate the same chain length H-PDMS-H was combined with ~3-10 mol% of *n*-propyltriethoxysilane (1.3 M in toluene). High-throughput mechanical testing was performed to determine the modulus of each elastomer. The average modulus at each crosslink density is depicted in Figure 6.5B. Replacing an aliphatic, single point trifunctional crosslinker with an aryl trifunctional crosslinker led to a ~50 % elevation of the Young's modulus (Figure 6.5B).

The question of synergistic effects between crosslinker and backbone was probed by combining H-PDMS-H with 20 mol% phenylmethyldimethoxysilane chain extender and 6-10 mol% crosslinker in 60 wells of a 96-welled plate; separate plates were used for different crosslinkers. Libraries were prepared from 4 different crosslinker types: aryl, 3 point – trifunctional aryl (1,3,5-trimethoxybenzene); aryl, 1 point – phenyl pendant (triethoxy(phenyl)silane); small alkyl – propyl (triethoxy(*n*-propyl)silane); and large alkyl – octyl (triethoxy(octyl)silane). SiH groups in H-PDMS-H first reacted with the methoxy functional chain extender releasing methane as a byproduct. The slower reaction with crosslinker (methoxybenzene or ethoxysilane functional groups) subsequently proceeded. The presence of pendant phenyl groups on the backbone (sourced from chain extenders) led to a ~ 40 % increase in moduli (Figure 6.5 ■◆ – phenyl pendant groups along PDMS backbone in C versus pure PDMS backbone in B).

As expected, elastomers possessing the highest modulus were observed when 1,3,5-trimethoxybenzene was used as the crosslinker. Having a phenyl group substituent on the crosslinker (phenyltriethoxysilane) produced elastomers with a pendant phenyl group at the crosslink points. This did not effectively work to improve modulus – the modulus was comparable to elastomers crosslinked using *n*-propyltriethoxysilane. Increasing the alkyl chain length substituent on the crosslinker worked to further decrease the elastic modulus (triethoxy(octyl)silane crosslinker).

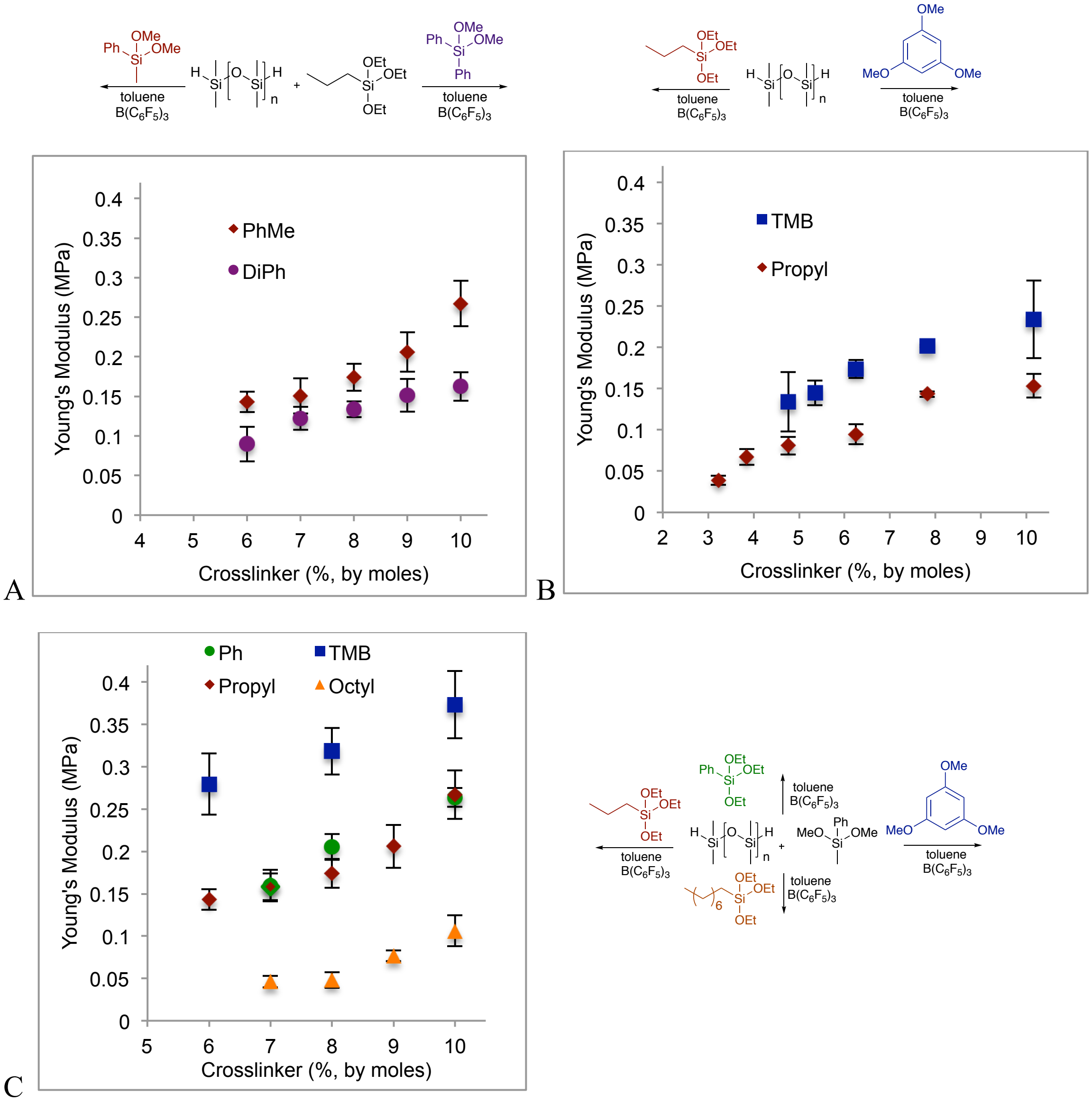

Figure 6.5 A: Average modulus data with error for elastomers synthesized from H-PDMS-H, chain extended with 20% phenylmethyldimethoxysilane (◆) or diphenyldimethoxysilane (●) and crosslinked with 6-10% triethoxy(*n*-propyl)silane; B: average modulus data with error for elastomers synthesized from H-PDMS-H crosslinked with trimethoxybenzene (■) or triethoxy(*n*-propyl)silane (◆); C: average modulus data with error for elastomers synthesized from reagents depicted to the right of the Chart; H-PDMS-H combined with 20 mol% PhMeSi(OMe)$_2$ chain extender and 6-10 mol% crosslinker: triethoxy(phenyl)silane (●), 1,3,5-trimethoxybenzene (■), triethoxy(*n*-propyl)silane (◆) and triethoxy(octyl)silane (▲)

6.5 Discussion

6.5.1 Robot Synthesis of Silicones

The Tecan Evo 200 Materials Screening System was an effective high-throughput synthesis method used to dispense and mix reagents into each well of a 96-welled plate in order to produce a large number of different silicone elastomers in a short time using the PR reaction. There are, however, some caveats. Most fluids used as silicone polymer precursors have much higher viscosity (> 100 cSt) than those used here. Therefore, it is not possible to directly aspirate and dispense standard silicone oils to develop pre-elastomer formulations using this system. Dilution with solvents to give low viscosity mixtures is impractical. However, the ability to create high molecular weight materials by chain extending lower MW compounds allows one to make complex libraries based on one shot addition of reagents. In this process, we benefit from the kinetics of the two processes – chain extension and crosslinking – that are occurring. Using faster reacting MeOSi groups for chain extension permits preferential growth of longer (high viscosity) chains on the fly before crosslinking sets in via the slower reacting SiOEt groups.

Second, one must be cautious when using the PR reaction for curing in these processes. In the absence of diluents, it is common to form foams in which the alkane byproduct is a blowing agent (Figure S6.8). The impact of the effect can be reduced by addition of solvent and use of less catalyst. These problems will not arise with other cure technologies with which gases are not created, including hydrosilylation.

Foam control was also exerted by the use of a deficit of alkoxy functional groups with respect to SiH in the reagent mixtures. Under these circumstances rapid chain growth and some crosslinking occurs in a PR process. However, the viscosity of the evolving product is sufficiently low that gases escape. The subsequent, slower $B(C_6F_5)_3$-catalyzed hydrolysis/condensation reaction took place to finish elastomers cure.

6.5.2 Tuning Silicone Physical Properties with Aryl Groups

It was possible to manipulate the physical properties of the resulting elastomer by selecting the total number of phenyl groups and establishing whether they were present along the chain as Ph_2SiO, PhMeSiO monomers, a single point of contract crosslinker $PhSiO_{3/2}$ or a three point contact crosslinker, $(1,3,5\text{-}MeO)_3C_6H_3$.

The presence of pendant phenyl groups along the backbone introduced via a chain extender (phenylmethyldiethoxysilane) worked to elevate the PDMS elastomer modulus. For networks cross-linked with triethoxy(*n*-propyl)silane, addition of 20 mol% phenylmethyl chain extender worked to increase the elastomer modulus by ~ 40 % compared to pure dimethylsilicone elastomers of the same crosslink density (Figure 6.5A). This effect is expected. Interchain interactions are much higher in phenylsilicones, as shown through the much higher T_g: methylsilicones ~ -122 °C; phenylmethylsilicones ~ -24 °C.[34-35] This effect is often ascribed to pi stacking, or phase separation of aryl rich domains. Addition of a second phenyl group on the same chain extender (diphenyldimethoxysilane) showed the same effect, but to a lower degree (Figure 6.5A). The latter response was somewhat surprising since the T_g of phenyl silicones typically increases with phenyl concentration ([Ph]) and the T_g of phenyl silicones with the same [Ph] exhibit similar T_g's, regardless of the phenyl substituent locations. Poly(phenylmethyl)siloxane exhibits a similar T_g (~ -22 °C) to an alternating copolymer (poly(diphenylsiloxane-*co*-dimethylsiloxane), alternating dimethylsiloxy and diphenylsiloxy units) of the same phenyl group to silicon ratio (Ph/Si = 1).[34, 36]

A more profound effect was the nature of the crosslinker itself. In a pure dimethylsilicone elastomer, changing from a propyltriethoxysilane crosslinker to cross-linked with trimethoxybenzene led to significant increase in modulus at the same crosslink density (Figure 6.5B). This is consistent with secondary crosslinking arising from association of aryl groups. Supporting this hypothesis is the effect of a single point trifunctional crosslinker. Elastomers crosslinked with $PhSi(OEt)_3$ had essentially the same modulus as *n*-$PrSi(OEt)_3$-crosslinked materials; both were lower than the trimethoxybenzene-crosslinked materials (Figure 6.5C). Longer, aliphatic crosslinkers led to further decrease in the modulus. The similarity in modulus expressed by elastomers crosslinked with $PhSi(OEt)_3$ and *n*-$PrSi(OEt)_3$ was somewhat surprising – the pendant phenyl group was expected to introduce more rigidity into the elastomer due to electronic interactions, compared with the propyl substituent. However the flexibility provided by the Si-O crosslinks is the prominent factor affecting elastomer stiffness here, resulting in phenyl and n-propyl substituted crosslinked silicone elastomers exhibiting similar Young’s modulus.

The presence of aryl groups in silicone elastomers is advantageous, particularly in applications like LEDs, where higher thermal stability is particularly important. Even subtle changes in the way in which the phenyl groups are located within the network change the physical performance of the network (Figure 6.5C). These high throughput studies show that, where the characterization is also rapid, it is very easy to rapidly explore effects of constituent location and quantity within silicone networks, and exploit that knowledge to design elastomers with desirable properties, including refractive index, thermal stability, and modulus.

6.6 Conclusions

High throughput synthesis and characterization can be used as an effective tool to optimize silicone elastomer synthesis and to target specific material properties. Property trends that arise from small changes in elastomer formulation can be easily analyzed and used predictively to create desirable elastomers. High throughput requires the use of low viscosity materials (< 100 cSt). However, the kinetically controlled use of chain extender and crosslinker can be used to control network structure and generate high molecular weight polymers in situ.

6.7 Acknowledgments

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S6.9 Appendix 5 – Supporting Information

Calculations for dispensing pre-elastomer reagents

250 µL = $V_a + V_b + V_c$; V=volume and a, b, c refer to different reagents.

With respect to relative molar ratios, the "total volume" is: $V_{T,r} = V_{a,r} + V_{b,r} + V_{c,r}$

$$V_{a,r} = \frac{Xmol_a * MW_a}{\rho_a}$$

Volume dispensed =

$$V_a = V_{a,r}(\frac{250\ \mu L}{V_{T,r}})$$

Combining the above equations:

$$V_a = \frac{Xmol_a * MW_a}{\rho_a} * \frac{250\ \mu L}{\frac{Xmol_a * MW_a}{\rho_a} + \frac{Xmol_b * MW_b}{\rho_b} + \frac{Xmol_c * MW_c}{\rho_c}}$$

If reagent solutions are being added, the equation becomes:

$$V_{a,r} = \frac{Xmol_a}{[a]}$$

X= moles of reagents a, b or c

MW=molecular weight of reagents a, b or c

Sample reagent volume (for a single well) calculation:

a = H-PDMS-H, b = phenymethyldimethoxysilane, c = 1,3,5-trimethoxybenzene

$$V_a = \frac{Xmol_a * MW_a}{\rho_a} * \frac{250\ \mu L}{\frac{Xmol_a * MW_a}{\rho_a} + \frac{Xmol_b}{[b]} + \frac{Xmol_c}{[c]}}$$

20 % chain extender (1.3 M solution of phenymethyldimethoxysilane) & 8 % crosslinker (1.3 M solution of 1,3,5-trimethoxybenzene).

$Xmol_a = 0.72$, $Xmol_b = 0.2$, $Xmol_c = 0.08$

$$V_{HPDMS} = \frac{(0.72)(727\frac{g}{mol})}{0.9\frac{g}{mL}} * \frac{250\ \mu L}{\frac{(0.72)\left(727\frac{g}{mol}\right)}{0.9\frac{g}{mL}} + \frac{0.2}{1.3\ M} + \frac{0.08}{1.3\ M}} = 184.30\mu L$$

$$V_{PhMeSi(OMe)2} = \frac{0.2}{1.3\ M} * \frac{250\ \mu L}{\frac{(0.72)\left(727\frac{g}{mol}\right)}{0.9\frac{g}{mL}} + \frac{0.2}{1.3\ M} + \frac{0.08}{1.3\ M}} = 46.22\mu L$$

$$V_{Ar(OMe)3} = \frac{0.08}{1.3\ M} * \frac{250\ \mu L}{\frac{(0.72)\left(727\frac{g}{mol}\right)}{0.9\frac{g}{mL}} + \frac{0.2}{1.3\ M} + \frac{0.08}{1.3\ M}} = 19.48\ \mu L$$

Table S6.1 Volumes of reagents added to wells of 96-welled plate to produce elastomers in Figure 6.5B

Crosslinker (%)	**Volume H-PDMS-H to each well (μL)**	**Volume 1.3 M crosslinker added to each well (μL)**
3	242.85	7.15
4	240.47	9.53
5	238.08	11.92
6	235.69	14.31
7	233.29	16.71
8	230.90	19.10
9	228.50	21.50
10	226.10	23.90

Table S6.2 Volumes of reagents added to wells of 96-welled plate to produce elastomers in Figure 6.5AC

Crosslinker (%)	**Volume H-PDMS-H to each well (µL)**	**Volume 1.3 M chain extender (20%) added to each well (µL)**	**Volume 1.3 M crosslinker added to each well (µL)**
6	189.23	46.17	14.60
7	186.77	46.19	17.04
8	184.30	46.22	19.48
9	181.83	46.24	21.93
10	179.36	46.26	24.38

Table S6.3 Liquid handling parameters inputted into the Freedom EVOware software for reagent pipetting on the Tecan Evo 200 Assays Material Screening System

<table>
<tr><th colspan="8">Liquid Handling System</th></tr>
<tr><th colspan="2"></th><th colspan="3">Transferring Silicones</th><th colspan="3">Mixing silicones & transferring catalyst</th></tr>
<tr><th colspan="2">Liquid Density (mg/µL)</th><td colspan="3">1.045</td><td colspan="3">1</td></tr>
<tr><th colspan="2">Detection Mode</th><td colspan="3">Detect twice with separate tips & retract</td><td colspan="3">Detect twice with separate tips & retract</td></tr>
<tr><th colspan="2">Liquid Conductivity</th><td colspan="3">Bad</td><td colspan="3">Good</td></tr>
<tr><th rowspan="2">Liquid Detection</th><th>Detection Speed (mm/s)</th><td colspan="3">60</td><td colspan="3">60</td></tr>
<tr><th>Double Distance (mm)</th><td colspan="3">4</td><td colspan="3">4</td></tr>
<tr><th rowspan="2">Clot Detection</th><th>Detection speed (mm/s)</th><td colspan="3">50</td><td colspan="3">50</td></tr>
<tr><th>Clot limit (mm)</th><td colspan="3">4</td><td colspan="3">4</td></tr>
<tr><th colspan="8">System Specifications for Aspiration</th></tr>
<tr><th colspan="2"></th><th colspan="3">Transferring Silicones</th><th colspan="3">Mixing Silicones & Transferring Catalyst</th></tr>
<tr><th colspan="2">DiTi Volume (µL)</th><td>1-10.01</td><td colspan="2">10.01-1000.01</td><td>1-5.01</td><td>5.01-10.01</td><td>10.01-200.01</td></tr>
<tr><th colspan="2">Pipetting</th><td>Single & Multi</td><td>single</td><td>multi</td><td colspan="3">Single & Multi</td></tr>
<tr><th colspan="2">Aspiration Speed (µL/s)</th><td>5</td><td colspan="2">80</td><td>5</td><td>20</td><td>50</td></tr>
<tr><th colspan="2">Delay (ms)</th><td>500</td><td colspan="2">10 000</td><td>500</td><td>500</td><td>500</td></tr>
<tr><th colspan="2">System Trailing Airgap (µL)</th><td>10</td><td>20</td><td>5</td><td>10</td><td>10</td><td>5</td></tr>
<tr><th colspan="2">Leading Airgap (µL)</th><td>10</td><td colspan="2">20</td><td>2</td><td>2</td><td>10</td></tr>
<tr><th colspan="2">Trailing Airgap (µL)</th><td>2</td><td colspan="2">2</td><td>2</td><td>2</td><td>2</td></tr>
<tr><th colspan="2">Excess Volume (µL)</th><td>0</td><td colspan="2">0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><th colspan="2">Conditioning Volume (µL)</th><td>0</td><td colspan="2">0</td><td>0</td><td>0</td><td>0</td></tr>
<tr><th colspan="2">Use Pinch Valve</th><td>No</td><td colspan="2">No</td><td>No</td><td>No</td><td>No</td></tr>
<tr><th colspan="2">Use Liquid Detection</th><td>No</td><td colspan="2">No</td><td>No</td><td>No</td><td>No</td></tr>
<tr><th colspan="2">Aspiration Position</th><td colspan="3">z max ± 0 mm offset, no tracking</td><td colspan="3">liquid level ± 2 mm offset, with tracking</td></tr>
</table>

X	center	center
Y	center	center
On PMP Clot error	user prompt	N/A
On Detection Error	N/A	user prompt
Use Exit Signal Detection	No	No
Mix Before Aspiration	No	No
Retract Tips to	z-travel, -5 mm	liquid level, - 5 mm
Retract Speed (mm/s)	5	5

System Specifications for Dispensing					
	Transferring Silicones		**Mixing Silicones & Transferring Catalyst**		
DiTi Volume (µL)	1-10.01	10.01-1000.01	1-5.01	5.01-10.01	10.01-200.01
Pipetting	Single & Multi		Single & Multi		
Dispense Speed (µL/s)	400	250	400	400	400
Breakoff Speed (µL/s)	200	250	200	200	350
Delay (ms)	200	10 000	200	500	200
Trailing Airgap after each Dispense	No	No	No	No	No
Use Pinch Valve	No	No	No	No	No
Use Liquid Detection	No	No	No	No	No
Dispense Position	z-dispense ± 0 mm offset, no tracking		z-dispense ± 0 mm offset, no tracking		
X	center		center		
Y	center		center		
Tip Touching	no tip touching		no tip touching		
Mix after Dispense	No		No		
Retract Tips to	z-dispense, -0 mm		z-dispense, -0 mm		
Retract Speed (mm/s)	50		50		

Synthesis of 1,4-Phenylenebis[methoxy(dimethyl)silane]

To absolute methanol (40.0 mL) was added Karstedt's catalyst solution (2% Pt in xylenes, 10.0 µL, 4.48 x 10^{-5} mmol) at room temperature. The mixture was then heated in a 50 °C oil bath with stirring under a nitrogen blanket for 15 min. A flask containing 1,4-bis(dimethylsilyl)benzene (4.00 g, 2.06 mmol) was flushed with nitrogen and added dropwise to the methanol with catalyst solution via a needle and syringe. The mixture was allowed to react and stir for 30 min. The solution was then concentrated under reduced pressure and purified by kugelrohr distillation at 68 °C under vacuum (0.1 mmHg), yielding a colorless oil product condensed on the secondary middle flask. Yield: 1.25 g, 24.1%; significant product hydrolysis occurred and so low yield pure product was distilled off of crude mixture.

^{1}H NMR ($CDCl_3$, 600 MHz, δ): 7.59 (s, 4 H), 3.45 (s, 6 H), 0.38 (s, 12 H); MS (m/z): 254.1157.

Competition Between 1,4-Phenylenebis[methoxy(dimethyl)silane] and p-Dimethoxybenzene as the Alkoxy Reagents

To dry toluene (10 mL) was added H-PDMS-H (2-3 cSt. 0.4733 g, 0.650 mmol), 1,4-phenylenebis[methoxydimethylsilane] (8.77 mL of 0.037 M solution in toluene, 0.325 mmol), *p*-dimethoxybenzene (2.54 mL of 0.128 M solution in toluene, 0.325 mmol) and 1,1-diphenylethylene (115 μL, 0.325 mmol) as an internal standard for ^{1}H NMR. The mixture was stirred at room temperature open to the atmosphere for 5 min. To the mixture was added tris(pentafluorophenyl)borane catalyst solution (40.0 μL, 3.12×10^{-3} mmol, 4.80×10^{-3} equivalents). As the reaction progressed ~ 1 mL aliquots were removed from the reaction vessel (approximately every 5 seconds) and added to vials containing a stir bar and neutral alumina (~ 0.5 g) to complex/neutralize tris(pentafluorophenyl)borane. After 15 min of stirring, each solution was filtered and concentrated. Each residue (product) was a colourless oil. The final polymer product was composed of methoxy aryl end groups with internal aryl ethers and arylsilyl groups in the PDMS backbone. ^{1}H NMR data was analyzed to track the change in integration of the alkoxy silyl peak and the alkoxy aryl peak in reference to the internal standard (Figure S6.6).

All products were analyzed by ^{1}H NMR (Table S6.4).

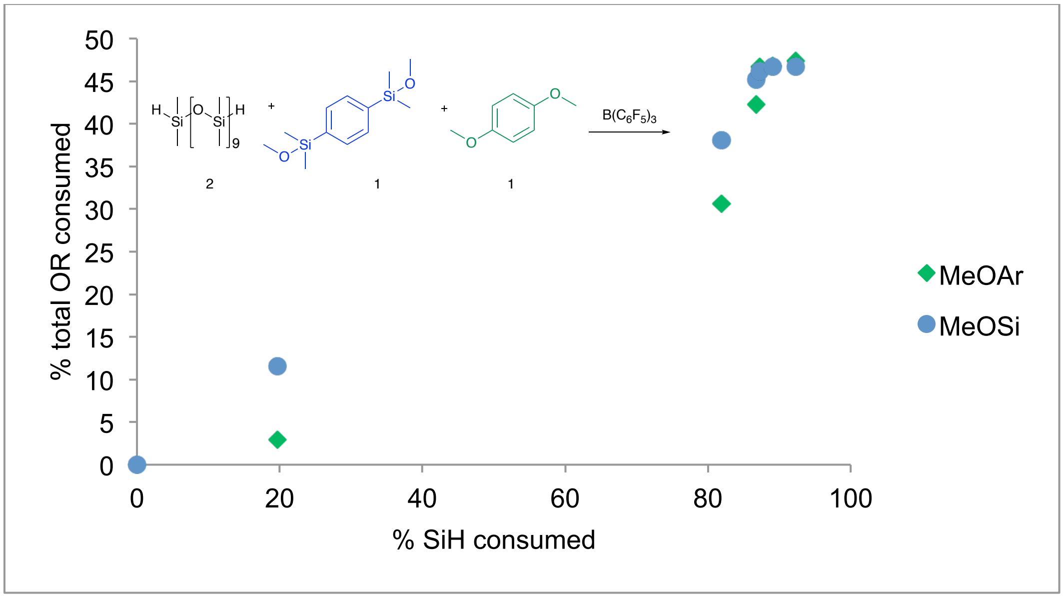


Figure S6.6 Relative reactivity of SiOMe (●) and ArOMe (◆) in the PR reaction

Table S6.4 ^{1}H NMR data for methoxy competition reactions

Fraction	**^{1}H NMR data (d8-toluene, 600 MHz, δ)**
Initial reaction mixture	7.58 (s, 4 H), 6.69 (s, 4 H), 4.99-4.97 (sep, 4 H, *J* = 2.8 Hz), 3.35 (s, 6 H), 3.30 (s, 6 H)
i	7.58 (s, 3 H), 6.69 (s, 4 H), 5.33 (s, 2 H) 4.99-4.97 (sep, 3 H, *J* = 2.8 Hz), 3.35 (s, 6 H), 3.30 (s, 4 H)
ii	7.69-7.47 (m, 3 H), 6.69 (s, 3 H), 5.33 (s, 2 H) 4.99-4.97 (sep, 1 H, *J* = 2.8 Hz), 3.35 (s, 3 H), 3.30 (s, 1 H)
iii	7.69-7.47 (m, 3 H), 6.69 (s, 3 H), 5.33 (s, 2 H) 4.99-4.97 (sep, 0.5 H, *J* = 2.8 Hz), 3.35 (s, 1 H), 3.30 (s, 0.2 H)
iv	7.69-7.47 (m, 3 H), 6.69 (s, 1 H), 5.33 (s, 2 H) 4.99-4.97 (sep, 0.5 H, *J* = 2.8 Hz), 3.35 (s, 0.68 H), 3.30 (s, 0.13 H)
v	7.69-7.47 (m, 3 H), 6.69 (s, 1 H), 5.33 (s, 2 H) 4.99-4.97 (sep, 0.4 H, *J* = 2.8 Hz), 3.35 (s, 0.67 H), 3.30 (s, 0.07 H)
vi	7.69-7.47 (m, 3 H), 6.69 (s, 1 H), 5.33 (s, 2 H) 4.99-4.97 (sep, 0.3 H, *J* = 2.8 Hz), 3.35 (s, 0.60 H), 3.30 (s, 0.07 H)
Final product ($CDCl_3$, 600 MHz, δ)	7.54 (s, 18 H), 6.84-6.82 (d, 4 H, *J* = 9.0 Hz), 6.77-6.76 (d, 4 H, *J* = 9.2 Hz), 6.75 (s, 7 H), 3.76 (s, 6 H), 0.34-0.32 (m, 67 H), 0.21-0.20 (d, 36 H, *J* = 3.1 Hz), 0.07 (s, 635 H)

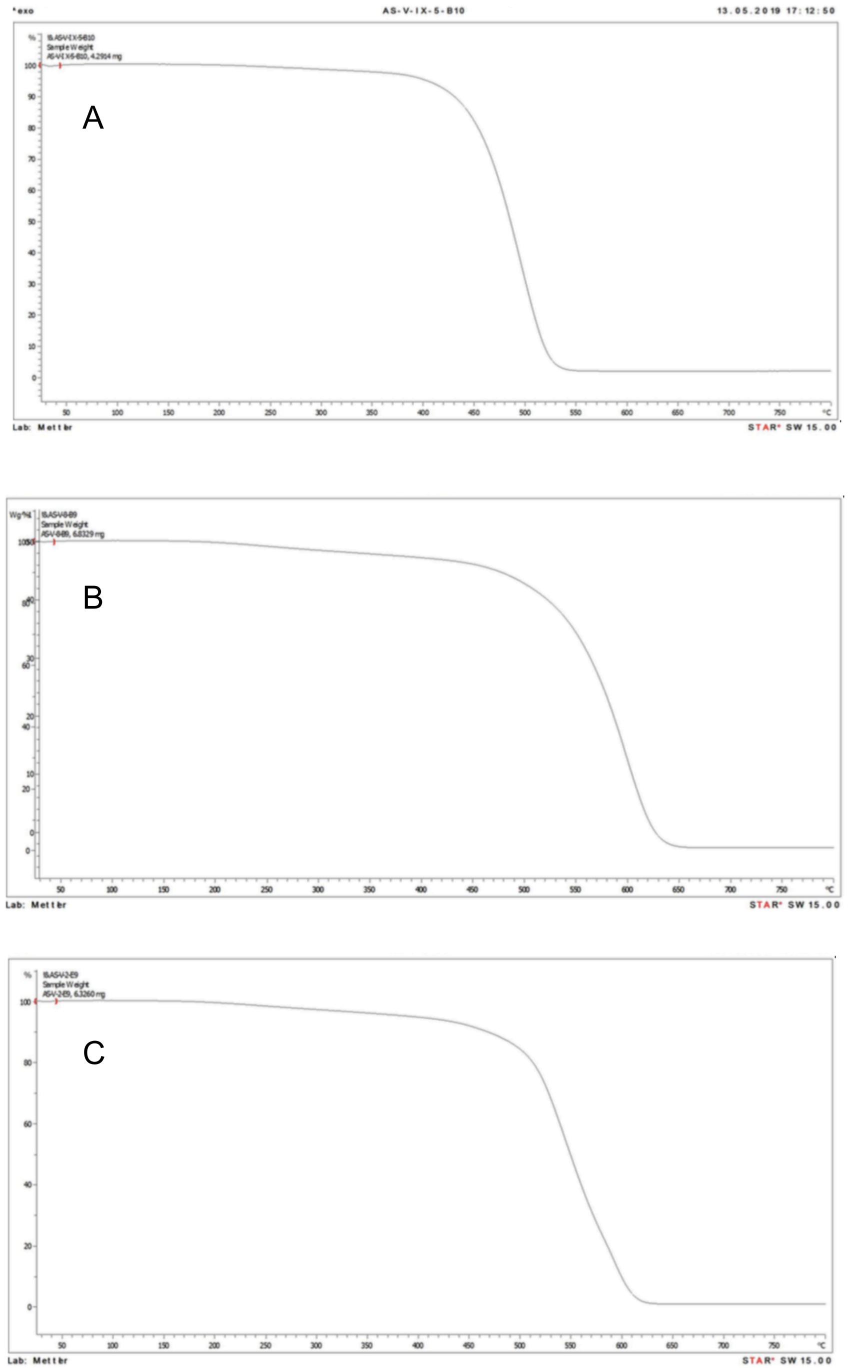


Figure S6.7 TGA traces for elastomers synthesized with 20% $PhMeSi(OMe)_2$ chain extender and crosslinked with 9% A) 1,3,5-trimethoxybenzene, B) phenyltriethoxysilane and C) *n*-propyltriethoxysilane.

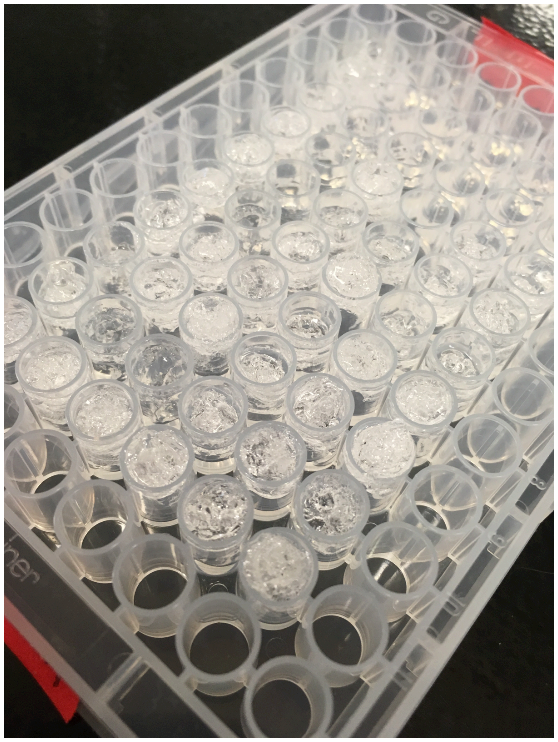


Figure S6.8 Foamed elastomer products – cure occurred quickly, resulting in trapped gaseous byproducts (bubbles)

Chapter 7: Sequential Functionalization of a Natural Crosslinker Leads to Designer Silicone Networks[††]

7.1 Abstract

Precise silicone networks are difficult to prepare from multiple starting materials because of poor spatial control over crosslink location, competing side reactions, and incompatible catalysts among other reasons. We demonstrate that cure processes catalyzed by $B(C_6F_5)_3$ (the Piers-Rubinsztajn reaction) and platinum-catalyzed hydrosilylation are perfectly compatible, and can be used in either order. It is possible to perform three different, selective, sequential reactions in the same pot using H-terminated silicones as chain extenders in all cases to give explicit networks. Eugenol, a readily available aromatic compound, acts as trifunctional crosslinker (HO, MeO, $HC{=}CH_2$) each functional group of which can be induced to undergo selective reaction. With platinum catalysis, the reaction of SiH groups with alkenes is fastest, while $B(C_6F_5)_3$ catalyzes reaction at phenols much faster than methoxybenzene. Thus, a variety of H-terminated telechelic siloxanes can be used to form chain extended polymers, or elastomers or foams in which morphology of the material and its constituent parts can be manipulated at will.

[††] Chapter reproduced from S.E. Laengert, A.S. Schneider, E. Lovinger, Y. Chen and M.A. Brook, Chemistry – An Asian Journal 2017, 12(11), 1208-1212 with permission from Wiley-WCH, copyright 2017. Schneider performed preliminary experiments studying relative reactivity between different functional groups on eugenol (phenol versus methoxybenzene with hydrosilanes via the PR reaction) and assisted with manuscript edits. Laengert performed all sequential polymerization and crosslinking experiments and was the primary author. Lovinger performed preliminary experiments with eugenol and small molecule siloxanes. Chen provided guidance during synthesis and characterization.

7.2 Introduction

As with most polymers, the current paradigm for the preparation of silicone polymers, including elastomers, should involve enhanced synthetic control such that desired properties can be attained. Structural control, however, is not a hallmark of silicone elastomers. The three commercial cure mechanisms normally utilized are radical, moisture cure (room temperature vulcanization RTV), and platinum-catalyzed hydrosilylation (PtHSi).[1] Radical cure leads to irreproducible, random networks. In selected cases, moisture cure allows the controlled incorporation of two different silicone polymers through the use of telechelic crosslinkers; more complex structures are difficult to attain. However, network errors occur when competitive hydrolysis leads to loss of spatial control of crosslinks at a given silicon atom (Figure 7.1A).

Platinum-catalyzed crosslinking (PtHSi), the most common route to high quality silicone elastomers, utilizes the combination of telechelic silicones with pendant functional chains. Unfortunately, the absolute concentration of functional groups on a given chain, and their relative locations along the chain cannot be readily controlled (Figure 7.1B). The resulting networks reflect the specific batch of pendant-functional polymers used. It is, therefore, difficult to reproducibly prepare precise networks from commercial materials.

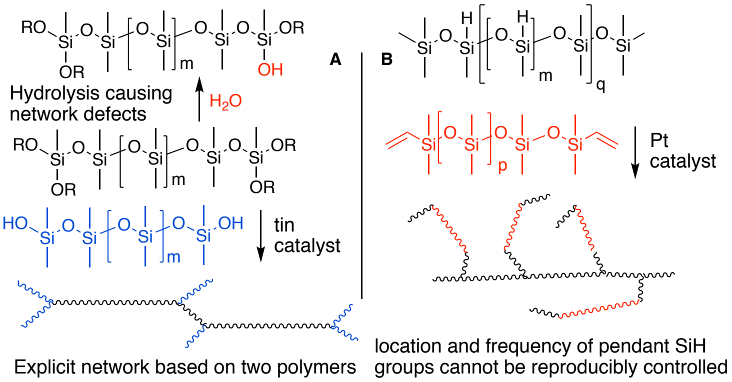


Figure 7.1 It is very challenging to produce precise networks either using A: moisture (RTV) cure or B: PtHSi.

It is possible to create networks containing a variety of silicone precursors in a somewhat controlled manner by using a combination of orthogonal cure technologies selected from silicone and organic chemistry; dual cure systems that combine any of the cure technologies noted above with amine/epoxy,[2-3] cationic epoxy polymerization,[4] thiol-ene click,[5] or azide/alkyne click[6-7] allow complex network materials to be prepared. Most of these processes, however, still suffer from random placement of crosslinking groups along a silicone backbone.

The Piers-Rubinsztajn[8] (PR) reaction has been shown to operate between SiH compounds and SiOR groups;[9-10] a variety of other functional groups will react under the same conditions[11-12] (Figure 7.1A). In all cases, the complex formed between $B(C_6F_5)_3$ (BCF) and a hydrosilane reacts with siloxonium ions to form siloxane bonds and either H_2 or an alkane (RH) byproduct (shown for phenolics, Figure 7.1B). BCF will also catalyze the hydrosilylation reaction with alkenes,[13] but only using high concentrations of catalyst (~5 mol%). We reasoned that, with an appropriate crosslinker bearing 3 different functional groups, it would be possible to control network structures simply by using readily available, (reasonably) well-defined telechelic rather than pendant functional silicones. The precision of the resulting networks would be limited only by the polydispersities of the linear telechelic starting materials.

Eugenol is a readily available organic material extracted from cloves and other plants.[14] It has three different functional groups that should react with SiH with very different efficiencies using either platinum catalysts or $B(C_6F_5)_3$. Platinum should preferentially promote SiH reactions with $RHC=CH_2$ groups, and react much less efficiently with ArOH,[15] while $B(C_6F_5)_3$ will catalyze reactions between SiH and ArOH or ArOMe, respectively. Use of this crosslinker would allow up to three different silicones to be sequentially linked to the central aromatic core, permitting the preparation of precise networks from commercial telechelic silicones; the products' properties could be tuned by selection of the chain lengths of the three silicones, backbone functionalization, and which silicone chain grafts via hydrosilylation.

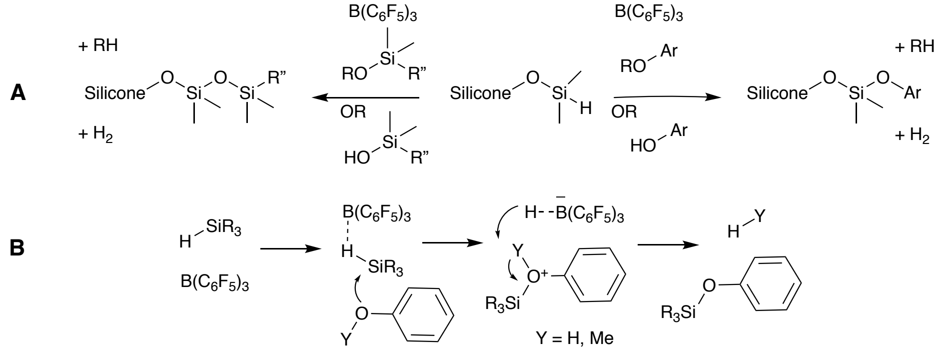


Figure 7.2 A) Examples of Piers-Rubinsztajn reactions; B) proposed mechanism of the PR reaction for phenols and methoxybenzene.

7.3 Results

Previous work has shown that both phenols[12] and methoxybenzene[9-10, 16] structures react under Piers-Rubinsztajn (PR) conditions to create aryloxysilanes (Figure 7.2). The process can occur with simple molecules or more complex natural materials including lignin.[17-20] Eugenol presents three distinct functional groups – the phenol, ArOMe and allyl groups – that, it was reasoned, could be induced to react selectively with different difunctional silanes (Figure 7.3). Prior to attempting to exploit eugenol as a crosslinker, it was necessary to ensure that sufficient selectivity existed between the three functional groups.

Eugenol was reacted with linear silicones bearing Me_2SiH groups at their termini; initially the use of the small model compounds $HMe_2SiOSiMe_3$ demonstrated a very high degree of functional group selectivity. Irrespective of the hydrosilane (hydrosiloxane) molecular weight, clean conversion of the phenol in the presence of $B(C_6F_5)_3$ was observed, without reaction of either the OMe or allyl groups. When telechelic hydrogen-terminated molecules including dimethylsilicones of various molecular weights ($HMe_2SiO(SiMe_2O)_nSiMe_2H$, n = 14, 81, 232, 378), or a phenylmethylsilicone tetramer ($HMe_2SiO(SiMePhO)_2SiMe_2H$) were reacted, the resulting products type **1** were telechelic silicones terminated by eugenol; only phenols reacted. The polydispersities (PDI) of the products matched those of the starting silicone (Figure 7.3A, Table 7.1).

Further chain extension occurred using a second PR reaction in which the same or a different silicone in the same pot consumed the MeO groups; workup between steps was not necessary (Figure 7.3AC, Table 7.1). The molecular weight of the linear products type **2**, as with any AA + BB condensation polymerization, depended on careful control of stoichiometry; linear polymers were isolated of molecular weights ranging from 25,000 to 660,000 g mol^{-1} (Table 7.1).

Crosslinking compounds **2** with telechelic hydrosilicones in the presence of Karstedt's Pt catalyst in the same pot (without workup) led to bubble free elastomers of type **3** (Figure 7.3ACF, Table 7.1). These experiments showed that the presence of $B(C_6F_5)_3$ did not affect the catalytic behavior of the platinum catalyst; without platinum, hydrosilylation was not observed.

The order of reactions could be altered at will because the platinum catalyst similarly did not affect the activity of the boron. For example, the platinum-catalyzed reaction of eugenol with telechelic hydrosilicones led to complete conversion of the allyl groups to give a regioisomeric mixture of telechelic arylpropylsiloxanes **1'** (the ' refers to a hydrosilylation step, only the β–isomer is shown, Figure 7.3B); the phenol and methoxy groups did not react under these conditions. Compounds **1'** were treated with two additional hydro-terminated silicones, sequentially, after addition of $B(C_6F_5)_3$ (Figure 7.3BEH, Table 7.1).

The situation was slightly more complicated if one uses PtHSi between two PR reactions (Figure 7.3ADG, Table 7.1). The platinum catalyst in step 2 does not appear to be affected by the presence of $B(C_6F_5)_3$ and C=C hydrosilylation was observed. However, the PR reaction in step 3 was slower than other PR reactions, suggesting boron catalyst degradation or inhibition along the way, but addition of an additional bolus of $B(C_6F_5)_3$ without any intervening workup led to a clean reaction in the same pot. Thus, the easiest processes to control involves hydrosilylation as the first or last step (Figure 7.3ACF or BEH, respectively).

The PR reaction with ROH or ArOMe generates gaseous by-products that may be utilized to blow foams.[18, 21] As a consequence, foams result when the last step of the 3 step sequences is a PR reaction (Figure 7.3G,H). If long chain silicones were utilized in the final step, the volumetric evolution of methane was small and either no foam, or an elastomer containing only a few bubbles was observed (F3, Figure 7.4). If short chain materials were used, by contrast, the higher quantity of evolved trapped gas manifested through formation of a less dense, more rigid foam (F1 or F2, Figure 7.4, Table 7.1).

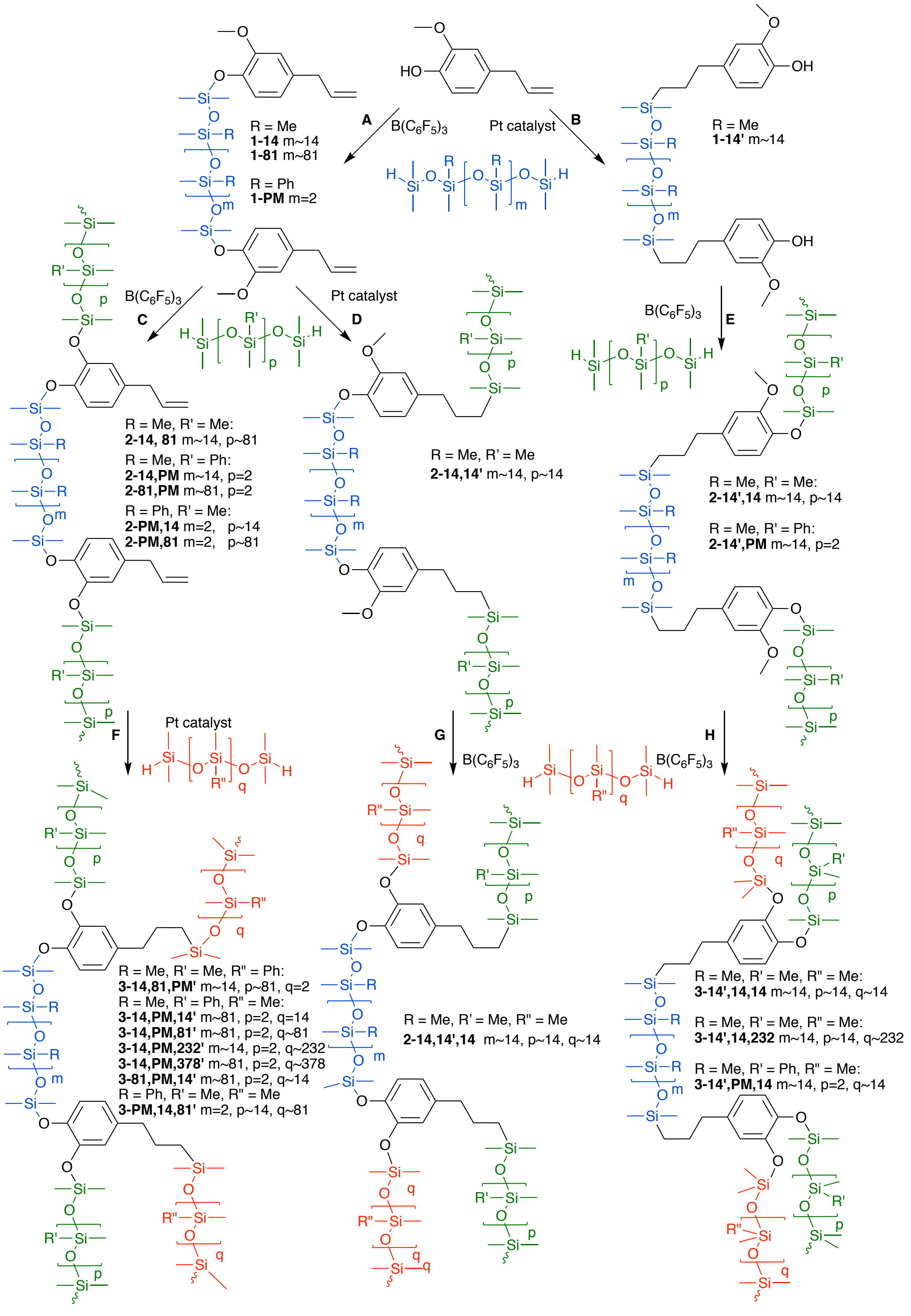
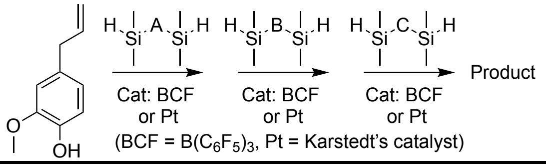


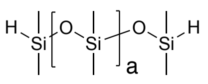
Figure 7.3 Network structural changes depend on order of addition

Table 7.1 Silicone elastomer formulations[a] (Figure 7.3)

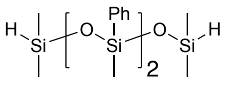


Homopolymer	Copolymer[a]	M_n[b]	Terpolymer	Hardness[c]
1-14	**2-14,81**	66100	**3-14,81,PM'**	73
	2-14,PM	84,700	**3-14,PM,14'**	84
			3-14,PM,81'	63
			3-14,PM,232'	46
			3-14,PM,378'	50
1-81	**2-81,PM**	459,000		
	Batch 2	75700	**3-81,PM,14'**	73
1-PM	**2-PM,14**	50100	**3-PM,14,81'**	74
	2-PM,81	660,800		
1-14	**2-14,14'**	27800	**3-14,14',14**	F1
1-14'	**2-14',14**	22700	**3-14',14,14**	F1
			3-14',14,232	F3
	2-14',PM	26600	**3-14',PM,14**	F2

[a] Nomenclature: **1** eugenol coupled with first silicone of DP x+2, e.g., **1-14** is a silicone of DP 16 terminated by silicones. **2** – reaction of **1** with a second silicone and **3**, after a third reaction. The use of ' denotes Pt-catalyzed hydrosilylation, otherwise a PR reaction is involved.



[b] **PDMS** a ~ **14**, a ~ **81**, a ~ **232**, a **~378**



Ph

[c] See Supporting Information, Shore OO Hardness, Foam type Figure 7.4.

The aversion to "Si-O-C" linkages in the silicone industry borders on affectation, but for good reason. Alkoxysilanes are widely used as precursors for moisture cure (Room Temperature Vulcanization RTV) elastomers.[22] Enhanced hydrolytic stability may be provided by use of bulky ligands adjacent to silicon,[23] but this approach is not considered practicable in industry. It was, therefore, initially expected that the elastomers produced in this 3 step, one pot process would be fragile in the presence of water.

An accelerated test was performed in which solid samples were immersed in boiling water for 12 hours. Surprisingly, after drying, there were no changes to either the modulus of the material nor to its weight (neither gain nor loss was observed within experimental error, full experimental details are found in the Supporting Information).

7.4 Discussion

The mechanism of the PR reaction involves complexation of SiH groups with $B(C_6F_5)_3$, displacement of the hydride by oxygen to form a silyl oxonium ion, and then hydride reduction form alkanes (or hydrogen) and a siloxane (Figure 7.2).[24] The silyloxonium ion formed from phenols is expected to be more reactive than the methoxy group simply because the hydride reaction with a protonated oxygen is expected to be much more facile than displacement of a methyl group at oxygen. Irrespective of the specific hydrosilane used, complete consumption of phenols were found to precede reactions with the OMe group of eugenol.

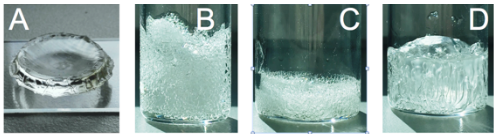


Figure 7.4 Photos of an elastomer A) **3-14,PM,378’** and foams B) **3-14,14’,14** high quality foam type F1, C) **3-14’,14,14** F2, and D) **3-14’,14,232** F3 (larger volume reflects more material, but with far fewer and larger bubbles), showing in the former cases that use of a shorter polymer leads to more efficient bubble capture and a more rigid foam.

Given the choice between the boron-catalyzed PR reaction and boron-catalyzed hydrosilylation (Figure 7.3C), the PR reaction was found to be far more facile. This is expected based on the known requirement for high catalyst concentrations to catalyze hydrosilylation (several %),[13] while we utilized only 0.02 mol% of $B(C_6F_5)_3$ for the PR reaction.

The platinum-catalyzed reaction (typically Speier's or Karstedt's catalyst) with SiH groups can also set up a competition between desired reaction at the allyl groups (e.g., Figure 7.3B) and at the phenol, to give SiOPh + ½ H_2. The latter reaction has been reported to occur much more slowly than the former,[25] and that outcome was observed here too. Clean hydrosilylation occurred without change in the phenol concentration.

The presence of the boron catalyst did not affect the PtHSi of alkenes (Figure 7.3AD). The third reaction in the sequence, however, was sluggish suggesting either boron catalyst degradation or inadvertent addition of a weak poison. However, the reaction rate could be increased in step 3 by addition of a new bolus of $B(C_6F_5)_3$ (Figure 7.3ADG). As this route offered no advantages, the most practical routes follow Figure 7.3ACF or BEF, in which case the two catalysts perform three explicit, orthogonal reactions in the same pot.

Elastomer or foams based on phenoxysilanes **3** were far more resistant to hydrolysis than might be expected based on steric or electronic arguments: sterically, the flat phenyl ring should not significantly restrict access of water to the silicon center; electronically, the stability of the phenol or phenolate product in water should make it a good leaving group. Cleavage of phenoxysilanes described in the literature support these contentions.[26] The observed enhanced stability in water is therefore attributed to the nature of the dimethylsilicone elastomers themselves. We infer the low solubility of water in silicone elastomers retards the rate of hydrolytic cleavage simply by keeping the water at bay under even under the aggressive conditions of boiling water.

Network structure can affect the physical properties of elastomers. This simple sequence of reactions allows the facile preparation of: functional telechelic silicones (Figure 7.3AB), alternating silicone copolymers (Figure 7.3 AC, AD, BE) of molecular weights up to 660,000 and elastomers (last step hydrosilylation, Figure 7.3ACF) or foams (last step PR)(Figure 7.3ADG, BEF). The properties of analogous materials, e.g., the Shore OO hardness of **3-14,81,PM'**, **3-81,PM,14'** and **3-PM,14,81'** are identical, as would be expected (Table 7.1), which shows the robustness of the method. A wide variety of readily available commercial telechelic materials permits the assembly of tight or loose networks with, so far, 2 types of silicones, dimethyl vs methylphenyl. In addition, in a single pot it is possible to make foams of various densities (Figure 7.4) and foams/elastomers of controlled modulus. The method of manufacture ensures complete and precise control of the network structure under mild (room temperature) conditions in a single reaction vessel, without the need for workup between steps.

7.5 Conclusions

The three functional groups on eugenol can be independently targeted for reaction to create silicone-based macromers, linear polymers and network structures – foams and elastomers – by application, in the chosen order, of the Piers-Rubinsztajn reaction and platinum-catalyzed hydrosilylation. It is therefore, straightforward to prepare libraries of silicone elastomers simply by changing the telechelic hydride-terminated silicone spacers, and the order of reactions. The resulting elastomers were surprisingly resistant to hydrolysis.

7.6 Experimental (see Supporting Information)

7.6.1 General Procedure for the PR Reaction (Figure 7.3A,C,E,G,H)

To an oven-dried 10 mL round-bottomed flask (with stir-bar) under a N_2 atmosphere was added dry toluene (1 mL) and eugenol (38.9 µL, 0.25 mmol) and $B(C_6F_5)_3$ catalyst (0.64 µL of a 40 mg/mL solution, 0.02 mol%); the colour changed to bright yellow. The Si-H terminated silicone (e.g., DMS-H11, 142.6 µL, 0.125 mmol) was added dropwise, pausing after ~20 % addition to allow induction time to pass (yellow colour disappears and bubbles form, 5-20 min. Where necessary (after the first or second of 3 steps), $B(C_6F_5)_3$ could be removed by addition of alumina, filtering and evaporation of solvent.

7.6.2 General Procedure for Platinum-Catalyzed Hydrosilylation (Figure 7.3B,D,F)

To dry toluene (1 mL) and eugenol (38.9 µL, 0.25 mmol) in an oven-dried 10 mL round-bottomed flask (with stir bar) under a N_2 atmosphere was added an Si-H terminated silicone (for example, DMS-H21, 773.2 µL, 0.125 mmol) and Karstedt's catalyst (1.0 µL of a 0.01M solution, 0.004 mol%). Reagents were mixed for 20 s and heated at 80 °C for 1 h.

Multiple steps. For a PR – PR sequence, the second bolus of hydridosilicone was added; for a PR – hydrosilylation sequence, the Pt catalyst and a second bolus of hydridosilicone was added.

7.7 Acknowledgments

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S7.9 Appendix 6 – Supporting Information

S7.9.1 Materials

Eugenol, $B(C_6F_5)_3$ and Karstedt's platinum catalyst $Pt_2(H_2C{=}CHSiMe_2OSiMe_2CH{=}CH_2)_3$ were provided by Aldrich. H-terminal functional silicones ($HMe_2SiO(Me_2SiO)_nSiMe_2H$) (DMS-H11, n = 14, MW = 1000 – 1100 g/mol, Viscosity = 7 - 10 cSt., "**14**" in compound numbers; DMS-H21, n = 81, MW = 6000 g/mol, Viscosity = 100 cSt., "**81**" in compound numbers; DMS-H25, n = 232, MW = 17200 g/mol, Viscosity = 500 cSt., "**232**" in compound numbers; DMS-H31, n = 378, MW = 28000 g/mol, Viscosity = 1000 cSt., "**378**" in compound numbers) and ($HMe_2SiO(MePhSiO)_nSiMe_2H$)(PMS-H03, MW = 300 - 500 g/mol, Viscosity = 2 - 5 cSt., "**Ph**" in compound numbers) were purchased from Gelest. Compounds were used as received. Toluene and tetrahydrofuran (Caledon) were dried over an activated alumina column.

S7.9.2 Characterization

^1H NMR were recorded at room temperature on a Bruker AV 600 spectrometer (at 600 MHz for ^1H) using deuterated solvent $CDCl_3$ (NMR data available in Supporting Information, Table S7.4, Table S7.5, Table S7.6). A Shore OO durometer (Rex Gauge Company, Inc. U.S. Patent 2421449) was used to measure hardness. Gel permeation chromatography (GPC) was carried out using a Waters Alliance GPC System 2695 calibrated with a polystyrene calibration kit S-M-10 (Lot 85) from Polymer Laboratories. The system was equipped with a Waters 2414 refractive index detector, a Waters 2996 photodiode array detector, and three Jordi fluorinated polydivinylbenzene mixed bed columns. Tetrahydrofuran was used as the eluent at a flow rate of 1.0 mL/min.

S7.9.3 Stock solution $B(C_6F_5)_3$

A 40 mg/mL stock solution of $B(C_6F_5)_3$ catalyst was made by dissolving 41.2 mg of tris(pentafluorophenyl)borane (Alfa Aesar) in 1.00 mL of dry toluene.

S7.9.4 Stock solution Karstedt's Catalyst

A 0.01M stock solution of Karstedt's Pt catalyst was made by adding 50.0 µL of a 0.1M solution of Karstedt's catalyst in vinyl-terminated PDMS (Sigma-Aldrich) to 450.0 µL of dry toluene.

S7.9.5 General procedure for elastomer prepared by a PR, PR, PtHSi sequence (Table S7.2)

Most experiments were run several times at different scales, from which samples for NMR and GPC were taken. The general procedures reported below describe reactions taken directly through the three steps in one pot.

Step 1: To an oven-dried 10 mL round-bottomed flask (with stir-bar) under a N_2 atmosphere was added dry toluene (1 mL), eugenol (38.9 µL, 0.25 mmol) and BCF catalyst (0.64 µL of a 40 mg/mL solution, 0.02 mol%); the colour changed to bright yellow. The Si-H terminated silicone (e.g., $HMe_2Si(OSiMe_2)_{14}OSiMe_2H$, 142.6 µL, 0.125 mmol) was added dropwise, pausing after ~20 % addition to permit the induction time to pass; the yellow colour disappeared and bubbles began to form. The remainder of the silicone was added slowly, and bubbling ceased after 5-20 min to give product **1-14**.

Step 2: Once bubbling has ceased, a second Si-H terminated silicone (e.g., $HMe_2Si(OSiMePh)_2OSiMe_2H$, 53.8 µL, 0.125 mmol) was added slowly, again pausing after ~20 % had been added to wait for bubbling to recommence. Then the remainder of the silicone was added slowly at a rate commensurate with even formation of bubbles to give product **2-14,Ph**.

Step 3: Once bubbling has ceased, the third Si-H terminated silicone (for example, $HMe_2Si(OSiMe_2)_{81}OSiMe_2H$, 773.2 µL, 0.125 mmol) was added all at once. In some cases, minor bubbling was observed (if insufficient HSi groups had been added in the first 2 steps - any residual methoxy groups were mopped up), which ceased within 5 min. Karstedt's catalyst (1.0 µL of a 0.01M solution, 0.004 mol%) was added, the reaction was mixed for 20 s, and then poured into a Teflon mold and placed in the oven at 80 °C to cure for 1 h and give product **2-14,Ph,81'**.

Note: depending on the specific catalyst batch, cure was sometimes affected at room temperature over a few hours. The Shore OO hardness of the elastomer was measured.

S7.9.6 General procedure for elastomer prepared by a PtHSi, PR, PR sequence (Figure 7.2)

Step 1: To an oven-dried 25 mL round-bottomed flask (with stir-bar) under a N_2 atmosphere was added dry toluene (4 mL), eugenol (2.487 mL, 16 mmol) and hydride-terminated PDMS (e.g., ($HMe_2Si(OSiMe_2)_{14}OSiMe_2H$, 9.129 mL, 8 mmol). Karstedt's catalyst (64 µL of 0.01 M Pt, 0.004 mol%) was then added. The reaction mixture was allowed to stir at room temperature for 10 h to give product **1-14'** h.

Step 2: To the previous reaction mixture **14'** (1.96 mL, 2.0 mmol) was added: BCF (5.12 µL of a 40 mg/mL toluene solution, 0.02 mol%); hydride-terminated PDMS (e.g., ($HMe_2Si(OSiMe_2)_{14}OSiMe_2H$, 1.141 mL, 1.0 mmol) was added portion-wise over 15 mins. Bubbling was observed from reaction mixture over about 30 min giving **2-14’,14**. Samples were retained for ^{1}H NMR and GPC.

Step 3: To **2-14’,14** reaction mixture (776 µL, 0.5 mmol) was added hydride-terminated PDMS (e.g., ($HMe_2Si(OSiMe_2)_{232}OSiMe_2H$, 4433 µL, 0.25 mmol), and the reaction was thoroughly mixed; it remained translucent. After 30 min the mixture was a viscous liquid so additional $B(C_6F_5)_3$ (1.28 µL of a 40 mg/mL toluene solution, 0.02 mol%) was added. A very soft, foam **3-14’,14,232** was formed within about 10 min.

S7.9.7 General procedure for elastomer prepared by PR, PtHSi, PR sequence (Figure 7.2)

Step 1: To an oven-dried 25 mL round-bottomed flask (with stir-bar) under a N_2 atmosphere was added dry toluene (3 mL), eugenol (2.487 mL, 16 mmol) and $B(C_6F_5)_3$ catalyst (41.0 µL of a 40 mg/mL solution, 0.02 mol%); the colour changed to bright yellow. The Si-H terminated silicone (e.g., $HMe_2Si(OSiMe_2)_{14}OSiMe_2H$, 9.129 mL, 8 mmol) was added dropwise, pausing after ~20 % addition to permit the induction time to pass; the yellow colour disappeared and bubbles began to form. The remainder of the silicone was added slowly, and bubbling ceased after 5-20 min to give product **1-14**. Samples were taken for ^{1}H NMR and GPC.

Step 2: Once bubbling has ceased, Karstedt’s catalyst (64 µL of 0.01 M Pt, 0.004 mol%) was added to the reaction mixture without quenching the $B(C_6F_5)_3$ catalyst present. (Alternatively, the $B(C_6F_5)_3$ catalyst can be quenched by adding a small amount of neutral alumina, stirring for 10 minutes, and filtering.) A second Si-H terminated silicone (e.g., $HMe_2Si(OSiMe_2)_{14}OSiMe_2H$, 9.129 mL, 8 mmol) was then added slowly over 5 min, with only minor bubbling occurring during the period of addition. The reaction was stirred for 10 h (no further bubbles were observed) to give product **2-14,14'**. Samples were taken for ^{1}H NMR and GPC.

Step 3: To **2-14,14'** reaction mixture (23.85 mL, 16 mmol) was added hydride-terminated PDMS, (e.g., $HMe_2Si(OSiMe_2)_{14}OSiMe_2H$, 9.129 mL, 8 mmol) and the reaction was thoroughly mixed; it remained translucent and produced minor bubbling. An additional bolus of $B(C_6F_5)_3$ (41.0 µL of a 40 mg/mL solution, 0.02 mol%) was added to the mixture and heat was applied. Within 5 – 10 seconds a brittle foam **3-14,14',14** was formed.

Table S7.2 Reaction parameters

Polymer	**Eugenol mmol, (vol in μL)**	**Polymer 1 mmol, (vol in μL)[a]**	**Polymer 2 mmol, (vol in μL)[a]**	**Polymer 3 mmol, (vol in μL)[a]**	**BCF mol% (vol in μL)[b]**	**Pt catalyst mol% (vol in μL)[c]**	**Toluene (mL)**
1-14	016 (2487)	**4** 8 (9130)			0.02 (41 μL 0.0032 mmol)		3
1-14’	16 (2487)	**4** 8 (9130)				0.004 (64 μL, 0.00064 μmol)	4
1-81	0.25 (38.9)	**81** 0.125 (773.2)			0.02 (0.64)		
1-Ph	0.25 (38.9)	**PM** 0.125 (53.8)			0.02 (0.64)		
3-14, 81,PM’	0.25 (38.9)	**14** 0.125 (142.6)	**81** 0.125 (773.2)	**PM** 0.125 (53.8)	0.02 mol% (0.64)	0.004 (1.0)	1
3-14, PM,14’	0.75 (116.6)	**14** 0.375 (427.9)	**PM** 0.375 (161.3)	**14** 0.375 (427.9)	0.02 (1.9)	0.0012 (0.9)	1
3-PM, 14,81’	0.25 (38.9)	**PM** 0.125 (53.8)	**14** 0.125 (142.6)	**81** 0.125 (773.2)	0.02 (0.64)	0.004 (1.0)	1
3-14, PM,232’	0.25 (38.9)	**14** 0.125 (142.6)	**PM** 0.125 (53.8)	**232** 0.125 (2217)	0.02 (0.64)	0.0072 (1.8)	2
3-14, PM,378’	0.25 (38.9)	**14** 0.125 (142.6)	**PM** 0.125 (53.8)	**378** 0.125 (3608)	0.02 (0.64)	0.0108 (2.7)	3
3-81, PM,14’	0.25 (38.9)	**14** 0.125 (142.6)	**PM** 0.125 (53.8)	81 0.125 (773.2)	0.02 (0.64)	0.0036 (0.9)	1
3-14, 14’,14	1.0 (155.4)	**14** 0.5 (570.6)	**14** 0.5 (570.6)	**14** 0.5 (570.6)	0.02 (0.64)	0.004 (4.0)	1
3-14’, 14,14	1.0 (155.4)	**14** 0.5 (570.6)	**14** 0.5 (570.6)	**14** 0.5 (570.6)	0.02 (2.56)	0.004 (4.0)	
3-14’, 14,232	1.0 (155.4)	**14** 0.5 (570.6)	**14** 0.5 (570.6)	**232** 0.5 (8866.0)	0.02 (2.56)	0.004 (4.0)	
3-14’, PM,14	1.0 (155.4)	**14** 0.5 (570.6)	**PM** 0.5 (215.1)	**14** 0.5 (570.6)	0.02 (2.56)	0.004 (4.0)	

[a] ($HMe_2SiO(Me_2SiO)_nSiMe_2H$): **14**, n = 14; **81**, n = 81; **232**, n = 232; **378**, n = 378; **PM** ($HMe_2SiO(MePhSiO)_2SiMe_2H$); numbers followed by a ‘ reflect platinum-catalyzed hydrosilylation, otherwise $B(C_6F_5)_3$ was used

[b] $B(C_6F_5)_3$: a 40 mg/mL solution in toluene

[c] $Pt_2(H_2C{=}CHSiMe_2OSiMe_2CH{=}CH_2)_3$: a 0.01M solution in toluene.

S7.9.8 Hydrolysis Test Procedure

Strips of elastomer measuring ~2 x 3 x 10 mm were cut out of a 2 mm thick sample of fully-cured bulk elastomer and weighed. The strips were then submerged in dichloromethane for 3 hours, replacing the solvent with fresh stock after each hour, to extract any leachable material. The swollen strips were removed from the DCM, left at room temperature for 30 min, placed in a vacuum oven at 635 mmHg and 60 °C overnight, and reweighed. Each elastomer was then placed in a vial of boiling distilled water in an oil bath set to 110 °C and left for 12 h, topping up the water every 30 min. The samples were then placed in the vacuum oven at 635 mmHg and 70 °C overnight, and reweighed. The strips were then submerged once again in dichloromethane for 3 hours, replacing the solvent with fresh stock after each hour, to extract any material having undergone hydrolysis. Finally, the strips were placed in a vacuum oven at 635 mmHg and 60 °C for 8 hours, and reweighed. See Table S7.3 for results of this hydrolysis test for a series of three elastomers.

Table S7.3 Changes in weight following boiling in water

Compound	Initial sample weight (mg)	Weight after first DCM extraction (mg)	Weight after 12-hour exposure to boiling water (mg)	Weight after second DCM extraction (mg)	Loss of weight between DCM extractions (%)
3-PM, 14, 81’	72.9	70.4	72.5	69.4	1.4
3-81, PM, 14’	77.4	74.1	77.1	74.0	1.5
3-14, 81, PM’	55.1	53.1	54.9	52.4	1.3

Table S7.4 ^{1}H NMR data of starting materials

Compound	**^{1}H NMR data ($CDCl_3$, 600 MHz) δ:**
Eugenol	6.86 (d, 1 H J = 8.5 Hz), 6.70 (s, 2 H), 6.00-5.93 (m, 1 H), 5.52 (s, 1 H), 5.10-5.06 (m, 2 H), 3.88 (s, 3 H), 3.33 (d, 2 H, J = 6.8 Hz)
PMS-H03 (**PM**)	7.67-7.35 (m, 9 H), 4.89-4.75 (m, 2 H), 0.40-0.38 (m, 6 H), 0.28-0.22 (m, 12 H)
DMS-H11 (**14**)	4.72-4.69 (sep, 2 H, J = 2.8 Hz), 0.19-0.18 (d, 14 H, J = 2.8 Hz), 0.07 (s, 72 H)
DMS-H21 (**81**)	4.72-4.69 (sep, 2 H, J = 2.8 Hz), 0.20-0.18 (d, 13 H, J = 2.8 Hz), 0.08 (s, 561 H)
DMS-H25 (**232**)	4.72-4.69 (sep, 2 H, J = 2.8 Hz), 0.20-0.18 (d, 18 H, J = 2.8 Hz), 0.08 (s, 1600 H)
DMS-H31 (**378**)	4.72-4.69 (sep, 2 H, J = 2.8 Hz), 0.20-0.18 (d, 25 H, J = 2.8 Hz), 0.08 (s, 3550 H)

Table S7.5 ^{1}H NMR data of telechelic polymers[a]

Compound	**^{1}H NMR data (CDCl$_3$, 600 MHz) δ:**
1-PM	7.58-7.54 (m, 2 H), 7.37-7.26 (m, 3 H), 6.82-6.74 (m, 1 H), 6.67-6.64 (m, 1 H), 6.60-6.54 (m, 1 H), 5.99-5.92 (m, 1 H), 5.09-5.05 (m, 2 H), 3.77-3.71 (m, 3 H), 3.32-3.30 (t, 2 H, *J* = 5.6 Hz), 0.33-0.06 (m, 11 H)
1-81	6.86-6.85 (d, 1 H, *J* = 8.0 Hz), 6.69-6.68 (d, 1 H, *J* = 1.5 Hz), 6.64-6.63 (d, 1 H, *J* = 8.0 Hz), 6.00-5.93 (m, 1 H), 5.09-5.05 (m, 2 H), 3.79 (s, 3 H), 3.33-3.32 (d, 2 H, *J* = 6.7 Hz), 0.22 (s, 6 H), 0.09 (s, 264 H)
1-14	6.87-6.85 (d, 1 H, *J* = 8.0 Hz), 6.69 (d, 1 H, *J* = 1.5 Hz), 6.65-6.64 (d, 1 H, *J* = 8.0 Hz), 6.00-5.93 (m, 1 H), 5.09-5.05 (m, 2 H), 3.80 (s, 3 H), 3.34-3.32 (d, 2 H, *J* = 6.7 Hz), 0.22 (s, 6 H), 0.09 (s, 38 H)
1-14'	6.84-6.83 (d, 1 H, *J* = 8.5 Hz), 6.68-6.67 (d, 2 H, *J* = 6.6 Hz), 5.46 (s, 1 H), 3.88 (s, 3 H), 2.57-2.55 (t, 2 H, *J* = 7.7 Hz), 1.65-1.59 (m, 2 H), 0.60-0.58 (m, 2 H), 0.23-0.05 (m, 49 H)

[a] Platinum-catalyzed hydrosilylation leads to a mixture of two (inseparable) isomers. NMR data of both is presented.

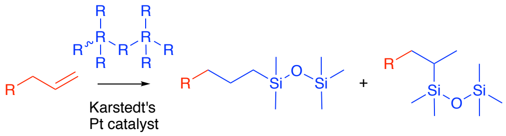

Table S7.6 ^{1}H NMR data of linear polymers

Compound	**^{1}H NMR data ($CDCl_3$, 600 MHz) δ:**
2-PM,14[a]	7.57-7.53 (m, 2 H), 7.36-7.27 (m, 3 H), 6.81-6.72 (m, 2 H), 6.59-6.51 (m, 1 H), 5.94-5.88 (m, 1 H), 5.05-5.01 (m, 2 H), 3.25-3.23 (t, 2 H, *J* = 6.0 Hz), 0.34-0.07 (m, 55 H)
2-81,PM[a]	7.58-7.54 (m, 2 H), 7.37-7.28 (m, 3 H), 6.86-6.84 (m, 1 H), 6.68-6.62 (m, 2 H), 6.00-5.79 (m, 1 H), 5.09-4.94 (m, 2 H), 3.79 (s, 0.4 H)*, 3.33-3.12 (m, 0.5 H), 3.20-3.15 (d, 0.5 H, *J* = 6.7 Hz), 3.15-3.10 (d, 1.0 H, *J* = 6.7 Hz), 0.35-0.08 (m, 287 H)
2-14,81	6.86-6.84 (d, 1 H, *J* = 8.0 Hz), 6.76 (d, 1 H, *J* = 1.8 Hz), 6.65-6.64 (d, 1 H, *J* = 8.0 Hz), 5.99-5.89 (m, 1 H), 5.09-5.02 (m, 2 H), 3.79 (s, 0.7 H)*, 3.33-3.32 (d, 0.5 H, *J* = 6.7 Hz), 3.27-3.26 (d, 1.5 H, *J* = 6.7 Hz), 0.21 (d, 12 H), 0.07 (s, 291 H)
2-14,14’	6.86-6.82 (m, 1 H), 6.66 (s, 1 H), 6.62-6.61 (d, 1 H, *J* = 8.0 Hz), 3.79 (s, 3 H), 2.57-2.54 (t, 2 H, *J* = 7.6 Hz), 1.66-1.59 (m, 2 H), 0.60-0.56 (m, 2 H), 0.22 (s, 7 H), 0.08 (s, 91 H)
2-14’,14	6.84-6.82 (d, 1 H, *J* = 8.0 Hz), 6.67 (m, 1 H), 6.63-6.61 (d, 1 H, *J* = 8.0 Hz), 3.79 (s, 3 H), 2.57-2.54 (t, 2 H, *J* = 7.6 Hz), 1.66-1.59 (m, 2 H), 0.60-0.57 (m, 2 H), 0.22 (s, 6 H), 0.08 (s, 89 H)
2-14’,PM	7.59-7.55 (m, 2 H), 7.37-7.15 (m, 3 H), 6.84-6.54 (m, 3 H), 3.80-3.72 (m, 3 H), 2.58-2.53 (m, 2 H), 1.66-1.59 (m, 2 H), 0.61-0.57 (m, 2 H), 0.34-0.05 (m, 61 H)

[a] In the spectra of compounds **2-81,PM** and **2-14,81** a singlet appears at 3.79 ppm arising from unreacted aryl methoxy groups on eugenol. This results if a stoichiometric deficit of Si-H is added in the chain extension step. This was addressed when making an elastomer/foam by providing extra H-PDMS-H for the third reaction.

Chapter 8: General Conclusions

Fluidic and elastomeric silicones are widely employed as polymeric materials due to their unique properties that stem from a silicon-oxygen backbone structure. The high thermal stability, oxidative resistance, low toxicity, moldability, and maintenance of fluidity across a broad temperature range, among others, make silicones attractive in a variety of applications in the electronic, automotive and medical fields.[1-5] Organosilicones combine the benefits of silicones with properties of organic groups and/or polymers.[2, 5] Incorporating aromatic groups into silicones works to elevate thermal stability, refractive index and improve mechanical properties.[5]

Linear phenylmethyl and dimethyl silicones are typically made using ring-opening polymerization (ROP), which employs strong acid/base initiators and chlorosilane termination steps.[6-7] Since the siloxane bond is susceptible to degradation by acids and bases, issues of chain redistribution accompany ROP methods, that is, the formation of cyclics often accompanies polymer formation during the process.[1] Alternative condensation polymerization techniques require chlorosilane starting materials that, when hydrolyzed, release HCl as a byproduct.[8-9]

The Piers-Rubinsztajn reaction is an alternative synthetic route to linear silicones, which provides the chemist with a controllable method to develop well-defined silicones while avoiding the use of chlorosilanes and avoids the introduction of Brønsted acids and bases that can be difficult to remove at the end of polymerization.[1, 10-13] The Piers-Rubinsztajn reaction involves the tris(pentafluorophenyl)borane ($B(C_6F_5)_3$)-catalyzed dehydrocarbonative siloxane bond formation between a hydrosilane and an alkoxysilane, releasing an alkane byproduct (R'$_3$Si-H + RO-SiR"$_3$ $\rightarrow$ R'$_3$Si-O-SiR"$_3$ + RH).[11-13] Silanols or alkoxybenzenes can be used in place of alkoxysilanes and these reactions can be used to develop both pure silicones and organosilicones.[14-15]

Water plays both an inhibitory and complementary role in the PR reaction. As a Lewis base, it coordinates to the Lewis acid B(C_6F_5)$_3$ forming a hydrate complex, which exists in a dynamic equilibrium with the frustrated pair.[13, 16] The PR reaction is initiated by coordination of a hydrosilane with B(C_6F_5)$_3$, a process, which was inhibited by water.[13] This process can be considered competitive in nature, but when given the choice, B(C_6F_5)$_3$ preferentially coordinates to a hydrosilane.[11, 17-18] Therefore, water only effectively inhibited the PR reaction when it is present in the B(C_6F_5)$_3$ catalyst stock solution (Chapter 2). Stock solutions are typically prepared in toluene; toluene can solubilize trace amounts of water. When B(C_6F_5)$_3$ and water coexist in solution they have the opportunity to coordinate. Then, at the time of desired catalyst use, the concentration of free B(C_6F_5)$_3$ will be lower than expected due to some B(C_6F_5)$_3$ existing in the hydrate form; rates of PR reactions depend upon concentration of free B(C_6F_5)$_3$ in solution. The use of alternative solvents that less readily solubilize water (such as PDMS) worked to preserve catalyst solutions over longer periods with frequent use. Due to the insolubility of B(C_6F_5)$_3$ in PDMS, M_3T^H was added to coordinate to B(C_6F_5)$_3$ giving a complex that was soluble in PDMS – complex is in equilibrium with frustrated Lewis pair and M_3T^H dissociates prior to B(C_6F_5)$_3$ catalytic activity in the PR reaction. Water that exists in solution with a hydride-functional silicone will competitively coordinate to B(C_6F_5)$_3$, but the hydrosilane coordination will win. Once the B(C_6F_5)$_3$ and hydrosilane form a complex, water can then act as a nucleophile, attacking the electrophilic silicon atom, displacing the borohydride forming an oxonium ion. Borohydride-mediated displacement of a hydrogen releases a silanol product, and a hydrogen gas byproduct (Figure 3.3A). This silanol can then participate in a PR reaction with a hydrosilane forming a siloxane bond (Figure 3.3B). This hydrolysis/condensation process was used to significantly chain extend low molecular weight silicones (Chapter 3). Slow ingress of water from the atmosphere (facilitated by toluene) worked to effectively grow polymer molecular weight. This process proved to be a superior hydrolysis method when compared to adding bulk water to a mixture of hydride-terminated silicone and $B(C_6F_5)_3$. The chain extension process is terminated once no SiH groups remain and only SiOH groups remain in solution. However, this process is living in the sense that addition of more hydrosilane will initiate further reactions.

Hydrolysis was used as a compliment to the PR reaction to produce block copolymers. Equimolar mixtures of H-PDMS-H and *p*-dimethoxybenzene quickly reacted via the PR reaction to form a central block – aryl ethers react much quicker than water, therefore competitive hydrolysis was not a factor (Chapter 4). Then, in the same open reaction vessel (without addition of supplementary $B(C_6F_5)_3$), more H-PDMS-H starting material was added and hydrolysis worked to grow chain ends and produce homosilicone end blocks. Block sizes were grown at will (and the RI of the product was tuned) by selection of the molar excess of flanking silicone used.

High refractive index polymers (RI > 1.5) are desirable for use in optical and electronic devices. The hydrolysis and PR reactions were used to develop phenyl rich silicones with refractive indices in the range 1.49-1.59 and M_ns up to 300 kDa – refractive indices were directly proportional to the Ph/Si ratio in the polymer (Chapter 5). Cyclic phenyl silicone byproduct formation was unavoidable but concentrations (of 6-30 %) were on par with or below previously reported values (from ROP). The phenyl rich silicones were prepared to have hydrosilane end group functionality. This allowed incorporation of phenyl rich silicones into block copolymers and offers the potential for crosslinking to produce high RI elastomers.

The PR reaction can facilitate chain extension followed by subsequent crosslinking in a single step by exploiting the relative reactivity of different functional groups. By using methoxysilane functional monomer chain extenders and ethoxysilane, or aryl ether functional crosslinkers, hydrosilanes proceed first through the chain extension mechanism then through crosslinking. Libraries of aryl silicone elastomers were prepared using combinatorial chemistry in order to gain insight into structure-property relationships in these materials (Chapter 6). Using high-throughput synthesis and characterization suites, plates of 60 elastomers were prepared in under 30 minutes and the mechanical properties of each elastomer was characterized. The liquid handling parameters of the robotic arms were optimized to aspirate and dispense silicone into wells of 96-welled plates. Small changes in crosslinker type and chain extender types were analyzed and statistically relevant Young's modulus data was obtained by performing 6+ repeats of a specific formulation – an average with error for each formulation was provided. Utilizing a trimethoxybenzene crosslinker worked to elevate the Young's modulus of silicone elastomers by 50 % at low crosslinker concentrations (6-10 %) when compared to phenyl-or alkyl-substituted trialkoxysilane crosslinkers. The aromatic ring worked to provide rigidity to the network in contrast to the flexible siloxane bonds produced from trialkoxysilane crosslinkers. The chain extension step was necessary to incorporate phenyl groups along the silicone backbone, but also because the high-throughput synthesis suite had difficulty handling high viscosity materials.

Structurally well-defined elastomers were prepared (Chapter 7) by exploiting the relative reactivity of 3 different functional groups on a single linker (eugenol). Eugenol contains a phenol, a methoxybenzene and a vinyl group. All 3 functional groups react with hydrosilanes – the phenol and methoxybenzene were able to react via the PR reaction and the vinyl group by hydrosilylation. By adding half an equivalent of telechelic hydride terminated siloxane and catalytic amounts of $B(C_6F_5)_3$ to eugenol, clean conversion of only phenol groups occurred to produce eugenol capped PDMS. By adding a second equivalent of hydride-terminated siloxane, chain extension was subsequently facilitated by the PR reaction with the methoxybenzene groups. In a final step, by adding a third equivalent of hydride-terminated siloxane with catalytic amounts of Karstedt's catalyst, linear organosilicones were crosslinked into bubble free elastomers with defined morphology. Addition of Karstedt's (platinum) catalyst to the solution containing $B(C_6F_5)_3$ (in other words, without removing PR catalyst prior to hydrosilylation) had no effect on elastomer synthesis; and vice versa. The order of reactions was interchanged to create elastomers of altered morphology, when the PR reaction was the last step foams were formed as opposed to elastomers. No evidence of platinum-catalyzed condensation between the hydrosilane and phenol was observed – hydrosilylation of olefins is much faster.

While the quest for the ‘holy grail’ of synthetic methods in silicone chemistry is still under investigation, we have demonstrated that the $B(C_6F_5)_3$-catalyzed PR and hydrolysis reactions provide the tools to develop well defined aryl silicones. Tuning silicone properties based on synthetic strategies is important. It permits the development and understanding of structure property relationships in silicone chemistry, which in turn allows formulations to be tailored to desired applications. The high-throughput synthetic methods developed here lay the groundwork for future work in combinatorial chemistry to quickly optimize synthetic procedures and permit further advancements in silicone polymer chemistry.

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