NEW ROUTES TO STRUCTURED SILICONES

THE PIERS-RUBINSZTAJN REACTION: NEW ROUTES TO STRUCTURED SILICONES

By

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A Thesis

Submitted to the School of Graduate Studies

In Partial Fulfillment of the Requirements

For the Degree of

Doctor of Philosophy

McMaster University ©

McMaster University Doctor of Philosophy (2013) Hamilton, Ontario (Department of Chemistry and Chemical Biology)

TITLE: The Piers-Rubinsztajn Reaction: New Routes to Structured Siicones

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NUMBER OF PAGES: xviii, 278

Abstract

Silicones are a class of polymeric materials broadly used in numerous commercial applications, primarily due to the significant advantages they poses over their carbon-based analogues. The technology utilized to synthesize them is rather mature, and most 'new' synthetic strategies involve only incremental changes to the existing norm. The high level of structural control that has become the hallmark of organic synthesis and increasingly of polymer chemistry is essentially absent from silicone chemistry. The origin of this deficiency is the susceptibility of silicone polymers to redistribution (metathesis/rearrangement) under acidic and basic conditions, which will destroy any existing controlled architectures. The Piers-Rubinsztajn reaction, catalyzed by tris(pentafluorophenyl)borane ($B(C_6F_5)_3$), involves the direct coupling between an alkoxysilane and hydrosilane forming a new siloxane linkage, ($R_3Si\text{-}OMe + H\text{-}SiR'_3 \rightarrow R_3Si\text{-}O\text{-}SiR'_3 + Me\text{-}H$). The reaction avoids any unwanted acidic/basic reaction conditions and has been shown previously to provide an efficient route to precise, well-defined silicones.

Herein, the functional tolerance of the Piers-Rubinsztajn reaction is reported. It has been shown that in the presence of Lewis basic functional groups (such as –OH, $-NH_2$, -SH) unwanted side reactions result. However in the presence of

haloalkanes and alkenes the reaction is fully tolerant, leading to the synthesis of over twenty new, well-defined functional silicones.

The ability to utilize prepared functional silicones in common organic transformations is also reported. It has been shown that prepared halocarbon-modified silicones can readily be converted to their subsequent azido derivatives and tethered to alkyne-modified poly(oxyethyene) (PEG or PEO) of a variety of molecular weights. This led to the synthesis of over fifteen new, well-defined silicone surfactants. Structure activity relationships have also been reported for the synthesized surfactants, showing that subtle manipulations to the silicone hydrophobe can substantially alter the properties the surfactants possess. The use of thiol-ene click chemistry which involves the reaction between prepared well-defined alkene containing silicones and thiol modified poly(oxyethylene) of varying molecular weights is also reported, providing another route to well-defined silicone based surfactants.

The use of the Piers-Rubinsztajn reaction in the synthesis of larger, well-defined silicone based macrostructures is also reported. It has been shown that through alternation between the Piers-Rubinsztajn reaction and platinum catalyzed hydrosilylation, well defined silicone dendrimers can be obtained with relative ease through a combination of both divergent and convergent growth methods.

Finally, a new method for the preparation of both silicone elastomers and silicone foams is reported. Through use of the Piers-Rubinsztajn reaction, elastomers can be readily obtained. A detailed analysis of the many factors that may alter the overall properties of the elastomers produced including solvent volume, crosslinker concentration and type and the molecular weight of the starting hydride terminated polydimethylsiloxane (H-PDMS-H) is discussed.

Taking advantage of the volatile hydrocarbon byproducts of the Piers-Rubinsztajn reaction, silicone foams can also be prepared using this method. A study analogous to that carried out on the silicone elastomers is also reported, showing that through subtle manipulations to the silicone foam formulations, significant changes to the materials properties can be obtained.

Acknowledgements

First and foremost I want to thank my PhD supervisor Dr. Michael A. Brook for giving me an opportunity to work is his lab. Mike's enthusiasm for chemistry and ability to inspire me to work out of my comfort zone has not only made me a better scientist, but also has made me a better person. I truly appreciate all the advice and support and will continually strive for more because of you. I also would like to thank my supervisory committee: Dr. Alex Adronov and Dr. John Valliant. All of the helpful advice and suggestions you both have given me over the years has helped shape my project into what it is now. I appreciate the time you both have taken to be on my committee. I would also like to thank the NMR facility and the mass spec facility for all your hard work dealing with my tricky samples.

To my labmates in the Brook lab over the years, I wouldn't have gotten this far without all of you. Special thanks to Vinodh for being the most relaxed person I will ever meet and teaching me how to chill out, Helen for being a great friend during the early days of my graduate career, Laura for your helpful suggestions and 'say it as it is' personality, Mark for making me laugh when times were tough, Jason for being a great friend, Marlena for being Marlena, and all those who I have missed, thank you.

I would also like to give a special thanks to all of the undergraduates that I have supervised over the last few years including but not limited to: Alex, Tara, Tomas, Tim and Robin. Although it was my job to mentor you, the friendships I have gained during the process won't be forgotten. I wish you all the greatest success in your graduate careers.

I would like to thank all of the friends I have met over the years from various places around McMaster campus: Patrica, Meera, Nik, Greg, Alan etc. – our trips to the Phoenix will never be forgotten.

I would also like to thank Dr. Dan Chen for always giving me advice and pointing me in the right direction when I would occasionally fall off track, you have been a great help. I would also like to thank Dr. Ferdinand Gonzaga. Although things aren't the same, your help and guidance in the early days of my graduate career were invaluable, and I thank you for that. Your ability to always get me to think positive about chemistry will forever shape the way I approach a chemical reaction.

I would also like to thank Amanda Fawcett. If there is one thing I have gained from McMaster it is you. Your love and support have consistently guided me through both the tough times and the good times. I can't imagine my PhD career without your desk behind mine. I thank you for all the wonderful memories and I look forward to all of the ones we have yet to make. I love you.

And last but certainly not least; I would like to thank my parents Mario and Denise Grande. The guidance and immense support you both have given me throughout my life and through the course of my PhD have been my backbone. I cannot express how grateful I am to have both of you as parents and I appreciate everything you have done for me. I wouldn't be where I am now without the love and encouragement both of you have given me. I thank you for this.

Declaration of Academic Achievement

The work performed by the author is described in the footers of each chapter in this document.

Published Manuscripts:

1. F. Gonzaga, L. Sadowski, T. Rambarran, J. B. Grande**,** A. Adronov, and M. A. Brook, *Journal of Polymer Science Part A, Polymer Chemistry*, 2013, **51** (6), 1272–1277.
2. A. S. Fawcett, J. B. Grande, and M. A. *Journal of Polymer Science Part A, Polymer Chemistry*, 2012, **51** (3), 644–652
3. J. B. Grande, A. S. Fawcett, A. J. McLaughlin, F. Gonzaga, T. P. Bender, and M. A. Brook, *Polymer*, 2012, **53** (15), 3135-3142.
4. J. B. Grande, F. Gonzaga and M. A. Brook, *Chemistry, A European Journal*, 2012, **18**, 1536-1541.
5. D. J. Keddie, J. B. Grande, F. Gonzaga, M. A Brook and T. R. Dargaville, *Organic Letters*, 2011, **13** (22), 6006-6009.
6. B. A. Kamino, J. B. Grande, M. A. Brook and T. P. Bender, *Organic Letters,* 2011, **13** (1), 154–157
7. M. A. Brook, J. B. Grande and F. Ganachaud, *Advances in Polymer Science*, 2011, **235**, 161-183
8. J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, *Chemical Communications*, 2010, **46**, 4988-4990
9. J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Transactions*, 2010, **39**, 9369-9378
10. D. B. Thompson, J. B. Grande and M. A. Brook, *Polymer Preprints*, **50** (2), 814-815

Manuscripts in Preparation:

1. J. B. Grande, T. Urlich, T. Dickie and M. A. Brook, *Angewandte Chemie* (to be submitted by August 2013)
2. J. B. Grande, L. Dodge and M. A. Brook, *Chemical Communications* – 2013 (invited review, to be submitted by August 2013)

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Chapter 1: Introduction[†]

1.1 Traditional methods for silicone chemistry rely on ionic chemistry

Silicones, polymers based on a ~R_2SiO~ repeat unit, constitute an important class of materials.[1, 2] Their additional cost, when compared to organic polymers, is justified by the exceptionally useful properties that the materials possess in terms of thermal, electrical, biological, surface and other behaviors.

These materials have been commercially produced since the 1940s, but little has changed in their manufacture in the intervening time. Silicone synthesis starts with nucleophilic substitution of chlorosilanes by water, leading to low molecular weight linear and cyclic products (Figure 1.1). These materials are finished into high molecular weight and functional materials, also using nucleophilic substitution, catalyzed by acidic or basic conditions.[2] Unlike many polymers that are formed under kinetic control, the 'equilibration' process used for silicone

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[†] Reference adapted from and reproduced with kind permission from Springer Science + Business Media. M. A. Brook, J. B. Grande and F. Ganachaud, *Adv. Polym. Sci.*, 2010, **235**, 161–183. John B. Grande was the sole author of this excerpt from the article mentioned above: contributions from other authors have been removed.

manipulation is completely reversible. While high molecular weight silicones are readily formed under acidic or basic conditions, they also undergo degradation under these conditions if water is present: the process is irreversible if low molecular weight cyclics (e.g., D_4, $(Me_2SiO)_4$) are able to leave the system, typically by evaporation.

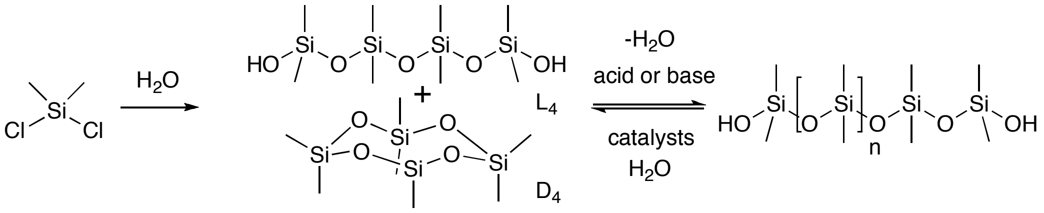


Figure 1.1. Traditional silicone synthesis

One consequence of the reactivity of silicones towards acidic or basic conditions is that it is exceptionally difficult to reliably assemble complex silicone structures. Almost inevitably, the reaction conditions used to create a structure also lead to structural fragmentation. Even linear polymers of narrow molecular weight are difficult to prepare in large scale and good yield. The very few reports of controlled silicone synthesis, for example, of a silicone dendrimer,[3] utilize difficult-to-reproduce and non-generic reaction conditions.

There is a need to create silicones with controlled 3D structures for a variety of purposes. As one example, the class of silicone polymers known as MQ resins[4‡] exhibits very interesting surface activity and are utilized in high value formulations including liquid crystals,[5] antifoaming compositions[6] and pressure sensitive adhesives[7]. The compounds are commercially generated as complex mixtures, so it is not possible to understand which structures would be most useful for a given application. There is therefore significant interest in generating explicit MQ resins and other structures. Traditional chemistry does not fulfill these needs in most cases.

1.2 New Chemistry for Silicone Synthesis

In a series of seminal papers, summarized in an authoritative review,[8] Piers demonstrated that the reduction by hydrosilanes of carbonyls (Figure 1.2A), thiocarbonyls, imines and other functional groups could be catalyzed by catalytic (but not insignificant 5-10 mol%) quantities of the hydrophobic Lewis acid $B(C_6F_5)_3$. As part of his careful synthetic and mechanistic studies, Piers noted that over-reduction of the intermediate alkoxysilane could lead to complete reduction to the alkane and the formation of a siloxane byproduct (Figure 1.2B).[9]

[‡] General Electric silicone nomenclature: M = Me_3Si, D = $Me_2SiO_{2/2}$, T = $MeSiO_{3/2}$ and Q = $SiO_{4/2}$. The subscript nomenclature is used to denote, for example with $SiO_{4/2}$, that there are four single bonds to oxygen from silicon, and that each oxygen bonds to another silicon through a single bond, i.e., $Si(OSi)_4$ rather than SiO_2, which might imply Si=O double bonds.

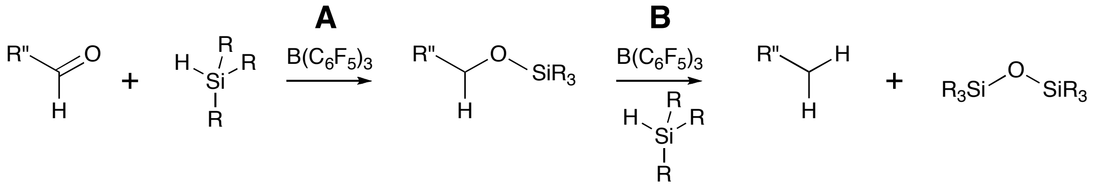


Figure 1.2. Origins of the Piers-Rubinsztajn reaction

Rubinsztajn and Cella looked at this outcome from the perspective of the silicon chemist. What may be by-products to organic chemists could be the synthetic target for a polymer chemist.[10-12] Thus, the Piers-Rubinsztajn reaction refers to the reaction between a hydrosilane and alkoxysilane that leads, with loss of an alkane, to a siloxane (Figure 1.2B). The process can be performed on small molecules or can lead to large, complex structures.

1.3 Mechanistic Considerations

1.3.1 From the Organic World

$B(C_6F_5)_3$ owes its Lewis acidity to the absence of necessary valence electrons to complete an octet and to the inductive effects provided by the perfluorosubstitution of the three aromatic rings. Most undergraduates when presented with such a highly electrophilic borane **1** would predict that its interactions would be dominated by strong Lewis bases such as amines, alcohols, ethers, etc. (Figure 1.3A,C). Parenthetically, we have been to many conferences where experts have espoused this conventional view. However, in addition to the traditional type of Lewis acidity, $B(C_6F_5)_3$ effectively and competitively forms complexes with hydrosilanes (Figure 1.3B) **2**, which is a much less easily predicted interaction based on Lewis acid theory, given that the silane possesses no Lewis basic electron pairs.

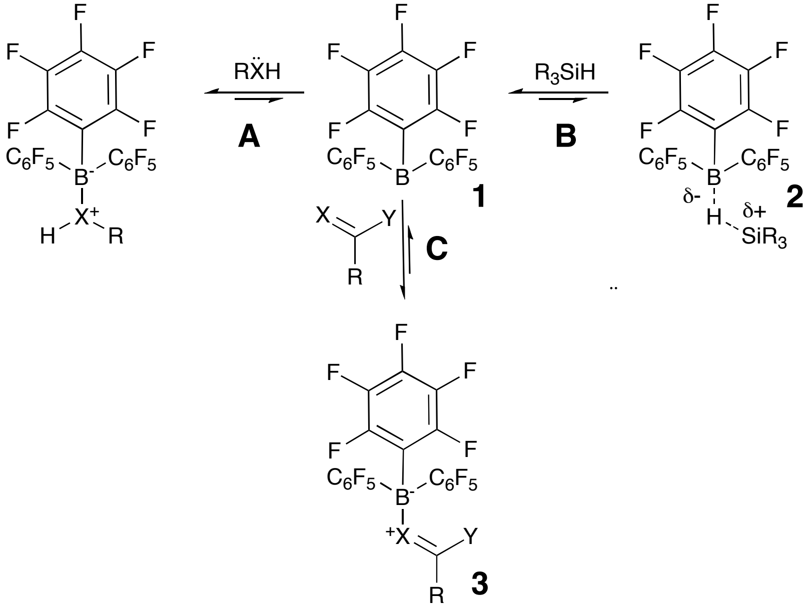


Figure 1.3. Lewis acid/base complexes of $B(C_6F_5)_3$

A comparison of $B(C_6F_5)_3$ with other Lewis acids using either the Childs strategy (complexation with crotonoaldehyde)[13, 14] or Gutman's acceptor number (AN)[15] – both NMR-based methods – suggest that the Lewis acidity of $B(C_6F_5)_3$ falls between $TiCl_4$ and BF_3. It is thus a very strong Lewis acid. In combination with the appropriate Lewis base, including phosphines[16] or 2,6-lutidine,[17] $B(C_6F_5)_3$ can even split H_2. In addition to electronic effects, the complexation behavior of $B(C_6F_5)_3$ is particularly sensitive to steric factors. When assessing its reactivity, perhaps the most important factor to consider is the very fast exchange in solution of the Lewis acid/Lewis base complexes of $B(C_6F_5)_3$ when compared to the NMR time scale.[8]

Piers examined the equilibria between $B(C_6F_5)_3$ and $B(C_6F_5)_3$-carbonyl complexes in a study of C=O hydrosilylation (Figure 1.3C, X = O, Y = H, Me, OEt). Equilibrium constants were found to favor the carbonyl complex **3** by about 10^2 depending on the nature of Y.[18] However, the rates of the hydrosilylation reaction were inversely proportional to the carbonyl concentration, suggesting that complexes such as **3** *inhibit* the reaction. These observations led to a mechanistic interpretation involving the reversible formation of a borohydride complex **2**, which is the active species in the subsequent reductive silylation process via **4** or **5**, shown for carbonyl reduction (Figure 1.4). Analogous processes have been invoked for the conversion of aldehydes/ketones to the alkane,[19] alcohols to alkoxysilanes,[20] and then to the alkane,[21] and the hydrosilylation of C=C bonds.[22]

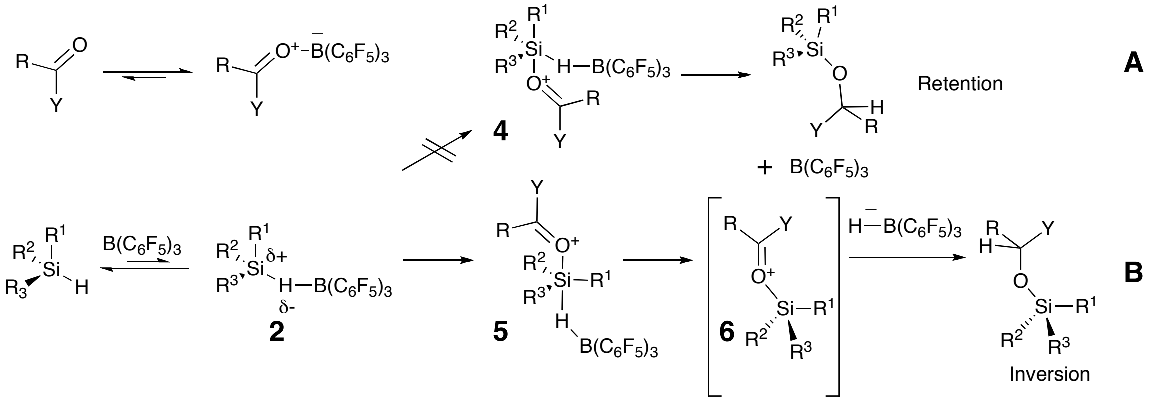


Figure 1.4. Proposed mechanism for C=O hydrosilylation catalyzed by $B(C_6F_5)_3$

Further support for this hypothesis comes from studies of the hydrosilylation of imines.[23] Less basic imines were found to undergo hydrosilylation more readily, consistent with the necessity for free $B(C_6F_5)_3$ in solution to complex with the hydrosilane giving **2**. NMR showed that less basic imines do not form complexes with the boron-based Lewis acid. Of greater significance, the hydridoborane complex $HB^-(C_6F_5)_3$ of ketimine derivatives could be detected directly using ^{11}B and ^{19}F NMR. The ^{29}Si NMR data of the same mixture showed the presence of a nitrogen/silicon complex analogous to **4** or **5**.

These data convincingly show that borohydride complexes of $B(C_6F_5)_3$ are key intermediates in the reduction of a variety of oxygen (and nitrogen) based organic functional groups. Piers[9] and others[24] have observed the formation of disiloxanes when large excesses of $HSiR_3$ are present in the reaction mixture. This observation, which is of less interest to synthetic organic chemists, provides a new strategy to synthesize silicones.

The use of enantiomerically pure silanes has permitted a more detailed view of this mechanistic picture. Rendler and Oestreich found that the hydride transfer from the Lewis acid-complexed silane takes place enantioselectively, favoring inversion at silicon.[25] Normally, substitution reactions with hydrosilanes occur with retention (Figure 1.4A).[26, 27] The process of retention has been rationalized to occur through a trigonal bipyramidal complex (either intermediate or transition state) in which the incoming nucleophile is apical, but the only-slightly-polarized hydrogen remains equatorial **4**.[28] Displacement of hydride by a heteroatom nucleophile thus occurs from the same face of the molecule, giving retention of stereochemistry. In the case of $B(C_6F_5)_3$ catalysis, however, the exceptional Lewis acidity of the highly polarized boron-H complex should favor placement of hydride in the apical position, anti to the incoming carbonyl **5** (Figure 1.4B). The substitution process is thus reminiscent (or may be) S_N2 with inversion of stereochemistry.

Reduction ultimately involves transfer of a hydride to a silyloxonium ion. It remains unclear whether this involves direct reaction of a second borohydride complex **2** with **5**, with a tetrahedral oxonium ion **6** or some other process. Irrespective, the data does not support the intermediacy of a free silylium ion intermediate.[23]

1.3.2 Additional Mechanistic Subtleties – The Silicone World

Rubinsztajn and Cella, looking at the results with alkoxysilanes described above through the lens of a silicone chemist, saw not a strategy for reduction of various functional groups including silyl ethers, but rather an opportunity to convert alkoxysilanes (= silyl ethers[29]) into silicones.[10] Here, distinctions are made between the previously described organic mechanistic information and the chemistry that occurs at silicon centers.

Chojnowski and coworkers demonstrated that the formation of small siloxanes catalyzed by $B(C_6F_5)_3$ is a second order process. The complexation of the boron to hydrosilane is a rapid equilibrium step that precedes the rate determining step.[30] They proposed a mechanism in which the boron-hydrosilane complex is attacked by the alkoxysilane nucleophile leading to a zwitterionic oxonium ion (Figure 1.5A).

The group of Kawakami observed in this process inversion of stereochemistry at the hydrosilane, and retention at the alkoxysilane partner during formation of a disiloxane (Figure 1.5B).[31] While retention at the oxygen bearing silicon is expected – inversion of the hydrosilane is somewhat unexpected as noted above. These processes can be understood by comparing Piers-Rubinsztajn disiloxane formation (Figure 1.5A) with the analogous carbonyl hydrosilylation shown in Figure 1.4. Formation of a pentacoordinate silyl-H oxonium complex **7** from **2** by addition of the alkoxysilane, is followed by substitution at the Si-H partner with inversion. Rearrangement to an alkane complex **8** is followed by decomposition to product.

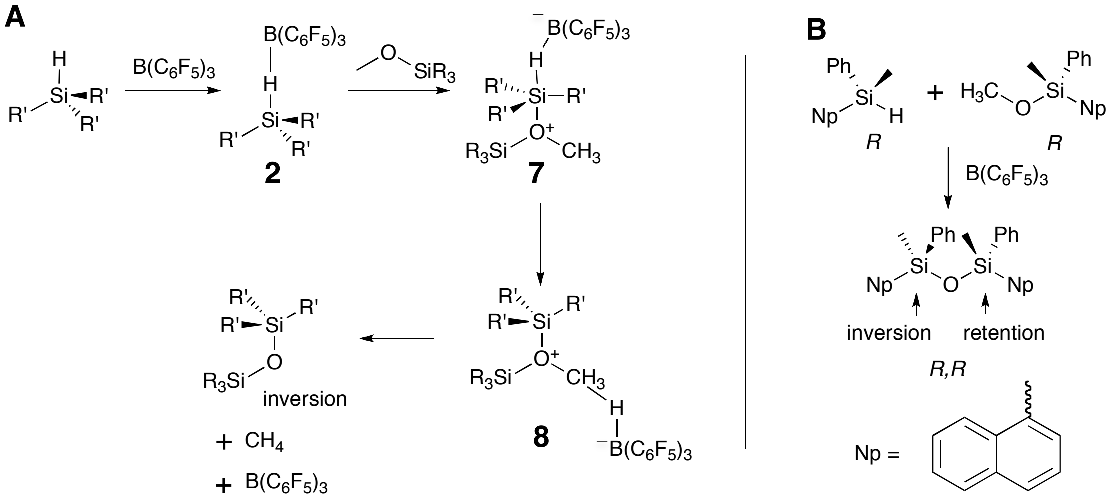


Figure 1.5. A: Proposed mechanism for dehydrocarbonative condensation, B: Stereoselective siloxane formation.

1.3.3 Metathesis

Unfortunately, the reaction is not quite as simple as implied above. When more than one type of silicon compound is present, metathesis (Figure 1.6A→c) can occur in addition to direct disiloxane formation (Figure 1.6A→b).[30, 32] That is, in addition to conversion of hydrosilane to silicone, it can also be converted to alkoxysilane. Chojnowski and coworkers rationalize both processes using a common intermediate. The borohydride-oxonium intermediate **9** can decompose in three distinct ways: hydride migration back to starting materials (Figure 1.6A→a); the desired hydride transfer to give the alkane and siloxane **10**; or migration of hydride to the other silyl group leading to metathesis **11**. The metathesis process is clearly disadvantageous as the formation of by-products removes a level of synthetic control from the reaction (Figure 1.6B).[30]

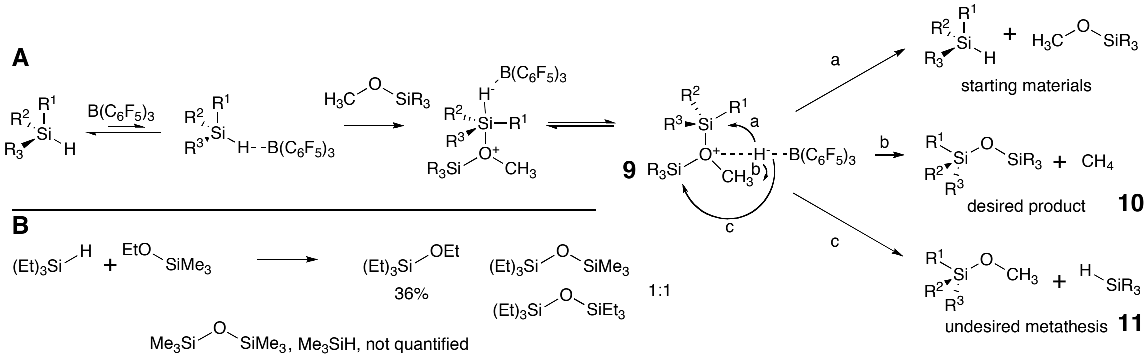


Figure 1.6. Metathesis in the Piers-Rubinsztajn process

Metathesis is particularly problematic with the hydrosilane reacting partners. For example, Cella and Rubinsztajn described linear, homologous polymer growth with concomitant loss of Me_2SiH_2 when starting from the simple, small silicone tetramethyldisiloxane (Figure 1.7A):[33] in certain circumstances such a process could be beneficial, but generally will lead to complex mixtures of products.[34, 35] The efficiency with which various silanes participate in such reactions has been determined by Chojnowski and coworkers.[32] An examination of the efficiency of insertion of various silanes into the ring-strained[36] silicone monomer D_3 showed the compounds to exhibit the following order of reactivity: $PhMeSiH_2$ > $HMe_2SiOSiMe_2H$ > $PhMe_2SiH$ > $HSiMe_2OSiMe_3$. Over time, larger linear and cyclic structures were formed, which increased in molecular weight over time (Figure 1.7B).

The efficiency of a metathesis at a given silicon nucleus is affected by the nature of the organic groups found there. Arylsilanes undergo metathesis less efficiently than methylsilanes. Vinylsilanes also undergo metathesis provided that low concentrations of $B(C_6F_5)_3$ (~ 1 mol%) are used. At higher concentrations of catalyst, the desired Piers-Rubinsztajn reactions occur compete with hydrosilylation of the vinyl group (see below, Figure 1.7C).[37] Fortunately, metathesis is not always observed.[§]

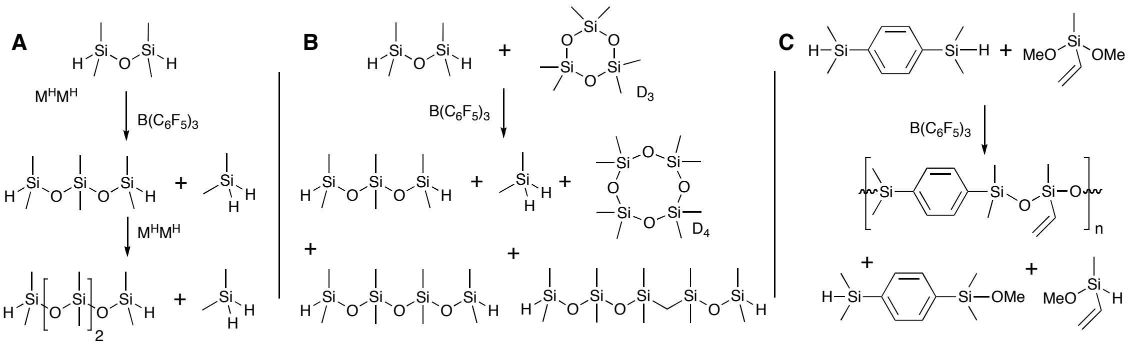


Figure 1.7. Structural manipulation through metathesis of various siloxanes

1.3.4 Steric Effects and Thermal Control

The Piers-Rubinsztajn reaction is normally initiated by adding $B(C_6F_5)_3$ to a mixture of alkoxysilane and hydrosilane. There is normally an induction time during which, presumably, the equilibria described above become established.

[§] We have discussed with Rubinsztajn and Chojnowski why, in their hands, metathesis is frequently encountered, while we typically do not observe metathesis. We have not been able to isolate the distinctions between our experimental processes. One possible distinction is the order of addition of reagents. Typically, we add catalyst to a mixture of the hydrosilane and alkoxysilane, while Chojnowski and coworkers use one of two alternate strategies (see Section 1.3.6). It is clear, however, that metathesis does not occur under all reaction conditions.

Thereafter, *there is a rapid evolution of flammable (alkane) gas that clearly has safety implications (hydrogen can form from the analogous reactions with silanols or alcohols under these conditions – see below).* The rates of reaction can be controlled both thermally and by the steric bulk found at both hydrosilane and alkoxysilane centers.

Steric control in the Piers-Rubinsztajn reaction was demonstrated by the reaction of tetraalkoxysilanes with small model silicones.[38] The unhindered methoxysilane **12** reacted completely with the slightly hindered $HSiMe_2$-terminated silicone **13** at room temperature to give the tetrasubstituted star **14**, as did ethoxy and propoxysilanes (Figure 1.8A). The lower yield observed with $Si(OMe)_4$ is a consequence of the high volatility of the starting material and challenges of isolation. In all three cases, pure compounds were isolated simply by removal of residual starting materials at low pressure (and the boron catalyst was removed by adsorption on neutral alumina). $Si(OMe)_4$ also cleanly reacted with the branched hydrosiloxane **15** to give the tetrasubstituted star **16** (Figure 1.8B). However, the bulkier $Si(OEt)_4$ did not react at all at room temperature, and could only be forced to the trisubstituted compound **17** at elevated temperatures. Attempts to stop substitution at the disubstituted compound, or to push the reaction thermally to the tetrasubstituted product **16**, were unsuccessful. These data are completely consistent with the intermediacy of oxonium ions like **9**. Steric pressure exerted either by the alkoxy group or the groups adjacent to the

SiH group will decrease the efficacy of the reaction. Chojnowski and coworkers note that more bulky silanes, including isopropoxy-derivatives, are yet more selective in reactions and require higher temperatures to initiate reaction.[30]

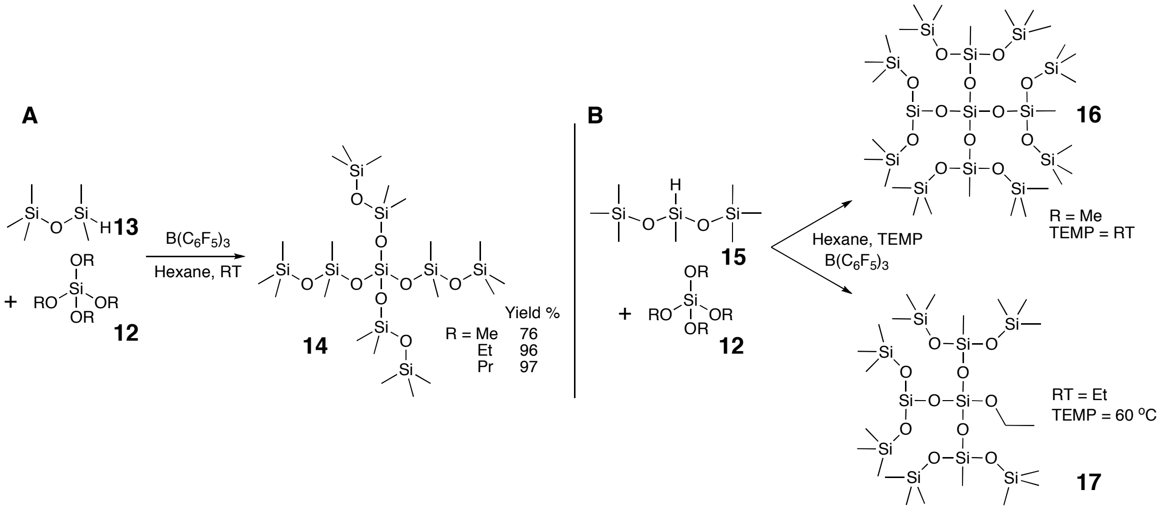


Figure 1.8. Steric control over siloxane formation

1.3.5 Silicone Synthesis

Rubinsztajn and co-workers reported in 2004 that Piers' observations that alkoxysilanes and organohydrosilanes will react in the presence of $B(C_6F_5)_3$ could be more generally applied to silicone synthesis (Figure 1.9).[10, 11, 39] Very low levels of catalyst were required, typically less than 1 mol%. Under these conditions the condensation process proceeds to produce nearly perfectly alternating siloxane polymers (i.e., no metathesis) containing phenyl moieties (58-95%), with M_w values of 10-50,000. By contrast, the use of dimethoxydimethylsilane was accompanied by "scrambling" (metathesis) of the silyl groups, which gave rise to more disordered structures. Metathesis was shown to be, among other things, dependent nature of the groups on the alkoxysilane reacting partner (see also Sections 1.3.3, 1.3.4).

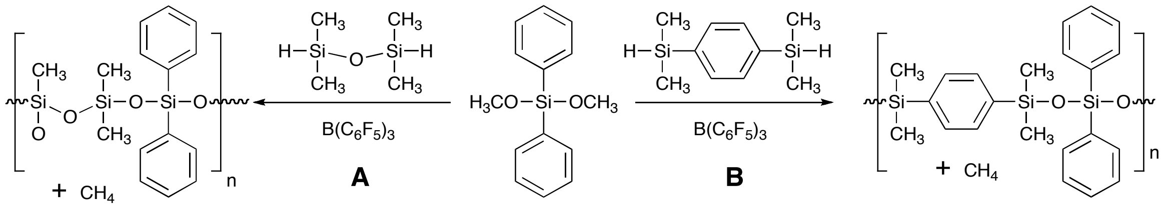


Figure 1.9: Polycondensation between diphenyldimethoxysilane and two different dihydrosilanes catalyzed by $B(C_6F_5)_3$

1.3.6 Resins

The Piers-Rubinsztajn reaction has also proven useful as a simple and mild method for the synthesis of highly branched alkoxy substituted polysiloxane resins consisting of a combination of M, D, T and Q‡ units, as noted by Chojnowski and co-workers.[40] Initial experiments with low levels of catalyst had long induction times, followed by very fast, uncontrollable reaction. Two distinct methods were developed to minimize the effect of impurities such as water, to control catalyst concentration, and to manage the highly exothermic nature of the reaction. Both methods used higher concentrations of catalyst to reduce the induction time necessary for reaction. Variant I involves the slow introduction of the hydrosilane to a mixture of alkoxysilane and $B(C_6F_5)_3$ in toluene. Variant II, which involves the addition of both hydrosilane and alkoxysilane to a solution of

$B(C_6F_5)_3$ uses yet higher catalyst concentrations, but is performed at lower temperatures, to minimize induction time (Figure 1.10A). The polydispersity of the products can be controlled through either manipulation of the silane:alkoxysilane ratio, or through temperature manipulation. For example, use of -25 °C as reaction temperature was accompanied both by higher tetraalkoxysilane conversion and a lower PDI of the resin.

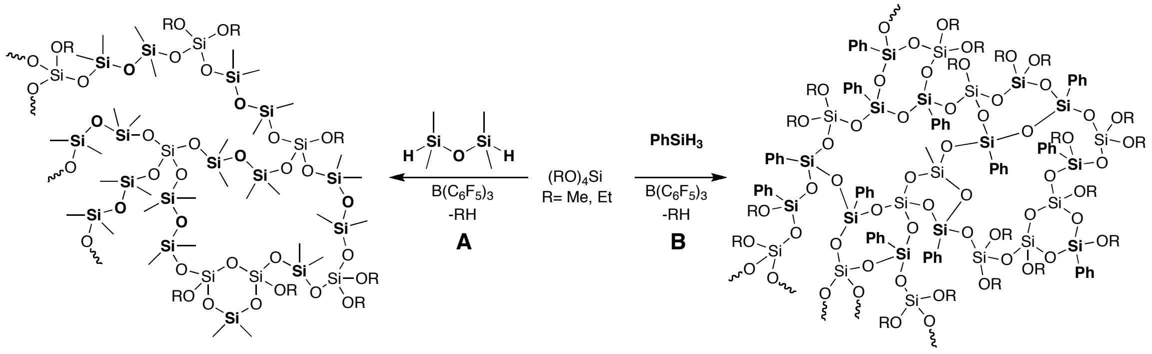


Figure 1.10: Generic scheme depicting the synthesis of DQ and TQ resins

More recently, Chojnowski's group has expanded this strategy to the preparation of more highly crosslinked TQ‡ resins. Phenylsilane ($PhSiH_3$):TMOS ($(MeO)_4Si$) were mixed in a molar ratio of less than 0.9 to yield alkoxy-rich products.[41] As with the DQ resins, the TQ resins are free of unwanted hydrophilic silanol groups, leading to an increase in polymer hydrophobicity, solubility in organic solvents, and long-term stability (Figure 1.10B).

During the growth of both of these resins, significant evidence was provided that an undesired, reversible metathetic process was occurring leading to functional group exchange. Mechanistic studies, described in more detail above, convincingly suggest the reaction proceeds through a disilyl-oxonium ion intermediate (similar to Figure 1.6).[30] At low conversion, evidence for exchange, resulting in a decrease in control associated with the condensation process, was provided by ^{29}Si NMR spectroscopy and GC analysis: new reactants, bearing two Si-H groups, two Si-OR groups, or a mixture of the two, were formed. This leads, for example in the case of DQ‡ resins, to unequal distribution of D units in the product polysiloxanes, rather than perfectly alternating systems.

1.3.7 Silicones with controlled 3D structures

With appropriate control of the reaction conditions, and in particular by exploiting the rules of steric control described in Section 1.3.4, the Piers-Rubinsztajn reaction can be employed to synthesize well-defined complex 3-D siloxane architectures. Small, readily available alkoxysilanes and silicones can be rapidly assembled into MDTQ‡ silicones (Figure 1.8): in our hands, metathesis was not observed.[38] These structures would be exceptionally difficult to synthesize using traditional means because of the susceptibility of siloxane bonds to strong electrophiles and nucleophiles, especially in the presence of water, and the ability of silicones to undergo redistribution under acidic or basic conditions.

A key intermediate for the synthesis of large structures was **17**. Although it is a Q‡ unit, it possesses a single residual ligand that will react in the presence of $B(C_6F_5)_3$. Only non-branched, terminal hydrosilanes are small enough to react with the ethoxysilane. Thus, linear or highly branched silicones are readily available by the rapid assembly of hydrosilane building blocks (Figure 1.11).

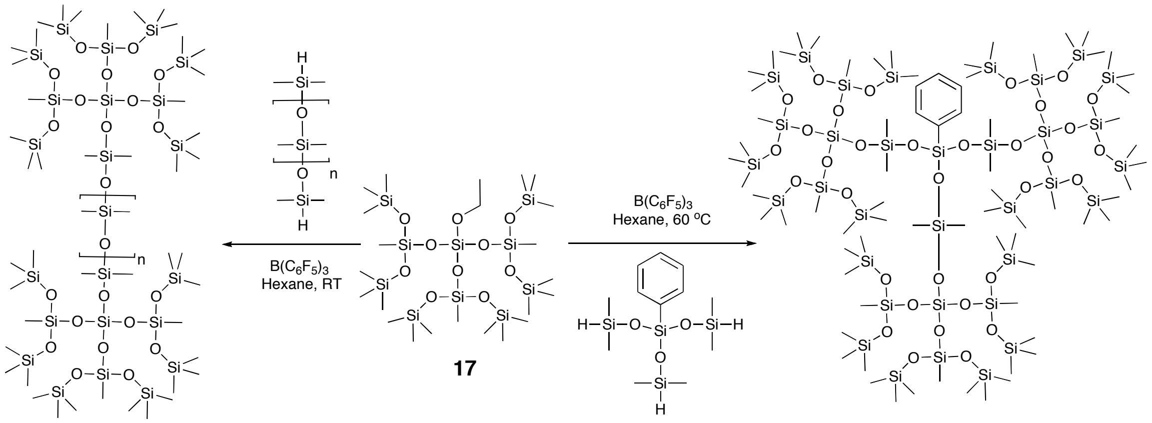


Figure 1.11: Synthesis of large, explicit silicones

1.4 Thesis objectives

1.4.1 Functional Silicones

Many interesting applications of silicones exploit their unusual surface activity. Mixtures of silicones and silica are used as defoaming agents;[42] MQ‡ resins can destabilize foams.[6] More interesting are functional silicones, particularly for their surface activity, including copolymers with polyethers, liquid crystals and others, which rely for their properties, in part, on organic groups or polymer chains. Typically, organofunctional silicones that allow for the direct tethering of organic moieties such as alkenes, halocarbons, thiols and hydrosilanes are prepared using equilibration methods as described above (Figure 1.1)[43]. The process allows for the preparation of three different types of functional silicones:

Functionality at the terminus (Figure 1.12A), functionality at one end (Figure 1.12B) or functionality along the backbone (Figure 1.12C).

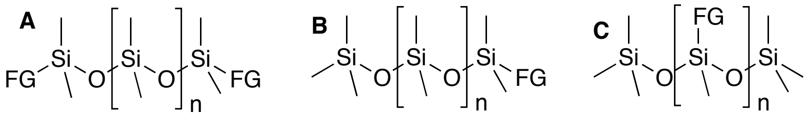


Figure 1.12. Three commonly prepared functional silicones A. Functionality at the terminus B. Monofunctional at one end C. Functionality along the backbone

Although this method allows for the direct incorporation of various functionality, it suffers from the same lack of synthetic control that plagues traditional poly(dimethylsiloxy)silane synthesis: ill-defined, polydisperse materials. The properties of the materials can therefore be associated to an average of the bulk material, and can be challenging to reproduce via batch-to-batch processing. It was therefore of interest to understand if the Piers-Rubinsztajn reaction could provide a new, alternative method for the synthesis of well-defined silicones bearing commonly incorporated functionality. Piers' studies on the mechanism of $B(C_6F_5)_3$-catalyzed hydrosilylation provide clues about the types of functional groups that will be tolerated during the synthesis of functional silicones.[9, 23] Very basic ligands will presumably shut the process down by irreversibly complexing with boron.[44] In addition, hydrosilylation of alkenes has been reported at high,[22] but not low,[45, 46] boron catalyst concentrations. Other then these, little was known about the functional group tolerance of the reaction. It was therefore of interest to understand the functional tolerance of the Piers-Rubinsztajn reaction, and determine if this could in fact be a highly effective route to well defined functional silicones. This systematic study is the bases of Chapter 2 in this document.

1.4.2 Silicone Surfactants

Originally introduced in the 1950's in the manufacture of polyurethane foam, silicone surfactants have since found application in many industrial process including – but not limited to- wetting agents, in which they are used to disperse chemicals on leaves[47, 48], in cosmetic formulations[49], as silicone based surfactants allow for a glossy yet dry feel, commonly associated with shampoos and shower gels and as defoaming agents[42].

Silicone surfactants are a class of amphiphilic compounds that consist of both hydrophobic and hydrophilic segments. The hydrophobic portion corresponds primarily to a poly(dimethyl)siloxane (PDMS) backbone and the hydrophilic groups can be a variety of organic moieites, including amines, phosphates, carboxylic acids, amino acids, etc., but is most commonly poly(oxyethylene) (PEG or PEO) and poly(oxypropylene)(PPO) oligomers (Figure 1.13).

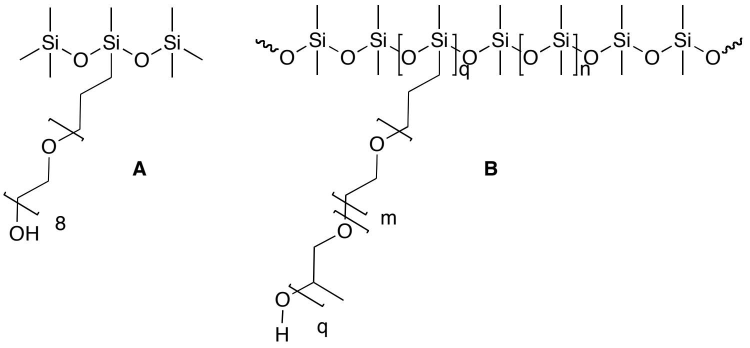


Figure 1.13. A. Typical well-defined superwetters B. Typical silicone based surfactants

The exceptional properties associated with silicone based surfactants originate from the flexibility of their polysiloxane backbone. This exceptional flexibility allows for the dimethyl groups tethered to the silicon atoms to more effectively present themselves at an interface, allowing for a substantial reduction of surface tension versus traditional hydrocarbon based surfactants (~ 20 dynes/cm vs ~30-32 dynes/cm)(Figure 1.14).[42, 47]

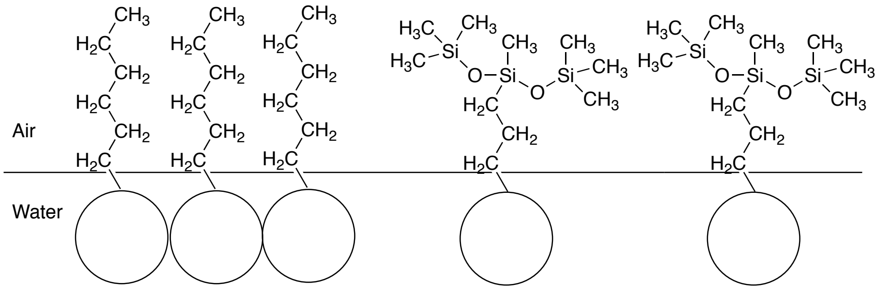


Figure 1.14. CH_2 groups primarily occupy the interface on hydrocarbon based surfactants resulting in surface tension of ~ 30 dynes/cm. CH_3 groups primarily occupy the interface in silicone based surfactants lowering the surface tension values to roughly 20 dynes/cm.

Silicone surfactants are commonly prepared using three common synthetic motifs. The first involves a simple transesterification between a silicone bearing an alkoxy group and a hydrophilic organic group containing an alcohol. The second method involeves the direct hydrosilylation of a Si-H containing silicone to a polar organic group bearing and allyl group. The third method involves indirectly attaching a reactive group to the siloxane backbone (such as an epoxy group), followed by exploiting this reactive group to attach a polar organic group.

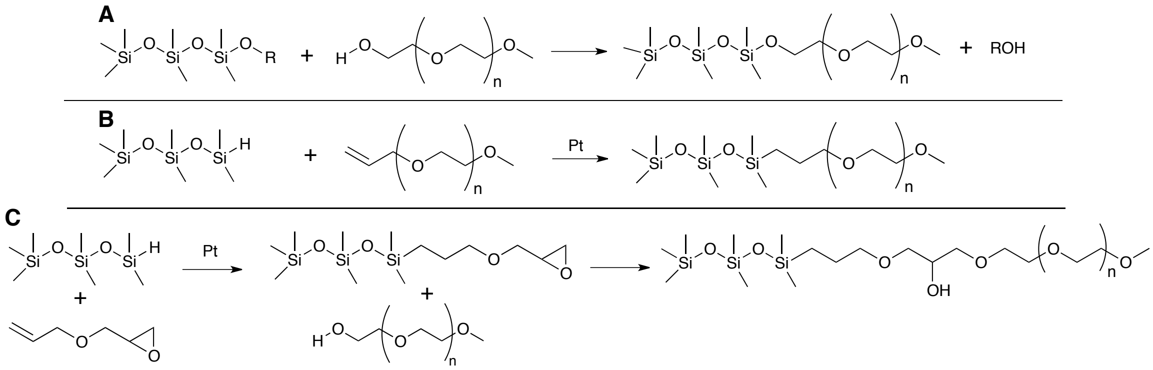


Figure 1.15. Methods to prepare amphiphillic silicone surfactants. A. Through use of a transesterification process B. Through platinum catalyzed hydrosilylation C. A two step method to firstly introduce a reactive group on to a silicone based polymer which can then be coupled to a hydrophilic organic group.

Although the three methods above provide highly effective routes to surface-active silicones, with the exception of superwetters (Figure 1.13A), most silicone surfactants are composed of ill-defined mixtures of products. This lack of synthetic control has made it exceptionally challenging to relate the structure of a silicone surfactant to the surface activity (structure activity relationship) it may posses. It was hypothesized that through an understanding of the functional tolerance associated with the Piers-Rubinsztajn reaction, well defined, functional silicones can be readily tethered to poly(oxyethylene). In Chapter 3, the ability to create- using azide/alkyne [3+2] cycloaddition (click chemistry)- a variety of precise silicone surfactants is explored. Analogous processes involving thiol-ene click chemistry leads to a different series of surfactants, as is examined in Chapter 4.

1.4.3 Silicone Based Dendrimers

As noted above, only a handful of examples of precise silicones of large molecular weight have been reported.[50, 51] The syntheses are beautiful, but not amenable to scale up. For example, a report published by the group of Masamune and coworkers in 1990 describe a simple, three step method allowing for the synthesis of large dendrimeric silicones with calculated molecular weights of up to 15,073 g/mol[3]. The process – as shown with octamethylcyclotetrasiloxane (D_4) for simplicity – can be directly applied to mono-, di- or tri functional silanes and involves ring opening hydrolysis of D_4 (Figure 1.16A), followed by conversion of obtained Si-H groups to Si-OH groups through the use of mild basic conditions (Figure 1.16B,i) or by using Pd/C as a catalyst (Figure 1.16B,ii). The final step of the process involves the direct coupling of the prepared silanol (Si-OH) with a chlorosilane (Si-Cl) to produce a new siloxane linkage. (Figure 1.16C). Through repetition of this process, large, monodisperse silicones can be readily prepared.

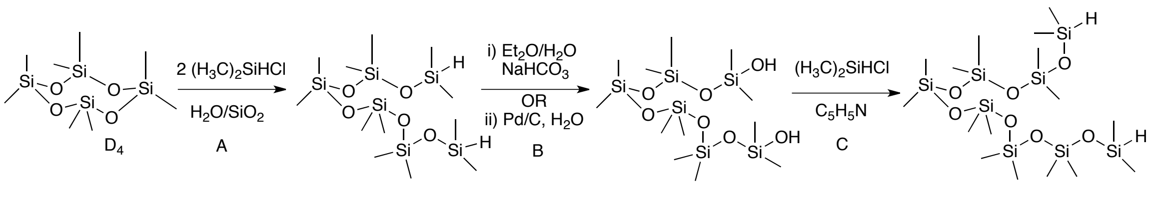


Figure 1.16. A. Ring opening hydrolysis of D_4 B. Conversion of Si-H to Si-OH using either i) mild basic conditions or ii) Pd/C as a catalyst C. Coupling of prepared silanols with dimethylchlorosilane.

Another route to precise silicones was reported by Muzafarov and coworkers and involves alternating reactions between silanolates and chlorosilanes, a method that has led to the one of the densest dendrimer structures reported.[52] Subsequent nucleophilic substitution of a trichlorosilane with sodiumoxymethyldiethoxysilane (Figure 1.17A) leads to a compound bearing six ethoxygroups. Treatment with $SOCl_2$ readily converts the ethoxy groups into chlorosilanes (Figure 1.17B). Repeating the process can lead to siloxane based dendrimers of up to the third generation[53].

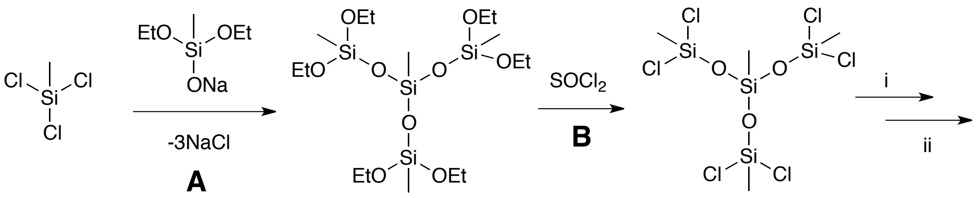


Figure 1.17 A. Reaction of methyltrichlorosilane with sodiumoxymethyldiethoxysilane B. Conversion of alkoxy groups to chlorosilanes through use of $SOCl_2$

Although these two reported methods provide elegant methods to large precise silicones, they do suffer from inherent drawbacks. For example, acidic or basic byproducts (Figure 1.16), or ensuring nucleophilic substitution only occurs at chlorosilane centers (Figure 1.17) tend to lower yields and increase the difficultly of dendrimer purification. In an effort to overcome these drawbacks, attention was turned to the Piers-Rubinsztajn reaction.

The Piers-Rubinsztajn reaction has been shown to provide precise small molecules that may include alkene functionalities. More importantly, as long as the concentration of $B(C_6F_5)_3$ remains low, hydrosilylation of olefins does not occur. This permits the possibility to combine the Piers-Rubinsztajn reaction with hydrosilylation, a reaction widely used in the silicone industry to create elastomers. In Chapter 5, the ability to prepare precise dendrimeric compounds using a convergent, divergent and a combination of both is examined.

1.4.4 Silicone Rubbers and Foams

Many other structural forms of silicones are important in industry. Among these are silicone elastomers and silicone foams, which find uses in many applications ranging from biomaterials[54, 55] to joints and sealants[2, 43]. Typical industrial methods to prepare silicone based elastomers rely heavily on room temperature vulcanization processes (RTV) involving use of platinum catalyzed hydrosilylation – the addition of a Si-H bond across a double bond (Figure 1.18A) - or a tin/titanium catalyzed hydrolysis/condensation reaction (Figure 1.18B). Silicone foams are prepared in much the same way, although active hydrogen compounds such as H_2O or ROH are required to be incorporated into the formulations.[56] These act as blowing agents to prepare foamed materials via the generation of H_2 throughout the curing process.

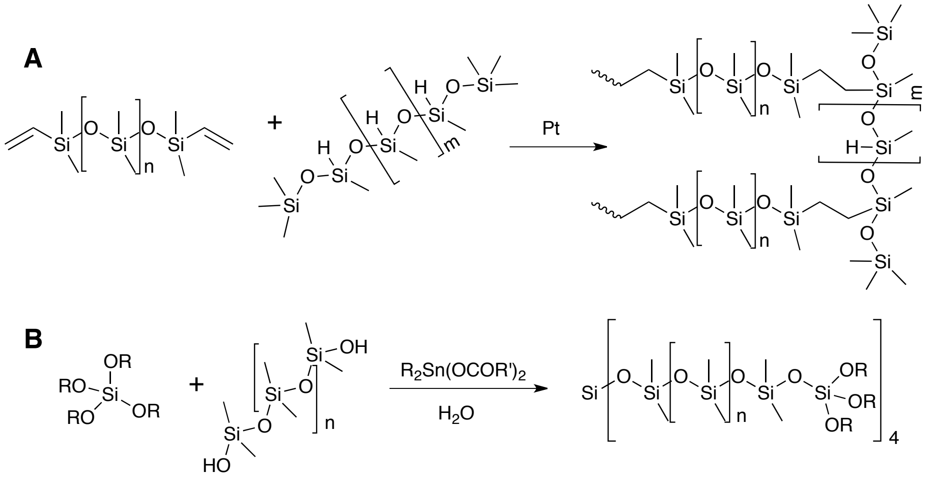


Figure 1.18 RTV preparation of silicone elastomers via A. Platinum catalyzed hydrosilylation and B. Tin moisture/condensation cure

Although these methods provide effective ways to both silicone elastomers and silicone based foams, there is a need to develop methods that would avoid the use of metal-based catalysts for reasons of expense (platinum) and environmental concern (tin). We have conducted research to examine and understand if the Piers-Rubinsztajn reaction can be used as an alternative platform to create silicone elastomers and silicone foams. Chapter 6 examines both the parameters and ability of the Piers-Rubinsztajn reaction to effectively prepare silicone-based elastomers. Chapter 7 of this thesis builds upon what was learned in Chapter 6 and explores the use of the Piers-Rubinsztajn reaction in the preparation of silicone based foams. [16]

1.5 References

1. S. J. Clarson and J. A. Semlyen, *Siloxane polymers*, PTR Prentice Hall, Englewood Cliffs, NJ, 1993.
2. W. J. Noll, *Chemistry and Technology of SIlicones*, Academic Press, New York, 1968.
3. H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, T. Tsumuraya and S. Masamune, *J. Am. Chem. Soc.*, 1990, **112**, 7077-7079.
4. M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000, pp. 1-26.
5. T. Ganicz, T. Pakula and W. A. Stanczyk, *J. Organomet. Chem.*, 2006, **691**, 5052-5055.
6. C. Araud, in *Polydimethylsiloxane resin antifoaming compositions*, ed. U. S. P. Office, Rhone-Poulenc Chimie, USA 5,082,590, 1992.
7. K. L. Ulman and X. Thomas, in *Advances in Pressure Sensitive Adhesive Technology*, ed. D. Satas, Satas, Warwick RI, 1995, pp. 133-157.
8. W. E. Piers, in *Advances in Organometallic Chemistry, Vol 52*, Elsevier Academic Press, San Diego, 2005, pp. 1-76.
9. D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090-3098.
10. S. Rubinsztajn and J. Cella, *Polym. Pre.*, 2004, **45 (1)**, 635-636.
11. S. Rubinsztajn and J. A. Cella, in *Silicone Condensation Reaction*, ed. E. Patent, General Electric, WO 2005118682, 2005.
12. S. Rubinsztajn and J. A. Cella, in *Silicone Condensation Reaction*, ed. U. S. P. Office, General Electric, USA Patent 7064173, 2006.
13. R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 801-808.
14. R. F. Childs, D. L. Mulholland and A. Nixon, *Can. J. Chem.*, 1982, **60**, 809-812.

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

16. G. C. Welch and D. W. Stephan, *J. Am. Chem. Soc.*, 2007, **129**, 1880-1881.

17. S. J. Geier and D. W. Stephan, *J. Am. Chem. Soc.*, 2009, **131**, 3476-3477.

18. D. J. Parks and W. E. Piers, *J. Am. Chem. Soc.*, 1996, **118**, 9440-9441.

19. S. Chandrasekhar, C. R. Reddy and B. N. Babu, *J. Org. Chem.*, 2002, **67**, 9080-9082.

20. J. M. Blackwell, K. L. Foster, V. H. Beck and W. E. Piers, *J. Org. Chem.*, 1999, **64**, 4887-4892.

21. V. Gevorgyan, M. Rubin, S. Benson, J. X. Liu and Y. Yamamoto, *J. Org. Chem.*, 2000, **65**, 6179-6186.

22. M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936-1940.

23. J. M. Blackwell, E. R. Sonmor, T. Scoccitti and W. E. Piers, *Org. Lett.*, 2000, **2**, 3921-3923.

24. V. Gevorgyan, M. Rubin, J. X. Liu and Y. Yamamoto, *J. Org. Chem.*, 2001, **66**, 1672-1675.

25. S. Rendler and M. Oestreich, *Angew. Chem. Int. Ed.*, 2008, **47**, 5997-6000.

26. A. R. Bassindale and P. G. Taylor, in *The Chemistry of Organic Silicon Compounds*, eds. S. Patai and Z. Rappoport, John Wiley & Sons, Chichester, UK, 1989, p. 839.

27. A. R. Bassindale, S. J. Glyne and P. G. Taylor, in *The Chemistry of Organic Silicon Compounds*, eds. Z. Rappoport and Y. Apeloig, John Wiley & Sons, Chichester, UK, 1998, p. 495.

28. R. J. P. Corriu, C. Guérin and J. J. E. Moreau, in *Topics in Stereochemistry*, eds. E. L. Eliel, S. H. Wilen and N. L. Allinger, Wiley, New York, 1984, pp. 43-198.

29. M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000, pp. 189-255.

30. J. Chojnowski, S. Rubinsztajn, J. A. Cella, W. Fortuniak, M. Cypryk, J. Kurjata and K. Kazmierski, *Organometallics*, 2005, **24**, 6077-6084.

31. S. Shinke, T. Tsuchimoto and Y. Kawakami, *Silicon. Chem.*, 2005, **3**, 243–249.

32. J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *J. Inorg. Organomet. P.*, 2007, **17**, 173-187.

33. J. Chojnowski, W. Fortuniak, J. Kurjata, S. Rubinsztajn and J. A. Cella, *Macromolecules*, 2006, **39**, 3802-3807.

34. J. Cella and S. Rubinsztajn, *Macromolecules*, 2008, **41**, 6965-6971.

35. S. Rubinsztajn, J. A. Cella, J. Chojnowski, W. Fortuniak and J. Kurjata, in *US Patent 7148370*, ed. U. P. Office, General Electric, USA, 2006.

36. M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000, pp. 256-308.

37. Chen Xunjun, Cui Yingde, Yin Guoqiang and Liao Liewen, *J. Appl. Polym. Sci.*, 2007, **106**, 1007-1013.

38. D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.*, 2008, **130**, 32-33.

39. S. Rubinsztajn and J. A. Cella, *Macromolecules*, 2005, **38**, 1061-1063.

40. J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *Macromolecules*, 2008, **41**, 7352-7358.

41. J. Kurjata, W. Fortuniak, S. Rubinsztajn and J. Chojnowski, *Eur. Polym. J.*, 2009, **45**, 3372-3379.

42. M. J. Owen, in *Silicon-Based Polymer Science: A Comprehensive Resource*, eds. J. M. Zeigler and F. W. G. Fearon, American Chemical Society, Washington, D.C., 1990, pp. 705-739.

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

44. W. E. Piers, in *Advances in Organometallic Chemistry*, Elsevier Academic Press, San Diego, 2005, pp. 1-76.

45. C. Xunjun, C. Yingde, Y. Guoqiang and L. Liewen, *J. Appl. Polym. Sci.*, 2007, **106**, 1007-1013.

46. X. Chen, Y. Cui, G. Yin, Z. Jia and Z. Liu, *Huagong Xuebao (Chinese Edition)*, 2008, **59**, 1143-1149.

47. R. M. Hill, *Silicone Surfactants*, Marcel Dekker New York, 1999.

48. R. M. Hill, *Curr. Opin. Colloid Interface Sci*, 2002, **7**, 255.

49. W. Silicones, Wacker Personal Care, http://www.wacker.com/cms/media/publications/downloads/6022_EN.pdf.

50. A. Morikawa, M. Kakimoto and Y. Imai, *Macromolecules*, 1991, **24**, 3469-3474.

51. J. P. Majoral and A. M. Caminade, *Chem. Rev.*, 1999, **99**, 845-880.

52. E. A. M. Rebrov, A.M.; Papkov, V.S.; Zhandanov, A.A, *Dokl. Akad. Nauk SSSR*, 1989, **309**, 376-380.

53. A. M. Muzafarov and E. A. Rebrov, *J. Polym. Sci. Pol. Chem.*, 2008, **46**, 4935-4948.

54. J. F. Kunzier, *Trends Polym Sci*, 1996, **4**, 52-60.

55. T. A. Mustoe, *Aesthetic Plastic Surgery*, 2008, **32**, 10.

56. J. J. Chruściel and E. Leśniak, *J. Appl. Polym. Sci.*, 2011, **119**, 1696-1703.

Chapter 2: Rapid Assembly of Explicit, Functional Silicones[**]

2.1 Abstract

The impressive surface activity of silicones can be enhanced by the incorporation of hydrophilic organic functional groups and polymers. Traditional routes to such compounds, which typically involve platinum-catalyzed hydrosilylation, suffer from incompatibility with certain functional groups. $B(C_6F_5)_3$ catalyzed condensation of hydrosilanes with alkoxysilanes offers new opportunities to prepare explicit silicone structures. We demonstrate here that conversion of alcohols to silyl ethers competes unproductively with alkoxysilane conversion to disiloxanes. By contrast, a wide range of structurally complex alkyl halide and oligovinyl compounds can be readily made in high yield. Thermal 3+2-cycloadditions and thiol-ene click reactions are used to convert these compounds into surface-active materials.

[**] J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Transactions*, 2010, **39**, 9369–9378 - Reproduced by permission of The Royal Society of Chemistry. Contribution – Grande was responsible for the complete experimental and write-up of the work completed in this chapter. Gonzaga was responsible and acknowledged for helpful suggestions and troubleshooting pertaining to the experimental work completed in this chapter. He was also responsible for the synthesis of compound **26**, and aided in the preparation of click product **27**.

2.2 Introduction

Silicone polymers are widely used in commerce. While they have many attributes that are unmatched by organic polymers, it is perhaps their surface activity in particular that has been the basis of most applications. With the exception of some surfactants that are based on small siloxanes, such as the superwetters[1,2] – commonly used to disperse agricultural chemicals on leaves – most silicone surfactants involve ill-defined mixtures of silicones polymers modified by oligo or poly(ethylene glycol)(PEG) or propylene glycol (PPG) chains (Figure 2.1).[3]

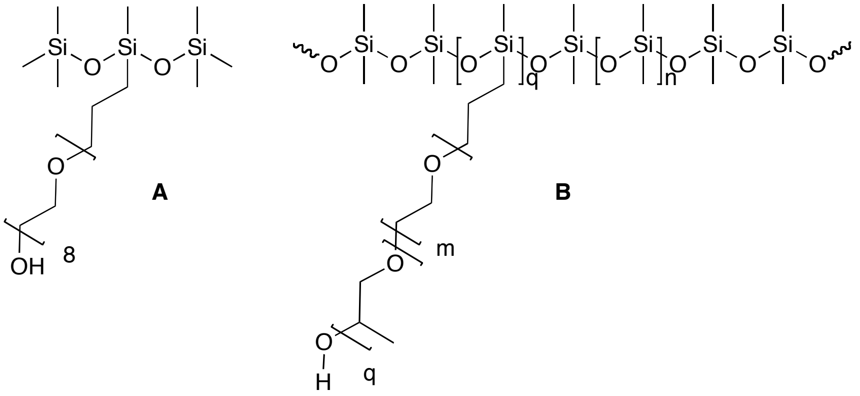


Figure 2.1. Typical silicone surfactants; A: superwetters; B: rake copolymers

A much wider range of surface activities is available when alternate hydrophiles to glycol oligomers are used, including such functional groups as amines, phosphates, sulfonates, carboxylic acids,[4,5] or clusters of acids[6,7] amino acids[8,9] and saccharides.[10–14] However, in these cases too, a clear correlation between structure and surface activity is generally not possible because the silicone constituents are typically poorly defined mixtures. Recently, we[15] and others[16–19] have described the preparation of silicone polymers using the Piers–Rubinsztajn reaction[20–23] in which an alkoxysilane is combined with a hydrosilane in the presence of $B(C_6F_5)_3$. Explicit silicone structures can be the result of such reactions.[15] We were interested in establishing if the Piers–Rubinsztajn process could also be used to create functional, explicit silicones that may be linked to hydrophilic organic moieties.[24] Such compounds could be the basis of a new class of well-defined silicone surfactants. An examination of the tolerance of $B(C_6F_5)_3$ to a variety of organic functional groups, and the conversion of functional silicones into surface active materials is described below.

2.3 Experimental Section

2.3.1 Materials

Allyltriethoxysilane, allyltrimethoxysilane, vinyltriethoxy-silane, methylphenylvinylsilane, dimethylphenylsilane, diphenylmethylsilane, pentamethyldisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, (3-glycidoxy)propyltrimethoxysilane and (3-iodopropyl)-trimethoxysilane,1,3-dimethyltetramethoxydisiloxane,(3-chloropropyl) methyl dimethoxysilane, vinyl-tetramethyldisiloxane were purchased from Gelest and used as received. vinyltrimethoxysilane (98%), tetramethyl orthosilicate (98%), tetraethyl orthosilicate (98%), (3-chloropropyl)trimethoxysilane (97%), (3-chloropropyl)-

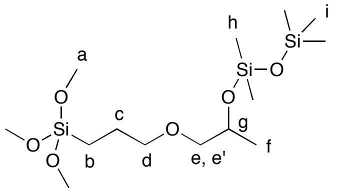
triethoxysilane (95%), 1-thioglycerol (98%), (3-aminopropyl)trimethoxysilane (97%), Propiolic acid (95%), poly(ethyleneglycol) methyl ether avg. mol. wt: 350, p-toluenesulfonic acid (98%), 2,2-dimethoxy-2-phenylacetophenone (99%), allyloxytrimethylsilane (98%), allyl benzyl ether (99%) , chromium (III) acetylacetonate, anhydrous dimethylformamide, sodium azide and tris(pentafluorophenyl)borane (95%) were purchased from Aldrich and used as received. Commercial solvents: hexane, dichloromethane and toluene were dried over activated alumina prior to use.

2.3.2 Instrumentation

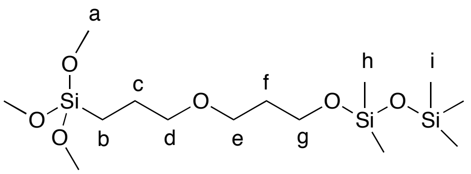
^{1}H NMR, ^{13}C NMR and ^{29}Si NMR experiments were recorded at room temperature and performed on Bruker Avance 200, 500 and 600 MHz nuclear magnetic resonance spectrometers, respectively. High-resolution MS Spectrometry was performed with a Hi-Res Waters/Micromass Quattro Global Ultima (Q-TOF mass spectrometer).

2.3.3 General Synthesis of Functional Silicones

Reaction of pentamethyldisiloxane with (3-glycidoxypropyl)-trimethoxysilane. To a solution of (3-glycidoxypropyl)trimethoxysilane (0.150 g, 0.63 mmol) in dry hexane (5 ml), was added pentamethyldisiloxane (0.376 g, 2.5 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (10 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.8 x 10^{-4} mmol). After a 30 s induction time, the reaction flask became warm, signifying the onset of an exothermic reaction, lasting roughly 10 min. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and examined via NMR. The obtained spectrum showed evidence of complete loss of epoxide, with no evidence of reaction at the methoxy moieties. The major and minor products deduced by proton and carbon NMR experiments are shown below.



Major



Minor

Major Product: (~ 88% by NMR) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.01-4.05 (m, 1 H, **g**, J = 6.0 Hz) 3.56 (s, 9 H's, **a**), 3.39-3.39-3.43 (m, 2 H's, **d**), 3.37 (dd, 1 H, **e,** J = 6.0, 9.6 Hz), 3.24 (dd, 1 H, **e',** J = 6.0, 9.6 Hz), 1.66 (m, 2 H's, **c**), 1.17 (d, 3 H's, **f**, J = 6 Hz), 0.65-0.68 (m, 2 H's, **b**), 0.09 (s, 9 H's, **i**), 0.07 ppm (s, 6 H's, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 76.53, 73.56, 67.23, 50.64, 22.93, 20.94, 5.39, 1.92, -0.15 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.07 (M), -13.56 (D), -42.01 ppm (T). HRMS (ES Positive mode): m/z $[M+H]^+$ calculated = 385.1898, found = 385.1878.

Minor Product: (~ 12% by NMR) ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.72 (t, 2 H, **g**, J = 6.4 Hz), 3.48 (t, 2 H, **e**, J = 6.4 Hz), 3.56 (s, 9 H's, **a**), 3.39-3.43 (m, 2 H's, **d**), 1.79 (m, 2 H, **f**) 1.66 (m, 2 H's, **c**), 0.67 (m, 2 H's, **b**), 0.09 (s, 9 H's, **i**), 0.06 ppm (s, 6 H's, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 73.12, 67.56, 59.33, 50.64, 33.61, 22.93, 5.39, 1.92, -0.17 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.31 (M), -13.02 (D), -42.01 ppm (T).

When the same reaction was run in dichloromethane (otherwise identical protocol), the outcome was somewhat different. Rather than the explicit reaction observed in hexane at the epoxide, the methoxy groups also started to react. The reaction was, therefore, not particularly useful in a synthetic sense. In either solvent, even with excess hydrosilane it was not possible to convert all OMe groups into disiloxanes.

2.3.3.1 Protected alcohols

Synthesis of trimethylsilyl protected (3-hydroxypropyl)-trimethoxysilane 6. In a round bottom flask equipped with a stir bar and water jacket condenser under a nitrogen atmosphere was added trimethoxysilane (2.5 g, 20.5 mmol) in dry toluene (8 ml). Allyloxytrimethylsilane (3.19 g, 24.5 mmol) was then added, followed by Karstedt's platinum complex (5 ml, 2% solution in xylenes, 1.0 mmol of Pt). The reaction was then monitored *via* NMR to ensure full conversion (3 h). Once complete, activated charcoal was added (~ 0.25 g) to the solution. The resulting mixture was stirred for an additional 2 h. The crude reaction mixture was filtered over Celite, and residual solvent and excess starting material was removed *in vacuo,* affording pure trimethylsilyl-protected (3-hydroxypropyl)trimethoxysilane (4.51 g, 88% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.55 (s, 9 H, ($\mathbf{H_3}CO)_3Si$), 3.52 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}O$-, *J* = 6.8 Hz), 1.60-1.63 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2O$-), 0.61-0.64 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2O$), 0.09 ppm (s, 9 H, $OSi(C\mathbf{H_3})_3$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 64.73, 50.45, 25.72, 4.94, -0.52 ppm. ^{29}Si NMR ($CDCl_3$, 99MHz, 1 % w/v $Cr(acac)_3$): δ 16.69 (M), -41.95 ppm (T).

Reduction of trimethylsilyl-protected (3-hydroxypropyl)-trimethoxysilane with pentamethyldisiloxane. To a solution of trimethylsilyl-protected (3-hydroxypropyl)-trimethoxysilane **6** (0.250 g, 0.99 mmol) in dry hexane (5 ml) was added pentamethyldisiloxane (0.661 g, 4.45 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (20 µl of a prepared solution containing 40 mg dissolved in 1 ml of toluene, 1.6 x 10^{-3} mmol). After a 60 s induction time, moderate evolution of gas and heat from the solution occurred, lasting roughly 5 min. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered, concentrated under reduced pressure and examined *via* ^{1}H NMR. The obtained spectrum showed complete cleavage of both methoxy and trimethylsiloxy groups consistent with a propyl-modified silicone. As this product was not of synthetic interest, it was not isolated. When fewer equivalents of hydrosilane were employed, little to no control was observed, giving mixtures of products **8, 9** and related silicones with various degrees of reaction at both methoxy and trimethylsiloxy moieties.

Synthesis of benzyl protected (3-hydroxypropyl)trimethoxysilane 7. In a round bottom flask equipped with a stir bar and water jacket condenser under a nitrogen atmosphere was added trimethoxysilane (9.07 g, 74.25 mmol) in dry toluene (15 ml). Allyl benzyl ether (10 g, 67.5 mmol) was then added, followed by Karstedt's platinum complex (5 ml, 2% solution in xylenes, 1.0 mmol of Pt). The reaction was then monitored *via* NMR to ensure full conversion (16 h). Once complete, solvent was removed under reduced pressure. The resulting mixture was then subjected to distillation (150°C, 2 mmHg) yielding pure benzyl-protected (3-hydroxypropyl)trimethoxysilane. (11.46 g, 88% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.27-7.29 (m, 4 H, phenyl), 7.23-7.26 (m, 1 H, phenyl), 4.45 (s, 2 H, $OC\mathbf{H_2}(C_6H_5)$), 3.51 (s, 9 H, $(\mathbf{H_3}CO)_3Si$), 3.40 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}O$-, *J* = 6.5 Hz), 1.66-1.70 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2O$), 0.63-0.66 ppm (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2O$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 138.64, 128.30, 127.57, 127.43, 72.73, 72.43, 50.49, 22.84, 5.34 ppm. ^{29}Si NMR ($CDCl_3$, 99MHz, 1 % w/v $Cr(acac)_3$): δ -42.11 ppm (T).

Reaction of benzyl-protected (3-hydroxypropyl)trimethoxysilane with pentamethyldisiloxane. To a solution of benzyl-protected (3-

hydroxypropyl)trimethoxysilane (0.100 g, 0.37 mmol) in dry hexane (5 ml), was added pentamethyldisiloxane **1** (0.33 g, 2.2 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (10 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.8×10^{-4} mmol). After a 30 s induction time, the reaction flask became warm, and evolution of gas occurred, signifying the onset of an exothermic reaction, lasting roughly 5 min. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered, concentrated under reduced pressure and examined *via* ^1H NMR. When only one equivalent of hydrosilane was added, both OMe and O-benzyl groups simultaneously reacted. Even with excess hydrosilane it was not possible to convert all OMe groups into disiloxanes. *Peaks associated with compound **10*** (although compound **10** was not isolated, characteristic peaks were observed *via* ^1H and COSY experiments).

^1H NMR ($CDCl_3$, 500 MHz): d 1.31–1.36 (m, 2 H, $(MeO)_3SiCH_2CH_2CH_3$), 0.853–0.882 (t, 2H, $(MeO)_3SiCH_2CH_2CH_3$, *J* = 7.5 Hz), 0.486–0.519 ppm (m, 2H, $(MeO)_3SiCH_2CH_2CH_3$).

*Peaks associated with compound **11*** (although compound **11** was not isolated, characteristic peaks were observed *via* ^1H and COSY experiments). ^1H NMR ($CDCl_3$, 500 MHz): d 3.51–3.49 (t, 2 H, $(MeO)_3SiCH_2CH_2CH_2$ O–, *J* = 7 Hz), 1.58–1.53 (m, 2 H, $(MeO)_3SiCH_2CH_2CH_2O$–), 0.57– 0.54 ppm (m, 2 H, $(MeO)_3SiCH_2CH_2CH_2O$–).

2.3.3.2 Haloalkanes

Synthesis of (3-chloropropyl)tris(pentamethyldisiloxy)silane 12. To a solution of chloropropyltriethoxysilane (0.500 g, 2.07 mmol) in dry hexane (10 ml), was added pentamethyldisiloxane (1.38 g, 9.34 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.95 x 10^{-3} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-chloropropyl)tris(pentamethyldisiloxy)silane (1.08 g, 1.81 mmol, 87.8% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.51 (t, 2 H, $O_2SiCH_2CH_2C\mathbf{H_2}Cl$, *J* = 7.0 Hz), 1.83-1.86 (m, 2 H, $O_2SiCH_2C\mathbf{H_2}CH_2Cl$), 0.62-0.65 (m, 2 H, $O_2SiC\mathbf{H_2}CH_2CH_2Cl$), 0.09 (s, 27 H, $OSi(C\mathbf{H_3})_3$), 0.07 (s, 18 H, $(C\mathbf{H_3})_2SiO_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 47.70 ($O_2SiCH_2CH_2\mathbf{C}H_2Cl$), 27.09 ($O_2SiCH_2\mathbf{C}H_2CH_2Cl$), 12.10 ($O_2Si\mathbf{C}H_2CH_2CH_2Cl$), 1.95 ($(\mathbf{C}H_3)_3SiO$), 1.26 ppm ($(\mathbf{C}H_3)_2SiO_2$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.05 (M), -21.90 (D), -70.19 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 612.2103, found = 612.2079.

Synthesis of (3-chloropropyl)tris(1,1,1,3,5,5,5-heptamethyl-trisiloxy)silane 13. To a solution of chloropropyltrimethoxysilane (0.500 g, 4.15 mmol) in dry hexane (10 ml), was added 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.98 g, 12.4 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.95 x 10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure chloropropyltris-(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (1.51 g, 90% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 3.51 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}Cl$, *J* = 7.1 Hz), 1.83-1.98 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2Cl$), 0.63-0.72 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2Cl$), 0.12 (s, 54 H, $OSi(C\mathbf{H_3})_3$), 0.07 (s, 9 H, $(C\mathbf{H_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 50 MHz): δ 47.65 ($O_3SiCH_2CH_2\mathbf{C}H_2Cl$), 26.97 ($O_3SiCH_2\mathbf{C}H_2CH_2Cl$), 12.14 ($O_3Si\mathbf{C}H_2CH_2CH_2Cl$), 1.91 ($(\mathbf{C}H_3)_3SiO$), -1.89 ppm ($(\mathbf{C}H_3)SiO_3$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.71 (M), -66.09 (D), -71.29 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 834.2643, found = 834.2667.

Synthesis of (3-chloropropyl)bis(1,1,1,3,5,5,5-heptamethyl-trisiloxy)methylsilane 14. To a solution of chloropropyldimethoxymethylsilane

(0.500 g, 2.73 mmol) in dry dichloromethane (10 ml), was added 1,1,1,3,5,5,5-heptamethyltrisiloxane (1.52 g, 6.84 mmol, 2.5 fold excess). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (20 μl of a prepared solution containing 40 mg dissolved in 1 ml of toluene, 1.6 x 10^{-3} mmol). After a 5 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-choloropropyl) di(1,1,1,3,5,5,5-heptamethyltrisiloxy)methylsilane (1.48 g, 91% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.50 (t, 2 H, $O_2SiCH_2CH_2C\mathbf{H_2}Cl$, *J* = 7.0 Hz), 1.82-1.88 (m, 2 H, $O_2SiCH_2C\mathbf{H_2}CH_2Cl$), 0.62-0.66 (m, 2 H, $O_2SiC\mathbf{H_2}CH_2CH_2Cl$), 0.102 (s, 36 H, $OSi(C\mathbf{H_3})_3$), 0.09 (s, 3 H, $O_2Si(C\mathbf{H_3})(CH_2CH_2CH_2Cl)$), 0.03 (s, 6 H, $(C\mathbf{H_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 47.81 ($O_2SiCH_2CH_2\mathbf{C}H_2Cl$), 26.80 ($O_2SiCH_2\mathbf{C}H_2CH_2Cl$), 15.13 ($O_2Si\mathbf{C}H_2CH_2CH_2Cl$), 1.81 ($(\mathbf{C}H_3)_3SiO$), -0.58 $O_2Si(\mathbf{C}H_3)(CH_2CH_2CH_2Cl)$), -2.0 ppm ($\mathbf{C}H_3SiO_3$). ^{29}Si NMR ($CDCl_3$, 99MHz, 1 % w/v $Cr(acac)_3$): δ 7.29 (M), -24.49 (D), -65.82 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 595.1837, found = 595.1819.

Synthesis of (3-chloropropyl)tris(dimethylphenylsilyloxy)silane 15. To a solution of chloropropyltriethoxysilane (0.100 g, 0.5 mmol) in dry hexane (4 ml), was added dimethylphenylsilane (0.308 g, 2.3 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (10 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.8 x 10^{-4} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure chloropropyltris(dimethylphenylsilyl)silane (0.260 g, 91% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): d 7.38–7.54 (m, 6 H, phenyl) 7.27–7.33 (m, 9 H, phenyl), 3.36 (t, 2 H, $O_2SiCH_2CH_2C\mathbf{H_2}Cl$, *J* = 6.8 Hz), 1.54–1.67 (m, 2 H, $O_2SiCH_2C\mathbf{H_2}CH_2Cl$), 0.31–0.57 (m, 2 H, $O_2SiC\mathbf{H_2}CH_2CH_2Cl$), 0.31 (s, 18 H, $OSi(CH_3)_2(C_6H_5)$). ^{13}C NMR ($CDCl_3$ 125 MHz): d 139.3, 133.2, 129.5, 127.9, 47.7, 26.9, 12.1, 0.64 ppm. ^{29}Si NMR (CDCl3 , 99 MHz, 1% w/v $Cr(acac)_3$): d -1.98 (M), -66.90 ppm (T). HRMS (ES Positive mode): *m/z* $[M+NH_4]^+$ calculated = 576.2009, found = 576.2003.

Synthesis of (3-iodopropyl)tris(diphenylmethylsiloxy)silane 16. To a solution of iodopropyltrimethoxysilane (1.0 g, 3.45 mmol) in dry hexane (10 ml), was added methyldiphenylsilane (3.07 g, 15.5 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.95 x 10^{-3} mmol). After a 6 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-iodopropyl)tris(diphenylmethylsiloxy)silane (2.18 g, 76% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46-7.48 (m, 12 H, phenyl), 7.38-7.41 (m, 6 H, phenyl,), 7.25-7.29 (m, 12 H, phenyl), 2.89 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}I$ $J = 7.0$ Hz), 1.59-1.64 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 0.54-0.55 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.52 ppm (s, 9 H, $OSi(C\mathbf{H_3})(C_6H_5)_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 137.21, 134.11, 129.76, 127.89, 27.83, 16.29, 10.77, -0.84 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -11.48 (M), -67.51 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 854.1834, found = 854.1863.

Synthesis of (3-iodopropyl)tris(methylphenylvinylsilyloxy)silane 17. To a solution of iodopropyltrimethoxysilane (0.500 g, 1.7 mmol) in dry hexane (10 ml), was added methylphenylvinylsilane (1.14 g, 7.75 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (20 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.6 x 10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure affording pure iodopropyl-tris(methylphenylvinylsilyloxy)silane (1.1 g, 93% yield).

^{1}H NMR (CDCl3, 500 MHz): d 7.49–7.51 (m, 6 H, phenyl), 7.36–7.39 (m, 3 H, phenyl), 7.29–7.32 (m, 6 H, phenyl), 6.15–6.23 (m, 3 H, $R_3SiC\mathbf{H}CHH$), 6.02–6.06 (m, 3 H, $R_3SiCHCH\mathbf{H}$), 5.75– 5.80 (m, 3 H, $R_3SiCHC\mathbf{H}H$), 3.03 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}I$, *J* = 7.0 Hz), 1.71–1.77 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2$ I), 0.57– 0.60 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.371 ppm (t, 9 H, $OSi(C\mathbf{H_3})(C_6H_5)(CHCH_2)$, *J* = 3.5 Hz). ^{13}C NMR ($CDCl_3$ 125 MHz): d 137.36, 136.89, 134.20, 133.74, 129.69, 127.84, 27.93, 16.16, 10.94, -1.18 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): d -13.38 (M), -67.49 ppm (T). HRMS (ES Positive mode): *m/z* $[M + NH_4]^+$ calculated = 704.1365, found = 704.1349.

2.3.3.3 Vinylsilanes

Synthesis of tris(phenyldimethylsilyloxy)vinylsilane 20. To a solution of vinyltrimethoxysilane (0.250 g, 1.68 mmol) in dry hexane (10 ml) and dichloromethane (5 ml) was added dimethylphenylsilane (0.919 g, 6.74 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (15 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2 x 10^{-3} mmol). After a 40 s induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure tris(phenyldimethylsilyloxy)vinylsilane (0.79 g, 1.55 mmol, 92%).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50-7.52 (m, 6 H, phenyl), 7.34-7.37 (m, 3 H phenyl), 7.28-7.31 (m, 6 H phenyl), 5.78-5.92 (m, 3 H, vinyl), 0.29 ppm (s, 18 H $(C_6H_6)(\mathbf{H_3}C)_2SiO$). ^{13}C NMR ($CDCl_3$ 125MHz): δ 139.45, 134.46, 133.30, 133.21, 129.37, 127.76, .71 ppm. ^{29}Si NMR (99 MHz 1 % w/v $Cr(acac)_3$): δ -1.58 (M), -78.86 (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 526.2085, found = 526.2051.

Synthesis of allyltris(dimethylphenylsilyloxy)silane 21. To a solution of allyltrimethoxysilane (0.500 g, 3.10 mmol) in dry hexane (10 ml) was added phenyldimethylsilane (1.67 g, 12.3 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (20 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.6 x 10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure allyltris(dimethylphenylsilyloxy)silane (1.38 g, 2.6 mmol, 86% yield)

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.54-7.56 (m, 6 H, phenyl) 7.38-7.41 (m, 3 H, phenyl), 7.33-7.36 (m, 6 H, phenyl) 5.70-5.75 (m, 1 H, $O_3SiCH_2C\mathbf{H}{=}CH_2$), 4.85-4.89 (m, 2 H, $O_3SiCH_2CH{=}C\mathbf{H_2}$), 1.55 (d, 2 H, $O_3SiC\mathbf{H_2}CH{=}CH_2$, *J = 8 Hz*), 0.34 ppm (s, 18 H's, $(C_6H_6)Si(C\mathbf{H_3})_2O$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.47, 133.48, 133.21, 129.41, 127.79, 133.48, 114.53, 22.33, 0.69 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -2.14 (M), -70.62 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 540.2242, found = 540.2267.

Synthesis of bis(methylphenylvinylsiloxy)methyldisiloxane 22. To a solution of 1,3-dimethyltetramethoxydisiloxane (0.250 g, 1.1 mmol) in dry hexane (5 ml), was added methylphenylvinylsi- lane (0.90 g, 6.1 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (15 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2 x 10^{-3} mmol). After a 4 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure affording pure bis(methylphenylvinylsiloxy)methyldisiloxane (0.63 g, 76% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.52-7.54 (m, 8 H, phenyl), 7.34-7.37 (m, 4 H, phenyl), 7.28-7.30 (m, 8 H, phenyl) 6.16-6.23 (m, 4 H, $SiC\mathbf{H}{=}CHH$), 5.99-6.02 (m, 4 H, $SiCHC{=}\mathbf{H}H$), 5.78-5.80 (m, 4 H, $SiCH{=}CH\mathbf{H}$), 0.370 (s, 12 H,

$(C_6H_5)(CH{=}CH_2)(C\mathbf{H_3})SiO)$, 0.04 ppm (d, 6 H, $O_3SiC\mathbf{H_3}$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 137.7, 137.1, 133.9, 133.7, 129.5, 127.8, -1.12, -2.01 ppm. ^{29}Si NMR ($CDCl_3$, 99MHz, 1 % w/v $Cr(acac)_3$): δ -13.81 (M), -65.83 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 772.2624, found = 772.2624.

Synthesis of $((M^{Vi}D)_2T)_2$ 23. To a solution of 1,3- dimethyltetramethoxydisiloxane (0.250 g, 1.10 mmol) in dry hexane (10 ml), was added vinyltetramethyldisiloxane (0.97 g, 0.061 mol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (15 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2 x 10^{-3} mmol). After a 90 s induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure $((MVi\ D)_2T)_2$ (0.85 g, 1.1 mmol, 96% yield).

^1H NMR ($CDCl_3$, 500 MHz): δ 6.13 (dd, 4H, $OSi(CH_3)_2(C\mathbf{H}CHH)$, *J* = 15, 19.8 Hz), 5.92 (dd, 4 H, $OSi(CH_3)_2(CHC\mathbf{H}H)$, *J* = 4.6, 15 Hz), 5.72 (dd, 4 H, $OSi(CH_3)_2(CHCH\mathbf{H})$, *J* = 4.6, 19.8 Hz), 0.153 (s, 24 H, $OSi(C\mathbf{H_3})_2(CHCH_2)$), 0.071 ppm (s, 30 H $(C\mathbf{H_3})SiO_3$, $(C\mathbf{H_3})_2SiO_2$). ^{13}C NMR ($CDCl_3$ 50 MHz): δ 139.48, 131.80, 1.29, 0.43, -2.09 ppm. ^{29}Si NMR (99 MHz 1 % w/v $Cr(acac)_3$): δ = -4.47 (M), -21.35 (D), -68.35 (T) ppm.

Synthesis of tetrakis(vinyltetramethyldisiloxy)silane 24. To a solution of tetraethyl orthosilicate (0.200 g, 0.96 mmol) in dry hexane (5 ml), was added vinyltetramethyldisiloxane (0.85 g, 5.28 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (10 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.81 x 10^{-4} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure tetrakis(vinyltetramethyldisiloxy)silane (0.520 g, 75% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): d 6.13 (dd, 4 H, R_3SiC**H**CHH, *J* = 15.0, 20.5 Hz), 5.93 (dd, 4 H, R_3SiCHCH**H**, *J* = 4.0, 15.0 Hz), 5.74 (dd, 4 H, R_3SiCHCH**H**, *J* = 4.0, 20.5 Hz), 0.166 (s, 24H, O(**H_3**C)$_2$Si(CHCH$_2$)), 0.09 ppm (s, 24 H, (C**H_3**)$_2$SiO$_2$)). ^{13}C NMR ($CDCl_3$ 125 MHz): d 139.47 (CH vinyl), 131.82 (CH_2 vinyl), 1.17 ($SiCH_3$), 0.45 ppm ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v Cr(acac)$_3$): d -4.34 (M), -20.95 (D), -110.18 ppm (D). HRMS (ES Positive mode): *m/z* $[M + NH_4]^+$ calculated = 746.2555, found = 746.2564.

Synthesis of $(M^YD)_4Si$, Y = $CH_2CH_2Si(OEt)_3$ 25. In a round bottom flask equipped with a stir bar and water jacket condenser with drying tube (Drierite desiccant) was added tetrakis(vinyltetramethyldisiloxy)silane (0.50 g, 0.68 mmol) in dry toluene (5 ml). Triethoxysilane (0.56 g, 3.4 mmol) was then added, followed by Karstedt's platinum complex (5 ml, 2% solution in xylenes, 1.0 mmol of Pt). The reaction flask was then immersed in an oil bath at 50°C. The reaction was allowed to proceed for 48 h, at which time activated charcoal was added (~ 0.25 g). The resulting solution was stirred for an additional 2 h. The crude reaction mixture was filtered over Celite, and residual solvent and excess starting material was removed *in vacuo,* affording pure $(M^YD)_4Si$, Y = CH_2 $CH_2Si(OEt)_3$ (0.74 g, 80% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): d 3.81 (q, 24 H, $(CH_3C\mathbf{H_2}O)_3SiO$, *J* = 7.0 Hz), 1.22 (t, 36 H, $(C\mathbf{H_3}CH_2O)_3SiO$, *J* = 7.0 Hz), 0.54 (s, 16 H, $O_3SiC\mathbf{H_2}C\mathbf{H_2}Si(CH_3\ )_2O$), 0.07 (s, 24 H, CH_2 $Si(C\mathbf{H_3})_2OSi(CH_3)_2OSi$), 0.06 ppm (s, 24 H, $CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2OSi$). ^{13}C NMR ($CDCl_3$ 125 MHz): d 58.50, 18.45, 9.21, 1.93, 1.17, -0.42 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): d 7.90 (M), -21.60 ppm (D), -45.01(T), -110.0 (Q) ppm.

2.3.4 Coupling to hydrophilic moieties

2.3.4.1 Thermal cycloaddition.

Synthesis of (3-azidopropyl)tris(pentamethyldisiloxy)silane 18*.* To a 10 ml round bottom flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(pentamethyldisiloxy)silane (0.500 g, 0.72 mmol) in anhydrous DMF (2 ml). To the solution was added sodium azide (0.095 g, 1.45 mmol). The mixture was then allowed to stir for 5 h at 90°C. To the mixture was added 20 ml of water and the desired product was extracted with 25 ml of hexane. The aqueous layer was washed three times with hexane (10 ml) to ensure maximum product recovery. The organic layers were combined and dried over magnesium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure affording pure (3-azidopropyl)tris(pentamethyldisiloxy)silane (0.38 g, 88% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.42 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ J = 7.0 Hz), 1.65-1.72 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 0.55-0.58 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.09 (s, 27 H's, $OSi(C\mathbf{H_3})_3$), 0.07 ppm (s, 18 H's, $(C\mathbf{H_3})_2SiO_2$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 54.20, 23.19, 11.61, 1.96, 1.28 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.06 (M), -21.88 (D), -70.20 ppm (T). HRMS (ES Positive mode): m/z $[M+Na]^+$ calculated = 624.2061, found = 624.2064

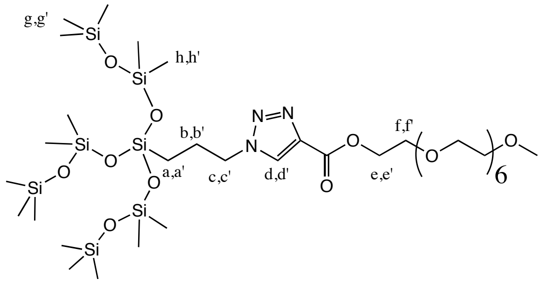
Synthesis of (3-azidopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane 19. To a 10 ml round bottom flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (1.0 g, 1.1 mmol) in anhydrous DMF (2 ml). To the solution was added sodium azide (0.141 g, 2.18 mmol). The mixture was then allowed to stir for 5 h at 90°C. To the mixture was added 40 ml of water and the desired product was extracted with 25 ml of hexane. The aqueous layer was washed three times with hexane (10 ml) to ensure maximum product recovery. The organic layers were combined and dried over magnesium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure affording pure pale yellow (3-azidopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (0.78 g, 87% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.23 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ J = 7.2 Hz), 1.70-1.73 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 0.57-0.60 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.11 (s, 54 H, $OSi(C\mathbf{H_3})_3$), 0.06 ppm (s, 9 H, $(C\mathbf{H_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 53.68, 22.40, 10.89, 1.44, -2.54 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.81 (M), -66.01 (T), -71.28 ppm (T).

Synthesis of propiolate terminated monomethoxy poly(ethyleneoxide), (av. mol. wt: 350) 26*.* In a round bottom flask containing monomethoxypoly(ethylene-oxide) (av. *mol. wt 350)* (7.0 g, 20 mmol), was successively added propiolic acid (2.8 g, 40 mmol), toluene (60 ml) and a catalytic amount of *para*-toluene sulfonic acid (0.2 g). The flask was equipped with a Dean Stark apparatus, and heated with azeotropic removal of water. Completion of the reaction was monitored by ^{1}H NMR, by comparison of the 3 protons of terminal methoxy compared to the appearance of the methylenic esters protons at 4.32 ppm (ca. 20 h). The mixture was then concentrated *in vacuo,* and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluent (up to 3%, v:v). The fractions containing the propiolate ester were combined, evaporated under reduced pressure to afford pure yellow propiolate, methyl-terminated poly(ethyleneoxide) (7.3 g, 91% yield).

^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.32 (t, 2 H, $COOCH_2$, J = 4.6 Hz), 3.74 to 3.50 (m, 29H, OCH_2CH_2), 3.35 (s, 3H, OCH_3), 2.96 to 2.93 ppm (m, 1H, *H*CCCOO). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 75.44, 74.60, 71.99, 70.65, 68.62, 65.32, 59.12 ppm.

Thermal cyclization of 18 with propiolate-modified PEG 27*.* To a 5 ml round bottom flask equipped with a magnetic stir bar and previously prepared azidopropyltris(pentamethyldisiloxy)silane (0.280 g, 0.47 mmol), was added propiolate, methyl-PEG (0.178 g, 0.47 mmol; av. mol. wt: 350, *mass calculated via NMR 382 g/mol)* and dry toluene (1 ml). The mixture was then stirred at 65°C and monitored *via* NMR for completion (typical time required is 48 h). Once complete, solvent was removed under reduced pressure, yielding pure **17** as two isomers, with a ratio of roughly 1:4. (0.324 g, 99.6% yield)



1,4 Isomer (~75%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.05 (s, 1 H, **d**), 4.49 (t, 2 H's, **e,** J = 5.0 Hz), 4.38 (t, 2 H's, **c,** J = 7.3 Hz), 3.82 (t, 2 H's, **f**, J = 5.0 Hz), 3.62-3.68 (m, ~ 24H's, -OC**H₂**C**H₂**O-), 3.53 (t, 2 H's, $-(CO)OCH_2CH_2OC\mathbf{H_2}CH_2O-$, J = 4.8 Hz), 3.36 (s, 3 H's, OC**H₃**), 1.96-2.03 (m, 3 H's, **b**), 0.49-0.53 (m, 2 H's, **a**), 0.063 (s, 27 H's, **g**), 0.05 ppm (s, 18 H's, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 159.10, 140.49, 128.08, 72.70, 71-28-71.48, 69.70, 64.81, 59.77, 53.69, 25.30, 11.90, 2.57, 1.90 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.24 (M), -21.52 (D), -70.99 ppm (T) .

1,5 Isomer (~25%): ^{1}H NMR ($CDCl_3$, 500 MHz): δ 8.13 (s, 1 H, **d'**), 4.68 (t, 2 H's, **c'**, *J* = 7.5 Hz), 4.44 (t, 2 H's, **e'**, *J* = 5.0 Hz), 3.79 (t, 2 H's, **f'**, *J* = 5.0 Hz), 3.62-3.68 (m, ~ 24H's, $-OC\mathbf{H_2}C\mathbf{H_2}O-$), 3.53 (t, 2 H's, $-(CO)OCH_2CH_2OC\mathbf{H_2}CH_2O-$, *J* = 4.8 Hz), 3.36 (s, 3 H's, $OC\mathbf{H_3}$), 1.93-1.97 (m, 3 H's, **b'**), 0.49-0.53 (m, 2 H's, **a'**), 0.051 (s, 27 H's, **g'**), 0.03 ppm (s, 18 H's, **h'**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 161.45, 138.78, 128.08, 72.70, 71.28-71.48, 69.52, 65.26, 59.77, 53.56, 25.30, 11.99, 2.57, 1.85 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.06 (M), -21.85 (D), -70.74 ppm (T) .

Thiol-ene click 29. To a solution of allyltris(1,1,1,3,5,5,5-heptamethyltrisiloxy)-silane (0.500 g, 0.64 mmol) in dry THF, previously passed through neutral alumina (1 ml), was added 1-thiogylcerol (0.103 g, 0.96 mmol) and 2,2-dimethoxy-2-phenylacetophenone (0.016 g, 0.0625 mmol). The mixture was then irradiated under ultraviolet light (254 nm) and monitored *via* NMR until complete disappearance of the allyl functionality was observed (typically 30– 40 min). Once complete, the mixture was subjected to column chromatography (10% acetone, 90% dichloromethane) to remove the photoinitiator and excess starting materials.

The collected fractions were combined and concentrated under reduced pressure yielding the sulfide-modified silicone (0.392 g, 69% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.76 (m, 1 H, $SCHH'C\mathbf{H}(OH)CHH''(OH)$), 3.73 (m, 1 H, $SCHH'CH(OH)C\mathbf{H}H''(OH)$), 3.52-3.55 (m, 1 H, $SCHH'CH(OH)CH\mathbf{H}''(OH)$), 2.68-2.72 (m, 1 H, $SC\mathbf{H}H'CH(OH)CHH''(OH)$), 2.56-2.60 (m, 1 H, $SCH\mathbf{H}'CH(OH)CHH''(OH)$), 2.53 (t, 2 H's, $O_3SiCH_2CH_2C\mathbf{H_2}S$, J = 7.5 Hz), 1.64-1.73 (m, 2 H's, $O_3SiCH_2C\mathbf{H_2}CH_2S$), 0.58-0.69 (m, 2 H's, $O_3SiC\mathbf{H_2}CH_2CH_2S$), 0.10 (s, 54 H's, $(C\mathbf{H_3})_3SiO$), 0.047 ppm (s, 9 H's, $(C\mathbf{H_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 69.60, 65.57, 36.01, 35.72, 23.63, 14.07, 1.91, -1.88 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 7.75 (M), -66.01 (T), -71.20 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated= 906.3145 found= 906.3204.

2.4 Results

2.4.1 Incorporation of functional synthetic handles

3-(Glycidoxy)propyltrimethoxysilane was reacted with one equivalent of pentamethyldisiloxane **1** in the presence of catalytic amounts of $B(C_6F_5)_3$. No evidence of disiloxane formation was observed: instead, selective reductive epoxide ring opening occurred (Figure 2.2), but only in hexanes as solvent. Surprisingly, there was no further reaction with the addition of excess 1: the major product remained 2A (A:B, 88:12). In the more polar solvent dichloromethane some competition occurred between the epoxide and the alkoxysilane: small amounts of disiloxane **3** were also formed. This trend in selectivity as a function of solvent polarity was also seen in the reaction of hydrosilanes with thiols ($R_3SiH + HS(CH_2)_3Si(OR) \rightarrow R_3SiS(CH_2)_3Si(OR)_3 + H_2$).[24]

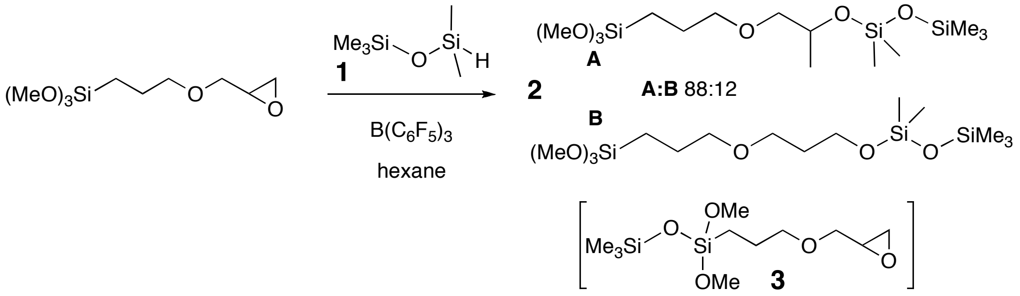


Figure 2.2. Reductive epoxide ring opening.

The relative efficiency of silylation between free alcohols and alkoxysilanes in the presence of $B(C_6F_5)_3$ was examined using **4,** which was prepared in low yield by platinum-catalyzed hydrosilylation of allyl alcohol with $HSi(OEt)_3$. Exposure of **4** to $B(C_6F_5)_3$ and one equivalent of **1** led preferentially to reaction at the alcohol giving **5** – the same process as occurs with platinum catalysts (Figure 2.2). By contrast, once the alcohol was protected as a silyl **6** or benzyl ether **7,** reactions of both methyl and propyl ethers occurred competitively. In the case of **6,** the propyloxy group was reduced competitively with the SiOMe group to give mixtures of **8**, **9** and related products: tris(trimethylsiloxy)propylsilane was the product with an excess of **1**. The benzyl ether **7** gave an unhelpful mixture of regioisomeric cleavage products, **10** and **11**. Complete conversion to trifunctional propylsilicones could not be induced with an excess of **1** (Figure 2.3).

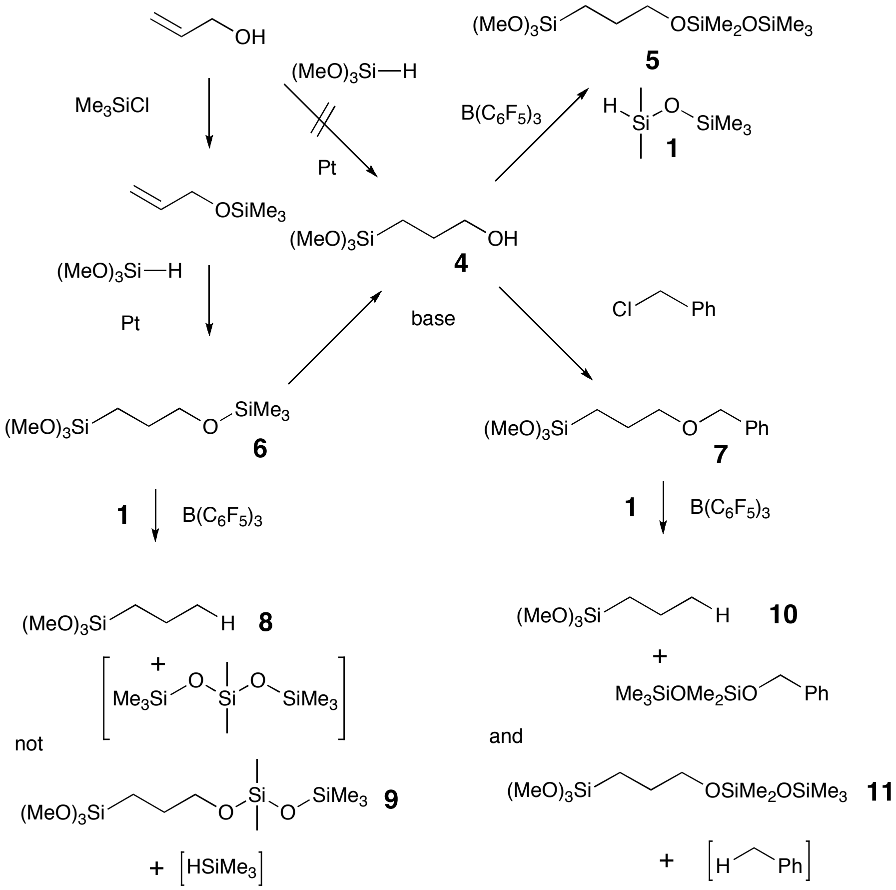


Figure 2.3. Competitive reduction of benzyl and silyl ethers (products in '[]' were removed during workup at low vacuum and are inferred).

2.4.2 Compatible functional groups

Haloalkanes. Alkoxysilane compounds that also contain alkyl halides, including both iodo and chloro compounds, react cleanly in high yields with hydrosilanes in the presence of $B(C_6F_5)_3$ to give functional siloxanes **12, 13, 14, 15, 16** and **17** (Figure 2.4). The alkyl halide can be further functionalized, as shown in the simple substitution of **12, 13** to give organoazides **18** and **19,** respectively. The latter compounds provide a facile linkage to hydrophilically modified and functional materials, as is discussed further below. The latter substitution (and cyclization) processes do not affect the structure of the silicone framework.

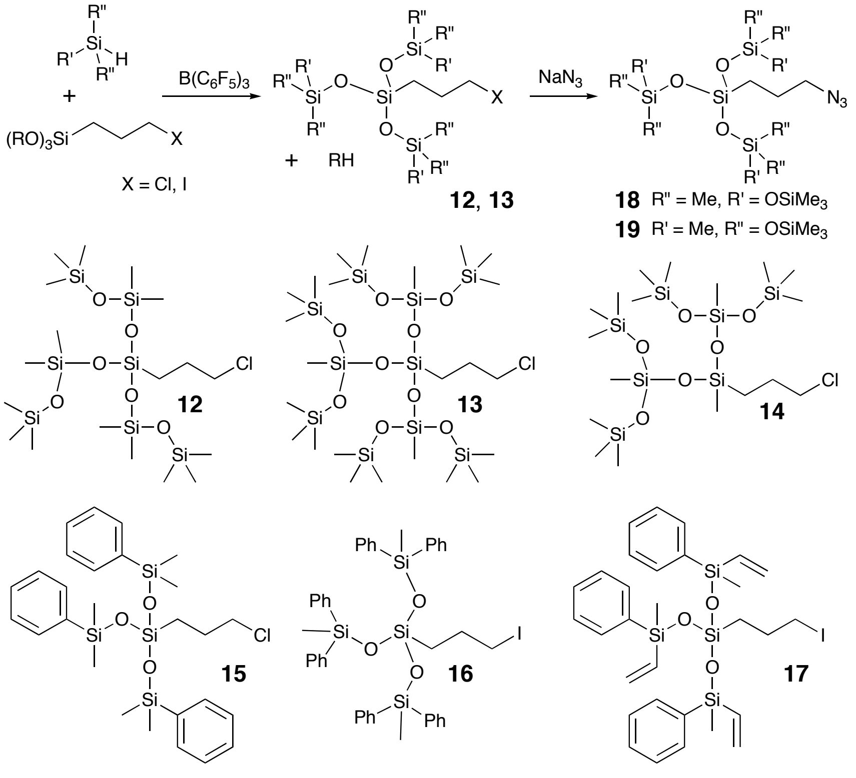


Figure 2.4. Alkyl halide-derived silicones

Alkenes. *Oligoalkene-functionalized silicones.* The hydrosilylation of alkynes, and particularly of alkenes, is broadly used in silicon chemistry to incorporate organic residues.[25] It has previously been reported that $B(C_6F_5)_3$ will catalyze the hydrosilylation of (thio)ketones, imines[26] and alkenes.[27,28] In addition, the hydrosilylation of alkenes catalyzed by $B(C_6F_5)_3$ has been described.[27] Therefore, it was not initially anticipated that vinyl-functional silicones could be prepared under the reaction conditions of the Piers–Rubinsztajn reaction. However, C=C hydrosilylation typically requires catalyst loadings of ~5wt%. At the concentrations of $B(C_6F_5)_3$ used here, ~0.5%, very clean disiloxane formation occurred leading to highly functionalized silicones with both single and multiple alkene groups (Figure 2.5) or mixed alkenes/alkyl halides **17** (Figure 2.4): no silylation of the olefins were observed during the Piers–Rubinsztajn silicone formation. The yields are excellent and complex materials, including silicone crosslinkers **20**, **21**, **22**, **23** and **24** (see also Figure 2.6), are readily prepared in a few steps.

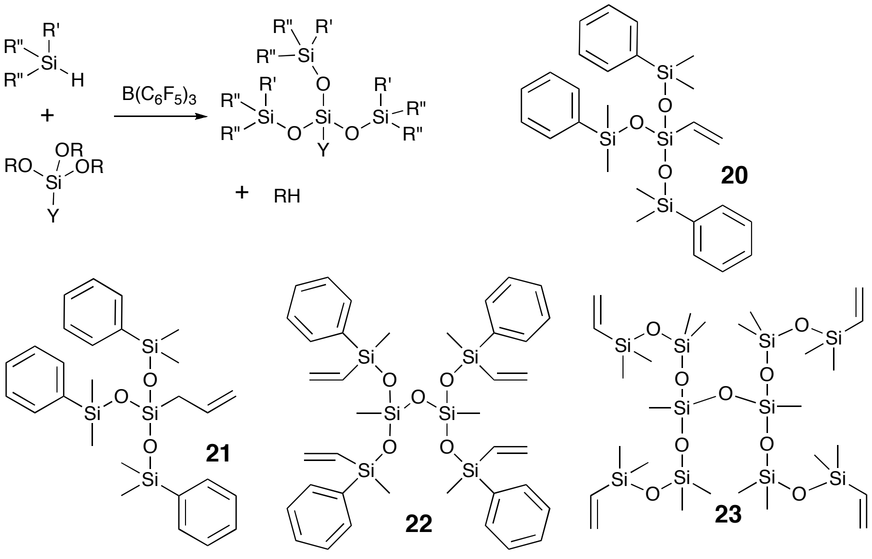


Figure 2.5. Oligoalkene preparation.

Silicone functionalization – strategies for polymer coupling

As noted above, the key objective of this work was finding appropriate functional groups and reaction conditions that would permit organofunctionalization of silicones. We show three complementary strategies that demonstrate this point.

Iterative hydrosilylation. Silicones bearing both SiH and $SiCHCH_2$ residues will self-polymerize in the presence of platinum or radical catalysts.[29,30] By contrast, the same compounds will selectively form siloxanes in the presence of $B(C_6F_5)_3$ without touching the alkenes. However, they can be converted into new alkoxysilanes[25] with platinum and compounds such as $HSi(OEt)_3$. Thus, a short iterative procedure can lead to large, highly functional compounds (Figure 2.6) while maintaining silicone structural integrity. This obvious route to dendrimeric structures is currently being developed.

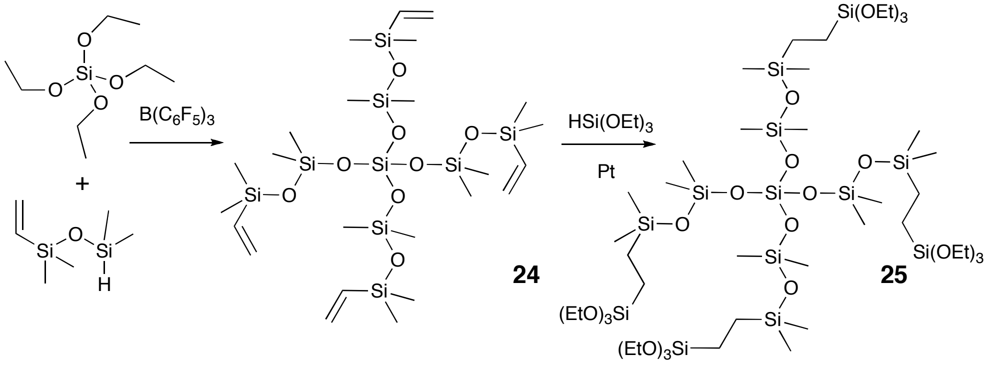


Figure 2.6. Iterative Piers–Rubinsztajn/hydrosilylation.

Azide "click" chemistry. Click chemistry[31] has become a standard method to link disparate molecules. Initially, a thermally activated process described by Huisgen.[32–34] It was reinvented by Sharpless who used a copper catalyst to both increase reaction selectivity and decrease reaction temperatures.[31,35–37] We have previously examined both the copper-catalyzed and thermal versions to functionalize[38] and crosslink silicones.[39]

The reaction between azide **18** and poly(ethylene glycol) propiolate ester **26** occurred in the absence of a copper catalyst at 65°C over 48 h to give the surface active graft copolymer **27** (Figure 2.7); the silicone structure was not affected during the process. Because of this accessibility of well-defined silicone materials, it should be possible to prepare a wide range of polymeric surfactants using this protocol. An examination of the surface activity of these and related compounds is currently under way and will form the basis of a future report.

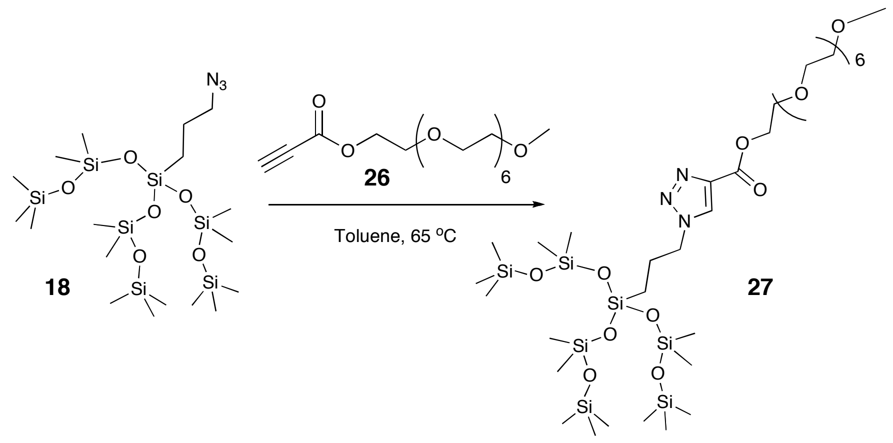


Figure 2.7. Concise preparation of organofunctional silicones.

Thiol-ene "click" capable silicones thioglycerol. More recently, the "click" moniker has been applied to the thiol-ene reaction (Figure 2.8).[40,41] Normally, this describes a radical chain addition of a thiol across an alkene to generate a sulfide. Thioglycerol cleanly added to **28**[24] in the presence of 2,2-dimethoxy-2-phenylacetophenone to give **29:** the process is photoinitiated at 254 nm. The thiol-ene reaction can therefore also be used to hydrophilize silicones under conditions that don't affect the silicone backbone.

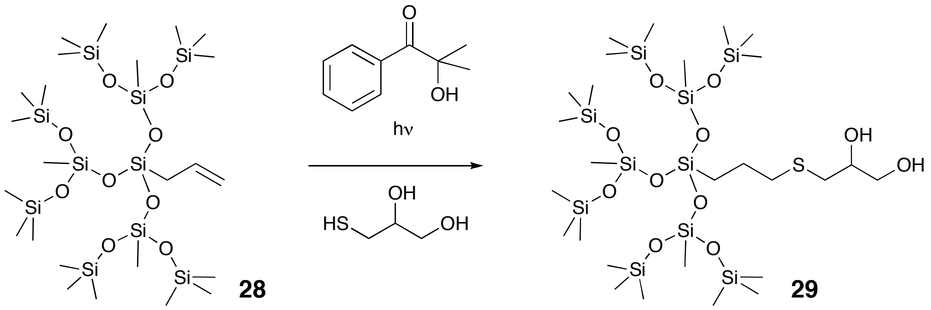


Figure 2.8. Thiol-ene click.

2.5 Discussion

The Piers–Rubinsztajn reaction is understood to involve the formation of a Si–H–B complex **30** which, in the presence of oxygen-based nucleophiles, leads of an oxonium ion **31** that subsequently degrades to a disiloxane and alkane, regenerating the catalyst (Figure 2.9). However, $B(C_6F_5)_3$ is a reasonably strong Lewis acid that can form Lewis acid–base complexes with other heteroatoms present in the reaction mixture **32.**[42] The interplay between formation of the required Si-H-B complex and other complexes controls the outcome of the reactions described above.

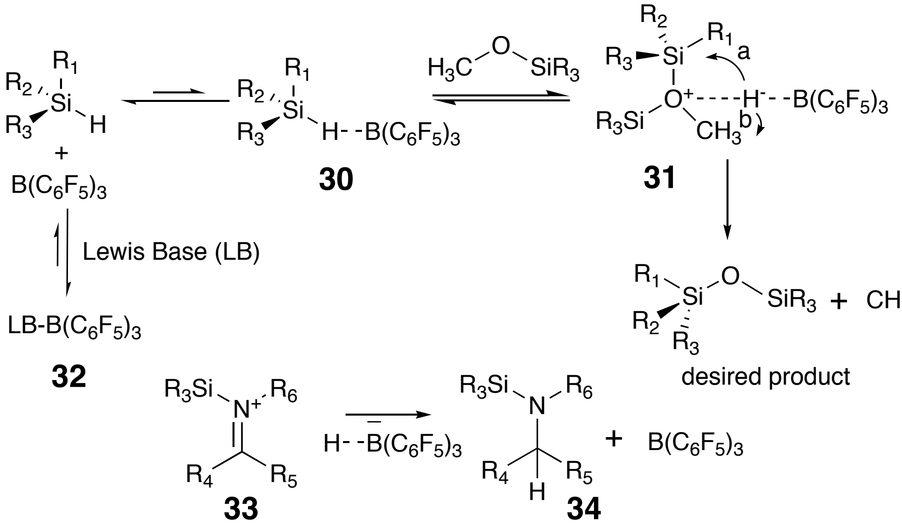


Figure 2.9. Proposed mechanism for $B(C_6F_5)_3$-catalyzed siloxane formation.

Neither halides nor olefins provide sufficiently basic Lewis bases to compete with alkoxysilanes. Thus, at the low concentrations of $B(C_6F_5)_3$ used in this study (0.5 wt%), only activation *via* silyloxonium formation occurs, leading to clean disiloxane formation. The process can be repeated multiple times without loss of fidelity to produce complex structures in high yield in one or two steps (Figure. 2.4-2.6).

Less efficient reactions were observed when more powerful Lewis bases were present. Piers, in his examination of the hydrosilylation of imines, for example, showed that strong Lewis bases such as nitrogen can shut down any reaction involving Si-H, because the equilibrium of N–B *vs.* H–B complexes lie almost exclusively on the side of the BN complex (Fig. 9, LB = RR'C=NR").[26] As the N basicity is reduced, the equilibrium with Si-H is established, and reduction occurs (**33** → **34**).

A similar set of complex equilibria will present in each of the cases studied here. The outcomes, in particular, the efficiency with which silicones are prepared, depend on the degree to which Si-H–B complexes and silylated oxonium ions can form in the presence of other Lewis bases.

No reaction was observed to occur between **1** and amino-propyltriethoxysilane (APTS) in the presence of $B(C_6F_5)_3$. We ascribe this, following Piers' results, to essentially irreversible complexation between boron and the nitrogen (Figure 2.9, LB = $H_2N(CH_2)_3$ $Si(OR)_3$). Under such circumstances formation of the necessary B–H–Si complex is precluded. To examine this in more detail, proton NMR of the reaction medium containing tris(pentafluorophenyl)boron with aminopropyltriethoxysilane (APTS) and **1** over 3.5 h, a very long time when compared to the *ca.* 5 min normally needed for completion of Piers–Rubinsztajn reactions. No change in the multiplicity and integration of the different signals of APTS was observed. The only minor change was a small chemical shift of the amino protons, which can be attributed to the formation of the B–N complex, from 1.09 ppm in the free form to 1.32 in the presence of catalyst. It would be reasonable to expect that such complexes **35** could be relatively strong Brønsted acids and lead to silicone degradation/redistribution. However, as noted, there was no evidence of this.

The epoxide opened exclusively in hexane, and reacted competitively with the SiOMe groups in dichloromethane. The major reaction in both cases can be considered to arise from a B–H complex analogous to **30** and a silyloxonium ion: the Piers–Rubinsztajn reaction is as much about silicon-based Lewis acids as about borohydrides. Reduction of the silyl complex **36** preferentially occurs at the least hindered carbon (Figure 2.10a), as would expected for nucleophilic driven reactions. In the more polar DCM, the less basic oxygen atoms of the SiOMe groups begin to compete, leading to some disiloxane formation (giving **3,** Figure 2.2).

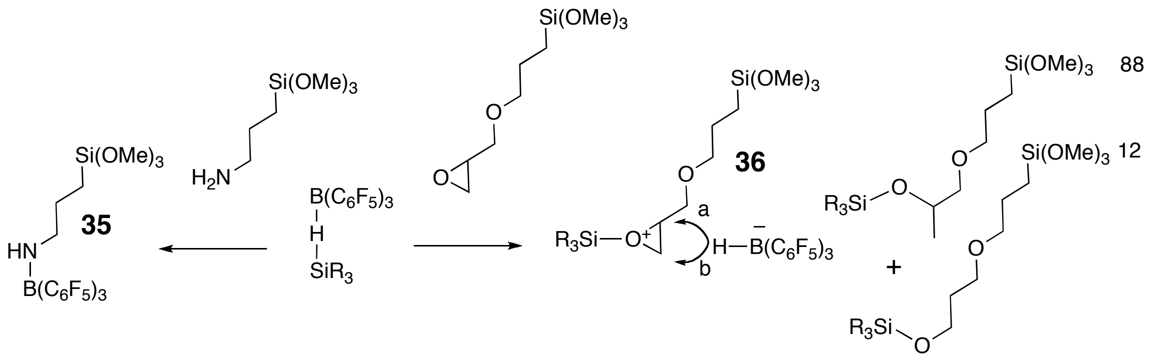


Figure 2.10. Epoxide-ring opening.

The most significant contributions of this work are related to the synthetic flexibility provided. As shown in Figure 2.6 (MW 1460), reasonably large silicones are available already after two steps. The orthogonality of the available processes suggest this strategy could be adopted to make explicit polymers or macrocrosslinkers.

The main objective of the work was to develop procedures to assembly amphiphilic polymers based on silicones. Both 3+2-cyclization reactions and thiol-ene reactions lend themselves to this objective (Figure 2.7 and Figure 2.8). As with hydrosilylation, they are orthogonal to dehydrogenative coupling, and both permit the linking of hydrophilic materials to silicones to give surface active materials.

2.6 Conclusions

The rapid assembly of explicit functional silicone polymers is facilitated by $B(C_6F_5)_3$ -catalyzed condensation of hydrosilanes and alkoxysilanes. Efficiency of the process is reduced when more efficient Lewis bases than alkoxysilanes are present, including alcohols and epoxides: ethers are competitive. However, useful functional groups including alkyl halides and olefins are readily incorporated into complex silicone structures, and can then be converted into surface active polymers using 3+2-cycloadditions and thiol-ene click reactions.

2.7 Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support and Silcotech Canada and Siltech Inc. for support and helpful discussions.

2.8 References

1. R. M. Hill, *Silicone Surfactants,* Dekker, New York, 1999.
2. R. M. Hill, *Curr. Opin. Colloid Interface Sci.,* 2002, **7,** 255–261.
3. P. M. Zelisko and M. A. Brook, *Langmuir,* 2002, **18,** 8982–8987.
4. A. J. O'Lenick, *J. Surfactants Deterg.,* 2000, **3,** 387–393.
5. A. J. O'Lenick Jr., in *Silicone Sulfate Polymers*, U. S. P. Office, Siltech Llc, US Patent 6777521*,* 2004.
6. F. Gonzaga, S. Singh and M. A. Brook, *Small,* 2008, **4,** 1390–1398.
7. R. S. Stan and M. A. Brook, in *Chelating Silicone Polymers*, McMaster University, US Patent 6,566,322, 2003.
8. G. Hu, F. J. LaRonde and M. A. Brook, *Silicon Chem.,* 2002, **1,** 215–222.
9. A. Provatas, J. G. Matisons and R. S. Smart, *Langmuir,* 1998, **14,** 1656–1663.
10. B. Sahoo, K. F. Brandstadt, T. H. Lane and R. A. Gross, *Org. Lett.,* 2005, **7,** 3857– 3860.
11. D. Henkensmeier, B. C. Abele, A. Candussio and J. Thiem, *Polymer,* 2004, **45,** 7053–7059.
12. D. Henkensmeier, B. C. Abele, A. Candussio and J. Thiem, *Macromol. Chem. Phys.,* 2004, **205,** 1851–1857.

13. D. Henkensmeier, B. C. Abele, A. Candussio and J. Thiem, *J. Polym. Sci. Polym. Chem.,* 2005, **43,** 3814–3822.

14. M. A. Brook, Y. Chen, K. Guo, Z. Zhang and J. D. Brennan, *J. Mater. Chem.,* 2004, **14,** 1469–1479.

15. D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.,* 2008, **130,**32–33.

16. J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *J. Inorg. Organomet. Polym. Mater.,* 2007, **17,** 173–187.

17. J. Cella and S. Rubinsztajn, *Macromolecules,* 2008, **41,** 6965–6971.

18 J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *Macromolecules,* 2008, **41,** 7352–7358.

19. S. Rubinsztajn and J. A. Cella, *Macromolecules,* 2005, **38,** 1061–1063.

20. D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.,* 2000, **65,** 3090–3098.

21. S. Rubinsztajn and J. Cella, *Polym. Prep.,* 2004, **45 (1),** 635–636.

22. S. Rubinsztajn and J. A. Cella, in *Silicone Condensation Reaction*, ed. E. Patent, General Electric, WO 2005118682, 2005.

23. S. Rubinsztajn and J. A. Cella, in *Silicone Condensation Reaction*, ed. U. S. P. Office, General Electric, USA Patent 7064173, 2006.

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

25. B. G. Marceniec, J.W. UrbaniakZ. W. Kornetka Comprehensive *Hand-book on Hydrosilylation Chemistry,* 1992, Pergamon*,* Oxford.

26. W. E. Piers, in *Advances in Organometallic Chemistry,* Elsevier Academic Press, San Diego, 2005, pp. 1–76.

27. M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.,* 2002, **67,** 1936–1940.

28. D. T. Hog and M. Oestreich, *Eur. J. Org. Chem.,* 2009, 5047–5056.

29. T. M. Stefanac and M. A. Brook, *Heteroat. Chem.,* 1998, **9,** 241–251.

30. T. M. Stefanac, M. A. Brook and R. Stan, *Macromolecules,* 1996, **29,** 4549–4555.

31. H. C. Kolb, M. G. Finn and K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2001, **40,** 2004–2021.

32. R. Huisgen, *Angew. Chem., Int. Ed. Engl.,* 1963, **2,** 633–645.

33. F. Santoyo-Gonzales and F. Hernandez-Mateo, in *Topics in Heterocyclic Chemistry,* ed. E. S. H. El Ashry, Springer-Verlag, Berlin, 2007, pp. 133–177.

34. K. V. Gothelf and K. A. Jorgensen, *Chem. Rev.,* 1998, **98,** 863–909.

35. Z. P. Demko and K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2002, **41,** 2113–2116.

36. Z. P. Demko and K. B. Sharpless, *Angew. Chem., Int. Ed.,* 2002, **41,** 2110–2113.

37. V. V. Rostovtsev, L. G. Green, V. V. Fokin and K. B. Sharpless, *Angew.Chem., Int. Ed.,* 2002, **41,** 2596–2599.

Chapter 3: Morphology-Controlled Synthesis of Poly(oxyethylene)silicone or Alkylsilicone Surfactants with Explicit, Atomically Defined, Branched, Hydrophobic Tails[**]

3.1 Abstract

Silicone surfactants are widely used in commerce because of the unusual surface activity when compared with fluorocarbon or hydrocarbon surfactants. However, most silicone surfactants are comprised of ill-defined mixtures, which preclude the development of an understanding of structure– surface activity relationships. Herein, we report a synthetic strategy that permits exquisite control over silicone structure by using the $B(C_6F_5)_3$-catalyzed condensation of hydro- and alkoxysilanes. Six different, precise hydrophobes were then mated to hydrophilic poly(oxyethylene)s of three different molecular weights by a metal-free click cyclization to generate a library of explicit silicone surfactants. These compounds

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[**] Reproduced with kind permission from John Wiley and Sons. J. B. Grande, F. Gonzaga and M. A. Brook, *Chemistry a European Journal*, 2012, **18,** 1536-1541. Grande was responsible for the synthesis and full characterization of all silicone based surfactants in this manuscript. Grande was also responsible for the experimental write up in this paper. Gonzaga was responsible for the synthesis of alkyne terminated PEO's of three molecular weights and the write up of the manuscript. Gonzaga is also acknowledged for the help with designing and implementing experimental procedures needed to obtain CMC values.

were calculated to have a relatively linear value range of the hydrophilic–lipophilic balance, ranging from about 8 to about 15. The solubility of some of the compounds was too low to measure a critical micelle concentration (CMC). The others exhibited a broad range of surface tension values at the CMC that depend both on the length of the hydrophilic head group and, more importantly, the nature of the hydrophobic tail. Subtle distinctions in surfactant-related properties, which can be attributed to the three-dimensional structures, can be seen for compounds with comparable numbers of hydrocarbons and silicon groups.

3.2 Introduction

Poly(oxyethylene) monoalkyl ethers are the most widely used nonionic surfactants. These surfactants, both oligomeric and polymeric, find applications in consumer products, particularly personal-care products, and a wide variety of industrial processes.[1] For surfactant design for specific purposes, advantage is taken of the well-established correlation between surface activity and sizes and structures of both the alkyl group and the poly(oxyethylene) hydrophile.

Silicone-based surfactants, which have hydrophobes of much lower surface energy than alkanes, have remarkable surface-activity properties. For example, dilute aqueous solutions of superwetters (for an example see Figure 3.1 A), which are commonly used to disperse agricultural chemicals on leaves, can rapidly spread across waxy leaves to 50 times the original droplet size.[2,3] With the exception of some silicone surfactants that are based on small, well-defined siloxanes, most silicone surfactants involve ill-defined mixtures of silicone polymers modified by oligo- or poly(ethylene glycol) (PEG) or propylene glycol (PPG) chains (Figure 3.1 B).[4] For the most part, this is because reliable syntheses for explicit silicones do not exist.

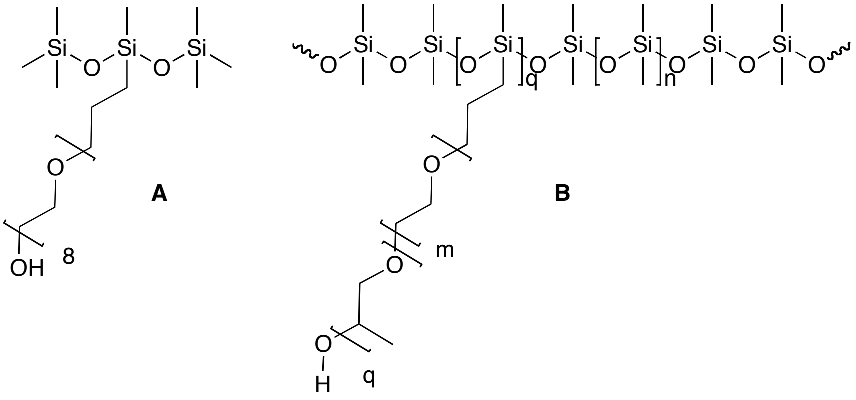


Figure 3.1. Typical silicone surfactants: A) superwetters and B) rake co- polymers.

The nature of surfactant aggregates found in solution strongly depends on geometric constraints during self-assembly, which derive from structural parameters, such as the volume and length of the apolar constituent.[5,6] Whereas the tailoring of the polar head groups of surfactants is a very widespread and usual feature in surfactant design, the fine tuning of the hydrophobic tails has proven considerably more challenging. In the hydrocarbon series, functionalized precursors (such as, iodo or bromo, alkyne or alkene) that would allow the creation of branching units or the introduction of aromatic systems (e.g., phenyl groups) or reactive groups (such as, allyl groups) at precisely defined positions in the hydrocarbon chain are not always available. The silicone series has a similar problem regarding controlled synthesis of the hydrophobe. In addition, and more problematic, is the fragility of silicone intermediates and products to acid- and base-catalyzed redistribution and other degradation reactions.[7] Even in cases for which it is possible to assemble precise, larger silicone fragments, the preservation of these structures requires that subsequent steps are undertaken at neutral pH, which has proven challenging.[8]

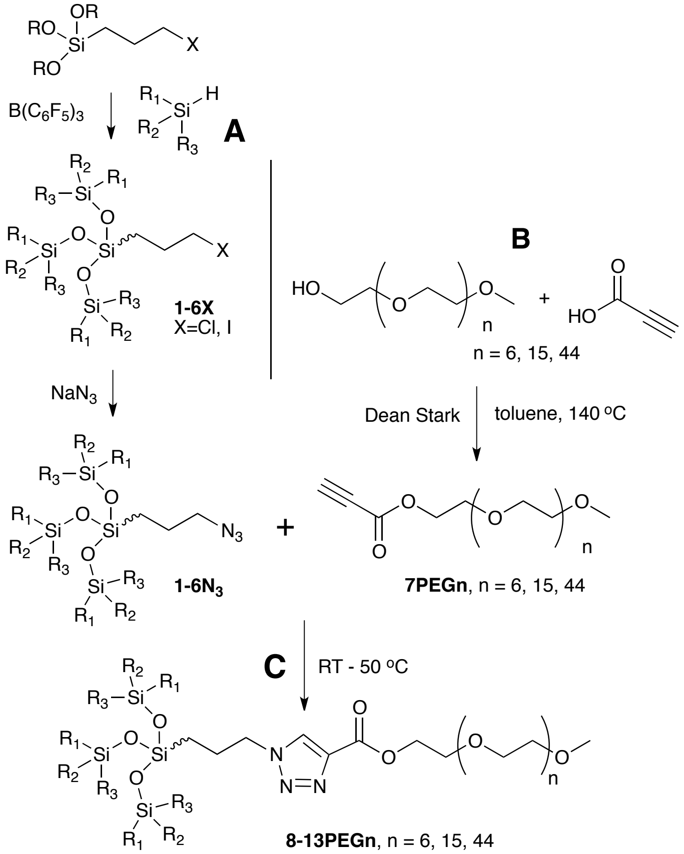
Recently, we[9] and others[10, 11, 12, 13] have described the preparation of silicone polymers by using the Piers–Rubinsztajn reaction.[14,15,16,17] Explicit silicone structures can be the result of such reactions.[9] We have demonstrated the tolerance of $B(C_6F_5)_3$ to a variety of organic functional groups, including allyl, chloro-, and iodoalkanes.[18] Equally important, additional functional groups can be incorporated into these silicones while their structures are preserved. For example, appropriately functionalized compounds will undergo click reactions, including metal-free addition of azides to alkynes and the thiolene reaction.[19]

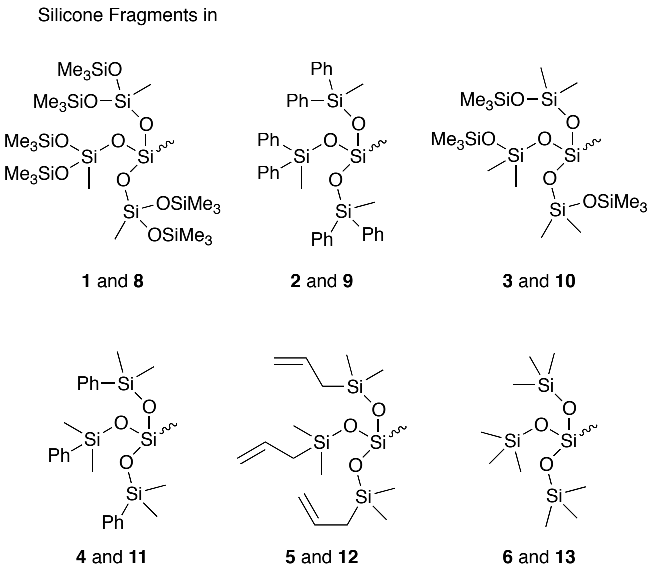
Herein we present a general, efficient, simple, and metal-free synthetic route to explicit silicone– or silicone–alkyl poly(oxyethylene) surfactants. The process relies on two separate, extremely efficient reactions: the Piers–Rubinsztajn reaction[20] to create explicit silicone hydrophobes and the Huisgen 1,3-dipolar cycloadditions of azides to alkynes—metal-free click chemistry—used to link the silicone to a hydrophile. In addition to the syntheses, the critical micelle concentration (CMC) and the value of surface tension (ST) at the CMC were determined for the prepared surfactants, and related to the morphologies of the surfactants.

3.3 Results and Discussion

The surfactant synthesis required independent preparation of well-defined azidopropyl silicones and propiolate-terminated PEGs, respectively. The routes to each of these key intermediates is first outlined, followed by a description of the coupling process, which involved a low temperature, metal-free (and catalyst-free) cycloaddition of the hydro- phobic azides to monopropiolate-terminated poly(oxyethylene)s of various molecular weights under almost solvent free conditions (Figure 3.2).

The hydrophobic portion of the surfactant was prepared in two steps by starting from simple, commercially available chloro- or iodopropylalkoxysilanes. These were coupled with hydrosilanes by using $B(C_6F_5)_3$ as a catalyst to provide a small library of complex silicones that possessed a single alkyl halide—the Piers–Rubinsztajn reaction (Figure 3.2A).[21] With the exception of azide **6-N$_3$**, which was prepared from tris(trimethylsiloxy)silane **6-Cl**, all azides **1-N$_3$** to **5-N$_3$** were prepared in high yields (typically ranging from 77 to 93%) by displacement of the alkyl halide by azide. It should be noted that the synthesis of such branched, explicit siloxane structures would be extremely tedious and, at the least, difficult with the use of conventional chlorosilane chemistry. The process permits the introduction of decreasing bulk and ramifications on the siloxane back- bone, as shown by the comparison in the structures of azides **1-N$_3$**, **3-N$_3$**, and **6-N$_3$**, with increasing numbers of trimethyl-silyl groups. Moreover, the functional-group tolerance[18,19] of the Piers–Rubinsztajn reaction permitted introduction of reactive groups, such as allyl (azide **5-N$_3$**) or a tunable amount of phenyl moieties (azides **2-N$_3$** and **4-N$_3$**; Figure 3.2).





1 and **8** **2** and **9** **3** and **10**

4 and **11** **5** and **12** **6** and **13**

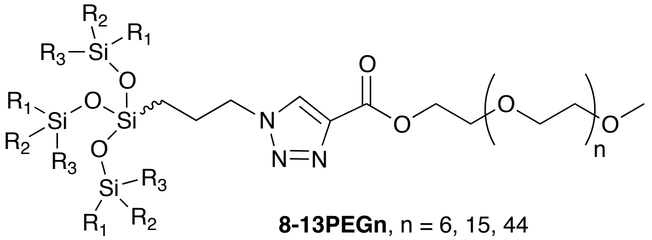
Figure 3.2. a) Synthesis of explicit azido silicones by using the Piers–Rubinsztajn reaction and/or nucleophilic displacement of halogens, followed by a click ligation. b) The explicit silicone fragments.

Surfactant polar head groups were prepared from monopropiolate-terminated poly(oxyethylene)s, with average molecular weights of 350, 750 and 2000. The synthetic route to such derivatives involves a classical Fischer esterification of the corresponding monomethoxy-terminated poly(oxyethylene) derivative (Figure 3.2B), followed by chromatographic purification (for the 350- and 750-molecular-weight precursors) or precipitation, for the highest-molecular-weight compounds.

Propiolate esters of poly(oxyethylene) were chosen due to the electron deficiency. We have shown previously that such activated alkynes undergo a metal-free click reaction (1,3-dipolar cycloaddition of azides to alkynes) at moderate (50°C) or even room temperature, without the need of a copper catalyst.[22,23,24]

The thermal cycloaddition of mono(propiolate) esters of poly(oxyethylene) proved to be extremely efficient; isolated yields that ranged from 79–99% were observed (Figure 3.2a C, Table 3.1). Moreover, the experimental procedure was straightforward: simple mixing of the two precursors in a small amount of toluene followed by mild heating allows the chemical ligation to proceed and gives the corresponding surfactants. The purification step benefits from two very interesting factors associated with the procedure. The first is inherent to this class of thermal cycloadditions; no byproducts are generated during the reaction. The second relies on the fact that a small excess of the azido derivative was used. This not only allowed the reaction to run faster and to ensure complete conversion of the poly(oxyethylene) propiolate into the surfactant, but also, due to the very large gap in polarity between the starting azidosiloxane (very non-polar, running with the solvent front in TLC and chromatography) and the cycloaddition product (amphiphilic, thus more polar), allows easy isolation of the product from the reaction mixture (i.e., a simple "chromatographic" filtration over silica gel; elution with CH_2Cl_2 eluted the azide, followed by elution with a methanol:CH_2Cl_2 mixture to elute the product). Last but not least, the entire procedure was designed to respect the integrity of the siloxane hydrophobic moiety. Siloxane bonds are extremely sensitive to acid- and base-catalyzed redistribution and other degradation reactions.[7] The isolated surfactants were analyzed by proton, carbon, and silicon NMR spectroscopy, which all indicate that the exact silicone structures of the starting azides were preserved in the corresponding surfactants. ^{29}Si NMR, in that respect, was essential as it proved, without any ambiguity, that every single M (monosiloxane R_3SiO-), D (disiloxane -$OSiR_2O$-), or T (trisiloxane $(RO)_3Si$-) unit was preserved during the synthetic process.

Table 3.1. Summary of prepared surfactants



8-13PEGn, n = 6, 15, 44

Entry	Hydrophobic tail	Polar head group	n	Surfactant yield [%][a]
1	**$1-N_3$**	**7PEG-6**	6	**8PEG-6** (79%)
2		**7PEG-15**	15	**8PEG-15** (81%)
3		**7PEG-44**	44	**8PEG-44** (83%)
4	**$2-N_3$**	**7PEG-6**	6	**9PEG-6** (89%)
5		**7PEG-15**	15	**9PEG-15** (90%)
6		**7PEG-44**	44	**9PEG-44** (78%)
7	**$3-N_3$**	**7PEG-6**	6	**10PEG-6** (99%)
8		**7PEG-15**	15	**10PEG-15** (87%)
9		**7PEG-44**	44	**10PEG-44** (84%)
10	**$4-N_3$**	**7PEG-6**	6	**11PEG-6** (83%)
11		**7PEG-15**	15	**11PEG-15** (88%)
12		**7PEG-44**	44	**11PEG-44** (93%)
13	**$5-N_3$**	**7PEG-6**	6	**12PEG-6** (91%)
14		**7PEG-15**	15	**12PEG-15** (90%)
15		**7PEG44**	44	**12PEG-44** (87%)
16	**$6-N_3$**	**7PEG-6**	6	**13PEG-6** (88%)
17		**7PEG-15**	15	**13PEG-15** (84%)
18		**7PEG-44**	44	**13PEG-44** (93%)

[a]Isolated yield.

The structural diversity of the prepared surfactants is reflected in the aggregation properties and calculated hydrophilic–lipophilic balance (HLB[25] and 3D-HLB)[26] values, as shown in Table 3.2 and Figure 3.3. For example, surfactants **8PEG-6** to **13PEG-6**, based on the smallest poly(oxyethylene) **7PEG-6**, present HLB values that range from 5.41 to 8.79 (3D-HLB, oil component values that range from 2.18 to 10.48). Such low values indicate a highly hydrophobic character. Experimentally, the following was observed: these surfactants were not measurably soluble in water, and thus the CMCs could not be determined. However, this lack of aqueous solubility does not rule out other applications. These amphiphilic derivatives are extremely well suited for the development of water-in-oil emulsions (typical values of HLB range from 4 to 6) or the wetting of powders into oil (HLB range 7–9).

Table 3.2. CMC data for the prepared surfactants

Entry	**Surfactant**	**CMC (M)**	**ST at CMC ($mN\cdot m^{-1}$)**	**HLB**[a]	**3D-HLB**[26]
1	**8PEG-6**	na	na	5.41	(5.41, 2.18)
2	**9PEG-6**	na	na	5.93	(5.93, 10.48)
3	**10PEG-6**	na	na	6.82	(6.82, 2.76)
4	**11PEG-6**	na	na	7.10	(7.10, 7.71)
5	**12PEG-6**	na	na	7.98	(7.98, 6.12)
6	**13PEG-6**	na	na	8.79	(8.79, 3.55)
7	**8PEG-15**	na	na	9.12	(9.12, 1.70)
8	**9PEG-15**	na	na	9.55	(9.55, 7.78)
9	**10PEG-15**	na	na	10.58	(10.58, 1.97)
10	**11PEG-15**	$7.2\cdot10^{-5}$	32.3	10.88	(10.88, 5.45)
11	**12PEG-15**	$6.1\cdot10^{-5}$	25.0	11.82	(11.82, 4.18)
12	**13PEG-15**	$5.7\cdot10^{-5}$	23.7	12.59	(12.59, 2.35)
13	**8PEG-44**	na*	na*	13.92	(13.92, 0.95)
14	**9PEG-44**	$8.3\cdot10^{-5}$	48.0	14.29	(14.29, 4.25)
15	**10PEG-44**	$0.9\cdot10^{-3}$	23.2	15.08	(15.08, 1.02)
16	**11PEG-44**	$4.0\cdot10^{-5}$	46.7	15.30	(15.31, 2.80)
17	**12PEG-44**	$2.4\cdot10^{-5}$	38.8	15.97	(15.97, 2.06)
18	**13PEG-44**	$1.2\cdot10^{-3}$	29.4	16.46	(16.46, 1.12)

[*] Attempts to obtain the CMC value for this surfactant were unsuccessful, even with its excellent solubility in water. [a] HLB values were calculated using Griffin's method.

For the three water-soluble surfactants, **11PEG-15**, **12PEG-15**, and **13PEG-15** extremely small CMC values were found, ranging from 57 (**13PEG-15**) to 72 μm (**11PEG-15**). These values easily compete with existing explicit trisiloxane surfactants that possess various lengths of poly(oxyethylene) chains. For example, an explicit MDM trisiloxane surfactant with four ethylene-oxide units as the hydrophilic head group have a CMC of 79 μm.[2] Moreover, it is well known that the surface activities of siloxane surfactants decrease with increasing length of the poly(oxyethylene) chain. Indeed, long hydrophilic ethylene-oxide chains are not completely located in the bulk water, but can penetrate partially into the surfactant film, thus preventing the formation of a tightly packed surfactant film. The CMC of a MDM trisiloxane surfactant with a 16-ethylene-oxide-units hydrophilic head group was found to be 1 mM. Surfactants **11PEG-15**, **12PEG-15**, and **13PEG-15** have similar hydrophilic components, yet their CMCs are more than two orders-of-magnitude lower than this value. Surfactant **13PEG-15** possesses a purely silicone hydrophobic tail, and accordingly, presents a ST value (23.7 mNm^{-1}) characteristic of silicone surfactants. The substitution of a methyl group by an allyl or a phenyl group produced an increase in the ST value at the CMC to 25.0 (**12PEG-15**) and 32.3 mNm^{-1} (**11PEG-15**), respectively. These results indicate that even a subtle manipulation in the morphology of the surfactants (e.g., an allyl moiety instead of a methyl) can be used to tailor the physical properties (Figure 3.3).

The ability to control the surfactant-related properties was further highlighted by the study of the aggregation of surfactants **8PEG-44**–**13PEG-44**, based on the approximate 2000-molecular-weight poly(oxyethylene) **7PEG-44**. These surfactants presented HLB values in the range 13.92–16.46 (3D-HLB oil component values range 0.95–4.25), characteristic of surfactants with good aqueous solubility and high detergency power (i.e., able to strongly stabilize oil-in-water emulsions). The CMC values for surfactants **10PEG-44** and **13PEG-44** are in the millimolar range, due to the reduced size of the hydrophobic moieties. On the other side, surfactants with a larger, hyperbranched hydrophobic tail, such as **9PEG-44**, **11PEG-44**, and **12PEG-44**, have extremely low CMC values, ranging from 24 *μ*m for **12PEG-44** to 83 *μ*m for **9PEG-44**. Interestingly, surfactants **11PEG-44** and **12PEG-44**, based on the 2000-molecular-weight poly(oxyethylene), exhibits CMC values (40 and 24 *μ*m, respectively) that are approximately half of those of the analogues based on the 750-molecular-weight poly(ethylene)oxide **11PEG-15** and **12PEG-15** (72 and 61 *μ*m, respectively). This behavior is unusual, as in the trisiloxane–oligo(ethylene oxide) surfactant series it was previously shown that CMC values increase with increasing hydrophilic chain length. However, this effect came with a large increase of the interfacial tension values at the CMC (from 25.0 to 38.8 mNm^{-1}, for **12PEG-15** and **12PEG-44**, respectively). Although aggregation occurs at a lower concentration for higher-molecular-weight poly(oxyethylene)s, the interfacial stabilization between water and the surfactant is not as efficient; this effect could also reflect changes in the type of surfactant aggregates that form (micelles, worm-like micelles). Values of ST at the CMC are small for **10PEG-44** and **13PEG-44** and characteristic of silicone surfactants: increased alkyl or aryl character of the hydrophobic moieties also increases the ST at the CMC (with values as high as 48.0 mNm^{-1} for **9PEG-44**).

The surfactants based on the intermediate-chain-length poly(oxyethylene) **7PEG-15**, not surprisingly, presented an intermediate character. Whereas aqueous solubility and thus micellization could be observed for the more hydrophilic surfactants, such as **11PEG-15**, **12PEG-15**, and **13PEG-15** (HLB values of 10.88, 11.82, and 12.59, respectively, 3D-HLB (10.88, 5.45), (11.82, 4.18), (12.59, 2.35)), it was not possible to determine CMC values for **8PEG-15** to **10PEG-15**, due to the high hydrophobicity of the extended, ramified hydrophobic tail.

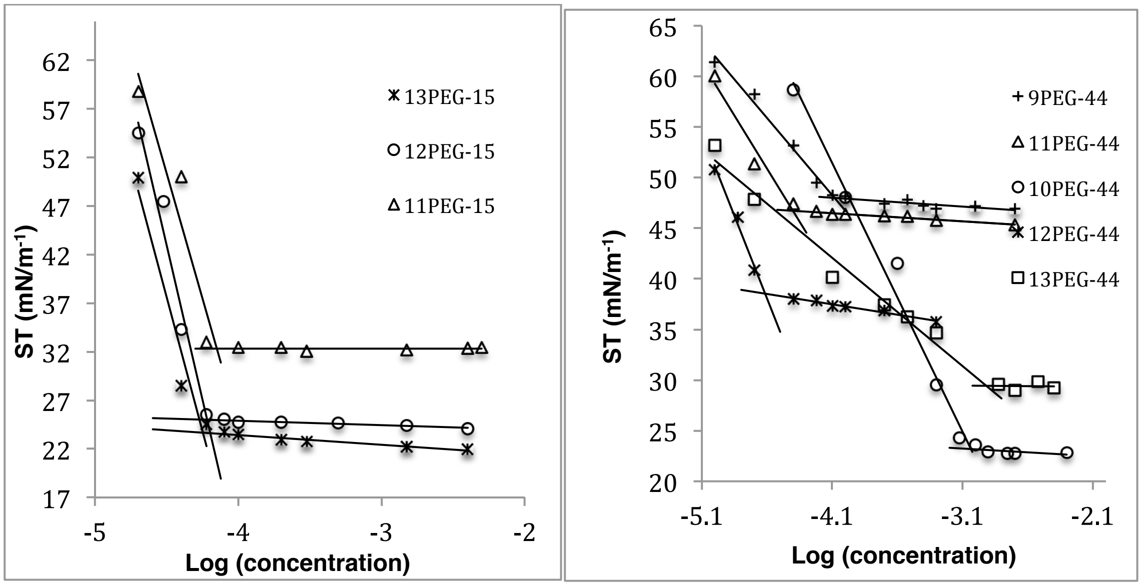


Figure 3.3. ST data for two series of surfactants with different hydrophilic tails, **7PEG-15**, and **7PEG-44**.

3.4 Conclusion

Taken together, all these results clearly show that this new class of hyperbranched, explicit silicone–ethylene oxide amphiphiles are extremely efficient surfactants. The methodology developed herein combines two extremely efficient coupling reactions that should allow the synthesis of tailor-made surfactants, at the wish of the experimentalist. This versatility allows for extensive tuning of surfactant morphology (alkyl versus silicone, degree of branching, size of the hydrophobic moiety), which leads to a great control over the aggregation properties and thus to a wide range of potential applications as detergents, oil-in-water or water-in-oil stabilizers, and so forth.

3.5 Experimental Section

Representative procedures for the synthesis of each type of building block used: explicit iodopropyl modified silicones, the corresponding azido derivatives, monopropiolate-terminated poly(oxyethylene)s and the surfactants prepared by metal-free click ligation, are given above. Detailed experimental procedures and spectroscopic characterizations of all synthesized compounds are provided in 9.1, Appendix I of this document.

Synthesis of 3-iodopropyl(tris(allyldimethylsiloxy))silane: Allyldimethylsilane (1.55 g, 15.5 mmol) was added to a solution of iodopropyltrimethoxysilane (1.00 g, 3.4 mmol) in dry hexane (10 mL). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (40 μL of a 0.078 m solution in toluene, 3.1 mmol). After a short induction time (about 100 s), rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina to remove $B(C_6F_5)_3$ (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed in vacuo, affording pure iodopropyl(tris(allyldimethylsiloxy))silane (1.61 g, 86 % yield).

^{1}H NMR (CDCl$_3$, 500 MHz): δ 5.79 (m, 3 H, $OSi(CH_3)_2CH_2C\mathbf{H}CH_2$), 4.86-4.91 (m, 6H, $OSi(CH_3)_2CH_2CHC\mathbf{H_2}$), 3.19 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}I$, J = 7.5 Hz), 1.81-1.87 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 1.59 (d, 6 H, $OSi(CH_3)_2C\mathbf{H_2}CHCH_2$, J = 10.0 Hz), 0.56-0.59 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.12 ppm (s, 18 H, $OSi(C\mathbf{H_3})_2CH_2CHCH_2$); ^{13}C NMR: ($CDCl_3$ 125 MHz) δ 134.15, 113.82, 28.29, 26.25, 16.18, 10.99, -0.16 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 4.92 (M), -68.01 (T) ppm. HRMS (ES Positive mode): m/z $[M^{+}Na]^{+}$ calc. = 565.0919, found = 565.0917.

Synthesis of 3-azidopropyl(tris(allyldimethylsiloxy))silane (5-N_3): A solution of 3-iodopropyl(tris(allyldimethylsiloxy))silane (1.00 g, 1.8 mmol) in anhydrous DMF (2 mL) was added to a 10 mL round-bottomed flask equipped with a magnetic stir bar. Sodium azide (0.24 g, 3.7 mmol) was added, and the mixture was stirred at room temperature. The reaction was monitored by ^{1}H NMR spectroscopy; once full substitution of the iodo group was achieved (reaction was completed within 24 h), water (20 mL) was added. The desired product was then extracted with hexanes (25 mL), and the water phase extracted again with hexanes (3 x 10 mL). The organic layers were combined and dried over sodium sulfate (10 g).The resulting solution was filtered and concentrated under reduced pressure (without heating) to yield 3-azidopropyltris(allyldimethylsiloxy))silane (0.78 g, 92.5% yield).

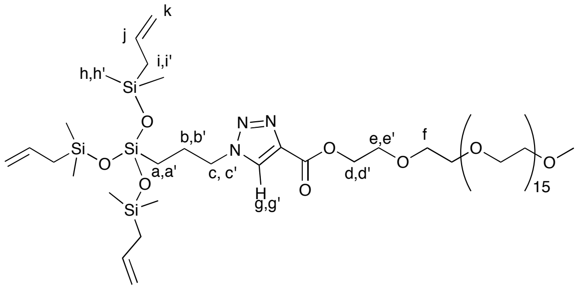
^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.78 (m, 3 H, $OSi(CH_3)_2CH_2C\mathbf{H}CH_2$), 4.86-4.91 (m, 6 H, $OSi(CH_3)_2CH_2CHC\mathbf{H_2}$), 3.23 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ J = 7.5 Hz), 1.61-1.66 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 1.59 (d, 6 H, $OSi(CH_3)_2C\mathbf{H_2}CHCH_2$, J = 10.0 Hz), 0.50-0.57 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.12 ppm (s, 18 H, $OSi(C\mathbf{H_3})_2CH_2$-$CHCH_2$); ^{13}C NMR: ($CDCl_3$ 125 MHz) δ 134.13, 113.79, 54.07, 26.24, 23.29, 11.61, -0.19 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 4.92 (M), -67.21 (T) ppm. LRMS (ES Positive mode): m/z $[M+K]^+$ calc. = 496.94, found = 496.3.

Synthesis of 7PEG-15: Propiolic acid (4.2 g, 60.0 mmol), toluene (90 mL), and a catalytic amount of p-toluenesulfonic acid (0.5 g, 2.6 mmol) was successively added in a round-bottomed flask containing monomethoxy poly(ethylene oxide) (av mol wt: 750, 15.0 g, 20.0 mmol). The flask, equipped with a Dean Stark apparatus, was heated with azeotropic removal of water. Completion of the reaction was monitored by ^{1}H NMR spectroscopy, by comparison of the three protons of the terminal methoxy with the appearance of the methylenic ester protons at 4.32 ppm (about 20 h). The solution was then cooled to room temperature, and washed three times with an aqueous potassium carbonate solution (50 mL). The organic phase was then dried over magnesium sulfate, concentrated in vacuo, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluent (up to 5% v:v). The fractions containing the propiolate ester were combined, evaporated under reduced pressure to afford pure monopropiolate, monomethoxy terminated poly(oxyethylene) (12.1 g, 77% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.34 (t, 2 H, $-COOC\mathbf{H}_2-$, J = 6.0 Hz), 3.74 to 3.55 (m, ~ 60 H, $-OC\mathbf{H}_2C\mathbf{H}_2O-$), 3.37 (s, 3 H, $OC\mathbf{H}_3$), 2.89 (s, broad, 1 H, $\mathbf{H}CCCOO$).

^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.68, 75.67, 74.56, 71.94, 70.57, 68.57, 65.24, 59.03. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 806.4749, found = 806.4768.

Synthesis of 12PEG-15



To a 5 mL round bottom flask equipped with a magnetic stir bar and previously prepared azidopropyltris(allyldimethyl-siloxy)silane (0.37 g, 0.82 mmol), was added prepared propiolate terminated monomethoxy poly(ethylene oxide) (0.500 g, 0.63 mmol; avg. mol. wt. 750, mass calculated via HRMS 788.47 g/mol) and dry toluene (~1 mL). The mixture was then stirred at 45 °C and monitored via NMR for completion (typical time required is 64 h). The mixture was then concentrated in vacuo, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluant (up to 3%, v:v). The fractions containing the desired compound were then evaporated under reduced pressure to affording pure pale yellow **12PEG15** as two isomers, with a ratio of roughly 1:4. (0.712 g, 90.2 % yield)

Major isomer 1,4 (~75%): ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.05 (s, 1 H, **g**), 5.73-5.78 (m, 3 H, **j**), 4.82-4.88 (m, 6 H, **k**), 4.50 (t, 2 H, **d**, *J* = 6.0 Hz), 4.36 (t, 2 H, **c,** *J* = 7.8 Hz), 3.79 (t, 2 H, **e**, *J* = 6.0 Hz), 3.59-3.68 (m, ~ 60 H, -OC**H$_2$**C**H$_2$**O-), 3.48-3.53 (m, 2 H, **f**), 3.36 (s, 3 H, OC**H$_3$**), 1.92-1.96 (m, 2 H, **b**), 1.56 (d, 6 H, **i**, *J* = 12 Hz), 0.43-0.47 (m, 2 H, **a**), 0.09 ppm (s, 18 H, **h**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 160.82, 139.90, 138.22, 133.95, 127.45, 113.93, 72.07, 70.70, 69.08, 64.23, 59.15, 53.08, 26.16, 24.80, 11.34, -0.17 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 5.80 (M), -67.63 (T). HRMS (ES Positive Mode): m/z [M+NH$_4$]$^+$ calc. = 1263.6818, found = 1263.6854. HLB value = 20*(719.925/1245.79) = 11.55.

Minor Isomer 1,5 (~25%): ^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.15 (s, 1 H, **g'**), 5.73-5.78 (m, 3 H, **j**), 4.82-4.88 (m, 6 H, **k**), 4.67 (t, 2 H, **c',** *J* = 9.0 Hz), 4.44 (t, 2 H, **d'**, *J* = 6.0 Hz), 3.72 (t, 2 H, **e'**, *J* = 6.0 Hz), 3.59-3.68 (m, ~ 24 H, -OC**H$_2$**C**H$_2$**O-), 3.48-3.53 (m, 2 H, **f**), 3.36 (s, 3 H, OC**H$_3$**), 1.89-1.91 (m, 2 H, **b'**), 1.53 (d, 6 H, **i',** *J* = 12.0 Hz), 0.43-0.47 (m, 2 H, **a**), 0.07 ppm (s, 18 H, **h'**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.49, 139.90, 138.22, 127.45, 134.09, 113.77, 72.07, 70.70, 68.88, 64.70, 59.15, 52.87, 26.16, 24.71, 11.34, -0.23 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 5.80 (M), -67.63 (T). HRMS (ES Positive Mode): m/z [M+NH$_4$]$^+$ calc. = 1263.6818, found = 1263.6854. HLB value = 20*(719.925/1245.79) = 11.55.

3.6 Acknowledgements

We thank the Natural Sciences and Engineering Research Council of Canada for financial support of this work.

3.7 References

1. R. Dong and J. Hao, *Chem. Rev.* 2010, **110**, 4978 – 5022.
2. R. M. Hill, *Silicone Surfactants*, Dekker, New York, 1999.
3. R. M. Hill, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 255 – 261.
4. P. M. Zelisko and M. A. Brook, *Langmuir*, 2002, **18**, 8982 – 8987.
5. W. Kunz, F. Testard and T. Zemb, *Langmuir,* 2009, **25**, 112 – 115.
6. J. N. Israelachvili, D. J. Mitchell, B. and W. Ninham, *J. Chem. Soc. Faraday T.,* 1976, **72**, 1525 – 1568.
7. M.A. Brook in *Silicon in Organic, Organometallic and Polymer Chemistry*, John Wiley & Sons, New York, 2000, pp. 256 – 308.
8. H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, T. Tsumuraya and S. Masamune, *J. Am. Chem. Soc.*, 1990, **112**, 7077 – 7079.
9. D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.*, 2008, **130**, 32 – 33.
10. J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *J. Inorg. Organomet. Polym. Mater.,* 2007, **17**, 173 – 187.
11. J. Cella and S. Rubinsztajn, *Macromolecules,* 2008, **41**, 6965 – 6971.
12. J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *Macromolecules,* 2008, **41**, 7352 – 7358.
13. S. Rubinsztajn and J. A. Cella, *Macromolecules,* 2005, **38**, 1061 – 1063.
14. D. J. Parks, J. M. Blackwell and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090 – 3098.
15. S. Rubinsztajn and J. Cella, *Polym. Prep.*, 2004, **45**, 635 – 636.
16. S. Rubinsztajn and J. A. Cella, in *Silicone Condensation Reaction*, ed. E. Patent, General Electric, WO 2005118682, 2005.
17. S. Rubinsztajn and J. A. Cella, in *Silicone Condensation Reaction*, ed. U. S. P. Office, General Electric, USA Patent 7064173, 2006.
18. J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, *Chem. Commun.*, 2010, **46**, 4988–4990.

19. J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Trans.*, 2010, **39**, 9369 – 9378.

20. M. A. Brook, J. B. Grande and F. Ganachaud, *Adv. Polym. Sci.*, 2010, **235**, 161–183.

21. J. Chojnowski, S. Rubinsztajn, J. A. Cella, W. Fortuniak, M. Cypryk, J. Kurjata and K. Kazmierski, *Organometallics,* 2005, **24**, 6077–6084.

22. F. Gonzaga, G. Yu, and M.A. Brook, *Macromolecules* 2009, **42**, 9220 – 9224.

23. F. Gonzaga, G. Yu and M.A. Brook, *Chem. Commun*. 2009, 1730 –1732.

24. Z. Li, T. S. Seo and J. Ju, *Tetrahedron Lett.*, 2004, **45**, 3143 – 3146.

25. W. C. Griffin, *J. Soc. Cosmet. Chem.*, 1949, **1**, 311 – 326.

26. The surface activities of silicone surfactants, because of the low solubility in both water and oil, are often better characterized by 3D-HLB numbers. A. J. O'Lenick, Jr., J. K. Parkinson, *Cosmetics Toiletries* ,1996, **111**, 37 – 44.

Chapter 4: Amphiphilic Silicone Architectures via Anaerobic Thiol-Ene Chemistry‡‡

4.1 Abstract

Despite broad application, few silicone-based surfactants of known structure or, therefore, surfactancy have been prepared because of an absence of selective routes and instability of silicones to acid and base. Herein the synthesis of a library of explicit silicone-poly(ethylene glycol) (PEG) materials is reported. Pure silicone fragments were generated by the $B(C_6F_5)_3$-catalyzed condensation of alkoxysilanes and vinyl functionalized hydrosilanes. The resulting pure products were coupled to thiol-terminated PEG materials using photogenerated radicals under anaerobic conditions.

[‡‡] Reprinted with permission from D. J. Keddie, J. B. Grande, F. Gonzaga, M. A. Brook and T. R. Dargaville, *Organic Letters*, 2011, **13** (22), 6006-6009. Copyright 2011 American Chemical Society. Contribution: Grande was responsible for the synthesis and characterization of all explicit vinyl functional silicones along with all explicit thiol-ene based surfactants. Grande was responsible for experimental write-up, experimental design and also helped with the write up of the manuscript. Keddie was responsible for the synthesis of thiol capped PEO (**13**, **14** and **15**), and the tethering of thiol capped PEO to ill-defined vinyl terminated PDMS polymers (**18**, **19** and **20**). Keddie was also responsible for the lead write up of the manuscript. Gonzaga is acknowledged for helpful discussions.

4.2 Introduction

Silicone surfactants (e.g., Figure 4.1A) are usually based on the poly(ethylene glycol) (PEG) modification of short-chain silicones[1,2] or of long-chain polymers modified randomly along the backbone.[3-6] While such compounds are considered “exotic” in the surfactant world, due both to price and composition, the compounds are essential in certain applications, including cosmetics, paints, and coatings and for the stabilization of bubbles in polyurethane foam structures.[7]

Like most silicones, silicone surfactants are comprised of complex mixtures of compounds[8-11] that can vary significantly in polydispersity index and, therefore, surfactancy. Normally, the compounds are prepared by grafting to an existing hydrosilane an allyl-terminated PEG chain using platinum-catalyzed hydrosilylation ($PEG\text{-}CH_2CH{=}CH_2 + HSiR_3 \rightarrow PEG(CH_2)_3SiR_3$). While the reaction is extremely efficient -in ideal cases, less than 10 ppm of Pt is required- platinum is expensive. In addition, two regioisomers are often generated in the hydrosilylation process. Worse, with the exception of only a very few low molecular weight materials as shown in Figure 4.1B, well-defined hydridosilicones are simply not available. Larger molecular weight silicone surfactants are sold as broad molecular weight mixtures of molecules bearing varying degrees of functionalization. There is, as a consequence, no general route to structurally well-defined silicone surfactants and little knowledge about structure activity relationships.[12]

Further complicating the situation is the intrinsic reactivity of silicone polymers. Either acids or bases can initiate a process in which silicones depolymerize in an equilibrium between chains and rings, for which the equilibrium constant is approximately 1.[13] Any processes that involve linking hydrophiles to well-defined silicones must therefore avoid both acidic and basic conditions.

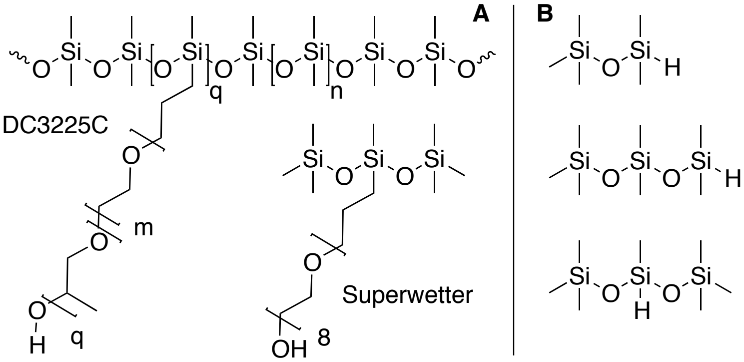
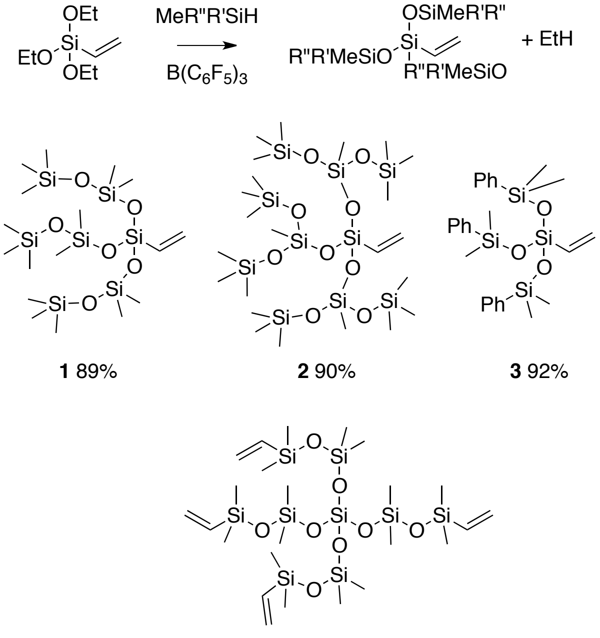


Figure 4.1 Structures of A: representataive, commercially available silicone surfactants, and, B: readily available functional hydrosiloxanes

Recently, we described a simple route to explicit, medium sized silicone structures,[14] including functional silicones,[15] that involves the $B(C_6F_5)_3$-catalyzed condensation of hydrosilanes and alkoxysilanes to give silicones and alkane byproducts (the Piers-Rubinsztajn reaction[16] (Figure 4.2)). The utilization of this route for the creation of structurally well-defined silicone amphiphiles could avoid the disadvantages of platinum-catalyzed processes and, in addition, would allow one to probe structure-surface activity relationships of the surfactants formed.



1 89%　**2** 90%　**3** 92%

4 75%

Figure 4.2 Using The Piers-Rubinsztajn Reaction to Prepare Explicit Vinylsiloxanes

Four different explicit silicones were produced using the Piers-Rubinsztajn coupling of alkoxy- and hydrosilanes (Figure 4.2).[16] Catalysis by $B(C_6F_5)_3$ of the condensation of vinyltriethoxysilane and the pentamethyldisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, or phenyldimethylsilane, respectively, led to siloxanes **1**, **2**, and **3** in good yield. Alternatively, the tetravinyl material **4** could be made in an analogous process with $Si(OEt)_4$. These and a commercial silicone terminated with vinyl groups served as substrates for the thiol-ene reaction (Figure 4.2).

The Piers-Rubinsztajn approach constitutes one part of the synthesis of well-defined surfactants. We sought a simple and efficient route for grafting these silicones to hydrophiles under conditions that do not affect silicone architecture: that is, under conditions that are neither acidic nor basic.[17] Several strategies presented themselves including the modular, metal free "click" reaction between azides and alkynes.[18] We reasoned that a thiol-ene "click" process[19,20] which has been broadly exploited in many technical areas,[21] including silicones,[22] should efficiently produce a wide range of molecular structures that can be isolated with limited workup. Therefore, we examined and describe below the synthesis of a library of amphiphilic silicones using thiol-ene chemistry, initiated by photolysis of 2,2-dimethoxy-2-phenylacetophenone (DMPA), between PEG thiols and well-defined silicone architectures, prepared by boron catalyzed coupling of lower alkoxy- and hydrosiloxanes.

A series of PEG oligomers, terminated at a single end by thiols, were synthesized from the corresponding PEG mono methyl ethers in three steps (see Figure 4.3). Synthesis of the PEG tosylates from the alcohol using the procedure previously reported by Keegstra et al.[23] proved facile and gave products **5-8** in high yield (88-91%) without the need for purification. Initial attempts to form the PEG thioacetates **9-12** directly, by refluxing the tosylates in dry MeOH[24] in the presence of KSAc, did not produce the desired products. After the solvent was changed to dry DMF,[25] however, the PEG thioacetates **9-12** could be isolated in moderate yield (32-40%). Subsequent acid hydrolysis of the thioesters using 10% aq HCl/MeOH furnished the target PEG thiols **13-16** in high yield (81-96%). Note that the low polydispersity of the original PEG was preserved in the products. For compounds **14** and **15**, for example, the average PEG oligomer values of 7 ± 1 and 16 ± 4, respectively, are also reflected in the mass spectra of the subsequent silicone product following the thiol-ene process (see below): high resolution mass spectra confirm the structure of the compound with **7** or **16** PEG units, respectively (See 9.2, Appendix II for compounds **22**, **28** and **31**), and low resolution mass spectra of both the PEG-thiol and thioether product show the same distributions of oligomers, separated by 44 mass units.

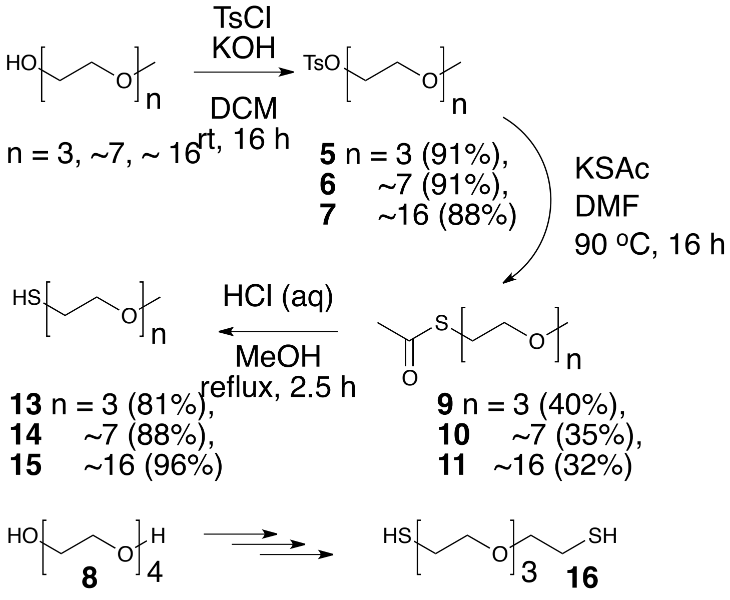


Figure 4.3 Synthesis of PEG thiols

Initial coupling reactions between discrete vinyl-functional siloxanes and alkyl thiols, such as undecanethiol and thioglycerol, under aerobic conditions based on the methodology reported by Campos et al.,[26] gave the desired products within 30 min under UV irradiation (data not shown). This was not surprising, as, the literature indicates that the thiol-ene reaction should not be significantly hindered by the presence of oxygen.[27] However, thiol-ene reactions with silicones are, apparently, not as pliable.[28] Survey experiments with a commercially available α,ω- divinyl PDMS **17** failed to lead to any products in the presence of oxygen after 2 h irradiation but, after degassing and reirradiation, the desired ABA block copolymers **18-20** formed in high yield (66-79%) within 1 h as shown by NMR (Figure 4.4): single regioisomers were observed. The stoichiometry used for this reaction was a 1.5:1 ratio of thiol to vinyl group to ensure complete conversion of the PEG-thiol, except for high molecular weight materials where a 1:1 ratio was used to eliminate the need to separate the polar unreacted PEG from the synthesized amphiphiles. When an excess of the PEG thiol was used (1.5 equiv thiol per vinyl group), the resulting products were difficult to separate from the excess starting material, especially when the larger PEG compounds were used (Figure 4.4).

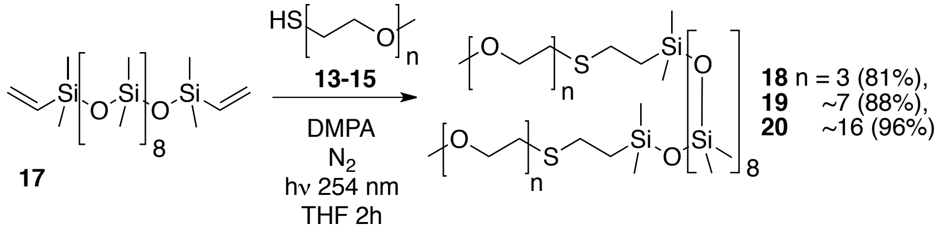


Figure 4.4 Thiol-ene coupling of PEG thiols with divinyl PDMS

Analogous reaction conditions were used to convert vinyl-functional silicones **1**-**3** into surface active silicones **21-29** using **3** PEG thiols **13-15** (Table 4.1, Figure 4.5). It was also possible to prepare the star-shaped silicones **30** and **31** from **4** and the bola-amphiphile **32** from tetraethyleneglycol dithiol **16** (Figure 4.5). The explicit silicone fragments were incorporated into the products unaltered, without the competing metathesis that accompanies acid or basic conditions. The formation of both the PEG-thiols and thioether reactions were in lower than expected yields for such reactions. This is a consequence of our desire to have absolutely pure materials, which will permit an understanding of structure/surface activity relationships. Several columns were required in the former case, and use of narrow distillation cuts in the latter case favored purity over yield of these polar molecules.

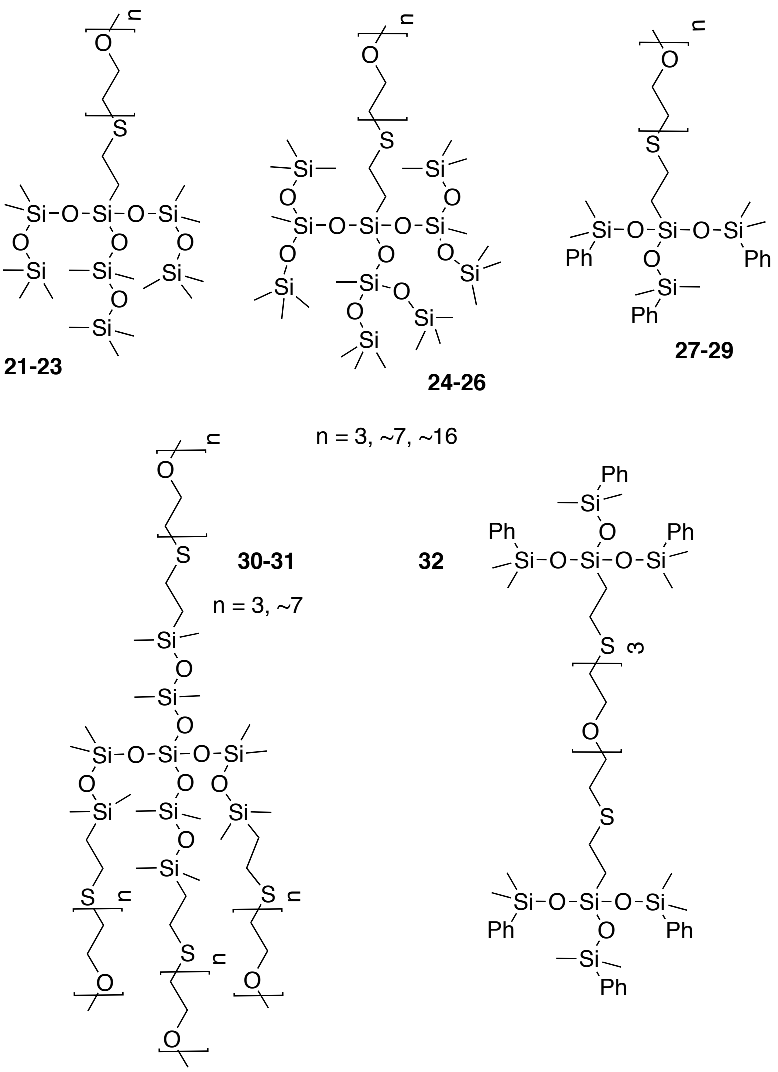
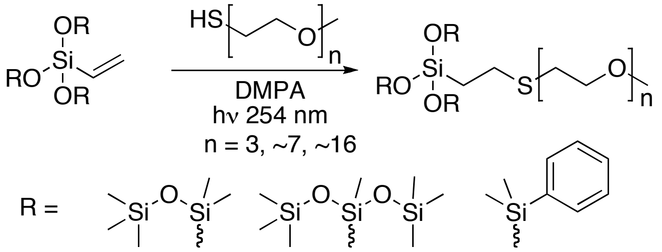
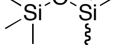
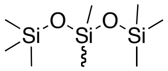
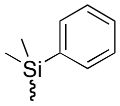


Figure 4.5 Explicit PEG-Silicone Surfactants

Low concentrations of $B(C_6F_5)_3$ facilitate the condensation of alkoxy- and hydridosilanes to give siloxane bonds under conditions that do not initiate the metathesis of the silicone: explicit structures can be prepared and isolated. Silicone compounds, with various 3D profiles- including linear, branched, or star- are thus readily available from simple starting materials. The elaboration of these compounds into hydrophilically modified materials can also be performed without degrading the silicone structures by the regioselective, photoinduced thiol-ene click reaction of thiol-terminated PEG oligomers of various molecular weights; we have described explicit structures, with different three dimensional profiles, of molecular weights ranging from about 1200 to about 3300 g mol^{-1}. Preliminary studies demonstrate that the products, particularly as the relative PEG fraction increases, are both soluble and stable in water. Such compounds are expected to have precise and predictable surface properties that depend upon their 3D structure and the ratio of hydrophilic to hydrophobic moieties, which will be the subject of future reports.

Table 4.1 Silicone-PEG Compounds



Starting silicone	R (Scheme above)	PEG-thiol (n)	product	yield (%)[a]
1		**13 (3)**	**21**	71
		14 (~7)	**22**	78
		15 (~16)	**23**	81
2		**13 (3)**	**24**	91
		14 (~7)	**25**	87
		15 (~16)	**26**	82
3		**13 (3)**	**27**	95
		14 (~7)	**28**	89
		15 (~16)	**29**	84
4	Figure 2	**13 (3)**	**30**	**82**
		14 (~7)	**31**	**72**
3		[b]	**32**	**89**

[a] Isolated yield. [b] tetraethyleneglycol dithiol *

4.3 Acknowledgments

We thank the Australian Research Council (grant DP0877988) and the Natural Sciences and Engineering Research Council of Canada for financial support.

4.4 Supporting Information

Experimental protocols, ^{1}H and ^{13}C NMR, HRMS data for compounds **21-32**, and LRMS for **22**, **28**, and **31**. This material is available in 9.2, Appendix II of this document.

4.5 References

1. R. Wagner, Y. Wu, G. Czichocki, H. Berlepsch, F. Rexin and L. Perepelittchenko, *Appl. Organomet. Chem.,* 1999, **13**, 201–208.
2. R. Wagner, Y. Wu, G. Czichocki, H. Berlepsch, B. Weiland, F. Rexin and L. Perepelittchenko, *Appl. Organomet. Chem,*, 1999, **13**, 611–620.
3. V. Hamciuc, L. Pricop, D.S. Pricop and M. Marcu, *J. Macromol. Sci. Pure Appl. Chem.*, 2001, **A38**, 79–89.
4. R.M. Hill, *Curr. Opin. Colloid Interface Sci.*, 2002, **7**, 255–261.
5. L. Pricop, V. Hamciuc, M. Marcu, A. Ioanid and S. Alazaroaie, *High Perform. Polym.*, 2005, **17**, 303–312.
6. M. Srividhya, K. Chandrasekar, G. Baskar and B.S.R Reddy, *Polymer,* 2007, **48**, 1261–1268.
7. R.M Hill in *Siloxane Surfactants. In Silicone Surfactants*, Ed. Marcel Dekker, Inc.: New York, 1999; p 360.
8. J. Chojnowski, M. Scibiorek, and J. Kowalski, *Makromol. Chem.*, 1977, **178**, 1351–66.
9. J. Chojnowski, and L. Wilczek, *Makromol. Chem.*, 1979, **180**, 117– 30.
10. P. Sigwalt, *Polym. J.*, 1987, **19**, 567–580.
11. L. Wilczek, S. Rubinsztajn and J. Chojnowski, *Makromol. Chem.*, 1986, **187**, 39–51.
12. R.M Hill in *Silicone Surfactants*; Dekker: New York, 1999.
13. J. Chojnowski, Polymerization. In *Siloxane Polymers*; Clarson, S. J., Semlyen, J. A., Eds.; Prentice Hall: Englewood Cliffs, NJ, 1993; pp 1-71.
14. D.B. Thompson, and M.A. Brook, *J. Am. Chem. Soc.*, 2008, **130**, 32–33.
15. J.B. Grande, D.B. Thompson, F. Gonzaga, M.A Brook, *Chem. Commun.,* 2010, **46**, 4988–4990.
16. M.A Brook, J.B Grande and F. Ganachaud, *Adv. Polym. Sci.*, 2010, **235**, 161–183.

17. M.A Brook in *Silicones. In Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 2000; pp 256-308.

18. F. Gonzaga, G. Yu and M.A Brook, *Chem. Commun.*, 2009, 1730– 1732.

19. K.L. Killops, L.M. Campos and C.J. Hawker, *J. Am. Chem. Soc.*, 2008, **130**, 5062–5064.

20. H.C. Kolb, M.G. Finn and K.B Sharpless, *Angew. Chem., Int. Ed.*, 2001, **40**, 2004–2021.

21. M. J. Kade, D. J. Burke and C. J. Hawker, *J. Polym. Sci. A, Polym. Chem.*, 2010, **48**, 743–750.

22. L. M. Campos, T. T. Truong, D. E Shim, M. D. Dimitriou, D. Shir, I. Meinel, J. A. Gerbec, H. T. Hahn, J. A. Rogers and C. J. Hawker, *Chem. Mater.*, 2009, **21**, 5319–5326.

23. E. M. D. Keegstra, J. W. Zwikker, M. R. Roest and L. W Jenneskens, *J. Org. Chem.*, 1992, **57**, 6678–80.

24. J. W. Bae, E. Lee, K. M. Park and K. D Park, *Macromolecules,* 2009, **42**, 3437–3442.

25. I. I. Cubero, M. T. P. Lopez-Espinosa and A. S. de Buruaga Molina, *Carbohydr. Res.,* 1996, **280**, 145–50.

26. L. M. Campos, K. L. Killops, R. Sakai, J. M.J. Paulusse, D. Damiron, E. Drockenmuller, B. W. Messmore, and C. J Hawker, *Macromolecules,* 2008, **41**, 7063–7070.

27. C. E. Hoyle, T. Y. Lee and T. Roper, *J. Polym. Sci. A, Polym. Chem.*, 2004, **42**, 5301–5338.

28. U. Mueller, A. Kunze, C. Herzig and J. Weis, *J. Macromol. Sci. Pure Appl. Chem.,* 1996, **A33**, 439–57.

Chapter 5: Silicone Dendrons and Dendrimers Using Orthogonal SiH Coupling Reactions[‡‡]

5.1 Abstract

Few syntheses of organosilicone dendrimers have been reported, in part, because the conditions used for synthesis also facilitate silicone degradation by acid- or base-catalyzed monomer metathesis. The Piers-Rubinsztajn reaction involving condensation of hydro- and alkoxysilanes catalyzed by $B(C_6F_5)_3$ permits the synthesis of highly branched structures, but without concomitant metathesis. This approach has been used to create dendrimers. A combination of divergent and convergent synthesis was used to create organofuntional silicone dendrons. These were combined to create dendrimers of molecular weight in excess of 10000 g/mol.

[‡‡] To be submitted to Angewandte Chemie. J. B. Grande, T. Urlich, T. Dickie and M. A. Brook, (2013). Grande was responsible for the synthesis and experimental writeup of all compounds in this chapter. Grande was also responsible for manuscript writing, with the editing done by Brook. Urlich and Dickie were responsible for helping with sample preparation, synthesis and experimental write-up.

5.2 Introduction

The benefits of well-structured dendrimeric structures arising from both convergent[1] and divergent syntheses are now well recognized.[2-6] PAMAMs, arguably the best explored materials because of their commercial availability, show particular utility for the delivery of bioactive compounds, small molecule drugs and for in vitro gene transfection.[7, 8] However, many other dendrimeric systems have been developed, targeted to a broad variety of applications, that utilize a very broad variety of chemistries.[9] A key requirement for any dendrimer synthesis is virtually perfect conversion during bond formation as each generation is added.[10, 11] An additional requirement is that the iterative reaction conditions leading to higher molecular weight (MW) materials must not affect the structure of the lower generation starting materials. It is the latter requirement, among others, that has challenged the development of silicone and carbosiloxane dendrimers.

Silicones are formed and readily degrade under both acidic and basic conditions.[12] Two beautiful, perhaps heroic, accounts of dendrimeric silicone synthesis have been reported. Although each provides elegant methods leading to larger molecular weight silicones, they suffer from some inherent drawbacks. For example, Masamune and co-workers in the early 1990's reported a simple three step process to prepare large molecular weight silicone dendrimers of calculated MW of up to 15073.[13] The assembly (partly shown in Figure 5.1 using D_4 for simplicity) hinges on the use of chlorosilanes, which are subject to facile hydrolysis through the presence of adventitious water. Thus, in addition to the introduction of defects, HCl is produced as a byproduct. The other key reaction uses an amine catalyst. Silicones are susceptible to degradation/redistribution in the presence of both acids and bases,[14] which of course can be detrimental to the prepared silicone architecture. The process, therefore, is not general.

Muzafarov and co-workers created one of the most dense dendrimer structures reported by taking advantage of sodiumoxyorganoalkoxysilanes.[15, 16] The main drawback associated with this strategy is the presence of basic moieties in the monomer and chlorosilane end groups in the evolving dendrimer, both of which are sensitive to water potentially leading to pH changes.[16]

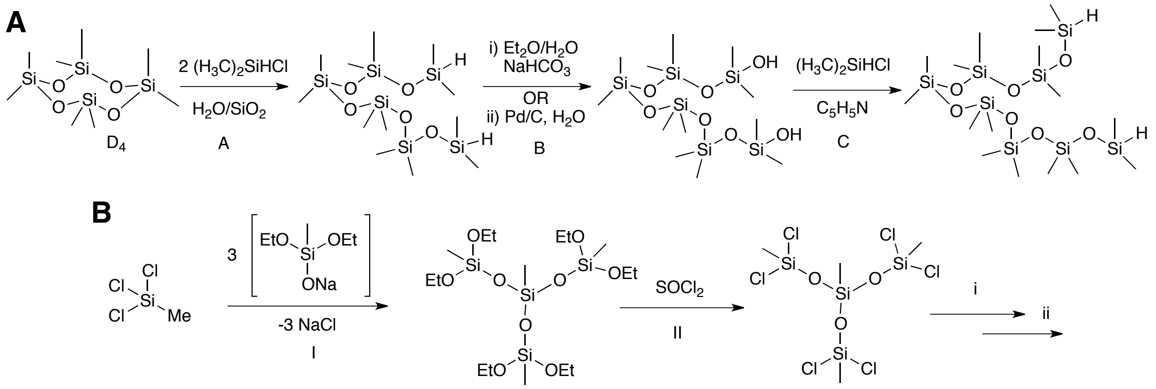


Figure 5.1 A: A three step process to prepare large MW dendrimers involving: i) ring opening hydrolysis; ii) conversion of Si-H to Si-OH using mild basic conditions on Pd/C; and, iii) coupling to chlorosilanes. B: the use of sodiumoxyorganoalkoxysilanes in the preparation of large MW dendrimers.

More recently, reports from the group of Kuroda have begun to provide routes to silicones of well-defined molecular architecture. In a first report, $BiCl_3$ has been shown to construct explicit alkoxysiloxane oligomers with relative ease, avoiding the formation of intermediate silanol groups[17] [18] (Figure 5.2A). In a second report, the use of a two-step silylation process is discussed [19, 20] (Figure 5.2B). Although these methods were initially shown to prepare smaller molecular weight materials, they begin to provide both new and facile methods to prepare well-defined siloxane based macrostructures of precise molecular architecture. However, they continue to be challenged by the low hydrolytic stability of chlorosilanes.

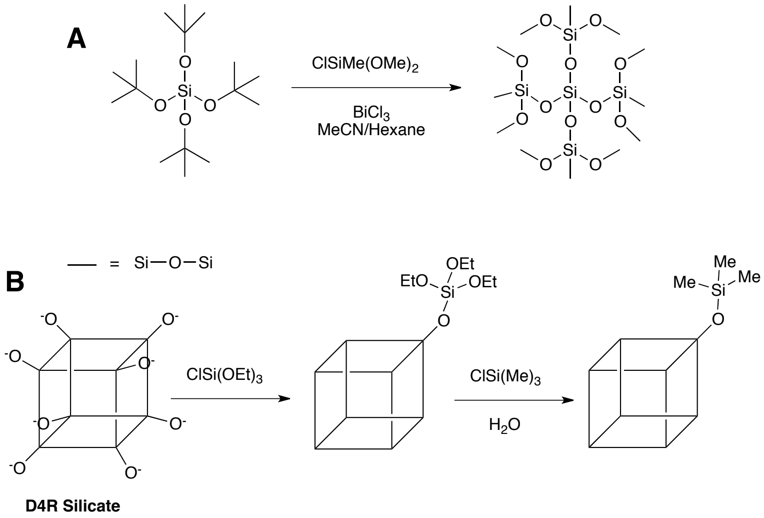


Figure 5.2. A. $BiCl_3$ can be used to prepare well-defined oligomers B. A two step silylation process to prepare well defined crystalline siloxane

The Piers-Rubinsztajn reaction allows the assembly of small, precise silicone structures,[21] including organofunctional silicones that possess vinyl or allyl groups[22,23] (Figure 5.3A,B). The conditions of the reaction do not lead to metathesis and, therefore, fulfill one of the key requirements for dendrimers synthesis. Controlled synthesis needs at least one additional reaction type, to allow iterative growth procedures that do not lead to ill-defined hyperbranched polymers. We chose to use platinum-catalyzed hydrosilylation, a highly efficient process (typically >98% yield). The only disadvantage of the reaction, in addition to the cost of the catalyst, is that the reaction is not completely regiospecific (Figure 5.3C).

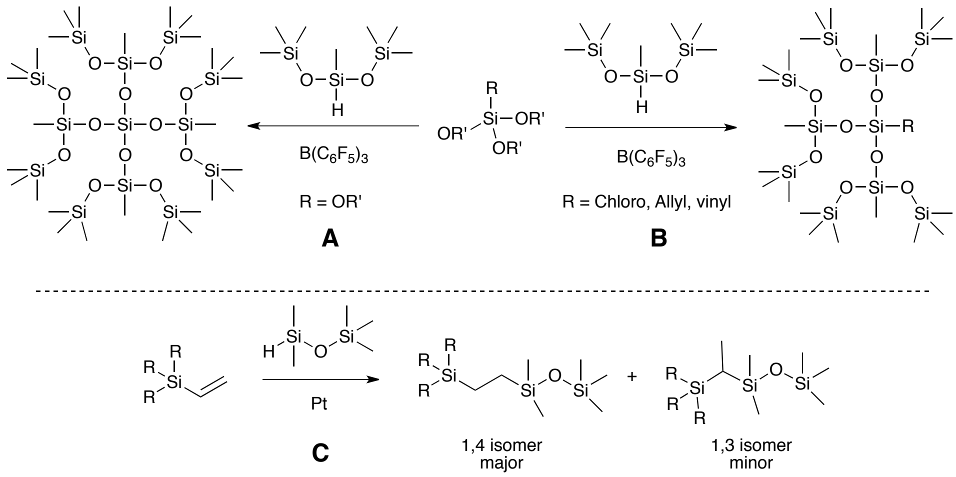


Figure 5.3. Using the Piers-Rubinsztajn reaction to prepare: A: non functional; and, B: functional silicone based compounds. C: platinum-catalyzed hydrosilylation can lead to the formation of both 1,4- and 1,3-isomers.

5.3 Results and Discussion

Prior to initiating dendrimer synthesis, it was necessary to ensure that the two reactions involving iterative conversion of alkoxysilanes to hydrosilanes using Piers-Rubinsztajn (PR), and hydrosilanes to vinylsilanes using hydrosilylation, were truly orthogonal. The key monomer used in this process was vinyltetramethyldisiloxane **1**. Compound **1** readily undergoes self-condensation by platinum-catalyzed hydrosilylation (Figure 5.4). $B(C_6F_5)_3$ can also induce hydrosilylation, but only at higher catalyst concentrations (> 5% mol).[24] No evidence of self-condensation of **1** in our hands was observed if $B(C_6F_5)_3$ concentrations were kept below ~1 % mol (Figure 5.4).

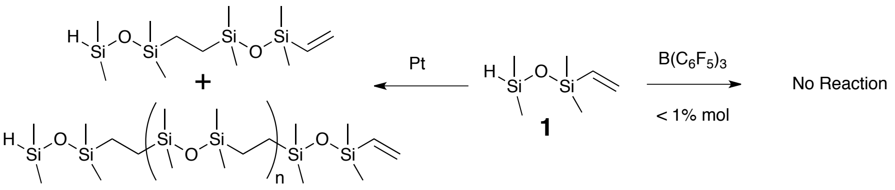


Figure 5.4. Hydrosilylation of **1** in the presence of platinum proceeds readily. In the presence of < 1% mol $B(C_6F_5)_3$ hydrosilylation is not observed.

Model studies, to demonstrate that the iterative sequence of PR/hydrosilylation was efficient, started with **1** and $Si(OEt)_4$: subsequent elaboration of the tetravinyl product **2**[25] with a series of hydrosilanes **3-5** led cleanly in isolated yields of 65-70% to a variety of star shaped silicones of molecular weights from about 1200-1600 g/mol (**6-8**, Figure 5.5A). In order to ensure the process could also be completed in the reverse order (i.e., hydrosilylation first, followed by the PR), H-$Si(OEt)_3$ was hydrosilylated with commercially available vinyltris(trimethylsiloxy)silane yielding **9**, followed by the direct tethering of **5** using the Piers-Rubinsztajn conditions, readily allowing for the clean synthesis of **10**.

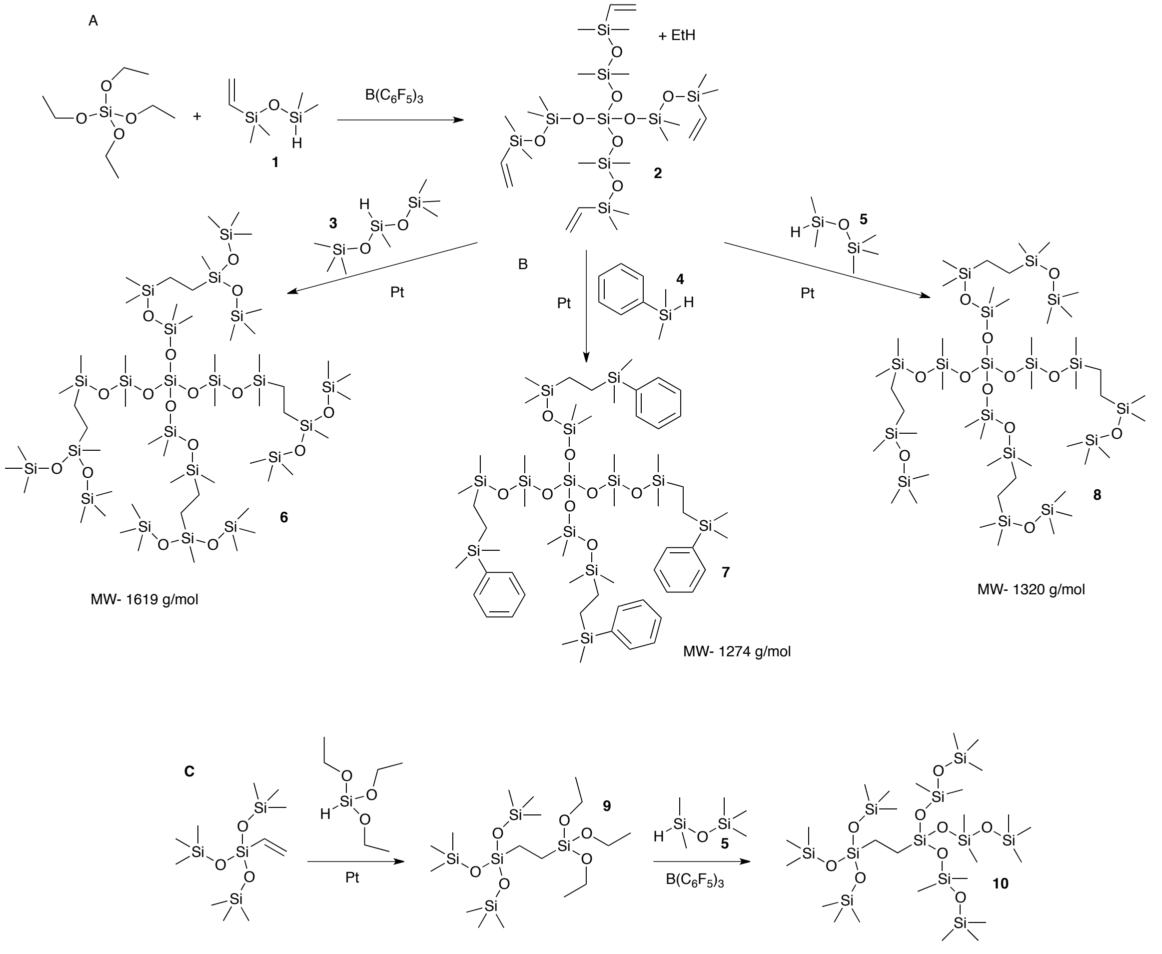


Figure 5.5. A. Preparation of tetrakis(vinyltetramethyldisiloxy)silane **2** B. hydrosilylation using 1,1,1,3,5,5,5-heptamethyltrisiloxane **3** C. phenyldimethylsilane **4** and D. pentamethyldisiloxane **5**. C: Iterative hydrosilylation then the PR reaction to give **10**.

Having demonstrated the Piers-Rubinsztajn and hydrosilylation were orthogonal, attention was turned to the synthesis of dendrimers and dendrons. Compound **2** was subjected first to hydrosilylation with triethoxysilane (H-Si(OEt)$_3$) to generate **11** and then to the Piers-Rubinsztajn with **1** yielding **12**, bearing twelve vinyl groups (Figure 5.6). It should be noted that the major isomer formed via hydrosilylation is the 1,4-product, however, the 1,3-isomer also formed in relatively small yields (~10-15%) as shown by ^{1}H NMR: the reaction mixture otherwise showed the absence of other products (Figure 5.6). The MALDI mass spectrum indicate the presence of single compound exhibiting $[M+Na]^+$ and $[M+CH_2CN+Na]^+$ peaks at 2,972.956 and 3,012.888 g/mol, respectively. There were no other peaks, for example, indicating dimers, other oligomers or dendrimers with defects. The GPC exhibited a small shoulder on the high molecular weight side of the curve that constitutes approx. ~10 % of the desired peak. We ascribe this to compounds in the mixture containing a higher than average portion of the 1,3-isomers.

G1 dendrimers of MW 4500-5600 could be prepared using this process, for example, capping **12** with hydrosilanes **3** (Figure 5.6, **13**) and **4**, **5** (Figure 5.7, to give **14**, **15**)(9.4-Appendix III), respectively. Efforts to expand this process to larger generation dendrimers by forming G2-type dendrimers, bearing 36 vinyl groups **16**, have been hampered by lower than expected yields. We ascribe this to the sensitivity of alkoxygroups to traces of moisture.

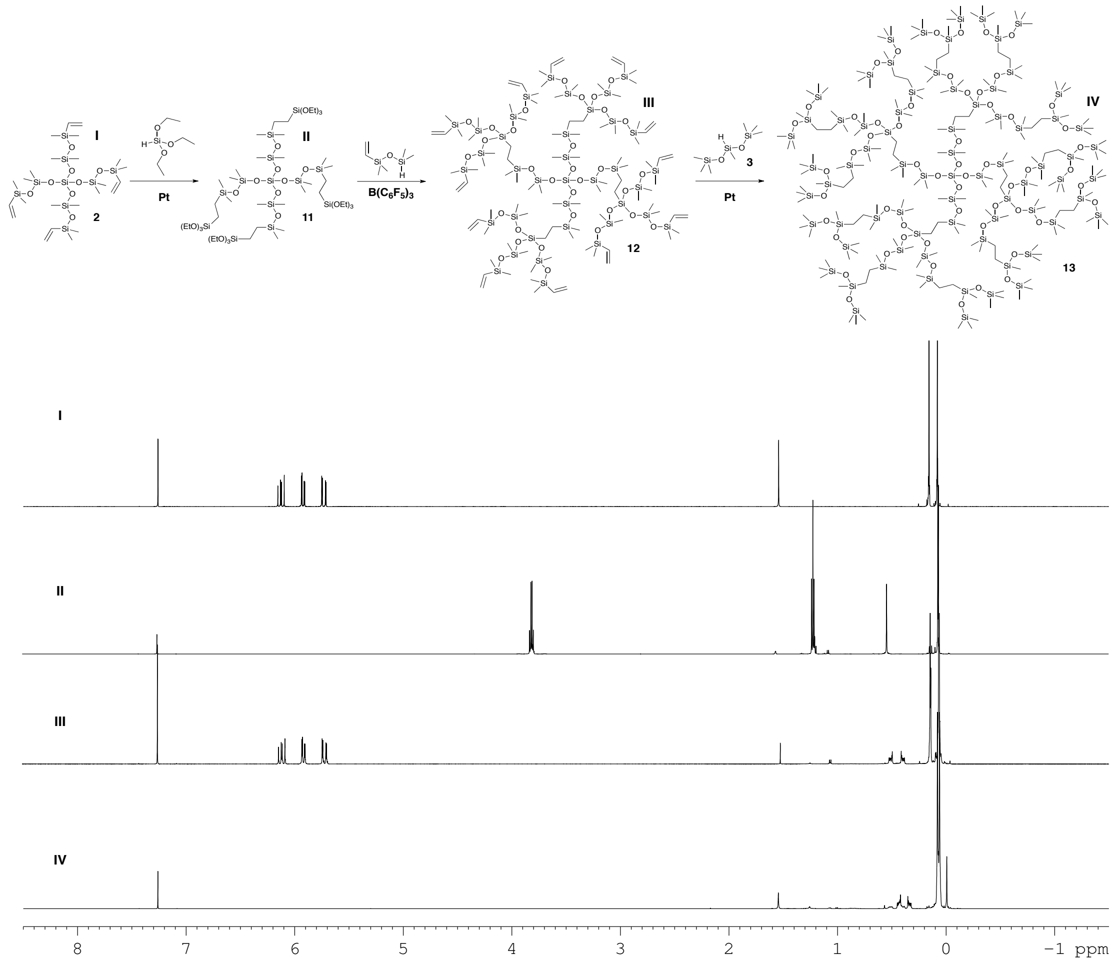
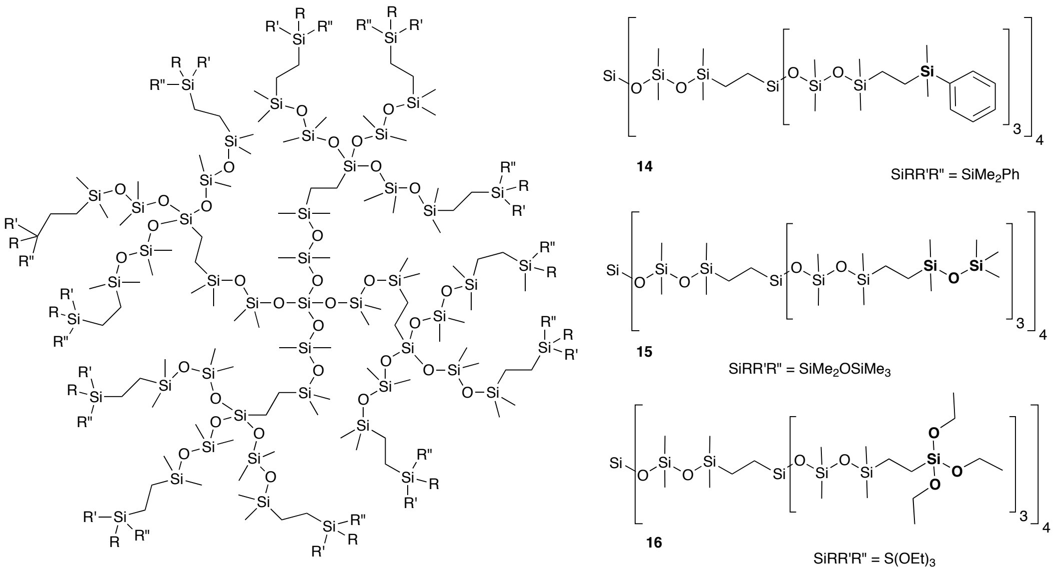


Figure 5.6. NMR of compounds containing four vinyl groups **2** (I), **11** containing twelve ethoxy groups (II), and **12** containing twelve vinyl groups (III). End capping **12** leads with **3** leads to **13** with MW of 5620 g/mol (IV).



14 SiRR'R" = $SiMe_2Ph$

15 SiRR'R" = $SiMe_2OSiMe_3$

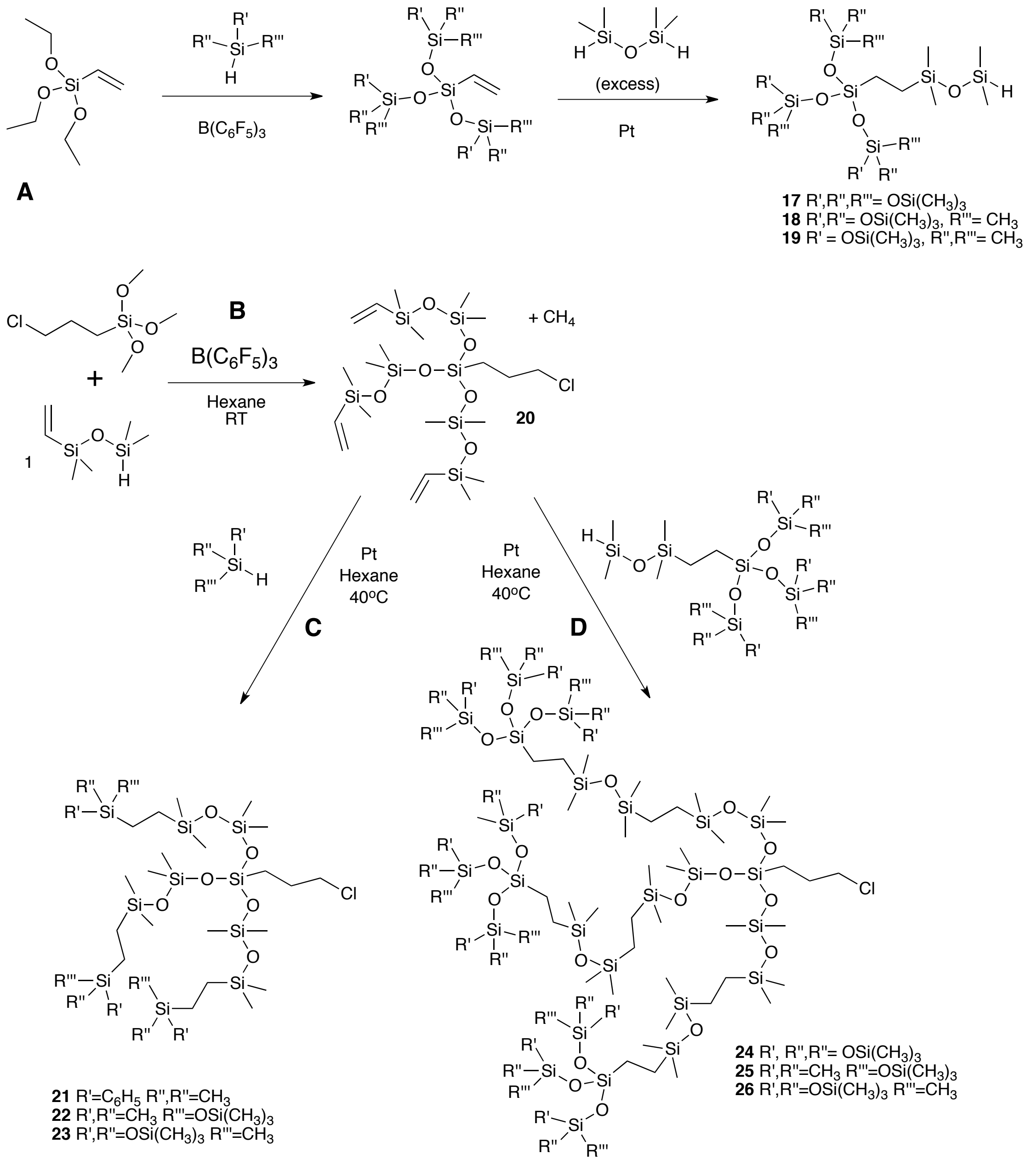
16 SiRR'R" = $S(OEt)_3$

Figure 5.7. End capping **12** with **4** and **5** can lead to precise silicones with MW ranging from 4500-5600 g/mol.

5.4 Combining Convergent and Divergent Processes: Functional Dendrons

In order to prepare larger molecular weight and functional silicone macrostructures, a convergent method for silicone dendrons was developed. The resulting silicone dendrons were designed to be monofunctional for use in larger dendrimers or other syntheses. Examples of monohydridocompounds, **17**, **18** and **19**, prepared in two steps, are shown in Figure 5.8A. Well-defined monovinyl functional silicones were firstly prepared via Piers-Rubinsztajn conditions starting from vinyltriethoxysilane [23] and then subsequently modified with hydrosilylation and a large excess of tetramethyldisiloxane (~ 30 eq of Si-H to vinyl): the compounds were isolated by distillation.

Dendrons bearing organic groups were also readily available. For example, the reaction of vinyltetramethyldisiloxane **1** with chloropropyltrimethoxysilane in the presence of $B(C_6F_5)_3$ gave chloropropyltris(vinyltetramethyldisiloxy)silane **20** in excellent yield (> 90%) after distillation under vacuum (~1 mmHg, 162 degrees centigrade, Figure 5.8B). Similar methods to those described above can be used to prepare even larger dendrons. The use of alternative commercially available starting materials **3-5** led to functional dendrons **21**, **22** and **23** (Figure 5.8C). The size of these compounds could be magnified by addition of the complex monofunctional Si-H containing dendrons **17**, **18** and **19** (Figure 5.8D). Thus, **24**, **25** and **26** can be prepared in two simple steps, with molecular weights ranging from 2000 to 3350 g/mol with various styles of branching and with available chloro groups available for subsequent reactions, such as in azide [3+2] cycloaddition[23].



17 R',R'',R'''= $OSi(CH_3)_3$
18 R',R''= $OSi(CH_3)_3$, R'''= CH_3
19 R' = $OSi(CH_3)_3$, R'',R'''= CH_3

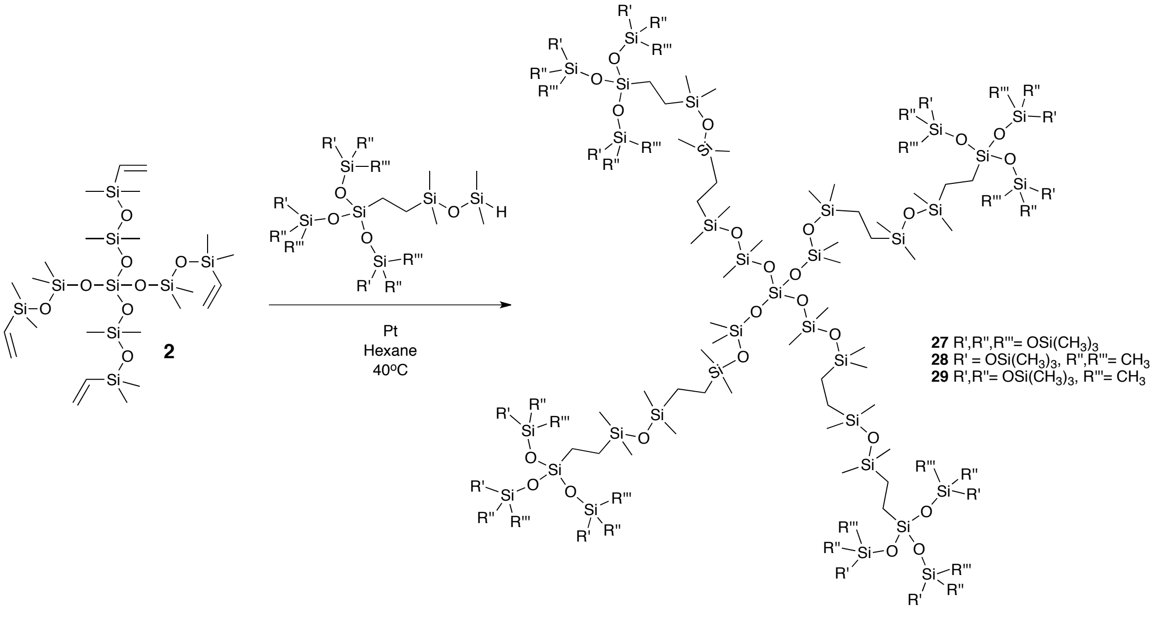
21 R'=C_6H_5 R'',R''=CH_3
22 R',R''=CH_3 R'''=$OSi(CH_3)_3$
23 R',R''=$OSi(CH_3)_3$ R'''=CH_3

24 R', R'',R''= $OSi(CH_3)_3$
25 R',R''=CH_3 R'''=$OSi(CH_3)_3$
26 R',R''=$OSi(CH_3)_3$ R'''=CH_3

Figure 5.8. Synthesis of A: monohydride dendrons and B-D: chloropropyl-functional dendrons

5.5 Dendrimers

Through the combination of both a divergent and convergent approach, the synthesis of carbosiloxane macrostructures with a large range of molecular weights can be realized. G1-type carbosiloxane dendrimers result from the simple combination of smaller, siloxane based cores, such as **2** with mono Si-H compounds **17**, **18** and **19** to give moderately sized siloxane macrostructures **27**, **28** and **29**.



27 R',R",R'''= $OSi(CH_3)_3$
28 R' = $OSi(CH_3)_3$, R",R'''= CH_3
29 R',R"= $OSi(CH_3)_3$, R'''= CH_3

Figure 5.9: By simply tethering prepared dendrons to tetravinyl core **2**, moderately sized carbosiloxane G1 type dendrimers **27, 28** and **29** can be prepared in few steps.

Larger dendrimers are similarly available. For example, by simply combining **12** with dendron **18**, a G2-like dendrimer, **30,** with a molecular weight of 13,773 g/mol exhibiting a PDI of 1.08 (Figure 5.10B) can be readily prepared. Likewise, compound **19** can also be combined with **12** to yield monodisperse macrostructures of molecular weights greater than 10,000 g/mol.

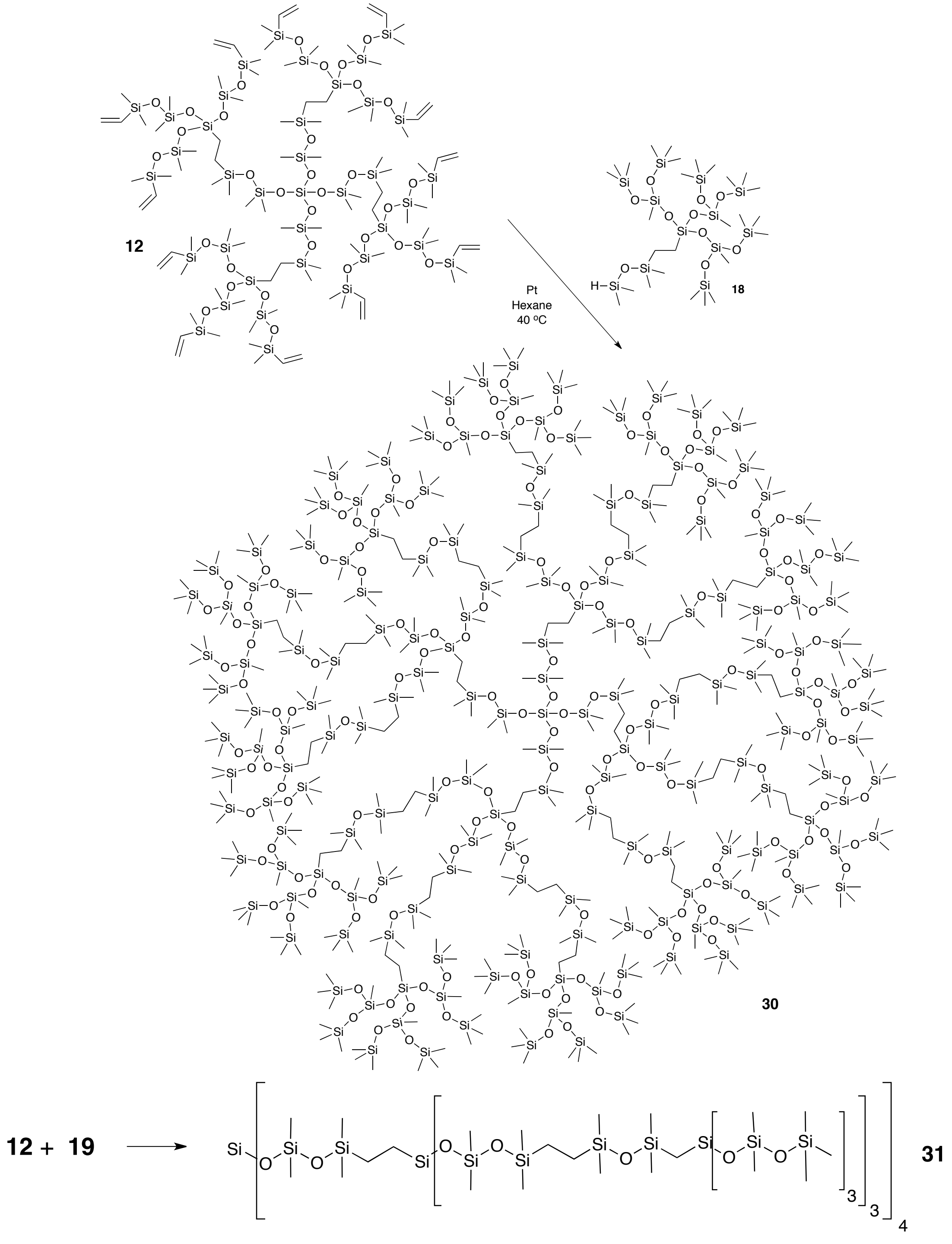


Figure 5.10. Tethering mono functional Si-H dendron **18** to **12** through hydrosilylation yields **30,** with a MW of 13,773. Likewise **12** can be coupled to **19** in a similar fashion yielding **31** with a MW of 11,103.

The combination of Piers-Rubinsztajn coupling and platinum-catalyzed hydrosilylation provides a simple and efficient strategy to assemble carbosiloxane macrostructures. The alternation of these two processes can be applied in both divergent and convergent strategies: dendrimers as large as 13,773 MW can be readily prepared in few steps. The functional tolerance of the Piers-Rubinsztajn reaction permits the synthesis of mono- and multi-functional silicones, which allows the ready preparation of large molecules with precise structures, which can be combined with other classes of small molecules and polymers.

5.6 Acknowledgements

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada. J.B. Grande is grateful for a NSERC PGS-D scholarship.

5.7 References

1. C. J. Hawker and J. M. J. Frechet, *J. Am. Chem. Soc.*, 1990, **112**, 7638-7647.
2. E. Buhleier, W. Wehner and F. Vogtle, *Synthesis-Stuttgart*, 1978, 155-158.
3. R. G. Denkewalter, J. Kolc and W. J. Lukasavage in Macromolecular highly branched homogeneous compound. Allied Corporation, 1983.
4. R. G. Denkewalter, W. J. Lukasavage and J. Kolc in Macromolecular highly branched homogeneous compound based on lysine units. US 4289872A, 1981.
5. J. R. Dewald and D. A. Tomalia in Dense star polymers having core, core branches, terminal groups. The Dow Chemical Corporation, US 4507466A, 1985.
6. G. R. Newkome, Z. Q. Yao, G. R. Baker and V. K. Gupta, *J. Org. Chem.,* 1985, **50**, 2003-2004.
7. A. Paul, W. Shao, S. Abbasi, D. Shum-Tim and S. Prakash, *Molecular Pharmaceutics*, 2012, **9**, 2479-2488.
8. J. M. Oliveira, A. J. Salgado, N. Sousa, J. F. Mano and R. L. Reis, *Prog. Polym. Sci.*, 2010, **35**, 1163-1194.
9. N. N. Ma, C. Ma, Y. Deng, T. Wang and N. Y. He, *J. Nanosci. Nanotechnol.*, 2013, **13**, 33-39.
10. F. Vogtle, S. Gestermann, R. Hesse, H. Schwierz and B. Windisch, *Prog Polym Sci*, 2000, **25**, 987-1041.
11. J. P. Majoral and A. M. Caminade, *Chem. Rev.*, 1999, **99**, 845-880.
12. M. A. Brook, *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000.
13. H. Uchida, Y. Kabe, K. Yoshino, A. Kawamata, T. Tsumuraya and S. Masamune, *J. Am. Chem. Soc.*, 1990, **112**, 7077-7079.
14. M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000, pp. 256-308.
15. E. A. M. Rebrov, A.M.; Papkov, V.S.; Zhandanov, A.A, *Dokl. Akad. Nauk SSSR*, 1989, **309**, 376-380
16. A. M. Muzafarov and E. A. Rebrov, *J. Polym. Sci. Pol. Chem.*, 2008, **46**, 4935-4948.

17. R. Wakabayashi, M. Tamai, K. Kawahara, H. Tachibana, Y. Imamura, H. Nakai and K. Kuroda, *J. Organomet. Chem.*, 2012, **716**, 26-31.
18. R. Wakabayashi, K. Kawahara and K. Kuroda, *Angew. Chem. Int. Ed.*, 2010, **49**, 5273-5277.
19. K. Kawahara, Y. Hagiwara, A. Shimojima and K. Kuroda, *J. Mater. Chem.*, 2008, **18**, 3193-3195.
20. K. Kawahara, Y. Hagiwara and K. Kuroda, *Chem. Eur. J.*, 2011, **17**, 13188-13196.
21. D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.*, 2008, **130**, 32-33.
22. J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, *Chem. Commun.*, 2010, **46**, 4988-4990.
23. J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Trans.*, 2010, **39**, 9369-9378.
24. M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem*, 2002, **67**, 1936-1940.
25. D. J. Keddie, J. B. Grande, F. Gonzaga, M. A. Brook and T. R. Dargaville, *Org Lett*, 2011, **13**, 6006-6009.

Chapter 6: Rapid, Metal-Free Room Temperature Vulcanization Produces Silicone Elastomers[§§]

6.1 Abstract

Silicone room temperature vulcanization elastomers are usually formed through either a platinum-catalyzed hydrosilylation or tin-catalyzed moisture cure. In this article, we show that it is possible to create robust, transparent silicone elastomers without the need for metal catalysts. Hydrogen-terminated silicone polymers are crosslinked by tri- or tetraalkoxysilane crosslinkers in a condensation process catalyzed by the presence of trispentafluorophenylborane catalyst to give elastomers and alkane by-products. This procedure allows for very fast cure times (< 30 s to a tack free state): the process is more conveniently controlled with the addition of a small amount of solvent. Physical and mechanical properties are readily modified by control of the chain length of the starting polymer, the functionality and nature of the alkoxy group on the crosslinker.

[§§] Reproduced with kind permission from John Wiley and Sons. A. S. Fawcett, J. B. Grande and M. A. Brook, *Journal of Polymer Science, Part A: Polymer Chemistry*, 2013, **51** (3), 644-652. Contributions: Grande and Fawcett contributed equally in optimizing, and designing all experimentation throughout this chapter, along with all characterization. Fawcett was lead in the writing of this manuscript and Grande assisted in writing the manuscript.

Organofunctional groups, useful for further polymer modification, can optionally be incorporated by judicious choice of readily available starting materials.

6.2 Introduction

Silicone elastomers are widely used in many applications ranging from biomaterials[1–3] to coatings and sealants, and so forth.[4–6] Although there are several methods available for their synthesis,[5,7,8] the most common of these are high-temperature radical cure, room-temperature vulcanization using either tin- or titanium-derived hydrolysis/condensation catalysts, or platinum-catalyzed hydrosilylation.[9] Each of these processes has its own disadvantages: for example, it can be difficult to control high-temperature curing to give reproducible networks. Although exquisite control over network structure is possible using metal-catalyzed crosslinking, for reasons of cost (platinum catalyst) or environmental concerns (tin catalysts are currently under scrutiny by regulatory agencies in many parts of the world[10]), there is a desire to avoid metals in room or elevated temperature crosslinking processes.

We have previously described the ability to make complex silicone structures, optionally containing functional groups, using the dehydrocarbonative coupling of alkoxysilanes with hydrosilanes ($R_3SiH + R'OSiR''_3 \rightarrow R_3SiOSiR''_3 + R'H$), a process catalyzed by $B(C_6F_5)_3$ (Figure 6.1A, B).[11–13] Others have also reported the synthesis of siloxane resins[14,15] and polymers[16,17] using this strategy. The reaction offers several advantages in the preparation of small molecules that include: rapid reaction times, simple removal of (gaseous) by-products, lower catalyst concentrations than Sn-based systems and the simplicity with which the 3D structures can be controlled by appropriate use of simple starting materials: complex structures can be prepared that are not available by traditional routes.[13] It seemed likely that this reaction could similarly offer benefits to the preparation of silicone polymers and elastomers (Figure 6.1C). We have therefore examined the ease with which α,ω-hydride-functional silicone polymers can be crosslinked with various alkoxysilanes as a function of molecular weight of the starting polymer, siloxane and catalyst concentrations, alkoxysilane reactivity, and choice of solvent to prepare uniform silicone elastomers.

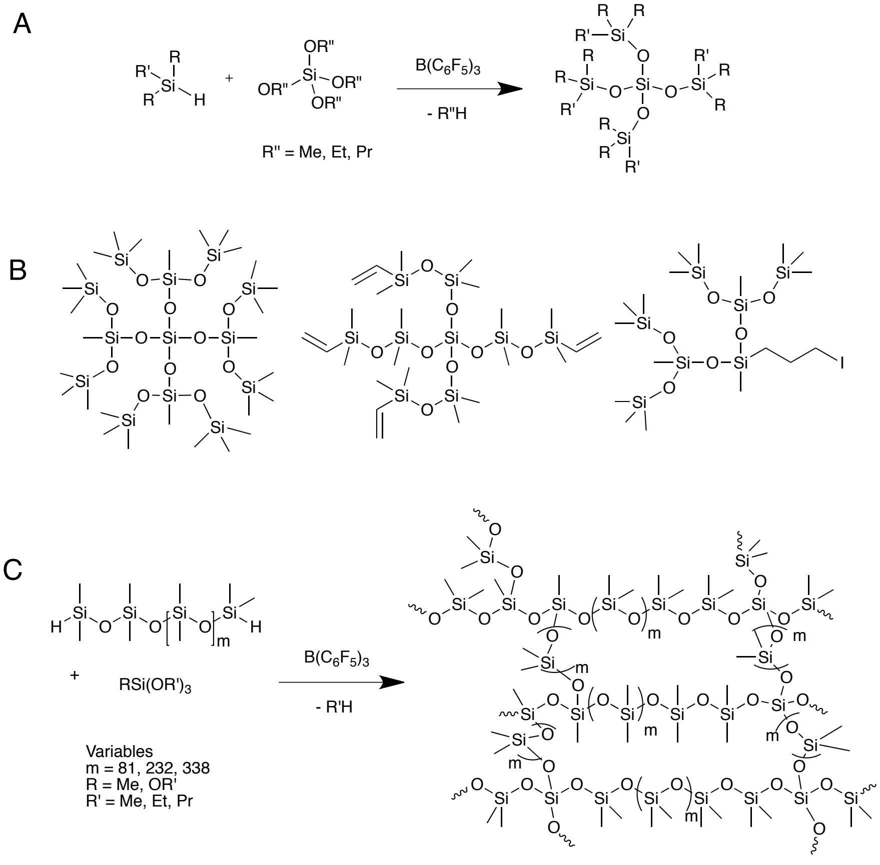


Figure 6.1 A: Reaction scheme depicting the dehydrocarbonative coupling used to synthesize PDMS elastomers. R = Me, OR'; R' = Me, Et, Pr. B: Examples of explicit silicones that can be synthesized using this process. C: Elastomer formation; product shown for R = OR'

6.3 Experimental

Tetraethyl orthosilicate (TEOS), tetrapropyl orthosilicate (TPOS), 1-pyrenemethanol, and tris(pentafluorophenyl)borane were purchased from Sigma-Aldrich and used as received. Methyltriethoxysilane (MTES), tetramethyl orthosilicate (TMOS), vinyltrimethoxysilane (VT), iodopropyltrimethoxysilane (IT), tetravinylsilane (TV), 1,1,3,3-tetramethyldisiloxane, 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane (D4), α,ω-hydride-terminated poly(dimethylsiloxane) (H-PDMS-H) 100, and 1000 centiStokes (cSt, ~ MW 5900 and 28,000, respectively)[18,19] were purchased from Gelest; hexanes, dichloromethane, diethyl ether, tetrahydrofuran, and toluene were purchased from Caledon.

NMR spectra were recorded using a Bruker Avance 500 or AV600 spectrometer. Shore A hardness measurements were made using a Durometer Hardness type “A2” from The Shore Instrument & Mfg. Co., NY. Shore OO experiments were taken using a Rex Durometer, Type OO, Model 1600 from Rex Gauge Co.

6.3.1 Synthesis of 500 cSt PDMS (Poly(dimethylsiloxane), ~16,000 MW)

To a mixture of 1,1,3,3,5,5,7,7-octamethylcyclotetrasiloxane, D4 (50.0 g, 0.158 mol Me_2SiO unit), and 1,1,3,3-tetramethyldisiloxane (0.483 g, 3.59 mmol) was added trifluoromethanesulfonic acid (0.05 mL, 0.085 g, 0.57 mmol) at room temperature. The mixture was then heated at 100 °C for 5 h, cooled to room temperature, and magnesium oxide (~2 g) was added to quench the acid. After 30 min, tetrahydrofuran (200 mL) was added to the mixture. The solution was then filtered and concentrated under reduced pressure. The residue was purified by removal of small molecular weight silicones using Kugelrohr distillation at 180 °C under vacuum (0.1 mmHg) for 5 h yielding a colorless oil (26.5 g, yield 62.8%).

1H NMR ($CDCl_3$, 600 MHz, δ): 4.70 (m, 2 H), 0.18 (d, 12 H), 0.08–0.05 (m, 1296 H).

6.3.2 General Synthesis of PDMS Elastomers

In a typical synthesis (shown for 1000 cSt SiH terminated PDMS with TEOS, 1:1 eq SiOEt:SiH, Table 6.2, Entry 6), TEOS (0.009 g, 0.04 mmol) was placed in a 25.0 mL vial with $B(C_6F_5)_3$ (15 μL of a 0.078 M solution, 239 ppm) and hexanes (2.0 mL). The contents of the vial were added to H-PDMS-H (1000 cSt, 2.50 g, 0.04 mmol SiH groups) that had been preweighed in a beaker, followed by rapid mixing. The contents were then poured into a Teflon-lined Petri dish (10 mm thick x 35 mm diameter) and placed under vacuum (571 Torr) to degas the mixture. The mixture was allowed to cure for 5 min at room temperature (20 °C) at which time the reaction was complete. The dish was then moved to a 50 °C oven overnight to remove any excess solvent.

Table 6.1 and Table 6.2 show the variables that were examined in an effort to correlate reagent types, concentrations, and reaction conditions with the ability to form uniform elastomers. Factors including: solvent volume (Table 6.1); catalyst concentration (a catalyst stock solution, 0.078 M, used to increase catalyst concentration in the elastomers, was prepared by dissolving the catalyst (40 mg, 0.07 mmol) in dry toluene (1 mL)); H-PDMS-H MW; type of crosslinker; molar ratio of crosslinker (SiOR) to SiH functional groups; and the effects of vacuum were examined (Table 6.1 and Table 6.2). The materials appeared to go to complete cure normally within 1–10 min (for example, bubble evolution ceased): hardnesses of the elastomers were measured after 24 h. In some instances, the elastomers required oven cure at 50 °C for 24 h to give a "tack-free" elastomer. An assessment of whether tack was coming from residual solvent or incomplete cure was not made.

6.3.3 A Comparison with Karstedt's Catalyst

A 30 ppm Pt solution was prepared by taking 10 μL of Karstedt's Catalyst (2.5% Pt in xylenes) and diluting in 1 mL of hexanes. A total of 0.33 mL of this stock solution was added to a vial containing $Si(CH=CH_2)_4$ (6.0 mg, 0.04 mmol) and 1.67 mL of hexanes. This solution was then quickly added to the hydrogen-terminated silicone, stirred, and poured into a Petri dish to cure following the protocol above (**29**, Table 6.2). The experiment was repeated at 50 °C to give **30**.

Table 6.1 Solvent Effects on Reaction Time[a]

Exp#	Hexane (mL)	Reaction Time (s)
1	0	20
2	0.1	32
3	0.5	38
4	1.0	43
5	2.0	43

[a] for 5,900 MW silane with TMOS (1:1) with 15μL/236ppm catalyst.

6.3.4 Synthesis of Fluorescent PDMS (Includes 10 mol % 1-Pyrenemethanol.)

1-Pyrenemethanol (0.001 g, 6.0×10^{-6} mol) was dissolved in toluene (0.6 mL) and added to H-PDMS-H (2.5 g, 8.9×10^{-5} mol) in a 20 mL vial. TMOS (0.009 g, 6 x

10^{-5} mol) and catalyst (15 µL, 239 ppm) were combined in a vial with hexane (1.4 mL). The crosslinker/catalyst solution was added to the silane, rapidly mixed, and poured into a Teflon- lined Petri dish and placed under vacuum to cure. After the initial curing reaction, 3 min, the Petri dish was placed into a 50 °C vacuum oven for 3 more days to remove any remaining toluene. A 1.27 cm disk was punched from the elastomer and placed in a cellulose thimble for a Soxhlet extraction, which was performed over 16 h with toluene as solvent. Following extraction and drying, images were taken using a Canon PowerShot SX120 IS camera, with irradiation by 365 nm light.

Table 6.2 Preparation of Silicone Elastomers

Exp #	Silane MW (g)[a]	X-linker (g)[b]	Ratio [SiOR]:[SiH]	Catalyst (µL/ppm)	Hexane (mL)	Rubber (Y/N)	Reaction Time (min:s)[c]	Shore A	Shore OO
6	28000 (2.5)	TE (0.009)	1:1	15/239	2.0	Y	1:42	18	67
7	28000 (2.5)	TE (0.014)	1.5:1	15/238	2.0	Y	2:00	13	63
8	16000 (2.5)	TE (0.024)	1.5:1	12/237	2.0	Y	1:10	21	70
9	5900 (2.5)	TE (0.066)	1.5:1	15/236	2.0	Y	1:20	25	68
10	28000 (2.5)	Me (0.006)	0.5:1	15/239	2.0	Y	4:48	20	78
11	5900 (2.5)	TE (0.022)	0.5:1	15/237	2.0	N[d]	-	-	-
12	16000 (2.5)	TE (0.008)	0.5:1	12/239	2.0	N[d]	-	-	
13	28000 (2.5)	Me (0.011)	1:1	15/238	2.0	Y	4:55	21	67
14	28000 (2.5)	Me (0.016)	1.5:1	15/238	2.0	Y	4:52	18	62
15	28000 (2.5)	Me (0.021)	2:1	15/238	2.0	Y	10:00	10	53
16	16000 (2.5)	TM (0.018)	1.5:1	12/238	2.0	Y	1:52	23	70
17	16000 (2.5)	TM (0.023)	2:1	12/237	2.0	Y	1:55	14	51
18	16000 (2.5)	TP (0.030)	1.5:1	12/237	2.0	Y	1:52	18	63
19	16000 (2.5)	Me (0.027)	1.5:1	12/237	2.0	Y	3:45	18	65
20	5900 (2.5)	VT (0.083)	2:1	15/232	2.0	Y	-	15	68
21	5900 (2.5)	IT (0.163)	2:1	15/225	2.0	Y	-	21	66
22	5900 (2.5)	TM (0.016)	0.5:1	15/238	2.0	N[d]	-	-	-
23	5900 (2.5)	TM (0.016)	0.5:1	9/143	5.0	Y	-	-	11
24	16000 (2.5)	TP (0.041)	2:1	12/236	2.0	Y	1:44	-	15
25	5900 (2.5)	Me (0.075)	1.5:1	15/233	2.0	Y	5:10	30	80
26	5900 (2.5)	TM (0.032)	1:1	15/236	2.0	Y	0:43	22	75
27	5900 (2.5)	TM (0.032)	1:1	1.9/30	0	Y	78:00	22	78
28	28000 (2.5)	TM (0.009)	1.5:1	15/239	2.0[e]	Y		8	60
29	28000 (2.5)	TV[f] (0.006)	1:1	30ppm	2.0	Y	19:08	12	62
30	28000 (2.5)	TV[g] (0.006)	1:1	30ppm	2.0	Y	9:00	12	62

[a] 28000 MW = 1000 cSt; 16000 MW = 500 cSt; 5900 MW = 100 cSt. [b] Me (methyltriethoxysilane), TM (tetramethyl orthosilicate), TE (tetraethyl orthosilicate), TP (tetrapropyl orthosilicate), IT (iodopropyltrimethoxysilane), VT (vinyltrimethoxysilane). [c] Small variations in temperature (2-4 °C) led to noticeable changes in reaction time; these values are thus reported ± 20 s. [d] The elastomers contained large bubbles. [e] 1.4 mL hexane with 0.6 mL toluene + 1-pyrenemethanol (0.001 g). [f] TV = $Si(CH=CH_2)_4$; these conditions match those of entry 6 (crosslinker is present in the same molar concentration), but using a 30ppm Pt solution to replace the boron catalyst. [g] The conditions reported in e were used, except the reaction was performed at 50 °C

6.4 Results

Synthetic protocols for siloxane bond synthesis using dehydrocarbonative coupling[11,12,20,21] simply involve mixing—often with a small amount of solvent (see below)—the hydrosilane, alkoxysilane, and a catalytic amount of $B(C_6F_5)_3$. After a short induction period, the reaction occurs with an exotherm and, occasionally (particularly with methoxysilanes) with vigorous release of an alkane gas. No protection from the local environment was needed. Normally, a small excess of the more volatile reagent is used, such that work-up (in the case of fluid products) is limited to addition of a small amount of neutral alumina to complex the catalyst, filtration, and evaporation of the residual volatile reagent (Figure 5.1). Although $B(C_6F_5)_3$ is normally removed from fluid silicones, we have not observed any evidence of silicone depolymerization/metathesis, even when the catalyst is left in the silicone over extended periods of time.

Preliminary experiments demonstrated that some procedural modifications would be necessary to evenly cure polymers into elastomers. Important process parameters to control included the order of addition of the reactants, the concentration of the $B(C_6F_5)_3$ catalyst, and the need to add small amounts of solvent to enhance the dispersion of $B(C_6F_5)_3$ and alkoxysilane crosslinker within the hydride-terminated PDMS silicone. A more important effect that speaks to the efficiency of the reaction was the slower reaction time observed when solvent was present, which permitted transfer of the pre-elastomer mixture to the curing vessel, typically a Petri dish. If solvent was not used, the reaction was sufficiently fast that cure often occurred to a significant degree during mixing, including partial or complete setting, which frequently led to inhomogeneous materials (e.g., less than 30 s, see Table 6.1). This suggests, however, that it may be possible to use the reaction in extrusion or injection molding processes where high-speed production is particularly important.

Early experiments also demonstrated that the order of addition of the reagents was important for clean elastomer formation. The optimal addition order involved combining the alkoxysilane crosslinker with the catalyst and then adding this mixture to H-PDMS-H. If the catalyst was added to the hydrosilane first, crosslinking immediately proceeded, making reproducible reactions difficult. Evenly cured materials formed more readily if the pressure was reduced shortly after mixing the ingredients: degassing silicone elastomers during cure is a common practice to avoid entrained bubbles.[4] In this reaction, the likelihood of bubbles in the product is exacerbated by the formation of alkane by-products. In some cases, it was not possible to form bubble-free elastomers unless significant deviations were made from standard formulations (see below).

A wide range of elastomeric materials could be prepared once these factors had been optimized, as described in Table 6.2 (Figure 5.1C, 9.4, Appendix IV). The factors that most influenced the mechanical properties of the product elastomers were: H-PDMS-H MW, crosslinker concentration, crosslinker reactivity, and solvent volume, which will be discussed in turn.

6.4.1 Reaction Rate, Use of Solvent, and Bubble Suppression

The rate of the reaction depended on a variety of factors including base polymer molecular weight, catalyst concentration, the character of the alkoxysilane crosslinker, and the use of hexane as diluent. Early explorations with the more reactive formulations (Table 6.1: **1**) demonstrated that solvent-free elastomers could be formed completely in 20 s. This exceptionally rapid rate was frequently disadvantageous as, in many cases, the elastomers were relatively inhomogeneous because it was not possible to efficiently mix the starting materials before the onset of cure. Only hand mixing was possible: the use of 10 static mixer syringe tips with either 5 or 10 elements was unsuccessful because cure occurred in the mixer.

As would be expected, lowering the catalyst concentration led to increases in reaction time. For example, using 30 ppm instead of 239 ppm of catalyst increased the reaction time to 78 min (Table 6.2: **27**). Although further manipulation of catalyst loading was possible, it proved to be more convenient both to facilitate mixing and moderate reaction times by addition of a small amount of solvent.

The first benefit of solvent addition was an increased level of control in the process as a consequence of mediation of cure kinetics: there was a concomitant reduction in reaction rate with decreasing reagent concentration (Table 6.1). Addition of hexanes also facilitated both catalyst and crosslinker dispersion and allowed the viscosity of the curing mixture to remain lower for longer periods of time, which led to a reduction in the incidence of entrapped bubbles. The addition of an appropriate amount of solvent could thus change outcomes from bubble containing to the desired uniform, bubble-free elastomers. For example, in an otherwise identical formulation containing 2.5 g of silicone, the use of 5 mL hexane instead of 2 mL, avoided the presence of bubbles in the product (Table 6.2: **22** vs. **23**, Figure 6.2A, B). Bubble formation was also controlled by crosslinker type and silicone MW as is discussed further below.

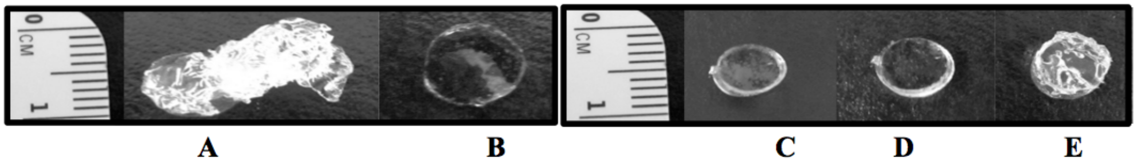


Figure 6.2: A foamed material (Table 6.2: **22**); B: The corresponding elastomer arises from changing the amount of added solvent and/or catalyst concentration (Table 6.2: **23**). Effect of PDMS MW on elastomer formation: entries on Table 6.2. C: entry **7** (1000 cSt), D: entry **8** (500 cSt), E: entry **9** (100 cSt) at a fixed [SiOR]:[SiH] ratio of 1.5:1.

6.4.2 H-PDMS-H Molecular Weight

As with any rubber, elastomeric properties were associated with the crosslink density that could be optimized by changing the molecular weight of the base silicone polymer. More rigid/brittle materials formed when shorter silicone chains were used, due to the shorter distance between crosslinks. For example, at a fixed crosslinker ratio of 1.5:1 [SiOEt]:[SiH] functional groups (from TEOS crosslinker and linear H-PDMS-H, respectively), the hardness of the elastomer products increased as the molecular weight of the silicone was decreased from 28,000 to 16,000 and 5900 MW H-PDMS-H: the Shore A hardness of the materials were 13, 21, and 25, respectively (Table 6.2: **7**, **8**, **9**, respectively; 9.4-Appendix IV, Figure 6.2C–E).

The lower MW starting H-PDMS-H (100 cSt, ~5900 MW) was more reactive than longer silicone chains due to a higher Si-H concentration in the reaction mixture, causing some of the alkane by-products to be entrapped in the resulting elastomer. For instance, the reaction time for a 5.9 kDa MW H-PDMS-H with reactive crosslinker TMOS with 2 mL of hexane is 43 s (Table 6.1: **5**, Figure 6.2E), while when the same conditions were used with a higher 28 kDa MW silicone hydride, the total reaction time increased to 1.4 min (Table 6.2: **6**). Performing the reaction under vacuum, to facilitate removal of the alkane gases, avoided the trapping of bubbles in most cases. With shorter H-PDMS-H chains (100 cSt), particularly with lower concentrations of crosslinker, bubble-containing materials were almost always formed demonstrating that the rate of cure is faster than the rate of bubble removal.[22]

6.4.3 Ratio of $Si(OR)_4$:H-PDMS-H

The final properties of the elastomer can also be manipulated by changing the concentration of crosslinker present. At lower crosslinker concentrations, for example, at a 0.5:1 molar ratio of [SiOR]:[SiH], the materials formed were softer and more elastic (Figure 6.3A,B) than elastomers formed with higher crosslinker concentrations (Table 6.2: Entry **10**, 9.4-Appendix IV). Even if complete reaction occurs with the four reactive sites on the crosslinker, residual unreacted silicone chains, or chains only tethered at one terminus, convey gel-like properties onto the material. At this low ratio, the products formed with 100 and 500 cSt H-PDMS-H, entry **11** and **12** respectively, generally contained large bubbles that could not be removed before the elastomer cured. With the optimal crosslink density resulting from a [SiOR]:[SiH] 1:1 ratio, harder elastomers formed for each given H-PDMS-H MW (Figure 6.3C). As the crosslinker ratio was further increased from 1:1 to 1.5:1 [SiOR]:[SiH], the elastomers became softer (Shore A decreased from 21 to 18, respectively, for 1000 cSt H-PDMS-H with MTES crosslinker, Table 6.2: **13**, **14**, Figure 6.3D). With yet higher crosslinker concentrations, 2:1, the crosslink density is further decreased and a much softer elastomer resulted (Shore A decreases to 10, Table 6.2: **15**, Figure 6.3E). In this case, the stoichiometry leads to a lightly crosslinked polymer that exhibits enhanced chain extension and crosslinker-capped chains, at the expense of crosslinks. The effect of both chain length and reduced crosslinker concentration can be seen by comparing Shore hardness values of the elastomers produced at 1.5:1 and 2:1 ratios with different H-PDMS-H MW: for 500 cSt H-PDMS-H MW the Shore A hardness decreased from 23 to 14, respectively, while for 1000 cSt hardnesses of 18 and 10 were observed (Table 6.2: **16**, **17,** 9.4 - Appendix IV).

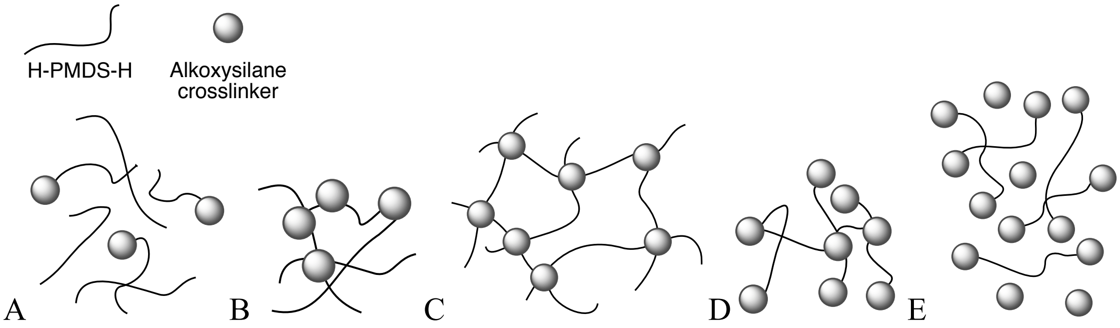


Figure 6.3. Models showing crosslink density changes associated with an increase in the concentration of alkoxysilane crosslinker. A: excess H-PDMS-H. B: [SiOR]:[SiH] ratio of 0.5:1. C: [SiOR]:[SiH] ratio of 1:1. D: [SiOR]:[SiH] ratio of 1.5:1. E: [SiOR]:[SiH] ratio of 2:1.

6.4.4 Alkoxysilane Crosslinker

The type of alkoxysilane crosslinker also affects the rate of the dehydrocarbonative coupling reaction: more sterically congested alkoxy groups react more slowly.[13] We examined a range of silicone crosslinkers to see if the rate effects were manifested during elastomer formation and, more importantly, if they led to significant changes in the properties of the resulting elastomers. It was found that more reactive crosslinkers, such as TMOS ($Si(OMe)_4$), led to elastomers that contained relatively high densities of bubbles or were less transparent, or both (e.g., Table 6.2: **16**, Figure 6.4B). The reaction process was too fast to allow bubbles to escape the curing material, even if solvent was used to slow the process. By contrast, use of the less reactive crosslinker, TPOS, slowed the reaction down to such an extent that in some instances the elastomers did not fully cure, and remained "tacky" (e.g., Table 6.2: **18**, Figure 6.4D), but no bubbles were entrained. MTES and TEOS were thus determined to be the optimal crosslinkers, as the ethoxy groups were large enough to retard the reaction such that clear, uniform elastomers formed that contained few or no bubbles, but reactive enough for the reaction to go to completion in a convenient time period (Figure 6.4A,C, respectively). An additional advantage of these two crosslinkers is that they can be used in different ratios: changing the ratio of tri- to tetra-functional silanes facilitates control of final elastomer hardness within a fixed [SiOR]:[SiH] ratio regime.

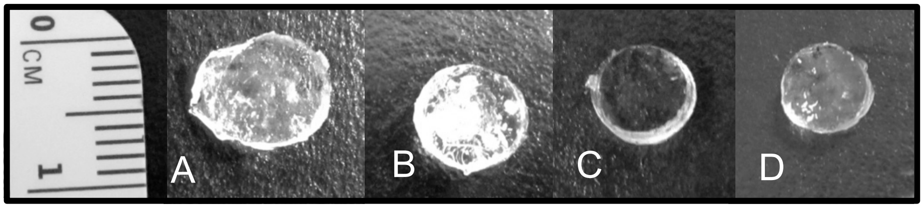


Figure 6.4. All elastomers were synthesized with 500 cSt PDMS, in a 1.5:1 ratio of [SiOR]:[SiH] in crosslinker:H-PDMS-H. Pictures show the effect of changing crosslinker reactivity: A: MTES **19**; B: TMOS **16**; C: TEOS **8**, D: TPOS **18** (see Table 6.2).

6.4.5 The Effect of Humidity

$B(C_6F_5)_3$ is a strong Lewis acid, which is known to efficiently complex with water and other Lewis bases.[23] The complexation with water leads to the formation of a relatively strong Brønsted acid. It was posited that the complexation would retard the coupling reaction and, possibly, the Brønsted acid could compromise the elastomer by catalyzing hydrolytic de-polymerization. As a consequence, the reaction was examined at various humidity levels. One of the most reactive formulations reacted in a chamber set at 75% humidity (Table 6.2: **26**). When the components were mixed and immediately placed into the humidity chamber there was only a slight delay (+ 5 s) in the total elastomer cure time. However, when the components of the reaction were left in the humidity chamber for 1 h before mixing, the elastomer cure time was significantly delayed (from 43 s to 16 min). The final hardness of the bubble-containing elastomer was the same as previously reported.

6.4.6 Comparison with Traditional Catalysts

As noted above, platinum catalysts are frequently used to prepare silicone elastomers from precursors functionalized with Si-H and Si-vinyl groups, respectively. To provide some comparison[24] between the process described above and traditional platinum-catalzyed addition cure, a formulation was prepared with 30 ppm of a platinum catalyst used to cure 28,000 MW hydrogen-terminated silicone with $Si(Vi)_4$ as crosslinker in hexane as diluent. As the molecular weight of silicone chains and functionality of the crosslinker are the same, the resulting network should be identical to formulation (**6**, Table 6.2). The initial experiment (**29**, Table 6.2) showed that cure took about an order of magnitude longer under comparable conditions with the $B(C_6F_5)_3$-catalyzed process, a situation only slightly improved by heating to 50 °C, entry **30**.

6.4.7 Functional Elastomers

Although the main focus of the research was the development of alternative routes to silicone elastomers, the $B(C_6F_5)_3$-catalyzed process conveniently allows incorporation of functional group synthetic handles: the chemistry used to form siloxane linkages does not affect some organic functional groups, including alkenes or alkyl halides (Figure 5.1B).[11] To demonstrate this premise, vinyltrimethoxysilane was used as a crosslinker to provide an elastomer bearing vinyl groups that are available for hydrosilylation reactions (Figure 6.5A, Table 6.2: **20**), the most common way to modify silicones.[5] Note that, while hydrosilylation can be catalyzed by $B(C_6F_5)_3$,[25] it was not observed with the low concentration of catalysts used. Similarly, iodopropyltriethoxysilane was incorporated in the silicone elastomer to provide a reactive site that could be used to create available sites for azide functionalization that can be used to react with alkynes in a click reaction (Figure 6.5B, Table 6.2: **21**).[26] The ability to incorporate synthetic functionality was further demonstrated by adding a fluorescent label which, through the Piers reduction,[27] becomes incorporated in the final elastomer.

In the low [SiH] regime, reductive cleavage to methylpyrene was not observed, and the fluorescent label remained in the elastomer after Soxhlet extraction with toluene (Table 6.2: **28**, Figure 6.5D).

6.5 Discussion

Silicone elastomers are normally cured by one of three means: high-temperature radical cure; tin-catalyzed moisture (condensation) cure; or platinum-catalyzed hydrosilylation (addition) cure. Each of these processes exhibits benefits and detriments.

Tin-catalyzed moisture cure is an efficient, but slow, elastomer-forming process. However, the tin catalysts are set for removal from commerce in Europe because of concerns about their environmental behavior.[10] From a materials' perspective, the challenge with this process is managing the moisture that is a co-constituent of the vulcanization process. As moisture is provided by the environment, cure always occurs from the ‘‘outside-in,'' and complete and homogeneous cure is not always easy to attain: it is typically slow.

Radical cure, which is very rapid, provides little control over network structure and requires postcure baking to (attempt to) remove residuals from the radical initiators. Platinum-based addition cure is typically associated with the highest level of network control. Elevated temperatures are frequently required to elicit cure and it is quite common to use a ‘‘postcure'' thermolysis to finish the curing process, and to drive off residual volatile compounds. Platinum catalysts—even at the low concentrations at which they are used—are expensive. Over time, the residual platinum in the silicone elastomer can aggregate to form colloidal platinum particles that cast a yellow tinge to the elastomer.

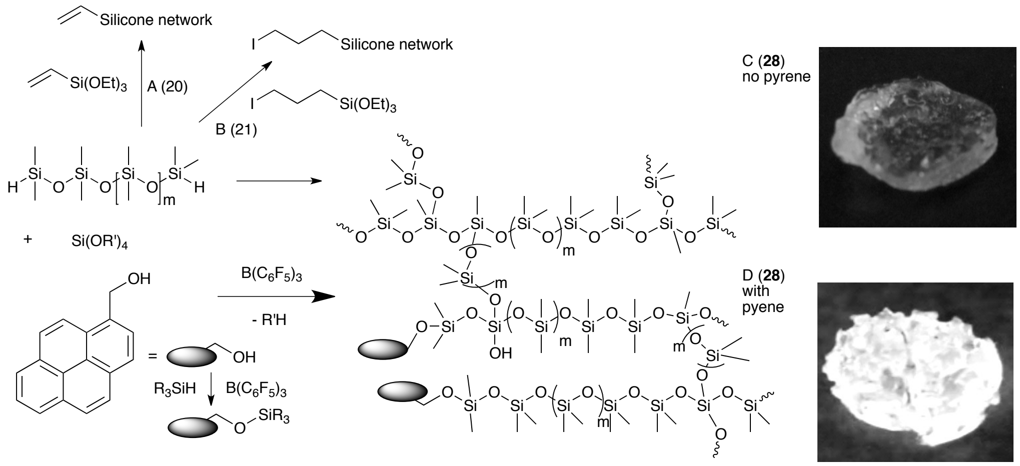


Figure 6.5. Functional silicones are readily prepared by use of functional crosslinkers A (Table 6.2: **20**), B (Table 6.2: **21**), C, D: non-functional (C: formulated without pyrenemethanol), and pyrene-modified silicone (D: Table 6.2: **28**). The rippling in the elastomers occurred after Soxhlet extraction with toluene and drying.

The outcome of the use of platinum catalysts under the optimized conditions used for the $B(C_6F_5)_3$-catalyzed process were instructive. The catalyst concentration—30 ppm—falls within the normal range of commercial elastomers. Platinum-catalyzed hydrosilylation is an efficient process in hexane as solvent, although the use of a solvent diluent is atypical for elastomer formation. As shown in Table 6.2, the reactions were significantly slower than the $B(C_6F_5)_3$, nearly an order of magnitude slower and, even at 50 °C, were about five times slower. This head-to-head comparison demonstrates the remarkable efficiency of the $B(C_6F_5)_3$-catalyzed condensation to give siloxanes.

The mechanism of the dehydrocarbonative coupling of hydrosilanes and alkoxysilanes involves the complexation of the Lewis acidic boron in $B(C_6F_5)_3$ with the silicon hydride.[12] The reaction proceeds efficiently despite the multitude of other Lewis bases present—silicone-based oxygens in particular: it is known that strong Lewis bases, including those based on nitrogen, completely suppress the process. Initially, there was concern that ambient water would intervene in the reaction as has been observed in other reactions catalyzed by $B(C_6F_5)_3$. At high levels of humidity, the process was retarded, which is attributed to a fraction of the catalyst being tied up with water and therefore unable to facilitate the coupling process. However, we did not observe any acid-catalyzed degradation[5] of the silicone backbone in previous work,[11,12,20] nor with the materials prepared here. We attribute this to the hydrophobic silicone environment. The water:$B(C_6F_5)_3$ complex will be comparably very polar and therefore likely of low solubility in the silicone environment: if the complex forms, it will not be sufficiently soluble in the silicone to catalyze silicone decomposition. This observation is particularly important for elastomers: it is impractical to remove catalysts from rubber and the presence of catalyst in the final product cannot compromise its integrity, as is the case here.

When the decarbonative coupling reaction was performed at ambient humidity and temperature, it was exceptionally rapid—much more rapid than the other silicone cure methodologies. For many applications, the rate of cure was actually impractically fast in a normal laboratory setting. However, this fast cure could be extremely beneficial in an industrial environment, such as with extrusion or injection molding, where speed and use of low temperatures is particularly advantageous.

In practice, it was necessary to slow the reaction down, both to avoid capturing bubbles formed from alkane byproducts and to facilitate mixing of the starting materials. The former aspect is most important because significant amounts of alkane are produced as by-products during the curing process. When the rate of bubble formation is comparable with the rate of cure (increasing viscosity leading to bubble capture), bubble-containing elastomers can result. However, to a large degree, the production of bubble free elastomers can be achieved simply by applying a small vacuum during elastomer production, by decreasing the viscosity of the elastomer body early on with the addition of a small amount of solvent, or slowing down the cure rate by reducing the amount of catalyst such that bubbles are better able to escape the curing material. However, it should also be noted that for certain formulations, bubble capture is not problematic, and rapid reaction occurs at room temperature to give transparent silicone elastomers (Table 6.2, 9.4 - Appendix IV). Of course, foam formation can be a desirable outcome.[26]

The decarbonative coupling process, as applied to elastomers, provides a variety of straightforward tools to manipulate the final rubber properties, while starting from simple, readily available precursors. Softer elastomers result from longer chain length between crosslinks or higher [SiOR]:[SiH] ratios; in the latter case increased surface tackiness is also enhanced as a consequence of more dangling chain ends (Figure 6.3D). Reaction rates can be moderated simply by using crosslinkers comprised of bulkier alkoxysilanes, less catalyst or more solvent. Crosslink density, in addition to the techniques just mentioned, is also readily tuned by using mixtures of tri- and tetra-functional crosslinkers. Manipulating the mechanical properties of the produced rubbers, most of which have to do with changing the network structure to increase the spacing between crosslinks, can be readily achieved by modifying the relative concentration of alkoxysilane crosslinker to H-PDMS-H silicone chain length. Shore hardness ranging from Shore OO 15, to Shore A 30 are readily available with the process (**24** and **25**, respectively, Table 6.2).

6.6 Conclusions

Formulators design silicone elastomers around a variety of desired properties: transparency, color, tackiness (for adhesion to a variety of surfaces), hardness, resistance to tear, and so forth. Increasingly, the ultimate fate of the material is also to be considered and, in the case of tin derivatives, there is increasing concern about environmental impact.[10] The process described above for silicone elastomer synthesis exhibits a variety of benefits. First, it avoids the use of metal catalysts entirely, and the concentrations of $B(C_6F_5)_3$[11] necessary for reaction are less than tin catalysts. Second, the process is very rapid, and the kinetics are easily manipulated by a variety of simple strategies. Finally, the process allows elastomers with different properties to be readily prepared using by manipulation of ratios of crosslinker to silicone chain, chain length, steric bulk of the alkoxygroups on the crosslinker, and reagent concentrations.

Silicone elastomers containing comparable or improved properties to the materials formed using tin- (moisture cure) or platinum-catalyzed (hydrosilylation cure) processes have been synthesized. The reaction of alkoxy-functional silane crosslinkers with SiH-functional silicones using small amounts of trispentafluorophenylborane as catalyst is a practical alternative to these metal-catalyzed processes and one that occurs much more rapidly at room temperature. Unless very highly reticulated materials are prepared, the gaseous alkane by-product can be removed from the process by vacuum or by slowing the cure process down using less catalyst or through the addition of solvent. The extent of cure, and hence control over the final consistency of the rubber, is readily achieved through catalyst concentration, crosslinker type and concentration, and MW of the siloxanes.

6.7 Acknowledgements

The authors acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada and 20/20: NSERC Ophthalmic Materials Network. A.S. Fawcett is grateful for a NSERC CGS-D scholarship and J.B. Grande is grateful for a NSERC PGS-D scholarship. The authors also thank Alexander J. McLaughlin for assistance with preliminary experiments.

6.8 References

1. C. A. Malpass, K. W. Millsap, H. Sidhu, and L. B. Gower, *J. Biomed. Mater. Res. B Appl. Mater.,* 2002, **63**, 822–829.
2. J.F. Kunzler, *Trends Polym. Sci.*, 1996, **4**, 52–59.
3. T. A. Mustoe, *Aesthetic Plast. Surg.*, 2008, **32**, 82–92.
4. H. Chen, M. A. Brook, H. D. Sheardown, Y. Chen and B. Klenkle, *Bioconjugate Chem.*, 2006, **17**, 21–28.
5. M. A Brook, *In Silicon in Organic, Organometallic and Polymer Chemistry*; Wiley: New York, 2000; pp 256–308.
6. W. J. Noll, *Chemistry and Technology of Silicones*; Academic Press: New York, 1968.
7. J. J. Chrusciel and E. Lesniak, *J. Appl. Polym. Sci.*, 2011, **119**, 1696–1703.
8. M. Zhang, T. Desai and M. Ferrari, *Biomaterials,* 1998, **19**, 953–960.
9. S. J. Clarson and J. A. Semlyen, *Siloxane Polymers*; Prentice Hall: Englewood Cliffs, NJ, 1993.
10. L. A. Utracki, *Polymer Blends Handbook*; Kluwer Academic Publishers: Dortrecht, Netherlands, 2002.
11. J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, *Chem. Commun.*, 2010, **46**, 4988–4990.
12. M. Iza, M. Bousmina and R. Jerome, *Rheol. Acta.,* 2001, **40**, 10–22.
13. D. B. Thompson and M. A. Brook, *J. Am. Chem. Soc.*, 2008,**130**, 32–33.
14. J. Chojnowski, S. Rubinsztajn, W. Fortuniak and J. Kurjata, *Macromolecules*, 2008, **41**, 7352–7358.
15. J. Kurjata, W. Fortuniak, S. Rubinsztajn and J. Chojnowski, *Eur. Polym. J.*, 2009, **45**, 3372–3379.
16. J. Cella and S. Rubinsztajn, *Macromolecules*, 2008, **41**, 6965–6971.
17. M. A. Hoque, Y. Kakihana, S. Shinke and Y. Kawakami, *Macromolecules,* 2009, **42**, 3309–3315.

18. R. B. Malla, B. J. Swanson, and M. T. Shaw, *Construct. Build. Mater.,* 2011, **25**, 4132–4143.

19. K. D. Safa, S. Tofangdarzadeh and A. Hassanpour, *J. Organomet. Chem.*, 2009, **694**, 4107–4115.

20. J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Trans.,* 2010, **39**, 9369–9378.

21. S. Rubinsztajn and J. A. Cella, Silicone Condensation Reaction. General Electric Company, U.S. Patent 7,064,173, June 20, 2006.

22. J. B. Grande, A. S. Fawcett, A. J. McLaughlin, F. Gonzaga, T. P. Bender and M. A. Brook, *Polymer,* 2012, **53**, 3135–3142.

23. W. E. Piers, *In Advances in Organometallic Chemistry*; Elsevier Academic Press: San Diego, 2005; Vol. **52**, pp 1–76.

24. We thank a referee for this suggestion.

25. M. Rubin, T. Schwier and V. Gevorgyan, *J. Org. Chem.*, 2002, **67**, 1936–1940.

26. R. B. Malla, M. R. Shrestha, M. T. Shaw and S. B. Brijmohan, *J. Mater. Civil Eng.*, 2011, **23**, 287–297.

27. D. J. Parks, J. M. Blackwell, and W. E. Piers, *J. Org. Chem.*, 2000, **65**, 3090–3098.

Chapter 7: Anhydrous Formation of Foamed Silicone Elastomers using the Piers-Rubinsztajn Reaction[‡‡‡]

7.1 Abstract

Elastomeric silicone foams are generally produced by the generation of hydrogen through reaction of Si-H groups with active hydrogen compounds, including water and alcohols, in a process catalyzed by platinum or tin complexes. It can be very difficult to control the rate and magnitude of bubble formation, particularly because of adventitious water. Silicone foams in a variety of densities (0.08-0.46 g/cm^3) were obtained using a newly developed Piers-Rubinsztajn reaction by combining α,ω-hydride-terminated poly(dimethylsiloxane) with an alkoxysilane crosslinker such as tetraethyl orthosilicate with catalysis by $B(C_6F_5)_3$. A single reaction leads both to crosslinking and bubble evolution. The reaction is not

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significantly impacted by humidity: foams are generated by the release of alkane gases derived from the alkoxysilane crosslinker, typically methane or ethane, rather than hydrogen. It was found that crosslinker reactivity and concentration, and silicone molecular weight, can be used to effectively control bubble nucleation, coalescence, viscosity build and, therefore, final foam density and the formation of open or closed cell foams. Better quality foams normally resulted when hexane, which acts as a blowing agent, was added to the pre-foam mixture. In addition to these advantages, and excellent reproducibility, the Piers-Rubinsztajn reaction benefits from a very fast induction time.

7.2 Introduction

Foamed silicone polymers exhibit very unusual properties when compared to organic analogs, which dictate their use in challenging applications ranging from joint sealants[1,2], insulators, mechanical shock absorbers in the aerospace, aircraft and transportation industry[3], to biomaterials for wound dressings[4,5]. Their high thermal stability, resistance to flame spreading, poor combustibility and electrical resistance are of particular use in transportation applications.

Silicone foam preparations can be classified, chemically, into two categories: (a) heat-activated foams and, (b) room temperature vulcanization (RTV)[3,6]. Heat-activated vulcanization usually consists of curing a higher molecular weight vinyl or methyl functionalized silicone polymer using a peroxide-vulcanizing agent[3,6,7] in the presence of a heat-activated blowing agent that is not affected by silicone cure[8-13]. Alternatively, in RTV systems polycondensation or polyaddition reactions occur between crosslinking agents containing a functional group on a silicon atom and silicone polymers containing hydrosilanes in the presence of a metal catalyst, typically based on platinum[7] or tin[3,7,14]. RTV foam systems are generally available as a two component mixture where, after mixing, elastomer cure occurs simultaneously with gas evolution.

Unlike the orthogonal chemical processes that occur in heat cured foams, RTV systems use the same chemical entity - typically a hydrosilane residue - for cure by hydrosilylation with an alkene and foam generation by reaction with active hydrogen compounds, such as H_2O and ROH, generating H_2 (Figure 7.1A). It remains very challenging to control the density and morphology of RTV silicone foams because of the need to control the kinetics of two separate processes: cure and foam/bubble generation. The most demanding aspect is avoiding adventitious water or other active hydrogen compounds that change both the crosslink density of the elastomeric foam and, more problematically, the relative cure/foam kinetics which lead to changes in foam density and structure (open/closed) from the desired outcome: reproducibility in foam generation can be problematic.

The condensation of alkoxysilanes with hydrosilanes (Figure 7.1B) giving alkane byproducts, catalyzed by $B(C_6F_5)_3$ - the Piers-Rubinsztajn reaction - can be used to create small well-defined silicone structures from simple starting materials[15-17]. This recently discovered reaction has been barely explored in silicone chemistry, particularly for the preparation of high molecular weight polymers. The few literature reports on the Piers-Rubinsztajn reaction suggest that it could have several potential advantages in the formation of silicone foams, including: rapid reaction times even at room temperature; facile formation of gaseous by-products that could act as blowing agents; very low sensitivity to the presence of water, which will therefore not act as a blowing agent; and the need for relatively low catalyst concentrations. Current RTV technologies use metal-based catalysts that may be disadvantageous on the basis of cost (platinum) or environmental (tin) reasons: the high temperatures required for heat generated foams can be avoided. *We note that the rapid generation of volatile and flammable byproducts means that particular care should be exercised with this process, particularly at larger scales.*

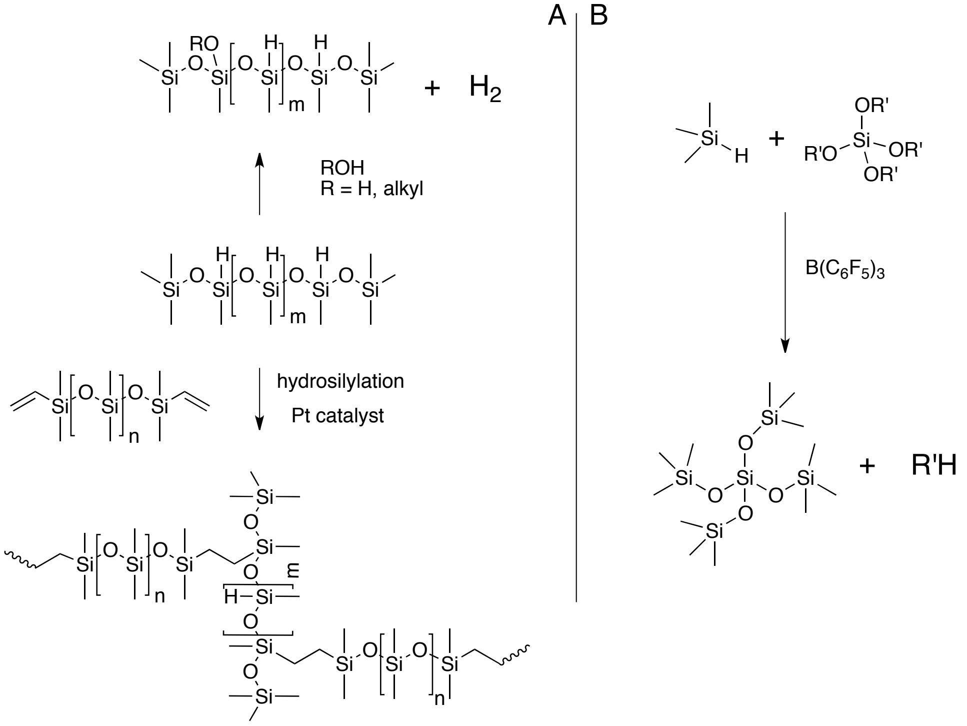


Figure 7.1. A: Gas evolution vs RTV cure. B: A model Piers-Rubinsztajn reaction. R' = Me, Et, Pr.

We have examined the applicability of this unusual condensation reaction as a synthetic route to RTV silicone foams. α,ω-Hydride-terminated poly(dimethylsiloxanes)(PDMS) were cross-linked with tetramethyl orthosilicate ($Si(OMe)_4$), tetraethyl orthosilicate ($Si(OEt)_4$), or tetrapropyl orthosilicate (Si(O*n*-Pr)$_4$), respectively. The ability to reproducibly crosslink polymers and simultaneously blow silicone foams under these reaction conditions was examined as a function of molecular weight of the starting hydride-terminated PDMS polymer, chemical nature of the alkoxy crosslinker, catalyst concentrations, and the presence and concentration of small amounts of the hydrocarbon solvent hexane. Foam structures and densities were correlated with the reagents used for foam manufacture.

7.3 Experimental

Tetramethyl orthosilicate (TMOS), tetraethyl orthosilicate (TEOS), tetrapropyl orthosilicate (TPOS), trifluoromethanesulfonic acid, magnesium oxide and trispentafluorophenylborane $B(C_6F_5)_3$ were purchased from Sigma-Aldrich, and used as received. Octamethylcyclotetrasiloxane (D_4), α,ω–hydride-terminated poly(dimethylsiloxane) (H-PDMS-H) 2-3, 7-10 and 100 centiStokes (cSt, approximate MW 730, 1,190 and 5,000 g mol^{-1}, respectively (silicones are commonly sold by their kinematic viscosity in cSt, which may be converted to viscosity by multiplying by the density of the fluid. 1000 cSt is thus 970 mPa s) were purchased from Gelest. Hexanes, tetrahydrofuran and toluene were purchased from Caledon. Solvents were dried over activated alumina before use.

Nuclear magnetic resonance spectra were recorded using a Bruker Avance 500 or 600 Avance spectrometer. SEM images were obtained using a Philips 515, JEOL 7000F, Focused Ion Beam, Zeiss NVision40 scanning electron microscope.

Synthesis of ~ 2570 g/mol Hydride-terminated H-PDMS-H (poly(dimethylsiloxane)) To a mixture of octamethylcyclotetrasiloxane D_4, (40.0 g, 0.135 mol (Me_2SiO) unit) and 1,1,3,3-tetramethyldisiloxane (2.79 g, 20.8 mmol) was added trifluoromethanesulfonic acid (0.02 ml, 0.038 g, 0.25 mmol) at room temperature. The mixture was then heated at 100°C for 5 h. Once complete, the mixture was cooled to room temperature. Tetrahydrofuran (~ 200 ml) and magnesium oxide (~2-3 g – to quench the triflic acid) were then added to the solution. The mixture was then filtered through a fritted funnel and concentrated under reduced pressure. The residue was purified by removal of small molecular weight molecules using Kugelrohr distillation at 140 °C under vacuum (0.1 mmHg) for 5 hours yielding a colorless oil (yield – 33.2 g).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.70 (m, 2 H, $OSi(CH_3)_2H$), 0.18 (s, 12 H, $H(CH_3)_2Si(OSi(CH_3)_2)_nOSi(CH_3)_2H$), 0.08 ppm (s, 200 H, $(OSi(CH_3)_2)_nOSi(CH_3)_2H$), ^{13}C NMR: ($CDCl_3$ 125 MHz) δ 0.90, 0.84, 0.74 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -6.69 (M), -19.68 (M), -21.73 (M) ppm.

Nomenclature: Numbered formulations contained hexane, e.g., **4** unless indicated by addition of 'n', e.g., **14n**, Table **1**, 9.5- Appendix V.

General Synthesis of Silicone Foam

In a typical synthesis (shown for 7-10 cSt H-PDMS-H with TMOS, 1:1 (eq SiH:SiOMe), (Table 7.1-entry **8**), H-PDMS-H (2.0 g, 1.70 mmol) and TMOS (0.127 g, 0.83 mmol) were placed in a 25.0 mL vial with hexanes (1 mL). The contents of the vial were stirred and $B(C_6F_5)_3$ (20 µL of a 0.078 M solution, 376 ppm) was quickly added. The contents were stirred gently until a few bubbles began to appear, then the mixture was left to complete the reaction (~30 s) during which time the volume of the mass increased by ca. 50%. *There was a relatively large exotherm during the process*. The vial was then broken to remove the foamed silicone elastomer. Alternatively, the foam could be formed in an open vessel by pouring the mixture immediately into a Petri dish that had been lined with Teflon. Table 7.1 (and 9.5-Appendix V) shows the variables that were examined in an effort to correlate reagent types, concentrations and reaction conditions with the ability to form foams. Factors including: solvent volume (concentration of reagents); MW of H-PDMS-H; type of crosslinker; and molar ratio of Si-H to crosslinker ($Si(OR)_4$), were systematically examined. The induction times between mixing of reagents and foam formation were measured, starting the time from the addition of $B(C_6F_5)_3$ to the solution of crosslinker and H-PDMS-H, until the first signs of gas evolution. Total reaction time refers to the total time from the addition of $B(C_6F_5)_3$ to the time a foam has been fully produced and reaction stopped – the evolution of gas ceased. The density of the silicone foams were measured following the procedure laid out by Chruściel *et al.*[3] as follows:

Density: $d = m/V$; *Volume (V) f*or a cylinder = $h(\pi r^2)$

Where m is the mass of the cylindrical sample, h is the height of the cylindrical sample and r is the radius of the sample.

Table 7.1 Experimental foam data

Entry #	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Induction Time (s)	Total time (s)	Density (g/cm^3)	Hardness[e]	Shore 00
			1:1.5							
1	730 (1.0)	TM (0.157)	1|1.5	10/345	1.0	13.1 ± 1.2	33.6 ± 0.9	0.23 ± 0.03	0	
2	1190 (2.0)	TM (0.191)	1|1.5	20/365	1.0	21.6 ± 5.7	32.2 ± 2.8	0.17 ± 0.02	0	
3	2570 (2.0)	TM (0.089)	1|1.5	20/382	1.0	16.1 ± 0.7	18.1 ± 1.9	0.32 ± 0.04	3	50
4	5000 (2.0)	TM (0.094)	1|1.5	20/382	1.0	N	-	-		
			1:1							
5	730 (1.0)	TM (0.104)	1|1	10/362	1.0	5.5 ± 2.2	15.9 ± 0.5	0.13 ± 0.03	0	
6	730 (1.0)	TE (0.143)	1|1	10/349	1.0	8.1 ± 2.1	25.4 ± 5.9	0.11 ± 0.01	0	
7	730 (1.0)	TP (0.182)	1|1	10/338	1.0	42.9 ± 5.9	75.7 ± 7.9	0.09 ± 0.01	0	
8	1190 (2.0)	TM (0.127)	1|1	20/376	1.0	10.3 ± 3.4	23.7 ± 1.6	0.17 ± 0.02	0	
9	2570 (2.0)	TM (0.059)	1|1	20/388	1.0	11.3 ± 2.6	14.9 ± 1.4	0.46 ± 0.04	3	51

Entry #	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Induction Time (s)	Total time (s)	Density (g/cm^3)	Hardness[e]	Shore 00
			1:2							
10	730 (1.0)	TM (0.201)	1ǀ2	10/333	1.0	31.8 ± 5.1	37.5 ± 4.2	0.14 ± 0.02	0	
11	2570 (2.0)	TE (0.162)	1ǀ2	20/370	1.0	37 ± 10	69 ± 12	0.30 ± 0.03	2	31
12	2570 (2.0)	TP (0.205)	1ǀ2	20/362	1.0	186 ± 95	453 ± 220	0.25 ± 0.07	2	35
			Solvent Free							
13n	1190 (2.0)	TM (0.127)	1ǀ1	20/376	-	13.6 ± 1.8	19.6 ± 1.9	0.34 ± 0.03	0	
14n	1190 (2.0)	TE (0.174)	1ǀ1	20/367	-	34.5 ± 8.4	43.6 ± 7.7	0.31 ± 0.01	0	
15n	1190 (2.0)	TP (0.222)	1ǀ1	20/360	-	170 ± 21	204 ± 34	0.21 ± 0.02	1	7
			vs Solvent							
16	1190 (2.0)	TE (0.174)	1ǀ1	20/367	1.0	12.0 ± 1.1	35.1 ± 2.8	0.13 ± 0.01	0	
17	1190 (2.0)	TP (0.222)	1ǀ1	20/360	1.0	27 ± 11	68.7 ± 5.7	0.15 ± 0.03	0	
			Half the solvent							
18	1190 (2.0)	TM (0.127)	1ǀ1	20/376	0.5	15.5 ± 1.2	19.3 ± 2.7	0.19 ± 0.01	1	3
			Double the solvent							
19	1190 (2.0)	TM (0.127)	1ǀ1	20/376	2.0	21.2 ± 1.2	24.0 ± 1.6	0.08 ± 0.01	0	

[a] Hydride terminated PDMS: 7-10 cSt (1,190 g mol-1), 2-3 cSt (730 g mol-1).[b] TM: Tetramethyl orthosilicate, TE: Tetraethyl orthosilicate, TP: Tetrapropyl orthosilicate.[c] ratio = PDMS hydride groups : alkoxysilane groups. [d] Catalyst solution: 40 mg of $B(C_5F_5)_3$ in 1 mL of dry toluene. [e] Hardness scale: For those samples for which a Shore 00 hardness could not be obtained we provide an empirical scale clarifying a range of hardness 0 = too soft to measure with Shore 00, 1 = Shore 00 values: 0-20, 2 = Shore 00 values – 20-40, 3 = Shore 00 values – 40-65. Many of the harder foams cracked during measurement.

7.4 Results and Discussion

The formation of a silicone (or any polymeric) foam requires the ability to match the kinetics of two independent processes: silicone crosslinking that builds the viscosity until the system first gels and then is converted into an elastomer; and, kinetics of bubble nucleation, coalescence and migration through the silicone. If too many bubbles are released before the viscosity increases sufficiently, or bubbles are not released until the elastomer is nearly formed, then few bubbles will be trapped and either a foam won't form at all, or the elastomeric material will be relatively bubble free. It was necessary therefore, to examine the relative kinetics of the two processes and vary them by changing both the reagent concentrations and the nature of the crosslinker.

It was previously shown that the Piers-Rubinsztajn reaction was very sensitive to the steric bulk of both the hydrosilane and alkoxysilane reaction partners: the larger the alkoxy group, the slower the reaction[18]. Although final crosslink density of the elastomer formed from H-PDMS-H and a tetraalkyl orthosilicate should not depend on crosslinker type, any reactivity differences between crosslinkers should provide a control element for the relative rates of condensation and gas generation. Therefore, three different alkoxysilanes $Si(OMe)_4$, $Si(OEt)_4$, $Si(O\text{-}nPr)_4$, which exhibit both different reaction rates in the process and which produce gases of different volatility and solubility in the silicone (methane, ethane and propane, respectively), were used to crosslink moderately sized hydride-terminated polydimethylsiloxanes (H-PDMS-H, MW 730-5000). Preliminary experiments demonstrated that addition of the solvent hexane allowed for the generation of more uniform silicone foams. Hexane was therefore added to many of the formulations (hexane-free foams are described below). The reaction parameters were systematically varied to determine the optimal conditions for foam generation. Although we judge the highest value foams to be relatively low density, closed cell foams that have good mechanical stability, others may find different structures of interest and we therefore report all the types of foams prepared. The foams were characterized by density, Shore OO hardness (for selected examples, and an empirical hardness scale for all samples) (Figure 7.2, Table 7.1, 9.5 Appendix V). The preliminary studies demonstrated that the factors which most influenced the mechanical properties of the product elastomers were: chain length (MW) of H-PDMS-H, crosslinker type, cross- linker concentration and solvent volume, each of which will be discussed in turn.

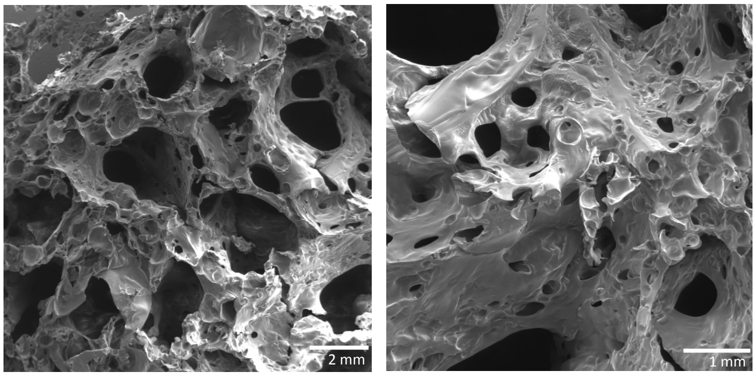


Figure 7.2. Elastomer formation around evolving volatile byproducts resulting in silicone foams **1**. The foam can be characterized in terms of total density, open or closed cell structure and mechanical performance.

7.4.1 H-PDMS-H molecular weight

The molecular weight of the H-PMDS-H was systematically increased from ~730 g/mol to ~5000 g/mol while keeping all other variables constant ($Si(OMe)_4$ crosslinker, hexane - 1.0 mL). As expected from polymer theory[19], which has particularly benefitted from the study of silicones[20], the distance between crosslinks[21], which tracks with H-PDMS-H chain length, dramatically affected the resulting foam structure and mechanical properties: we have recorded, where possible, Shore OO hardness and provided an empirical scale for hardness for other samples (Table 7.1). In general, foam hardness tracked with density, but was also affected by bubble size and dispersity. These silicone foams, which were not reinforced by silica fillers, were therefore in some cases friable such that measuring hardness was precluded.

The use of H-PDMS-H MW ~730 g/mol **1**, led to a fairly brittle silicone foam (Figure 7.3A) compared to **2**, in which MW ~ 1190 g/mol was used, which was less rigid and brittle (Figure 7.3B, brittle foams cracked when mechanically bent). Increasing the molecular weight further to MW ~2570 g/mol, such as in foam **3**, led to materials that were more ductile and flexible in nature, and capable of undergoing repeat compressions without any cracking or tearing (Figure 7.3C). If, however, the size of the starting H-PDMS-H was significantly increased, such as in **4** (MW = 5000 g/mol), foams were not produced at all. Instead, virtually bubble free elastomers resulted (Figure 7.3D, Table 7.1, 9.5-Appendix V). Thus, one can tune the properties of the prepared foamed elastomer, depending on the particular application, by simply varying the molecular weight of the starting hydrosilane. This also allows one to prepare bubble free silicone elastomers.

The effect of the molecular weight of the starting H-PDMS-H on the induction or total times of foam generation was marginal. For example, when lower molecular weight H-PDMS-H (730 g/mol) was used **1**, the induction time was 13.1 ± 1.2 s, with a total reaction time of 33.6 ± 0.9 s. When H-PDMS-H with a molecular weight of 1190 g/mol was used **2**, the induction time the reaction increased only to 21.6 ± 5.7 s with a total reaction time of 32.2 ± 2.8 s. Further increasing the H-PDMS-H molecular weight to ~2570 g/mol **3** led to an induction time of 16.1 ± 0.7 s, and a total reaction time of 18.1± 1.9s.

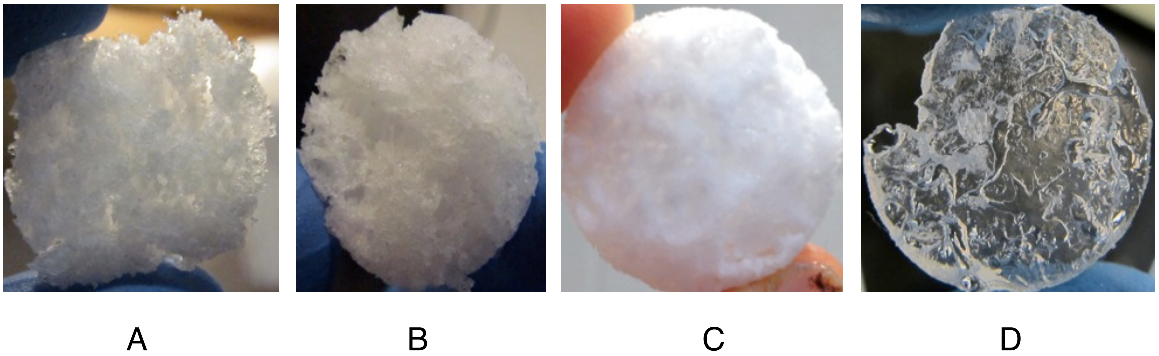


Figure 7.3 Effect of varying starting H-PDMS-H (molecular weight), while keeping all other variables constant. A: (**1**, 730), B: (**2**, 1190), C: (**3**, 2570), D: (**4**, 5000 g/mol), respectively.

7.4.2 Effect of the starting crosslinker

The nature of the starting crosslinker had a dramatic effect on the rate of the foaming process and the resulting morphology. The rate of the Piers-Rubinsztajn reaction is affected by the steric demand of the hydrosilane which is invariant in the experiments described here, the concentrations of reagents and, most importantly, the steric demand of the alkoxysilane[16,18]. As the cross-linker was changed from unhindered alkoxysilanes such as $Si(OMe)_4$ to $Si(OEt)_4$ and then to the more sterically congested centers in $Si(O\text{-}nPr)_4$, the reactions occurred more slowly, the resulting silicone foams had larger bubbles, foams were usually lower in density, became more open celled structures and were more brittle (Figure 7.4A-C). There was a larger exotherm in the reactions that exploited $Si(OMe)_4$, when compared to those using $Si(OEt)_4$ or $Si(O\text{-}nPr)_4$.

When a more reactive crosslinker such as $Si(OMe)_4$ was used to prepare silicone foams, regardless of the starting H-PDMS-H molecular weight, both induction times and times for reaction completion were short, usually occurring in less than a minute with a noticeable exotherm. In these cases, it was expected that the low solubility of generated methane gas in silicone fluid[22-25] coupled with a larger thermal spike due to the highly exothermic nature of the reaction when $Si(OMe)_4$ is used as a crosslinker, and rapid build in viscosity during elastomer cure, would preclude significant coalescence or departure of the methane gas bubbles: closed cell silicone foams with small cell sizes result (Figure 7.4A, Table 7.1 entry **5**, 9.5- Appendix V, 7 examples).

The use of $Si(OEt)_4$ as the crosslinker was accompanied by increased induction and total reaction times: the resulting foams were produced in less than 2.5 min (Table 7.1 entry **6**, 9.5- Appendix V 7 examples) with a slightly lower exotherm. The increase in reaction time apparently gave bubbles more time to coalesce before being locked into the elastomeric matrix. Bubble sizes as judged by optical microscopy for a given formulation, and which differed only in the type of crosslinker used, were about two times larger when $Si(OEt)_4$ rather than $Si(OMe)_4$ was used (Figure 7.4B).

Changing the crosslinker to $Si(O\text{-}nPr)_4$ further enhanced these effects. The resulting reaction mixtures exhibited substantially longer induction times that averaged around 1.5 min and total reaction times about 3-3.5 min. Cell sizes were also significantly larger (about 2.5 times larger than when $Si(OMe)_4$ was used as crosslinker, Table 7.1 entry **7**, 9.5 Appendix V, 7 examples) as a consequence of greater opportunity for bubble coalescence over longer time periods. Loss of the alkane by dissolution in the silicone during cure may also play a role, as is discussed below.

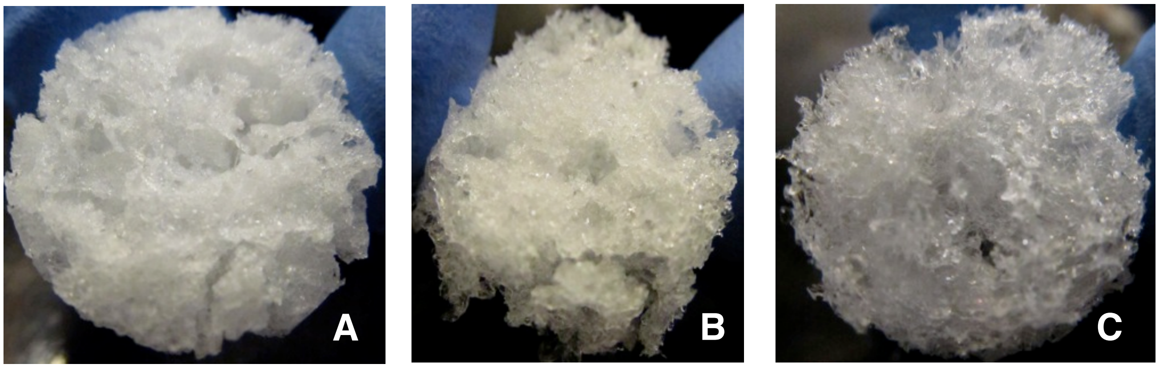


Figure 7.4. Effect of altering the crosslinker in the preparation of silicone foams. A: Crosslinker - TMOS **5**, B: Crosslinker - TEOS **6**, C: Crosslinker - TPOS **7**. Increasing the steric bulk at the alkoxysilane results in silicone foams with larger cell sizes and lower densities.

7.4.3 Effect of the $(RO)_4Si$:H-PDMS-H ratio

The ratio between H-PDMS-H and $Si(OR)_4$ was shown to be a significant factor in both the reaction process and characteristics of the resulting silicone foams. At a SiOR:SiH ratio of 0.5:1, the silicone products were viscous silicone liquids, regardless of the molecular weight of the starting H-PDMS-H and irrespective of the alkoxysilane crosslinker used (9.5-Appendix V). Presumably, on average, non-crosslinked stars form ($Si(O\text{-}PDMS\text{-}H)_4$).

When the SiOR:SiH ratio was changed to 1:1, fairly brittle foams resulted when H-PDMS-H with a molecular weight of 730 g/mol was used. Increasing the molecular weight to 1190 g/mol at this same SiOR:SiH ratio yielded more ductile foams (cf., MW 730, **5**; MW 1190, **8**, Table **1**). However, when the starting H-PDMS-H molecular weight was of even higher MW, ~2500 g/mol **9**, very flexible and robust foams were formed[21]. This is to be expected: foam brittleness can be overcome simply by increasing the molecular weight of the H-PDMS-H - the distance between crosslink sites - at a constant SiOR:SiH ratio[26].

Further increasing the SiOR:SiH ratio to 1.5:1 or 2:1 produced more ductile foams that were also more robust than foams formed with lower amounts of crosslinker: an increase in crosslinker concentration to this range results in fewer crosslink sites, ultimately leading to more elastomeric, less resinous and less brittle materials (Figure 7.5). This was especially evident in foams produced starting from H-PDMS-H with molecular weight of 730 g/mol (**1** - $Si(OMe)_4$:H-PDMS-H = 1.5:1 **10** - $Si(OMe)_4$:H-PDMS-H = 2:1); as the degree of crosslinking decreased, the more flexible the foams became. It should be noted that although very flexible foams were prepared with a SiOR:SiH ratio of 2:1 with a starting H-PDMS-H molecular weight of ~2500 g/mol, foams **11** and **12** remained slightly tacky even after curing. This can be attributed to the relatively large distance between crosslinks at higher SiOR:SiH ratios and to dangling unreacted polymer chains.

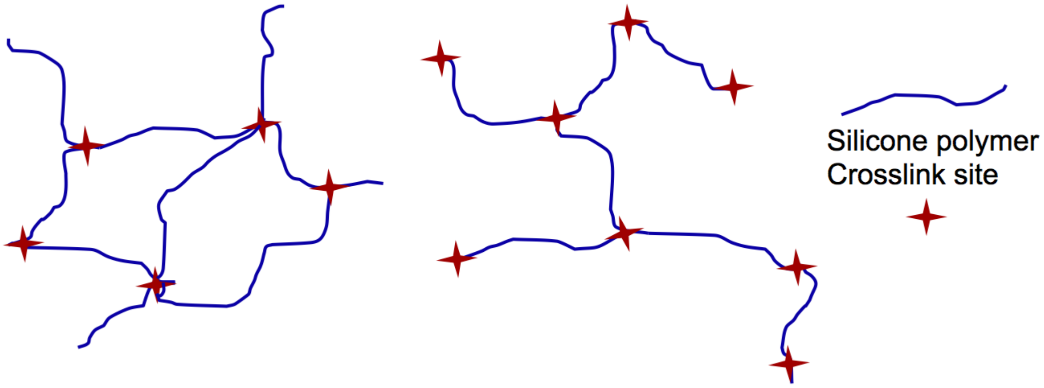


Figure 7.5. Crosslink density changes with an increase in the concentration of alkoxy crosslinker (TMOS). (A) shows a ratio of 1:1 SiOR:SiH, (B) shows a ratio of 2:1, fewer cross-links create a softer silicone foam.

7.4.4 Varying the hexane content of silicone Foam formulations

The foams described above were synthesized using hexane (1 ml in a total formulation of ~2 g) to facilitate reagent miscibility, to aid in the preparation of uniform silicone foams, and to also act as a blowing agent. As shown in previous studies[15-18], the Piers-Rubinsztajn reaction is highly exothermic and, in the current reaction, particularly with $Si(OMe)_4$ as crosslinker, can result in fairly high reaction temperatures (> 60°C). The addition of hexane into the formulations acts as a heat sink. As a consequence, however, in addition to the volatile organic byproducts released from the reaction, the hexane can act as a blowing agent (if its boiling point of 68°C is surpassed) depending on the reaction conditions used. Although the use of hexane has largely been beneficial in preparing uniform foams, it was of interest to determine if foams could also be produced from lower

VOC formulations that did not benefit from the added blowing effect from the hexane (Table 7.1, 9.5- Appendix V).

The impact of hexane on the foaming process was readily seen using $Si(OMe)_4$ and H-PDMS-H MW 1190 g/mol prepared with various amounts of hexane: **13n** (0 ml), **18** (0.5 ml), **8** (1 ml), **19** (2.0 ml) (Figure 7.6A). Typical induction times for solvent free reactions were fairly consistent with the silicone foams prepared with hexane, regardless of the crosslinker used. Overall reaction times noted for foams that used $Si(OMe)_4$ as a crosslinker were also similar whether or not hexane was present (**8** 23.7 ± 1.6 v. **13n** 19.6 ± 1.9 s). By contrast, slightly longer reaction times were observed in the absence of hexane when more sterically congested crosslinkers were used, using formulations containing H-PDMS- H MW of 1192 g/mol with a SiOR:Si-H ratio of 1:1 (TPOS: **15n** 204 ± 34 v. **7** 75.7 ± 7.9s).

As noted, when a sufficiently strong exotherm occurs, hexane can also act as a blowing agent. In the absence of hexane, therefore, higher density foams resulted. For example, **8** has a density of 0.17 ± 0.02 g/cm^3, compared to its solvent free analog **13n**, with a density of 0.34 ± 0.03 g/cm^3. It is also evident that, in the absence of hexane, foams were comprised of smaller pore sizes, and a larger fraction of closed cells (**8** v. **13n**, Figure 7.7). As the concentration of VOCs is increased further in the silicone formulations, more porous, less dense silicone foams result.

General trends for silicone foam densities were similar whether or not hexane was present. For example, foams prepared with formulations containing H-PDMS-H MW of 1190 g/mol and Si(OR):H-PDMS-H ratio's of 1:1, had densities decrease from 0.34 ± 0.03 g/cm^3, to 0.31 ± 0.01 g/cm^3 and 0.21 ± 0.02 g/cm^3 for **13n** ($Si(OMe)_4$), **14n** ($Si(OEt)_4$) and **15n** ($Si(O\text{-}nPr)_4$, respectively. These may be compared to the hexane-containing formulations: **8** 0.17 ± 0.02 g/cm^3 (Si(OMe)4), **16** 0.13 ± 0.01 g/cm^3 ($Si(OEt)_4$) and **17** 0.15 ± 0.03 g/cm^3 ($Si(O\text{-}nPr)_4$, respectively. These observations can be ascribed to faster elastomer crosslinking with less sterically congested crosslinkers giving to smaller bubble sizes, more bubbles, and ultimately lower density silicone foams.

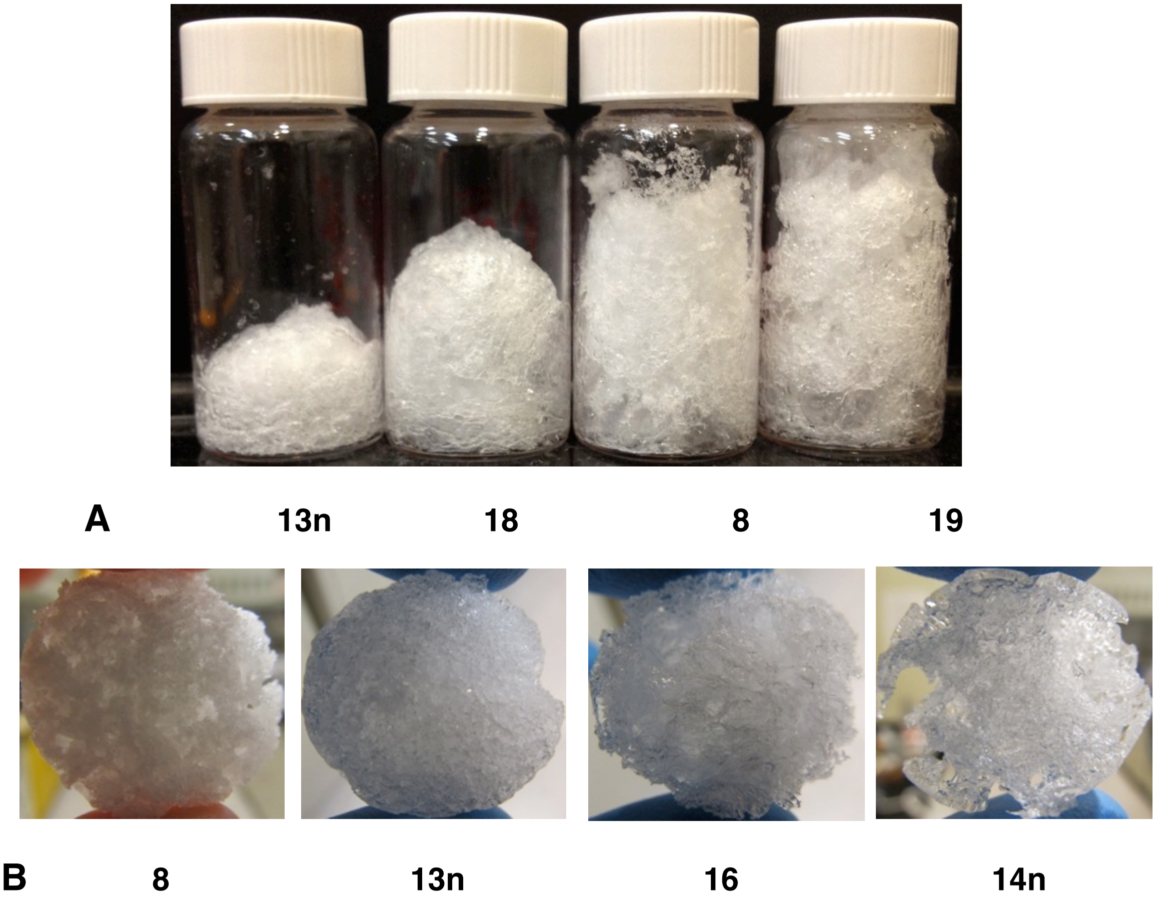


Figure 7.6 A: Comparison of foam formulations prepared with four different hexane concentrations (0, 0.5, 1, 2 ml/formulation). B: Comparison of foams created with $Si(OMe)_4$ **8**, and without, **13n** solvent, visually showing a decrease in cell size and an increase in density. Analogous formulation prepared from $Si(OEt)_4$ with, **16** and without, **14n** hexane show the use of more sterically hindered crosslinkers in solvent free conditions leads to less uniform silicone foams.

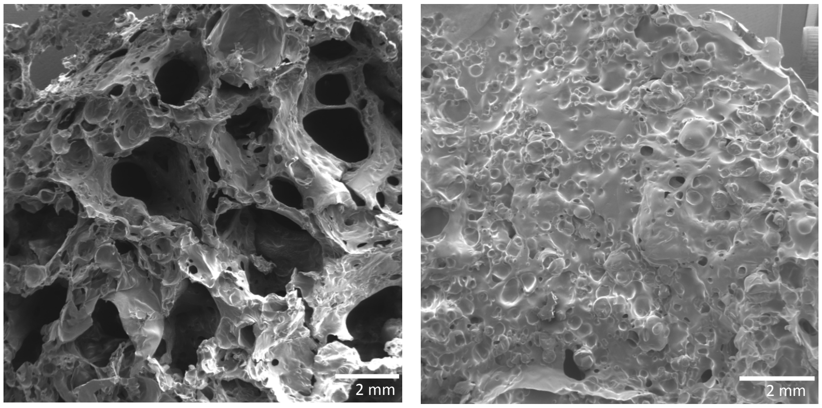


Figure 7.7. SEM images of the surface of foams **8** and **13n**, respectively. Compound **8** shows generally larger pore sizes compared with solvent free analogue **13n**.

It was not possible to prepare high quality foams when the more sterically congested alkoxysilane crosslinkers $Si(OEt)_4$ and $Si(O\text{-}nPr)_4$ were used in the absence of hexane. The foams typically exhibited more open cells and, in some cases, contained large voids: there was sufficient time for the volatile byproducts (ethane, propane) to coalesce into larger bubbles, but insufficient time for the majority of the bubbles to leave the matrix before being trapped by cure. With either crosslinker, silicone foams prepared in the absence of solvent were not as uniform as those prepared with solvent. For example, **16** is a uniform foam while its solvent free analog **14n** (H-PDMS-H - 1192 g/mol, Si(OR):Si-H 1:1, crosslinker - $Si(OEt)_4$) contains small areas of elastomer that have no bubbles (Figure 7.6B). This could be due to a higher initial viscosity in the formulation when solvent is not present, resulting in less efficient mixing and non-uniform foams. More likely, however, the higher solubility's of the evolving gases (ethane, propane vs.

methane)[3,22-24] in silicone provide a different mechanism by which gas bubbles can be lost from the system: they dissolve into the surrounding matrix or, through Ostwald ripening[27], large bubbles increase in size at the expense of smaller bubbles.

The Piers-Rubinsztajn reaction provides several elements to manipulate the formation of foamed structures. Factors that accelerate the kinetics of gas evolution and cure process, including more reactive crosslinkers and use of shorter silicone chains (thus higher [SiH] in the medium), were associated with a higher concentration of small bubbles. By contrast, the use of less reactive crosslinkers and/or longer silicone chains (~5000 g/mol) did not result in foams at all or, in the best cases, very tacky open celled structures.

The key factors to be considered when choosing the brittleness/flexibility of the prepared foams are the H-PDMS-H MW, and the SiOR:SiH ratio: the former is most important. Shorter chain lengths (e.g., H-PDMS-H MW 730 g/mol) result in higher crosslink density, ultimately giving more brittle foams. By lengthening the H-PDMS- H chain, the crosslink density decreases, leading first to more rigid (H-PDMS-H MW 1190 g/mol), and ultimately more flexible and ductile (H-PDMS-H MW 2500 g/mol) silicone foams.

Crosslink density can also be controlled through the manipulation of the SiOR:SiH ratio, and by alteration of the starting H-PDMS-H molecular weight. For example, when the molecular weight of the H-PDMS-H is kept at 730 g/mol and the crosslinker ratio is varied, significant differences in foam structures arise. A ratio of 0.5:1 (Si(OR):SiH) led to no silicone foam generation, and resulted in a viscous silicone liquid. Increasing this ratio to 1:1, allows for a very high crosslink density, ultimately yielding very brittle and ridged foams. Further increasing this ratio to 1.5:1 and then ultimately 2:1, leads to more ductile/flexible materials capable of undergoing repeat compressions without cracking or tearing, because there is a balance between increased crosslinks, and the increasing number dangling polymer chains at higher crosslinker concentrations. These effects of altering the crosslink density by varying the SiOR:SiH ratio hold true for each of the molecular weights used. That is, for each of the given ratios, increasing the molecular weight of the starting H-PDMS-H leads to a decrease in the hardness of the foams (more flexible materials are obtained).

In addition to manipulating the mechanical properties of the prepared silicone foams, one can easily control foam density by addition of solvent, alteration of the H-PDMS-H molecular weight and changing the reactivity of the crosslinker by using crosslinkers with different sterics. However, the interplay between factors to control density is somewhat more complicated than other parameters. Factors that permit evolved gas to escape from the matrix lead to densification. These include physical escape because gas bubbles are generated and escape faster than being trapped by cure; coalescence of bubbles will change overall density when they located near an external matrix interface and break; and, finally, gas solubility and diffusion from the matrix is more efficient for the alkane byproduct propane > ethane > methane.

In general, although there are exceptions (Table 7.1), higher density foams are achieved through formulations containing less solvent, larger molecular weight H-PDMS-H and less sterically hindered (more reactive e.g., TMOS v TPOS) crosslinkers that react more rapidly, which quickly increases the viscosity of the formulation during cure. High reactivity and low foam expansion result in fairly dense materials. The observed hardness generally tracks with density, but is also affected by the average cell sizes and crosslink density. Gradual increases in both solvent concentration and crosslinker sterics ($Si(OEt)_4$ and $Si(O\text{-}nPr)_4$) normally lead to less dense silicone foams.

Cell size is also an important characteristic of silicone foams. Bubble size can be readily manipulated through crosslinker sterics and solvent effects. The cell size is understood to be related to two factors, the speed at which the reaction progresses, and the relative permeability of the volatile gaseous byproducts in the forming silicone elastomer. In general, the less sterically hindered the alkoxysilane crosslinker, the faster the reaction $Si(OMe)_4 > Si(OEt)_4 > Si(OPr)_4$. At higher cure rates, the elastomeric network forms so rapidly that the gaseous byproducts are trapped in high density as small bubbles; there is insufficient time to migrate through the network or coalesce to form larger bubbles. Alternatively, if the reaction kinetics are suppressed, through use of more sterically congested crosslinkers (TEOS, TPOS), the elastomer network forms more slowly, allowing more bubbles to slowly coalesce, leading to larger cell sizes. Ostwald ripening[27] of bubbles based on the silicone soluble ethane/propane byproducts of the latter two crosslinkers provides another mechanism for bubbles to increase in size. As shown in previous studies, condensable gases in silicone polymers that are elastomeric in nature permeate more readily compared to smaller non-condensable gases[23,24].

Finding formulations that lead solely to open or closed cell silicone foams has been rather challenging. In most cases, silicone foams are produced with both a mixture of open and closed cells. However, it has been determined that if the solvent (hexane) concentration is reduced, and a reactive crosslinker such as TMOS is used, one can produce primarily closed cell silicone foam formulations (Figure 7.6B). With less blowing agent, a more densely packed material results. This coupled with the lower permeability of methane through the forming silicone network[22-24], leads to the formation of densely packed, primarily closed cell foams.

The final silicone foam structure, when prepared using the Piers-Rubinsztajn reaction, is readily manipulated by controlling a variety of factors. The first step of foam formation is the initial bubble nucleation, which is controlled by adjusting the rate of gas evolution (crosslinker reactivity). Once the system begins crosslinking the viscosity increases proportionally - diminishing the ability of the nucleated bubbles to move through the elastomeric system. The amount of bubble coalescence then becomes proportional to the viscosity, which is controlled by the crosslink site concentration (the number of crosslink sites per/siloxane unit can be changed with H-PDMS-H MW and the ratio of SiOR:SiH), and to the ability of gases to dissolve into and migrate through the silicone matrix. The final step of foam formation occurs when the elastomeric portion has crosslinked to such an extent that the bubbles can no longer effectively migrate.

Two methods are traditionally used to blow silicone foams. First, foaming agents that play no part in the reaction are used which are activated by various means such as heat. Second, as in the case of most silicone foams, hydrogen gas is released as the result of a competitive reaction to crosslinking via hydrosilylation[3,6,7,10,13,14]. In this case, two separate reactions with two rate constants compete for the same SiH groups. While this process is very efficient, adventitious water or other agents often distort the process by favoring foaming at the expense of crosslinking and compromise reproducibility.

The Piers-Rubinsztajn process for foams avoids the challenges that occur with traditional forming strategies. It is possible to manipulate the outcome of a single process, in which both the blowing agent and crosslinking process occurs, in spite of the fact that a single reaction is required for both bubble generation and crosslinking. Within the process it is straightforward to control bubble nucleation, coalescence and trapping following simple formulation rules. The final foam structure can have a high or low bubble density, which can be further manipulated by the addition of excess blowing agent (hexane) that lowers the viscosity during initial foaming, but nearing the end of the reaction provides an extra source of bubbles before the final elastomer cure. The final mechanical properties of the foam can be controlled using crosslink density.

7.5 Conclusion

A new method has been developed for the preparation of silicone foams. Commercial hydrogen-terminated silicones can be cross-linked in varying ratios using $Si(OR)_4$, where R = Me, Et, Pr. By varying starting molecular weight of H-PDMS-H, changing the crosslink density and crosslinker/H-PDMS-H ratio, or by controlling solvent effects, the gaseous byproducts can be trapped in the silicone matrix generating foams with varying densities, rigidity, tackiness/brittleness and open or closed cell structure. The process avoids challenges in traditional methods with adventitious water, and generates foams rapidly and in high yield.

7.6 Acknowledgements

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada. J.B.G and A.S.F would also like to thank NSERC for a PGS-D and CGS-D scholarship, respectively.

7.7 References

1. M. B. Malla, M. R. Shrestha, M. T. Shaw and S. B. Brijmohan *J. Mater. Civil. Eng.*, 2011, **23**, 287-97.
2. R. B. Malla, B. J. Swanson and M. T. Shaw, *Constr. Build. Mater.,* 2011, **25** (11), 4132-43.
3. J. J. Chruscie and E. Lesniak, *J. of Appl. Polym. Sci.*, 2011, **119** (3), 1696-703.
4. A. S. Fawcett, H. Y. So and M. A. Brook, *Soft Matter.,* 2010, **6** (6), 1229-37.
5. Mustoe TA. *Aesthet. Plast, Surg.,* 2008, **32**, 82-92.
6. C. L. Lee, R. G. Niemi and K. M. Kelly, *J. Cell. Plast.*, 1977, **13** (62), 62-7.
7. W. J. Noll In *Chemistry and Technology of Silicones*. New York: Academic Press; 1968.
8. C. A. Berridge, *Spongeable Polysiloxane Composition and Process of Producing Sponge Therefrom*. US 2857343: General Electric, 1958.
9. C. A. Berridge, *Preparation of Sponge Rubber From High Temperature Mixed Silicone Rubber-Silica Composition*. US 2875163: General Electric, 1959.
10. K. R. Hoffman, *Siloxane Structural Foams*. US 2655485: Dow Corning, 1953.
11. R. C. Wade and P. L. Blanchard, *Polymer Compositions Comprising an Alkali Metalborohydride and Stearic Acid and Preparation of Cellular Rubber-Like Articles Therefrom.* US 2951819: Metal Hydrides Inc., 1960.
12. F. J. Modic, *Foamable Organopolysiloxane Composition and Foamed Product Obtained Therefrom*. US 3425967: General Electric Company, 1969.
13. T. Wada, K. Itoh and N. Kuga, *Silicone Elastomeric Compositions and a Method for Preparing Silicone Sponge Rubbers Therefrom*. US 3425967: Shinetsu Chemical Company, 1972.
14. M. A. Brook in *Silicon in Organic, Organometallic, and Polymer Chemistry*. New York: Wiley; 2000.

15. M. A. Brook, J. B. Grande and F. Ganachaud, *Adv. Polym. Sci.*, 2010, **235**, 161-83.

16. J. B. Grande, F. Gonzaga and M. A. Brook, *Dalton Trans,* 2010, **39** (39), 9369-78.

17. J. B. Grande, D. B. Thompson, F. Gonzaga and M. A. Brook, *Chem. Commun.*, 2010, **46** (27), 4988-90.

18. D. B. Thompson and M.A. Brook, *J. Am. Chem. Soc.*, 2008, **130** (1), 32-3.

19. L. H. Sperling in *Introduction to Physical Polymer Science*. 4th ed. New York: Wiley-Interscience; 2005.

20. J. E. Mark and B. Erman, *Polymer Networks: Elastomers.* In: J. Chalmers, R. Meier editors. Molecular characterization and analysis of polymers. 1st ed, vol. **53**. Elsevier Science; 2008. p. 337-83.

21. M. A. Sharaf, J. E. Mark and E. Ahmed, *Colloid Polym. Sci.,* 1994, **272**, 504-15.

22. I. G. Economou, Z. A. Makrodimitri, G. M. Kontogeorgis and A. Tihic, *Mol. Simulat.*, 2007, **33**, 851-60.

23. T.C. Merkel, V.I. Bandar, K. Nagal, B.D. Freeman and I. Pinnau *J. Polym. Sci. Pol. Phys.,* 2000, **38**, 415-34.

24. I. Pinnau and Z. He, *J. Membrane. Sci.*, 2004, **244**, 227-33.

25. We thank a referee for this suggestion.

26. J. R. Falender, G. S. Y. Yeh and J. E. Mark *J. Am. Chem. Soc.*, 1979, **101**, 7353-6.

27. S. Tcholakova, Z. Mitrinova, K. Golemanov, N. D. Denkov, M. Vethamuthu and K. P. Ananthapadmanabhan, *Langmuir,* 2011, **27**, 14807-19.

Chapter 8: General Conclusions

Silicones possess unparalleled properties compared to their carbon-based analogues, which make them advantageous in many industrial applications. Nonetheless, the sensitivity of the siloxane bond to both acidic and basic environments translates to working with ill defined, largely polydisperse materials; primarily because reliable methods to prepare well-defined silicones simply do not exist. By taking advantage of the unique capacity for $B(C_6F_5)_3$ to activate hydrosilanes, the Piers-Rubinsztajn reaction avoids conditions which can lead to silicone degradation; providing a new method to prepare explicit, siloxane-based materials.

In Chapter 2 of this thesis, the functional tolerance of the Piers-Rubinsztajn (PR) reaction is reported. It has been shown that Lewis basic functional groups such as amines and alcohols tend to shutdown the PR reaction, presumably complexing with the catalyst. The reaction, however, has shown to be functionally tolerant to either halocarbons or alkenes, providing a novel method to prepare over tewnty, well-defined functional silicones bearing either single or multiple functional groups. It should be noted that in the presence of a low concentration of $B(C_6F_5)_3$ hydrosilylation of alkenes is not observed.

In Chapter 3, previously prepared halocarbon containing functional silicones, described in Chapter 2 are subjected to nucleophillic substitution with sodium azide; ensuring that through common organic transformations, the structural integrity of the well-defnined silicone backbones can be preserved. Azido-derivatives were then “clicked”, via a [3+2] cycloaddition to alkyne modified poly(oxyethylene) (PEO) of varying molecular weights, providing a novel method to synthesize well-defined silicone surfactants. It was shown that through subtle manipulations of the silicone hydrophobe, substantial differences in the overall properties of the surfactants can be achieved – a first of its kind.

Chapter 4 of this thesis follows an analogous approach to that of Chapter 3 in which the goal is to develop new routes to silicone based surfactants. Prepared well-defined alkene containing silicones were subjected to thiol-ene reaction conditions in the presence of thiol-modified poly(oxyethylene) (PEO) of various molecular weights. It was demonstrated that this process is both highly effective and readily preserves the structural integrity of the silicone hydrophobe. The process was also readily adapted to prepare bola- or star-shaped amphiphiles.

In Chapter 5, attention is turned to understanding if the Piers-Rubinsztajn reaction can serve as an effective route to silicone-based dendrimers. It was shown that in conjunction with platinum catalyzed hydrosilylation, a divergent dendrimer growth method could be employed, allowing for the synthesis of G1-type dendrimers with MW averaging around 5000 g/mol. Through a combination of both a convergent and divergent dendrimer growth approach, G2 type dendrimers with MW’s as large as 10,000 g/mol were readily prepared. The process was adaptable to multifunctional cores, and allowed for the preparation of moderately sized silicone dendrons bearing reactive chloro focal points.

Chapter 6 and Chapter 7 of this thesis slightly stray from the preparation of well-defined silicones, and begin to show the versatility of the Piers-Rubinsztajn reaction as a novel, highly effective method to rapidly prepare both silicone elastomers and silicone foams. Parameters that alter crosslink density, reaction speed, dilution etc., were examined and showed that the Piers-Rubinsztajn reaction provides a viable route to prepare silicone elastomers. By taking advantage of the reaction's volatile hydrocarbon based byproducts, which can serve as an "internal" blowing agent, silicone foams were also synthesized using a similar strategy. By simply reducing the molecular weight of the starting hydride terminated polydimethylsiloxane (H-PDMS-H) foams with varying density were rapidly synthesized.

The results discussed in this thesis describe novel methods to prepare well-defined, functional silicones. Using this technology, understanding how silicones' shape, size or structure can ultimately affect their overall properties can now be realized. Future work will continue to build on this process, with hopes of further developing the Piers-Rubinsztajn reaction for the preparation of new, more advanced, silicone based materials.

Chapter 9: Appendix

9.1 Appendix I - Supporting information for Chapter 3: Morphology-Controlled Synthesis of Poly(oxyethylene)silicone or Alkylsilicone Surfactants with Explicit, Atomically Defined, Branched, Hydrophobic Tails

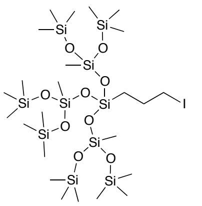
Experimental Section

Instrumentation. ^{1}H NMR, ^{13}C NMR and ^{29}Si NMR experiments were recorded at room temperature and performed on Bruker Avance 200, 500 or 600 MHz nuclear magnetic resonance spectrometers, respectively. Coupling constants (*J*) are recorded in Hertz (Hz). The abbreviations s = singlet, d = doublet, t = triplet, dd = doublet of doublets, m = multiplet, are used in reporting the spectra. High-resolution MS Spectrometry was performed with a Hi-Resolution Waters/Micromass Quattro Global Ultima (Q-TOF mass spectrometer). Critical Micelle Concentrations were recorded using a Kruss Drop shape analysis system DSA 10.

Materials. Iodopropyltrimethoxysilane, allyldimethylsilane, pentamethyldisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, chloropropyl-tris(trimethylsiloxy)silane were purchased from Gelest and used as received. Propiolic acid (95%), poly(ethylene glycol) methyl ether (average molecular weights of 350, 750 and 2000), p-toluenesulfonic acid (98%), chromium (III) acetylacetonate, anhydrous dimethylformamide, sodium azide and tris(pentafluorophenyl)borane (95%) were purchased from Aldrich and used as received. Commercial solvents: hexanes, dichloromethane and toluene were dried over activated alumina prior to use. All syntheses were carried out in dry apparatus under a dry nitrogen atmosphere utilizing conventional bench-top techniques. Water was purified by a Millipore purification system (resistance = 18.1 MΩ.cm).

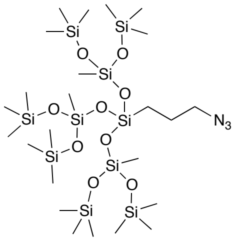
Synthesis of functional silicones and alkyl-silanes

(**3-Iodopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane 1-I**



To a solution of iodopropyltrimethoxysilane (2.5 g, 8.6 mmol) in dry hexane (15 mL), was added 1,1,1,3,5,5,5-heptamethyltrisiloxane (8.62 g, 38.8 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μL of a solution containing 40 mg dissolved in 1 mL of toluene, 1.95×10^{-3} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-iodopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (6.06 g, 77.4% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.18 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}I$, *J* = 7.2 Hz), 1.90-1.97 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 0.62-0.66 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.11 (s, 54H, $OSi(C\mathbf{H_3})_3$), 0.05 ppm (s, 9H, $O_2SiC\mathbf{H_3}$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 28.03, 16.40, 10.59, 1.93, -1.90 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.31 (M), -66.52 (T), -72.77 (T) ppm. HRMS (ES Positive mode): m/z [$M+NH_4^+$] calc. = 926.2023, found = 926.2032.

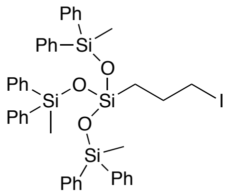
(3-Azidopropyl)tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane 1-N_3



To a 10 mL round bottom flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(1,1,1,3,5,5,5-hetpamethyltrisiloxy)silane (1.00 g, 1.10 mmol) in anhydrous DMF (2 mL). To the solution was added sodium azide (0.14 g, 2.18 mmol). The mixture was stirred 5 hours at 90 °C. Then, 40 mL of water and the desired product was extracted with 25 mL of hexanes. The aqueous layer was extracted three more times with hexanes (10 mL). The combined organic layers were dried over magnesium sulfate (10 g), filtered and concentrated under reduced pressure to afford pure 3a (0.78 g, 87% yield) as a pale yellow liquid.

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.23 (t, 2 H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ J = 7.2 Hz), 1.70-1.73 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 0.57-0.60 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.11 (s, 54 H, $OSi(C\mathbf{H_3})_3$), 0.06 ppm (s, 9 H, $(C\mathbf{H_3})SiO_3$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 53.68, 22.40, 10.89, 1.44, -2.54 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.81 (M), -66.01 (T), -71.28 ppm (T). HRMS (ES Positive mode): m/z [$M+NH_4^+$] calc. = 841.3070, found = 841.3041.

3-Iodopropyltri(methyldiphenylsiloxy)silane 2-I

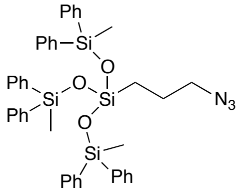


To a solution of iodopropyltrimethoxysilane (1.0 g, 3.45 mmol) in dry hexane

(10 mL), was added methyldiphenylsilane (3.07 g, 15.5 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μL of a solution containing 40 mg dissolved in 1 mL of toluene, 1.95 x 10^{-3} mmol). After a 6 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-iodopropyl)tris(diphenylmethylsiloxy)silane (2.18 g, 76% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.46-7.48 (m, 12H, phenyl), 7.38-7.41 (m, 6H, phenyl,), 7.25-7.29 (m, 12H, phenyl), 2.89 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}I$ *J* = 7.0 Hz), 1.59-1.64 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 0.54-0.55 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.52 ppm (s, 9H, $OSi(C\mathbf{H_3})(C_6H_5)_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 137.21, 134.11, 129.76, 127.89, 27.83, 16.29, 10.77, -0.84 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -11.48 (M), -67.51 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 854.1834, found = 854.1863.

3-Azidopropyltri(methyldiphenylsiloxy)silane 2-N_3



To a 10 mL round-bottomed flask equipped with a magnetic stir bar was added a solution of 3-iodopropyltris(methyldiphenylsiloxy)silane **6a** (1.55 g, 1.85 mmol) in anhydrous DMF (3 mL). Then, sodium azide (0.24 g, 3.70 mmol) was added. The mixture was stirred 24 h at 55 °C. The reaction was monitored by proton NMR: once full substitution of the iodo group was achieved, the solution was cooled to room temperature, and 20 mL of water was added. The desired product was then extracted with 25 mL of hexanes, and the water phase extracted again with 3 x 10 mL of hexanes. The organic layers were combined and dried over sodium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure (without heating) to yield pure 3-azidopropyltris(tridimethylphenylsiloxy)silane (1.19 g, 85% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.35-7.37 (m, 12H, phenyl), 7.26-7.29 (m, 6H, phenyl), 7.15-7.18 (m, 12H, phenyl), 2.80 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ J = 6.3 Hz), 1.28-1.31 (m, 2H, $OSi(CH_3)_2CH_2C\mathbf{H_2}CH_2N_3$), 0.40 (s, 9H, $((C_6H_6)_2(C\mathbf{H_3})SiO)_3Si$), 0.35-0.37 ppm (m, 2H, $OSi(CH_3)_2C\mathbf{H_2}CH_2CH_2N_3$). ^{13}C NMR: δ ($CDCl_3$ 150 MHz) δ 137.20, 134.08, 129.75, 127.87, 53.79, 22.90, 11.68, -0.87 ppm; ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ -11.06 (M), -67.07 (T) ppm. LRMS (ES Positive mode): m/z $[M+NH_4]^+$ found = 769.4.

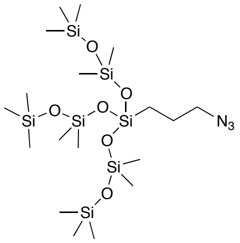
(3-Iodopropyl)tris(pentamethyldisiloxy)silane 3-I

To a solution of iodopropyltrimethoxysilane (3.0 g, 0.01 mol) in dry hexane (15 mL), was added pentamethyldisiloxane (7.66 g, 0.05 mol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μL of a solution containing 40 mg dissolved in 1 mL of toluene, 1.95 x 10^{-3} mmol). After a 1.5 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-iodopropyl)tris(penta-methyldisiloxy)silane (6.21 g, 87.5% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.20 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}I$, J = 7.0 Hz), 1.88-1.94 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 0.60-0.64 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.10 (s, 27H, $OSi(C\mathbf{H_3})_3$), 0.07 ppm (s, 18H, $O_2Si(C\mathbf{H_3})_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 28.22, 16.32, 10.82, 2.00, 1.29 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v

$Cr(acac)_3$): δ 7.05 (M), -21.89 (D), -71.08 (T) ppm. HRMS (ES Positive mode): m/z $[M]^+$ calc. = 687.1194, found = 687.1191.

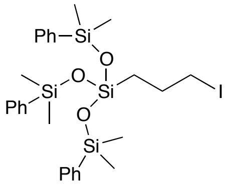
(3-Azidopropyl)tris(pentamethyldisiloxy)silane 3-N_3



To a 10 mL round-bottomed flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(pentamethyldisiloxy)silane (0.500 g, 0.72 mmol) in anhydrous DMF (2 mL). To the solution was added sodium azide (0.095 g, 1.45 mmol). The mixture was then allowed to stir for 5 h at 90 °C. To the mixture was added to 20 mL of water and the desired product was extracted with 25 mL of hexane. The aqueous layer was washed three times with hexane (10 mL) to ensure maximum product recovery. The organic layers were combined and dried over magnesium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure affording pure (3-azidopropyl)tris(penta-methyldisiloxy)silane (0.38 g, 88% yield).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 3.42 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ J = 7.0 Hz), 1.65-1.72 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 0.55-0.58 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.09 (s, 27H, $OSi(C\mathbf{H_3})_3$), 0.07 ppm (s, 18H, $(C\mathbf{H_3})_2SiO_2$). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 54.20, 23.19, 11.61, 1.96, 1.28 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.06 (M), -21.88 (D), -70.20 ppm (T). HRMS (ES Positive mode): m/z $[M+Na]^+$ calc. = 624.2061, found = 624.2064.

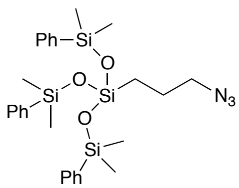
3-Iodopropyltris(dimethylphenylsiloxy)silane 4-I



To a solution of iodopropyltrimethoxysilane (2.0 g, 6.89 mmol) in dry hexane (10 mL), was added dimethylphenylsilane (4.23 g, 31.0 mmol). The mixture was stirred at room temperature for 5 min before the addition of $B(C_6F_5)_3$ (25 μL of a solution containing 40 mg dissolved in 1 mL of toluene, 1.95 x 10^{-3} mmol). After a 1 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated on a rotary evaporator. The remaining solvent and excess reagents were removed *in vacuo,* affording pure (3-iodopropyl)tris(dimethylphenylsiloxy)silane (3.70 g, 83 % yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.51-7.55 (m, 6H, phenyl), 7.32-7.40 (m, 9H, phenyl), 3.05 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}I$, *J* = 7.5 Hz), 1.71-1.77 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 0.55-0.58 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.32 ppm (s, 9H, $OSi(C\mathbf{H_3})(C_6H_5)_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.28, 133.15, 129.51, 127.86, 28.09, 16.22, 10.93, -0.64 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ -1.51 (M), -67.29 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 668.1365, found = 668.1391.

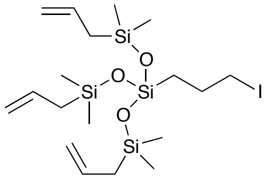
3-Azidopropyltris(dimethylphenylsiloxy)silane 4-N_3



To a 50 mL round-bottomed flask equipped with a magnetic stir bar was added a solution of 3-iodopropyltris(dimethylphenylsiloxy)silane **5a** (2.00 g, 3.08 mmol) in anhydrous DMF (5 mL). Then, sodium azide (0.40 g, 6.17 mmol) was added. The mixture was stirred 24 h at 55 °C. The reaction was monitored by proton NMR: once full substitution of the iodo group was achieved, the solution was cooled to room temperature, and 20 mL of water was added. The desired product was then extracted with 25 mL of hexanes, and the water phase extracted again with 3 x 10 mL of hexanes.. The organic layers were combined and dried over sodium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure (without heating) to yield pure 3-azidopropyltris(tridimethylphenylsiloxy)silane (1.41 g, 81.5 % yield).

^{1}H NMR (CDCl$_3$, 200 MHz): δ 7.48-7.53 (m, 6H, phenyl) 7.29-7.38 (m, 9H, phenyl), 3.04 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$, *J* = 7.1 Hz), 1.45-1.53 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 0.43-0.52 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.30 (s, 18H, $OSi(C\mathbf{H_3})_2(C_6H_5)$). ^{13}C NMR (CDCl$_3$ 125 MHz): δ 139.3, 133.1, 129.5, 127.9, 53.9, 23.1, 11.6, 0.62 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ -1.97 (M), -66.94 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 583.2412, found = 583.2407.

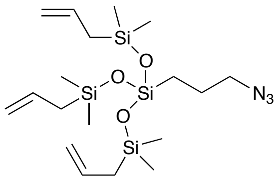
(3-Iodopropyl)tris(allyldimethylsiloxy)silane 5-I



To a solution of iodopropyltrimethoxysilane (1.0 g, 3.4 mmol) in dry hexane (10 mL) was added allyldimethylsilane (1.55 g, 15.5 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (40 μL of a prepared solution containing 40 mg dissolved in 1 mL of toluene, 3.1 x 10^{-3} mmol). After a 1 min, 45 second induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure iodopropyltris(allyldimethylsiloxy)silane (1.61 g, 86% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.79 (m, 3H, $OSi(CH_3)_2CH_2C\mathbf{H}CH_2$, *J* = 10.0 Hz), 4.86-4.91 (m, 6H, $OSi(CH_3)_2CH_2CHC\mathbf{H_2}$), 3.19 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}\mathbf{I}$, *J* = 7.5 Hz), 1.81-1.87 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2I$), 1.59 (d, 6H, $OSi(CH_3)_2C\mathbf{H_2}CHCH_2$, *J* = 10.0 Hz), 0.56-0.59 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2I$), 0.12 ppm (s, 18H, $OSi(C\mathbf{H_3})_2CH_2CHCH_2$); ^{13}C NMR: δ ($CDCl_3$ 125 MHz) δ 134.15, 113.82, 28.29, 26.25, 16.18, 10.99, -0.16 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 4.92 (M), -68.01 (T) ppm. HRMS (ES Positive mode): m/z $[M^+Na]^+$ calc. = 565.0919, found = 565.0917.

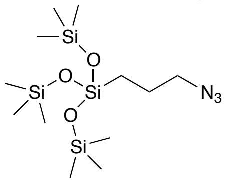
(3-Azidopropyl)tris(allyldimethylsiloxy)silane 5-N_3



To a 10 mL round-bottomed flask equipped with a magnetic stir bar was added a solution of (3-iodopropyl)tris(allyldimethylsiloxy)silane (1.0 g, 1.83 mmol) in anhydrous DMF (2 mL). To the solution was added sodium azide (0.24 g, 3.70 mmol). The mixture was stirred for 24 h at room temperature. Once full substitution was achieved, 20 mL of water was added to the mixture. The desired product was then extracted with 25 mL of hexanes. The aqueous layer was washed three more times with hexane (10 mL). The organic layers were combined and dried over sodium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure to afford pure (3-azidopropyl) tris(allyldimethylsiloxy)silane (0.78 g, 92.5% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.78 (m, 3H, $OSi(CH_3)_2CH_2C\mathbf{H}CH_2$, *J* = 10.0 Hz), 4.86-4.91 (m, 6 H, $OSi(CH_3)_2CH_2CHC\mathbf{H_2}$), 3.23 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$ *J* = 7.5 Hz), 1.61-1.66 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 1.59 (d, 6H, $OSi(CH_3)_2C\mathbf{H_2}CHCH_2$, *J* = 10.0 Hz), 0.50-0.57 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.12 ppm (s, 18H, $OSi(C\mathbf{H_3})_2CH_2CHCH_2$); ^{13}C NMR: δ ($CDCl_3$ 125 MHz) δ 134.13, 113.79, 54.07, 26.24, 23.29, 11.61, -0.19 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 4.92 (M), -67.21 (T) ppm. MS (ES Positive mode): m/z $[M^+K]^+$ calc. = 496.84, found = 496.3.

(3-Azidopropyl)tris(trimethylsiloxy)silane 6-N_3



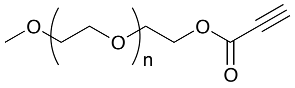
To a 50 mL round-bottomed flask equipped with a magnetic stir bar was added a solution of 3-chloropropyltris(trimethylsiloxy)silane (3.00 g, 8.03 mmol) in anhydrous DMF (4 mL). Then, sodium azide (1.04 g, 16.07 mmol) was added. The mixture was stirred for 48 h at 65 °C. The reaction was monitored by proton NMR: once full substitution of the chloro group was achieved, the solution was cooled to room temperature, and 20 mL of water was added. The desired product was then extracted with 25 mL of hexanes, and the water phase extracted again with 3 x 10 mL of hexanes. The organic layers were combined and dried over sodium sulfate (10 g). The resulting solution was filtered and concentrated under reduced pressure (without heating) to yield pure 3-azidopropyltris-(trimethylsiloxy)silane (2.67 g, 87.5% yield).

^{1}H NMR ($CDCl_3$, 500 MHz): δ 3.23 (t, 2H, $O_3SiCH_2CH_2C\mathbf{H_2}N_3$, *J* = 7.0 Hz), 1.62 (m, 2H, $O_3SiCH_2C\mathbf{H_2}CH_2N_3$), 0.50 (m, 2H, $O_3SiC\mathbf{H_2}CH_2CH_2N_3$), 0.10 ppm (s, 27H,

$(CH_3)_3SiO$). ^{13}C NMR: δ ($CDCl_3$ 125 MHz) δ 54.12, 23.33, 11.67, 1.86 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.49 (M), -67.20 (T) ppm. HRMS (ES Positive mode): m/z $[M^{+}Li]^{+}$ calc. = 386.1759, found = 386.1763.

Synthesis of mono-propiolate terminated poly(oxyethylene)s:

Propiolate-terminated monomethoxy poly(ethylene oxide) 7PEG-6

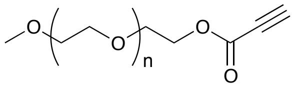


n~6

In a round-bottomed flask containing monomethoxypoly(ethylene-oxide) *(av. mol. wt: 350*) (7.00 g, 20.0 mmol), was successively added propiolic acid (4.20 g, 60.0 mmol), toluene (60 mL) and a catalytic amount of para-toluene sulfonic acid (0.50 g, 2.6 mmol). The flask was equipped with a Dean-Stark apparatus, and heated with azeotropic removal of water. Completion of the reaction was monitored by ^{1}H NMR, by comparison of the 3 protons of terminal methoxy with to the appearance of the methylenic esters protons at 4.32 ppm (*ca.* 20 h). The solution was then cooled to room temperature, and washed three times with 50 mL of an aqueous potassium carbonate solution. The organic phase was then dried over magnesium sulfate, concentrated *in vacuo*, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluant (up to 3%, v:v). The fractions containing the propiolate ester were combined, evaporated under reduced pressure to affording pure yellow propiolate terminated monomethoxy poly(ethylene oxide), (7.3 g, 91 % yield)

^{1}H NMR ($CDCl_3$, 200 MHz): δ 4.32 (t, 2H, $COOCH_2$, J = 4.6 Hz), 3.74 to 3.50 (m, 29H, OCH_2CH_2), 3.35 (s, 3H, OCH_3), 2.96 to 2.93 (m, 1H, $HCCCOO$). ^{13}C NMR ($CDCl_3$, 50 MHz): δ 75.44, 74.60, 71.99, 70.65, 68.62, 65.32, 59.12. HRMS (ES Positive mode): m/z $[M+NH_4]^{+}$ calc. = 410.2390, found = 410.2408.

Propiolate-terminated monomethoxy poly(ethylene oxide) 7PEG-15

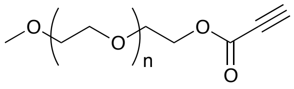


n~16

In a round-bottomed flask containing monomethoxypoly(ethylene-oxide) *(av. mol. wt: 750*) (15.0 g, 20.0 mmol), was successively added propiolic acid (4.2 g, 60.0 mmol), toluene (90 mL) and a catalytic amount of para-toluene sulfonic acid (0.5 g, 2.6 mmol). The flask was equipped with a DeanStark apparatus, and heated with azeotropic removal of water. Completion of the reaction was monitored by ^{1}H NMR, by comparison of the 3 protons of terminal methoxy with the appearance of the methylenic ester protons at 4.32 ppm (*ca.* 20 h). The solution was then cooled to room temperature, and washed three times with 50 mL of an aqueous potassium carbonate solution. The organic phase was then dried over magnesium sulfate, concentrated *in vacuo*, and the crude product directly loaded onto a chromatography column packed with silica gel. Elution started with pure dichloromethane, then increasing amounts of methanol were added to the eluant (up to 5%, v:v). The fractions containing the propiolate ester were combined, evaporated under reduced pressure to afford pure monopropiolate-terminated monomethoxy poly(ethylene oxide), (12.1 g, 77 % yield)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 4.34 (t, 2H, -COOCH_2-, J = 6.0 Hz), 3.74 to 3.55 (m, ~ 60H, -OCH_2CH_2O-), 3.37 (s, 3H, OCH_3), 2.89 (s, broad, 1H, *H*CCCOO). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.68, 75.67, 74.56, 71.94, 70.57, 68.57, 65.24, 59.03. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 806.4749, found = 806.4768.

Propiolate-terminated monomethoxy poly(ethylene oxide) 7PEG-44



n~44

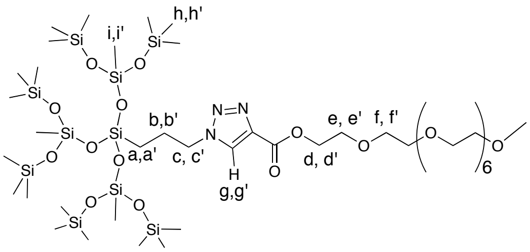
In a round-bottomed flask containing monomethoxypoly(ethylene-oxide) *(av. mol. wt: 2000*) (20.0 g, 10 mmol), was successively added propiolic acid (2.8 g, 40 mmol), toluene (70 mL) and a catalytic amount of para-toluene sulfonic acid (0.75g, 3.9 mmol). The flask was equipped with a Dean-Stark apparatus, and heated with azeotropic removal of water. Completion of the reaction was monitored by ^{1}H NMR, by comparison of the 3 protons of terminal methoxy with to the appearance of the methylenic ester protons at 4.27 ppm. Once the reaction was complete, the mixture was then concentrated in vacuo, and the crude product was dissolved in a minimal amount of dichloromethane. The mixture was then added drop wise to a beaker containing ice-cold diethylether (150 mL). Once completed, the mixture was allowed to stir for a further 20 min to ensure complete precipitation. The precipitate was then collected using a fritted funnel and dried under reduced pressure. The white powder was redissolved in DCM, and the precipitation procedure (drop by drop addition into ice-cold diethyl ether) was repeated. The precipitate was collected in a fritted funnel, dried under reduced pressure in a dessicator to afford the title compound (16.8g; 82%) as a white powder.

^{1}H NMR ($CDCl_3$, 500 MHz): δ 4.27 (t, 2H, -COOC*H*$_2$-, *J* = 5.0 Hz), 3.47 to 3.68 (m, ~ 233 H, -OC*H*$_2$C*H*$_2$O-), 3.31 (s, 3H, -OC*H*$_3$), 3.01 ppm (s, 1H, *H*CCCOO). ^{13}C NMR ($CDCl_3$, 125 MHz): δ 152.59, 75.62, 74.48, 71.88, 70.60, 68.50, 65.14, 58.97 ppm. HRMS (ES Positive mode): m/z $[M+H]^+$ calc. = 2065.2008, found = 2065.1916.

Synthesis of surfactants by metal-free Click chemistry:

Surfactant **8PEG-6**: was prepared according to the general procedure given in the Experimental section, from azide **1-N$_3$** (0.44 g, 0.53 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-6 (**0.16 g, 0.41 mmol; *average molecular weight calculated via ^{1}H NMR 382g/mol*)).

Yield: 0.39 g (79.0%), pale yellow oil.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

<u>Major isomer 1,4 (~75%)</u>

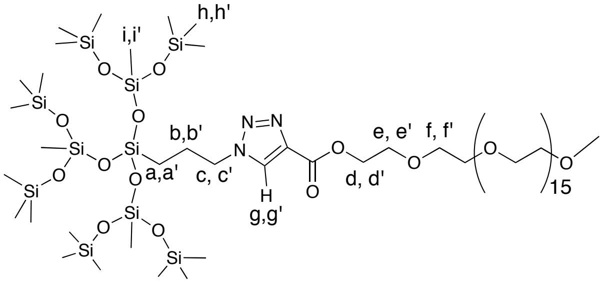
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.05 (s, 1 H, **g**), 4.49 (t, 2H, **d,** *J* = 5.4 Hz), 4.38 (t, 2H, **c,** *J* = 7.2 Hz), 3.83 (t, 2H, **e**, *J* = 5.4 Hz), 3.63-3.67 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.54 (t, 2H, **f**, *J* = 5.4 Hz), 3.37 (s, 3H, OC**H$_3$**), 2.01-2.06 (m, 2H, **b**), 0.54-0.58 (m, 2H, **a**), 0.084 (s, 54H, **h**), 0.047 ppm (s, 9H, **i**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 160.76, 139.80, 127.356, 72.04, 70.62-70.74, 69.04, 64.11, 59.13, 53.10, 24.50, 11.21, 1.88, -1.89 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.55 (M), -66.34 (T), -72.30 ppm (T). HRMS (ES Positive Mode): m/z [M+Na]$^+$ calc. = 1172.4565, found = 1172.4523. 3D HLB value = % Hydrophillic = (339.393/1254.67)*100 = 27.05%/5 = 5.41. % Oil = (137.151/1254.67)*100 = 10.93%/5 = 2.18)

<u>Minor Isomer 1,5 (~25%)</u>

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.12 (s, 1 H, **g'**), 4.69 (t, 2H, **c',** *J* = 7.0 Hz), 4.44 (t, 2H, **d',** *J* = 4.8 Hz**)**, 3.79 (t, 2H, **e'**, *J* = 4.8 Hz), 3.63-3.67 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.54 (t, 2H, **f'**, *J* = 5.4 Hz), 3.37 (s, 3H, OC**H$_3$**), 1.96-2.03 (m, 2H, **b'**), 0.54-0.58 (m, 2H, **a'**), 0.075 (s, 54H, **h'**), 0.031 ppm (s, 18H, **i'**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.42, 130.03, 127.36, 72.04, 70.62-70.74, 68.89, 64.54, 59.13, 52.94, 24.57, 11.35, 1.86, -1.94 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.29 (M), -66.53 (D), -72.30 ppm (T). HRMS (ES Positive Mode): m/z [M+Na]$^+$ calc. = 1172.4565, found = 1172.4523. HLB value = 20*(323.413/1254.67) = 5.15.

Surfactant **8PEG-15**: was prepared according to the general procedure given in the Experimental section, from azide **1-N$_3$** (0.39 g, 0.47 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-15 (**0.29 g, 0.36 mmol; *average molecular weight calculated via HRMS 788.947 g/mol*).

Yield: 0.48g, (81.0%), pale yellow paste.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

<u>Major isomer 1,4 (~75%)</u>

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.03 (s, 1 H, **g**), 4.49 (t, 2H, **d,** *J* = 5.1 Hz), 4.37 (t, 2H, **c,** *J* = 7.5 Hz), 3.81 (t, 2H, **e**, *J* = 5.4 Hz), 3.62-3.67 (m, ~ 60H, -OC**H$_2$**C**H$_2$**O-), 3.53 (m, 2H, **f**,), 3.36 (s, 3H, OC**H$_3$**), 2.01-2.04 (m, 2H, **b**), 0.53-0.55 (m, 2H, **a**), 0.07 (s, 54H, **h**), 0.031 ppm (s, 9H, **i**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 160.75, 139.81, 127.34, 72.05, 70.36-70.84, 69.04, 64.09, 59.13, 53.09, 24.48, 11.19, 1.87, -1.93 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 7.98 (M), -65.92 (T), -72.22 ppm (T). HRMS (ES Positive Mode): m/z [M+K]$^{2+}$ calc. = 826.8425, found = 826.8408. HLB value = 20*(719.925/1613.615) = 8.92.

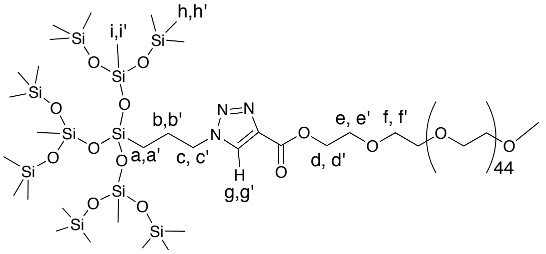
<u>Minor Isomer 1,5 (~25%)</u>

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.10 (s, 1 H, **g'**), 4.67 (t, 2H, **c',** *J* = 7.4 Hz), 4.42 (t, 2H, **d',** *J* = 4.8 Hz), 3.78 (t, 2H, **e'**, *J* = 4.8 Hz), 3.62-3.67 (m, ~ 60H, -OC**H$_2$**C**H$_2$**O-), 3.53 (m, 2H, **f**,), 3.36 (s, 3H, OC**H$_3$**), 1.94-2.01 (m, 2H, **b'**), 0.53-0.55 (m, 2H, **a'**), 0.06 (s, 54H, **h'**), 0.015 ppm (s, 9H, **i'**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.4, 138.02, 127.31, 72.05, 70.63-70.84, 68.89, 64.54, 59.13, 52.93, 24.55, 11.33, 1.84, -1.97 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 7.71 (M), -66.11 (T), -71.88 ppm (T). HRMS (ES Positive Mode): m/z [M+K]$^{2+}$ calc. = 826.8425, found = 826.8408. 3D HLB value = % Hydrophillic =

(735.88/1613.62)*100 = 45.60%/5 = 9.12. % Oil = (137.151/1613.62)*100 = 8.49%/5 = 1.70)

Surfactant **8PEG-44**: was prepared according to the general procedure given in the Experimental section, from azide **1-N$_3$** (0.26 g, 0.24 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-44 (**0.51 g, 0.25 mmol; *average molecular weight calculated via 1H NMR 2065.19 g/mol*), in ~2 mL of dry toluene (time to reach completion was slightly longer for Propiolate-terminated PEO of molecular weight 2000, typically up to 72 h).
Yield: 0.46g, (83.0%), pale yellow solid.

^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.



Major isomer 1,4 (~75%)

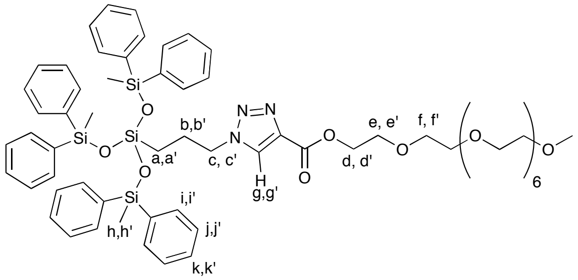
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.03 (s, 1 H, **g**), 4.49 (t, 2H, **d,** J = 5.1 Hz), 4.37 (t, 2H, **c,** J = 7.2 Hz), 3.82 (t, 2H, **e**, J = 5.1 Hz), 3.64-3.68 (m, ~ 176H, -OC**H$_2$**C**H$_2$**O-), 3.53-3.55 (m, 2H, **f**), 3.37 (s, 3H, OC**H$_3$**), 2.00-2.05 (m, 2H, **b**), 0.53-0.56 (m, 2H, **a**), 0.08 (s, 54H, **h**), 0.04 ppm (s, 9H, **i**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 160.86, 139.93, 127.44, 72.17, 70.79, 69.13, 64.21, 59.25, 53.20, 24.59, 11.30, 1.97, -1.83 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 7.99 (M), -65.91 (T), -72.20 ppm (T). HRMS (ES Positive Mode): m/z [M+H]$^{2+}$ found = 1440.7813. 3D HLB value = % Hydrophillic = (2013.15/2891.12)*100 = 69.63%/5 = 13.92. % Oil = (137.151/2891.12)*100 = 4.74%/5 = 0.95)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.11 (s, 1 H, **g'**), 4.68 (t, 2H, **c',** *J* = 7.5 Hz), 4.43 (t, 2H, **d',** *J* = 4.8 Hz), 3.78 (t, 2H, **e'**, *J* = 5.1 Hz), 3.64-3.68 (m, ~ 176H, -OC**H$_2$**C**H$_2$**O-), 3.51-3.52 (m, 2H, **f'**), 3.37 (s, 3H, OC**H$_3$**), 1.93-1.99 (m, 2H, **b'**), 0.53-0.56 (m, 2H, **a'**), 0.07 (s, 54H, **h'**), 0.02 ppm (s, 9H, **i'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 158.52, 138.14, 128.17, 72.17, 70.79, 69.14, 64.38, 59.25, 53.05, 24.67, 11.45, 1.97, -1.86 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 7.72 (M), -66.01 (T), -71.88 ppm (T). HRMS (ES Positive Mode): m/z $[M+H]^{2+}$ found = 1440.7813. HLB value = 20*(2012.15/2891.12) = 13.9.

Surfactant **9PEG-6**: was prepared according to the general procedure given in the Experimental section, from azide **2-N$_3$** (0.37 g, 0.49 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-6 (**0.150 g, 0.38 mmol; *average molecular weight calculated via ^{1}H NMR 382g/mol*)).

Yield: 0.39 g (89.4 %), yellow oil.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

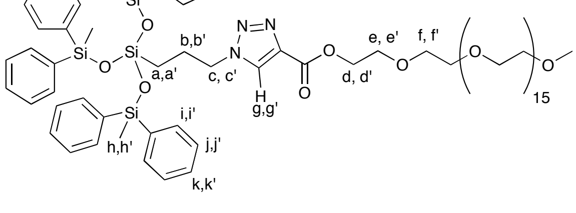
Major isomer 1,4 (~75%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.48 (s, 1 H, **g**), 7.36-7.43 (m, 18H, **j, k**), 7.23-7.27 (m, 12H, **i**), 4.54 (t, 2H, **d**, *J* ~ 5.1 Hz), 3.92 (t, 2H, **c**, *J* = 7.5 Hz), 3.86 (t, 2H, **e**, *J* = 4.8 Hz), 3.63- 3.71 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.54-3.55 (m, 2H, **f**), 3.38 (s, 3H, OC**H$_3$**), 1.46-1.51 (m, 2H, **b**), 0.50 (s, 9H, **h**), 0.31-0.34 ppm (m, 2H, **a**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.79, 136.96, 134.06, 129.91, 127.95, 127.17, 72.05, 70.69, 69.14, 64.21, 59.17, 52.69, 24.07, 11.36, -0.90 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ -10.59 (M) -67.02 ppm (T). HRMS (ES Positive Mode): m/z [M+H]$^+$ calc. = 1144.4663, found = 1144.4647. 3D HLB value = % Hydrophillic = (339.393/1144.58)*100 = 29.65%/5 = 5.93. % Oil = (599.77/1144.58)*100 = 52.40%/5 = 10.48)

Minor Isomer 1,5 (~25%)

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.10 (s, 1 H, **g'**), 7.36-7.43 (m, 18H, **j', k'**), 7.23-7.27 (m, 12H, **l'**), 4.33 (t, 2H, **d'**, *J* ~ 4.8 Hz), 4.4 (t, 2H, **c'**, *J* = 7.2 Hz), 3.7-3.71 (m, 2H, **e'**), 3.63- 3.71 (m, ~ 24H, -OC$\mathbf{H_2}$C$\mathbf{H_2}$O-), 3.54-3.55 (m, 2H, **f'**), 3.38 (s, 3H, OC$\mathbf{H_3}$), 1.65-1.68 (m, 2H, **b'**), 0.45 (s, 9H, **h'**), 0.41-0.44 ppm (m, 2H, **a'**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.27, 139.63, 137.12, 134.06, 129.72, 127.84, 72.05, 70.69, 68.83, 64.59, 59.17, 52.69, 24.34, 11.44, -0.90 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ -10.99 (M), -66.60 ppm (T). HRMS (ES Positive Mode): m/z [M+H]$^+$ calc. = 1144.4663, found = 1144.4647. HLB value = 20*(323.413/1144.58) = 5.65.

Surfactant **9PEG-15**: was prepared according to the general procedure given in the Experimental section, from azide **2-N$_3$** (0.41 g, 0.55 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-15 (**0.33 g, 0.42 mmol; *average molecular weight calculated via HRMS 788.947 g/mol*$^{)}$.
Yield: 0.58g, (90.0%), pale yellow oil.



Major isomer 1,4 (~75%)

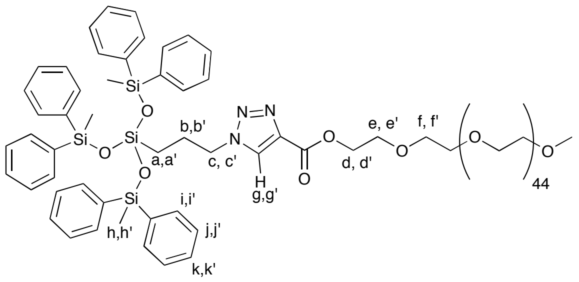
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.47 (s, 1 H, **g**), 7.33-7.44 (m, 18H, **j, k**), 7.21-7.27 (m, 12H, **i**), 4.54 (t, 2H, **d**, *J* ~ 4.8 Hz), 3.92 (t, 2H, **c**, *J* = 7.5 Hz), 3.86 (t, 2H, **e**, *J* = 4.8 Hz), 3.61- 3.66 (m, ~ 60H, -OC**H**$_2$C**H**$_2$O-), 3.55-3.56 (m, 2H, **f**), 3.38 (s, 3H, OC**H**$_3$), 1.46-1.51 (m, 2H, **b**), 0.50 (s, 9H, **h**), 0.31-0.34 ppm (m, 2H, **a**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.78, 136.941, 134.05, 129.92, 127.94, 127.16, 72.06, 70.65, 69.14, 64.20, 59.17, 52.70, 24.08, 11.36, -0.89 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ -10.59 (M) -67.03 ppm (T). HRMS (ES Positive Mode): m/z $[M+NH_4]^+$ calc. = 1557.7288, found = 1557.7360. 3D HLB value = % Hydrophillic = (735.88/1541.10)*100 = 47.75%/5 = 9.55. % Oil = (599.77/1541.10)*100 = 38.92%/5 = 7.78)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.10 (s, 1 H, **g'**), 7.33-7.44 (m, 18H, **j', k'**), 7.21-7.27 (m, 12H, **l'**), 4.33 (t, 2H, **d'**, *J* ~ 4.8 Hz), 4.41 (t, 2H, **c'**, *J* = 7.2 Hz), 3.71-3.73 (m, 2H, **e'**), 3.63- 3.66 (m, ~ 60H, -OC**H**$_2$C**H**$_2$O-), 3.55-3.56 (m, 2H, **f'**), 3.38 (s, 3H, OC**H**$_3$), 1.64-1.70 (m, 2H, **b'**), 0.45 (s, 9H, **h'**), 0.41-0.44 ppm (m, 2H, **a'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 158.27, 139.63, 137.11, 134.06, 129.71, 127.84, 127.17, 72.06, 70.65, 69.14, 64.58, 59.17, 52.70, 24.34, 11.45, 0.89 ppm.^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ -11.00 (M), -66.61 ppm (T). $[M+NH_4]^+$ HRMS (ES Positive Mode): m/z $[M+NH_4]^+$ calc. = 1557.7288, found = 1557.7360.

Surfactant **9PEG-44**: was prepared according to the general procedure given in the Experimental section, from azide **2-N$_3$** (0.24 g, 0.31 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-44 (**0.500 g, 0.24 mmol; *average molecular weight calculated via 1H NMR 2065.19 g/mol*), in ~2 mL of dry toluene (time to reach completion was slightly longer for Propiolate-terminated PEO of molecular weight 2000, typically up to 72 h).

Yield: 0.53 g, (77.8 %), pale yellow solid.



Major Isomer 1,4 (75%)

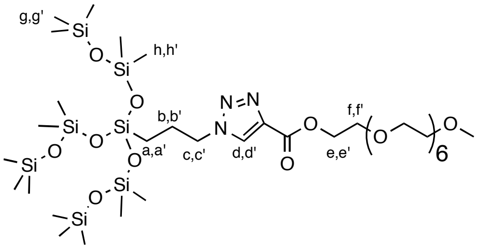
^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.46 (s, 1 H, **g**), 7.31-7.42 (m, 18H, **j, k**), 7.20-7.26 (m, 12H, **i**), 4.52 (t, 2H, **d**, *J* ~ 5.7 Hz), 3.90 (t, 2H, **c**, *J* = 8 Hz), 3.85 (t, 2H, **e**, *J* = 6 Hz), 3.58- 3.76 (m, ~ 176H, $-OC\mathbf{H_2}C\mathbf{H_2}O-$), 3.54-3.57 (m, 2H, **f**), 3.37 (s, 3H, $OC\mathbf{H_3}$), 1.45-1.50 (m, 2H, **b**), 0.48 (s, 9H, **h**), 0.30-0.33 ppm (m, 2H, **a**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.74, 136.93, 134.02, 129.87, 127.90, 127.13, 72.02, 70.65, 69.09, 64.15, 59.11, 52.64, 24.02, 11.32, -0.94 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ -10.55 (M) -67.06 ppm (T). HRMS (ES Positive Mode): m/z $[M+3H]^{3+}$ calc. = 939.8255, found = 939.3066. 3D HLB value = % Hydrophillic = (2013.15/2817.34)*100 = 71.4%/5 = 14.29. % Oil = (599.77/2817.34)*100 = 21.28%/5 = 4.25)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.08 (s, 1 H, **g'**), 7.31-7.42 (m, 18H, **j, k**), 7.20-7.26 (m, 12H, **i**), 4.31 (t, 2H, **d'**, *J* ~ 5.0 Hz), 4.39 (t, 2H, **c'**, *J* = 6.0 Hz), 3.76-3.72 (m, 2H, **e'**), 3.58- 3.76 (m, ~ 176H, $-OC\mathbf{H_2}C\mathbf{H_2}O-$), 3.51-3.52 (m, 2H, **f'**), 3.37 (s, 3H, $OC\mathbf{H_3}$), 1.63-1.69 (m, 2H, **b'**), 0.44 (s, 9H, **h'**), 0.40-0.43 ppm (m, 2H, **a'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 158.23, 139.59, 137.08, 134.02, 129.68, 127.80, 127.13, 72.02, 70.65, 68.78, 64.54, 59.11, 53.54, 24.28, 11.40, -0.94 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ -11.00 (M), -66.67 ppm (T). HRMS (ES Positive Mode): m/z $[M+3H]^{3+}$ calc. = 939.8255, found = 939.3066.

Surfactant **10PEG-6**: was prepared according to the general procedure given in the Experimental section, from azide **3-N$_3$** (0.28 g, 0.47 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-6 (**0.18 g, 0.47 mmol; *average molecular weight calculated via ^{1}H NMR 382g/mol*)).

Yield: 0.32 g (99.6%), pale yellow oil.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

Major isomer 1,4 (~75%)

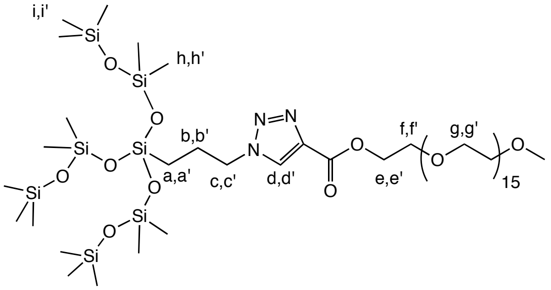
^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.05 (s, 1 H, **d**), 4.49 (t, 2H, **e,** *J* = 5.0 Hz), 4.38 (t, 2H, **c,** *J* = 7.3 Hz), 3.82 (t, 2H, **f**, *J* = 5.0 Hz), 3.62-3.68 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.53 (t, 2H, -(CO)OCH$_2$CH$_2$OC**H$_2$**CH$_2$O-, *J* = 4.8 Hz), 3.36 (s, 3H, OC**H$_3$**), 1.96-2.03 (m, 2H, **b**), 0.49-0.53 (m, 2H, **a**), 0.063 (s, 27H, **g**), 0.05 ppm (s, 18H, **h**). ^{13}C NMR (CDCl$_3$ 125 MHz): δ 159.10, 140.49, 128.08, 72.70, 71-28-71.48, 69.70, 64.81, 59.77, 53.69, 25.30, 11.90, 2.57, 1.90 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.24 (M), -21.52 (D), -70.99 ppm (T). 3D HLB value = % Hydrophillic = (339.393/994.61)*100 = 34.12%/5 = 6.82. % Oil = (137.151/994.61)*100 = 13.78%/5 = 2.76)

Minor Isomer 1,5 (~25%)

^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.13 (s, 1 H, **d'**), 4.68 (t, 2H, **c',** *J* = 7.5 Hz), 4.44 (t, 2H, **e',** *J* = 5.0 Hz), 3.79 (t, 2H, **f'**, *J* = 5.0 Hz), 3.62-3.68 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.53 (t, 2H, -(CO)OCH$_2$CH$_2$OC**H$_2$**CH$_2$O-, *J* = 4.8 Hz), 3.36 (s, 3H, OC**H$_3$**), 1.93-1.97 (m, 2H, **b'**), 0.49-0.53 (m, 2H, **a'**), 0.051 (s, 27H, **g'**), 0.03 ppm (s, 18H, **h'**). ^{13}C NMR (CDCl$_3$ 125 MHz): δ 161.45, 138.78, 128.08, 72.70, 71.28-71.48, 69.52, 65.26, 59.77, 53.56, 25.30, 11.99, 2.57, 1.85 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.06 (M), -21.85 (D), -70.74 ppm (T). HLB value = 20*(323.413/994.583) = 6.50.

Surfactant **10PEG-15**: was prepared according to the general procedure given in the Experimental section, from azide **3-N_3** (0.50 g, 0.82 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-15 (**0.50 g, 0.63 mmol; *average molecular weight calculated via HRMS 788.947 g/mol*$^{)}$.

Yield: 0.88g, (87.0%), pale yellow paste.



^{1}*H NMR* indicates the presence of two isomers, with a ratio of 1:4.

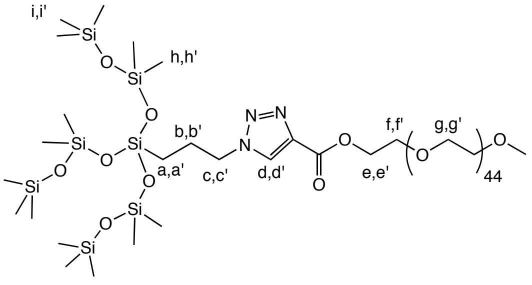
<u>Major isomer 1,4 (~75%):</u>

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (s, 1 H, **d**), 4.49 (t, 2H, **e,** *J* = 4.8 Hz), 4.38 (t, 2H, **c,** *J* = 7.2 Hz**)**, 3.82 (t, 2H, **f**, *J* = ~4.8 Hz), 3.61-3.68 (m, ~ 60H, -OC**H_2**C**H_2**O-), 3.52-3.54 (m, 2H, -(CO)OCH_2CH_2OC**H_2**CH_2O-, **g**), 3.36 (s, 3H, OC**H_3**), 1.96-2.02 (m, 2H, **b**), 0.49-0.53 (m, 2H, **a**), 0.059 (s, 27H, **i**), 0.06 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.79, 139.82, 138.12, 127.42, 72.04, 70.63-70.82, 69.04, 64.15, 59.12, 53.04, 26.64, 11.25, 1.93, 1.25 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.66 (M), -21.11 (D), -70.59 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^{2+}$ calc. = 704.3490, found = 704.3445. 3D HLB value = % Hydrophillic = (735.88/1391.10)*100 = 52.89%/5 = 10.58. % Oil = (137.151/1391.10)*100 = 9.85%/5 = 1.97)

Minor Isomer 1,5 (~25%)

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.12 (s, 1 H, **d'**), 4.68 (t, 2H, **c',** *J* = 7.2 Hz), 4.44 (t, 2H, **e',** *J* = 4.8 Hz), 3.78 (t, 2H, **f'**, *J* = 4.8 Hz), 3.61-3.68 (m, ~ 60H, -OC$\mathbf{H_2}$C$\mathbf{H_2}$O-), 3.52-3.54 (m, 2H, -(CO)OCH$_2$CH$_2$OC$\mathbf{H_2}$CH$_2$O-, **g'**), 3.36 (s, 3H, OC$\mathbf{H_3}$), 1.92-1.97 (m, 2H, **b'**), 0.49-0.53 (m, 2H, **a'**), 0.050 (s, 27H, **i'**), 0.03 ppm (s, 18H, **h'**). ^{13}C NMR (CDCl$_3$ 125 MHz): δ 158.44, 139.82, 138.12, 127.42, 72.04, 70.63-70.82, 68.87, 64.60, 59.12, 52.91, 24.64, 11.34, 1.91, 1.21 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.47 (M), -21.44 (D), -70.32 ppm (T). HRMS (ES Positive mode): m/z [M+NH$_4$]$^{2+}$ calc. = 704.3490, found = 704.3445. HLB value = 20*(719.925/1391.09) = 10.3.

Surfactant **10PEG-44**: was prepared according to the general procedure given in the Experimental section, from azide **3-N$_3$** (0.19 g, 0.32 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-44 (**0.51 g, 0.25 mmol; *average molecular weight calculated via 1H NMR 2065.19 g/mol)*, in ~2 mL of dry toluene (time to reach completion was slightly longer for Propiolate-terminated PEO of molecular weight 2000, typically up to 72 h).
Yield: 0.54g, (84.0%), pale yellow solid.



^{1}*H NMR* indicates the presence of two isomers, with a ratio of 1:4.

Major isomer 1,4 (~75%)

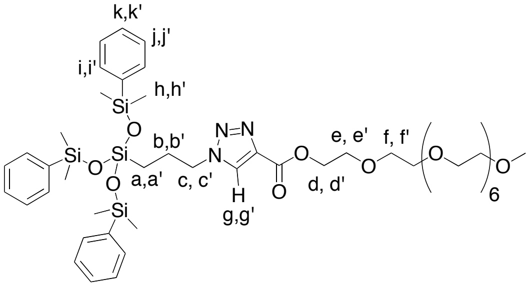
^{1}H NMR (CDCl$_3$, 500 MHz): δ 8.02 (s, 1 H, **d**), 4.45 (t, 2H, **e,** *J* = 5.0 Hz), 4.34 (t, 2H, **c,** *J* = 7.5 Hz**)**, 3.77 (t, 2H, **f**, *J* = 5.0 Hz), 3.58 (m, ~ 176H, -OC$\mathbf{H_2}$C$\mathbf{H_2}$O-), 3.49 (t, 2H, **g**, *J* = 5.0 Hz), 3.32 (s, 3H, OC$\mathbf{H_3}$), 1.94-1.97 (m, 2H, **b**), 0.45-0.49 (m, 2H, **a**), 0.02 (s, 27H, **i**), 0.01 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 160.67, 139.70, 127.34, 71.93, 70.57, 68.94, 64.04, 59.02, 52.93, 24.53, 11.13, 1.83, 1.15 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 7.61 (M), -21.16 (D), -70.61 ppm (T). 3D HLB value = % Hydrophillic = (2013.15/2668.60)*100 = 75.43%/5 = 15.08. % Oil = (137.151/2668.60)*100 = 5.14%/5 = 1.02)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.08 (s, 1 H, **d'**), 4.64 (t, 2H, **c'**, *J* = 7.5 Hz), 4.40 (t, 2H, **e'**, *J* = 5.0 Hz), 3.72 (t, 2H, **f'**, *J* = 5.0 Hz), 3.58 (m, ~ 176H, -OC**H₂**C**H₂**O-), 3.44 (t, 2H, **g'**, *J* = 5.0 Hz), 3.32 (s, 3H, OC**H₃**), 1.87-1.92 (m, 2H, **b'**), 0.45-0.49 (m, 2H, **a'**), 0.01 (s, 27H, **i'**), -0.01 ppm (s, 18H, **h'**). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 158.34, 138.02, 127.34, 71.93, 70.57, 68.75, 64.50, 59.02, 52.79, 24.53, 11.22, 1.83, 1.11 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 7.43 (M), -21.45 (D), -70.35 ppm (T). HLB value = 20*(2012.95/2668.6) = 15.08.

Surfactant **11PEG-6**: was prepared according to the general procedure given in the Experimental section, from azide **4-N₃** (0.56 g, 0.99 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-6 (**0.30 g, 0.76 mmol; *average molecular weight calculated via ^{1}H NMR 382g/mol*)).

Yield: 0.73 g (83 %), pale yellow oil.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

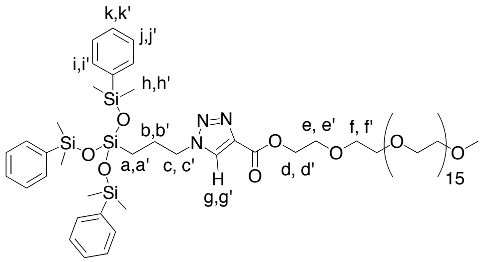
Major isomer 1,4 (~75%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.70 (s, 1 H, **g**), 7.45-7.49 (m, 6H, **i**), 7.26-7.39 (m, 9H, **j, k**), 4.52 (t, 2H, **d**, *J* ~ 4.8 Hz), 4.08 (t, 2H, **c**, *J* = 6.0 Hz), 3.85 (t, 2H, **e**, *J* = 4.9 Hz), 3.58- 3.72 (m, ~ 24H, -OC**H₂**C**H₂**O-), 3.48-3.55 (m, 2H, **f**), 3.37 (s, 3H, OC**H₃**), 1.62-1.69 (m, 2H, **b**), 0.34-0.37 (m, 2H, **a**), 0.30 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.84, 139.77, 139.09, 133.12, 129.69, 127.94, 127.32, 72.09, 70.72 (PEO), 69.15, 64.24, 59.18, 52.86, 24.40, 11.31, 0.52 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -1.02 (M) -67.27 ppm (T). HRMS (ES Positive Mode): m/z $[M+H]^+$ calc. = 958.4193, found = 958.4177. 3D HLB value = % Hydrophillic = (339.393/955.55)*100 = 35.51%/5 = 7.10. % Oil = (368.47/955.55)*100 = 38.56%/5 = 7.71)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 (s, 1 H, **g'**), 7.45-7.49 (m, 6H, **i'**), 7.26-7.39 (m, 9H, **j', k'**), 4.54 (t, 2H, **c'**), 4.39 (t, 2H, **d'** *J* = 6.0 Hz), 3.76 (t, 2H, **e'**, *J* ~ 6.0 Hz), 3.58- 3.72 (m, ~ 24H, -OC**H₂**C**H₂**O-), 3.48-3.55 (m, 2H, **f**), 3.37 (s, 3H, OC**H₃**), 1.77-1.82 (m, 2H, **b'**), 0.43-0.46 (m, 2H, **a'**), 0.27 ppm (s, 18H, **h'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 156.49, 139.23, 139.09, 138.21, 133.12, 129.49, 127.84, 72.09, 70.72 (PEO), 68.88, 64.67, 59.18, 52.86, 24.55, 11.41, 0.59 ppm.^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -1.46 (M), -66.94 ppm (T). HRMS (ES Positive Mode): m/z $[M+H]^+$ calc. = 958.4193, found = 958.4177. HLB = 20*(323.413/955.55) = 6.76.

Surfactant **11PEG-15**: was prepared according to the general procedure given in the Experimental section, from azide **4-N₃** (0.46 g, 0.82 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-15 (**0.50 g, 0.63 mmol; *average molecular weight calculated via HRMS 788.947 g/mol*$^)$.
Yield: 0.75g, (88.0%), pale yellow paste.



^{1}*H NMR* indicates the presence of two isomers, with a ratio of 1:4.

Major isomer 1,4 (~75%)

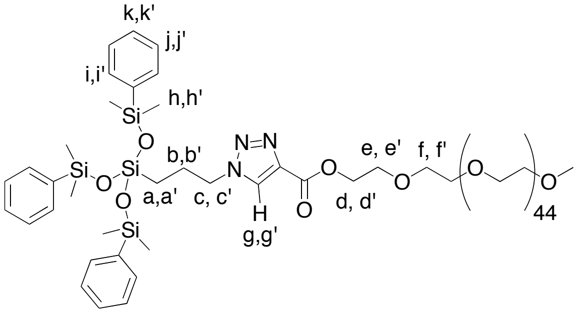
^{1}H NMR (CDCl$_3$, 600 MHz): δ 7.69 (s, 1 H, **g**), 7.45-7.48 (m, 6H, **i**), 7.26-7.38 (m, 9H, **j, k**), 4.52 (t, 2H, **d**, J = 4.8 Hz), 4.08 (t, 2H, **c**, J = 8.5 Hz), 3.84 (t, 2H, **e**, J = 4.9 Hz), 3.59- 3.71 (m, ~ 60H, -OC**H$_2$**C**H$_2$**O-), 3.54 (m, 2H, **f**), 3.37 (s, 3H, OC**H$_3$**), 1.62-1.67 (m, 2H, **b**), 0.33-0.35 (m, 2H, **a**), 0.29 ppm (s, 18H, **h**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 160.78, 139.70, 139.02, 133.06, 129.63, 127.88, 127.27, 72.03, 70.67 (PEO), 69.08, 64.17, 59.12, 52.78, 24.34, 11.25, 0.46 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ -1.04 (M) -67.29 ppm (T). HRMS (ES Positive Mode): m/z [M+NH$_4$]$^+$ calc. = 1371.6818, found = 1371.6831. 3D HLB value = % Hydrophillic = (735.88/1352.07)*100 = 54.43%/5 = 10.88. % Oil = (368.47/1352.07)*100 = 27.25%/5 = 5.45)

Minor Isomer 1,5 (~25%)

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.11 (s, 1 H, **g'**), 7.45-7.48 (m, 6H, **i'**), 7.26-7.38 (m, 9H, **j', k'**), 4.53 (t, 2H, **c'**, J = 7.8 Hz), 4.38 (m, 2H, **d'**), 3.75 (t, 2H, **e'**, J = 4.9 Hz), 3.59- 3.71 (m, ~ 60H, -OC**H$_2$**C**H$_2$**O-), 3.54 (m, 2H, **f**), 3.37 (s, 3H, OC**H$_3$**), 1.76-1.81 (m, 2H, **b'**), 0.42-0.45 (m, 2H, **a'**), 0.26 ppm (s, 18H, **h'**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.36, 139.16, 139.02, 138.15, 133.06, 129.42, 127.77, 72.03, 70.67 (PEO), 68.81, 64.60, 59.12, 52.78, 24.48, 11.35, 0.53 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ -1.47 (M), -66.95 ppm (T). HRMS

(ES Positive Mode): m/z $[M+NH_4]^+$ calc. = 1371.6818, found = 1371.6831. HLB value = 20*(719.925/1352.07) = 10.6.

Surfactant **11PEG-44**: was prepared according to the general procedure given in the Experimental section, from azide **4-N$_3$** (0.18 g, 0.31 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-44 (**0.50 g, 0.24 mmol; *average molecular weight calculated via 1H NMR 2065.19 g/mol)*, in ~2 mL of dry toluene (time to reach completion was slightly longer for Propiolate-terminated PEO of molecular weight 2000, typically up to 72 h).
Yield: 0.77g, (93.0%), pale yellow solid.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

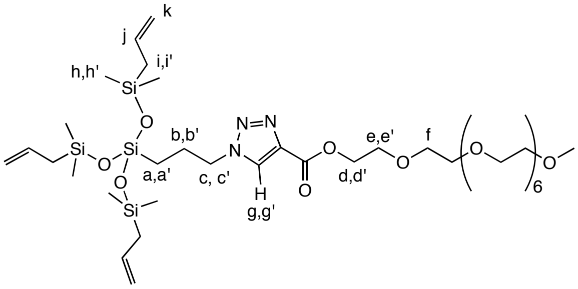
<u>Major isomer 1,4 (~75%)</u>

^{1}H NMR ($CDCl_3$, 600 MHz): δ 7.69 (s, 1 H, **g**), 7.45-7.48 (m, 6H, **i**), 7.27-7.38 (m, 9H, **j, k**), 4.52 (t, 2H, **d**, *J* ~ 6.0 Hz), 4.08 (t, 2H, **c**, *J* = 8.5 Hz), 3.85 (t, 2H, **e**, *J* = 4.9 Hz), 3.58- 3.68 (m, ~ 176H, -OC**H$_2$**C**H$_2$**O-), 3.54 (m, 2H, **f**), 3.37 (s, 3H, OC**H$_3$**), 1.62-1.67 (m, 2H, **b**), 0.34-0.36 (m, 2H, **a**), 0.29 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.71, 139.94, 132.98, 129.57, 127.82, 127.240, 71.95, 70.54, 69.02, 64.11, 59.06, 52.73, 24.29, 11.17, 0.42 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -1.06 (M) -67.25 ppm (T). HRMS (ES Positive Mode): m/z $[M+3H]^{3+}$ calc. = 877.4739, found = 876.1533. 3D HLB value = % Hydrophillic = (2013.15/2628.31)*100 = 76.59%/5 = 15.31. % Oil = (368.47/2628.31)*100 = 14.01%/5 = 2.80)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 (s, 1 H, **g'**), 7.45-7.48 (m, 6H, **i'**), 7.26-7.38 (m, 9H, **j', k'**), 4.54 (t, 2H, **c'**), 4.39 (m, 2H, **d'**), 3.75 (t, 2H, **e'**, J = 4.9 Hz), 3.58-3.68 (m, ~ 176H, -OC**H₂**C**H₂**O-), 3.52 (m, 2H, **f'**), 3.37 (s, 3H, OC**H₃**), 1.76-1.81 (m, 2H, **b'**), 0.43-0.46 (m, 2H, **a'**), 0.26 ppm (s, 18H, **h'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 156.52, 139.60, 138.94, 132.98, 129.36, 127.70, 71.95, 70.54, 68.75, 64.55, 59.06, 53.53, 24.42, 11.28, 0.49 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -1.48 (M), -66.91 ppm (T). HRMS (ES Positive Mode): m/z $[M+3H]^{3+}$ calc. = 877.4739, found = 876.1533. HLB value = 20*(2012.15/2628.31)= 15.3

Surfactant **12PEG-6**: was prepared according to the general procedure given in the Experimental section, from azide **5-N₃** (0.21 g, 0.45 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-6 (**0.15 g, 0.38 mmol; *average molecular weight calculated via ^{1}H NMR 382g/mol*)).
Yield: 0.30 g (91.4%), pale yellow oil.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

Major Isomer 1,4 (~75%)

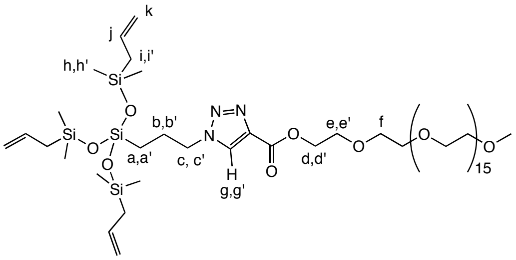
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (s, 1 H, **g**), 5.70-5.78 (m, 3H, **j**), 4.81-4.88 (m, 6H, **k**), 4.50 (t, 2H, **d**, J = 6.0 Hz), 4.36 (t, 2H, **c,** J = 9 Hz), 3.82 (t, 2H, **e**, J = 6 Hz), 3.63-3.67 (m, ~ 24H, -OC**H₂**C**H₂**O-), 3.52 (t, 2H, **f**, J = 6 Hz), 3.36 (s, 3H, OC**H₃**), 1.92-1.95 (m, 2H, **b**), 1.56 (d, 6H, **i,** J = 12 Hz), 0.43-0.46 (m, 2H, **a**), 0.09 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.82, 139.90, 138.22, 133.95, 127.45, 113.92, 72.06, 70.70, 69.08, 64.24, 59.14, 53.08, 26.16, 24.80, 11.34, -

0.17 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 5.80 (M), -67.65 (T). HRMS (ES Positive Mode): m/z [M+NH$_4$]$^+$ calc. = 867.4459, found = 867.4499. 3D HLB value = % Hydrophillic = (339.393/850.28)*100 = 39.91%/5 = 7.98. % Oil = (260.350/850.28)*100 = 30.61%/5 = 6.12)

Minor Isomer 1,5 (~25%)

^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.14 (s, 1 H, **g’**), 5.70-5.78 (m, 3H, **j**), 4.81-4.88 (m, 6H, **k**), 4.67 (t, 2H, **c’,** *J* = 9 Hz), 4.44 (t, 2H, **d’**, *J* = 6.0 Hz), 3.79 (t, 2H, **e’**, *J* = 6 Hz), 3.63-3.67 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.52 (t, 2H, **f**, *J* = 6 Hz), 3.36 (s, 3H, OC**H$_3$**), 1.88-1.91 (m, 2H, **b’**), 1.54 (d, 6H, **i’,** *J* = 10 Hz), 0.43-0.46 (m, 2H, **a**), 0.07 ppm (s, 18H, **h’**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.52, 139.90, 138.22, 127.45, 134.09, 113.77, 72.06, 70.70, 68.88, 64.71, 59.14, 52.87, 26.16, 24.71, 11.34, -0.23 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 5.40 (M), -67.27 (T). HRMS (ES Positive Mode): m/z [M+NH$_4$]$^+$ calc. = 867.4459, found = 867.4499. HLB value = 20*(323.413/850.278) = 7.60.

Surfactant **12PEG-15**: was prepared according to the general procedure given in the Experimental section, from azide **5-N$_3$** (0.3 g, 0.82 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-15 (**0.50 g, 0.63 mmol; *average molecular weight calculated via HRMS 788.947 g/mol*$^{)}$.
Yield: 0.71g, (90.2%), pale yellow paste.



^{1}*H NMR* indicates the presence of two isomers, with a ratio of 1:4.

Major isomer 1,4 (~75%)

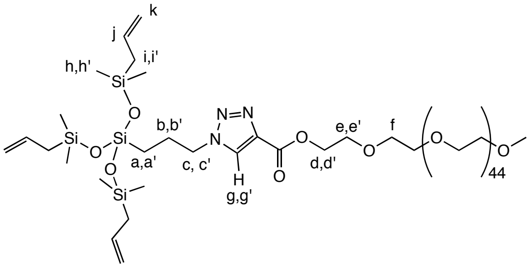
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (s, 1 H, **g**), 5.73-5.78 (m, 3H, **j**), 4.82-4.88 (m, 6H, **k**), 4.50 (t, 2H, **d**, *J* = 6.0 Hz), 4.36 (t, 2H, **c,** *J* = 7.8 Hz), 3.79 (t, 2H, **e**, *J* = 6 Hz), 3.59-3.68 (m, ~ 60H, -OC**H₂**C**H₂**O-), 3.48-3.53 (t, 2H, **f**), 3.36 (s, 3H, OC**H₃**), 1.92-1.96 (m, 2H, **b**), 1.56 (d, 6H, **i,** *J* = 12 Hz), 0.43-0.47 (m, 2H, **a**), 0.09 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.82, 139.90, 138.22, 133.95, 127.45, 113.93, 72.07, 70.70, 69.08, 64.23, 59.15, 53.08, 26.16, 24.80, 11.34, -0.17 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 5.80 (M), -67.63 (T). HRMS (ES Positive Mode): m/z $[M+NH_4]^+$ calc. = 1263.6818, found = 1263.6854. 3D HLB value = % Hydrophillic = (735.88/1245)*100 = 59.10%/5 = 11.82. % Oil = (260.35/1245)*100 = 20.91%/5 = 4.18)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.15 (s, 1 H, **g'**), 5.73-5.78 (m, 3H, **j**), 4.82-4.88 (m, 6H, **k**), 4.67 (t, 2H, **c',** *J* = 9 Hz), 4.44 (t, 2H, **d'**, *J* = 6.0 Hz), 3.72 (t, 2H, **e'**, *J* = 6 Hz), 3.59-3.68 (m, ~ 24H, -OC**H₂**C**H₂**O-), 3.48-3.53 (m, 2H, **f**), 3.36 (s, 3H, OC**H₃**), 1.89-1.91 (m, 2H, **b'**), 1.53 (d, 6H, **i',** *J* = 12 Hz), 0.43-0.47 (m, 2H, **a**), 0.07 ppm (s, 18H, **h'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 158.49, 139.90, 138.22, 127.45, 134.09, 113.77, 72.07, 70.70, 68.88, 64.70, 59.15, 52.87, 26.16, 24.71, 11.34, -0.23 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 5.80 (M), -67.63 (T). HRMS (ES Positive Mode): m/z $[M+NH_4]^+$ calc. = 1263.6818, found = 1263.6854. HLB value = 20*(719.925/1245.79) = 11.55.

Surfactant **12PEG-44**: was prepared according to the general procedure given in the Experimental section, from azide **5-N₃** (0.14 g, 0.31 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-44 (**0.50 g, 0.24 mmol; *average molecular weight calculated via 1H NMR 2065.19 g/mol)*, in ~2 mL of dry toluene (time to reach completion was slightly longer for Propiolate-terminated PEO of molecular weight 2000, typically up to 72 h).

Yield: 0.52g, (87.0%), pale yellow solid.



^1H NMR indicates the presence of two isomers, with a ratio of 1:4.

Major isomer 1,4 (~75%)

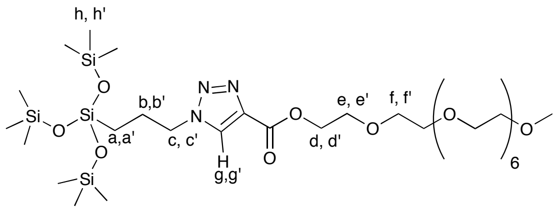
^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (s, 1 H, **g**), 5.70-5.78 (m, 3H, **j**), 4.81-4.88 (m, 6H, **k**), 4.49 (t, 2H, **d**, *J* = 6.0 Hz), 4.35 (t, 2H, **c,** *J* = 6 Hz), 3.82 (t, 2H, **e**, *J* = 6 Hz), 3.63-3.71 (m, ~ 176H, -OC**H₂**C**H₂**O-), 3.51-3.54 (m, 2H, **f**), 3.36 (s, 3H, OC**H₃**), 1.92-1.96 (m, 2H, **b**), 1.55 (d, 6H, **i,** *J* = 10 Hz), 0.43-0.45 (m, 2H, **a**), 0.08 ppm (s, 18H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.81, 139.20, 138.22, 133.94, 127.44, 113.93, 72.06, 70.69, 69.07, 64.23, 59.15, 53.07, 26.15, 24.79, 11.33, -0.17 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 5.80 (M), -67.65 (T). HRMS (ES Positive Mode): m/z $[M+NH_3+Na]^{2+}$ calc. = 1282.2168, found = 1282.2238. 3D HLB value = % Hydrophillic = (2013.15/2521)*100 = 79.8%/5 = 15.97. % Oil = (260.35/2521)*100 = 10.32%/5 = 2.06)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.13 (s, 1 H, **g'**), 5.70-5.78 (m, 3H, **j**), 4.81-4.88 (m, 6H, **k**), 4.66 (t, 2H, **c',** *J* = 7.8 Hz), 4.44 (t, 2H, **d'**, *J* = 6.0 Hz), 3.79 (t, 2H, **e'**, *J* = 6 Hz), 3.63-3.71 (m, ~ 176H, -OC**H₂**C**H₂**O-), 3.48-3.51 (m, 2H, **f**), 3.36 (s, 3H, OC**H₃**), 1.90-1.92 (m, 2H, **b'**), 1.54 (d, 6H, **i',** *J* = 10 Hz), 0.43-0.45 (m, 2H, **a**), 0.07 ppm (s, 18H, **h'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 155.07, 139.90, 138.22, 134.08, 127.44, 113.77, 72.06, 70.69, 68.87, 64.70, 59.15, 52.86, 26.16, 24.70, 11.33, -0.23 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 5.40 (M), -

67.27 (T). HRMS (ES Positive Mode): m/z $[M+NH_3+Na]^{2+}$ calc. = 1282.2168, found = 1282.2238. HLB value = 20*(2012.65/2521) = 15.9.

Surfactant **13PEG-6**: was prepared according to the general procedure given in the Experimental section, from azide **6-N$_3$** (0.63 g, 1.65 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-6** (0.50 g, 1.3 mmol; *average molecular weight calc. via ^{1}H NMR 382g/mol*)).
Yield: 0.86 g (88 %), pale yellow oil.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

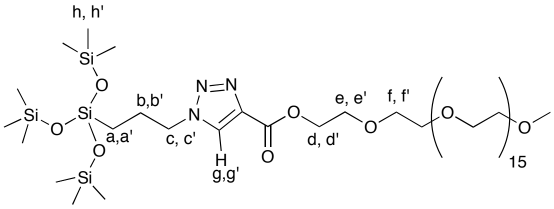
Major isomer 1,4 (~75%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (s, 1H, **g**), 4.48 (t, 2H, **d,** J = 6.0 Hz), 4.35 (t, 2H, **c,** J = 8.3 Hz), 3.81 (t, 2H, **e**, J = 6.0 Hz), 3.56-3.68 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O-), 3.52 (m, 2H, **f**), 3.35 (s, 3H, OC**H$_3$**), 1.89-1.95 (m, 2H, **b**), 0.40-0.44 (m, 2H, **a**), 0.07 ppm (s, 27H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.82, 139.83, 127.46, 72.03, 70.81 (PEO), 69.05, 64.19, 59.11, 53.04, 24.81, 11.32, 1.83 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 8.45 (M), -67.58 ppm (T). HRMS (ES Positive Mode): m/z $[M]^+$ calc. = 772.3723 found = 772.3724. 3D HLB value = % Hydrophillic = (339.393/772.18)*100 = 43.95%/5 = 8.79. % Oil = (137.151/772.181)*100 = 17.76%/5 = 3.55)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.12 (s, 1H, **g'**), 4.66 (t, 2H, **c',** J =8.6 Hz), 4.43 (t, 2H, **d',** J = 6.0 Hz), 3.78 (t, 2H, **e'**, J = 6.0 Hz), 3.56-3.68 (m, ~ 24H, -OC**H$_2$**C**H$_2$**O), 3.52 (m, 2H, **f**), 3.35 (s, 3H, OC**H$_3$**), 1.86-1.90 (m, 2H, **b'**), 0.40-0.44 (m, 2H, **a'**), 0.05 ppm (s, 27H, **h'**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 158.47, 138.20, 127.46, 72.03, 70.81 (PEO), 69.05, 64.65, 59.11, 52.92, 24.73, 11.36, 1.83 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.98 (M), -67.23 ppm (T). HRMS (ES Positive Mode): m/z [M]$^+$ calc.= 772.3723 found = 772.3724. HLB value = 20*(323.413/772.18) = 8.37.

Surfactant **13PEG-15**: was prepared according to the general procedure given in the Experimental section, from azide **6-N$_3$** (0.31 g, 0.82 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-15 (**0.50 g, 0.63 mmol; *average molecular weight calc. via HRMS 788.947 g/mol)*.
Yield: 0.62g, (83.5%), pale yellow paste.
^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.



Major isomer 1,4 (~75%)

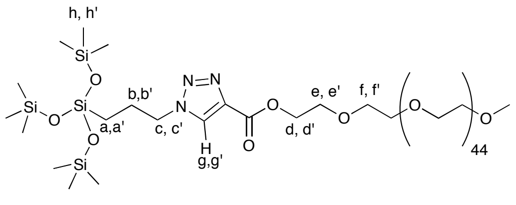
^{1}H NMR (CDCl$_3$, 600 MHz): δ 8.06 (s, 1H, **g**), 4.49 (t, 2H, **d,** *J* = 6.0 Hz), 4.36 (t, 2H, **c,** *J* = 7.2 Hz), 3.82 (t, 2H, **e**, *J* = 6.0 Hz), 3.58-3.67 (m, ~ 60H, -OC**H$_2$**C**H$_2$**O-), 3.52 (m, 2H, **f**), 3.36 (s, 3H, OC**H$_3$**), 1.91-1.96 (m, 2H, **b**), 0.41-0.44 (m, 2H, **a**), 0.08 ppm (s, 27H, **h**). ^{13}C NMR (CDCl$_3$ 150 MHz): δ 160.84, 139.84, 127.48, 72.05, 70.68 (PEO), 69.07, 64.21, 59.13, 53.06, 24.82, 11.33, 1.85 ppm. ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 8.45 (M), -67.61 ppm (T). 3D HLB value = % Hydrophillic = (735.88/1168.66)*100 = 62.96%/5 = 12.59. % Oil = (137.151/1168.66)*100 = 11.73%/5 = 2.35)

<u>Minor Isomer 1,5 (~25%)</u>

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.13 (s, 1 H, **g'**), 4.66 (t, 2H, **c',** *J* = 6.0 Hz), 4.44 (t, 2H, **d',** *J* = 6.0 Hz**)**, 3.79 (t, 2H, **e'**, *J* = 6.0 Hz), 3.58-3.67 (m, ~ 60H, -OC**H$_2$**C**H$_2$**O-), 3.52 (m, 2H, **f**), 3.36 (s, 3H, OC**H$_3$**), 1.87-1.91 (m, 2H, **b'**), 0.41-0.44 (m, 2H, **a'**), 0.06 ppm (s, 27H, **h'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 158.48, 138.22, 127.48, 72.05, 70.68 (PEO), 68.52, 64.66, 59.13, 52.93, 24.75, 11.38, 1.81 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.98 (M), -67.24 ppm (T). HRMS (ES Positive mode): m/z [M^+] calc.= 772.3723 found = 772.3724

Surfactant **13PEG-44**: was prepared according to the general procedure given in the Experimental section, from azide **6-N$_3$** (0.17 g, 0.82 mmol) and monopropiolate-terminated poly(oxyethylene) **7PEG-44 (**0.70 g, 0.34 mmol; *average molecular weight calculated via 1H NMR 2065.19 g/mol)*, in ~2 mL of dry toluene (time to reach completion was slightly longer for propiolate-terminated PEO of molecular weight 2000, typically up to 72 h).

Yield: 0.77 g (93.0%), pale yellow solid.



^{1}H NMR indicates the presence of two isomers, with a ratio of 1:4.

<u>Major isomer 1,4 (~75%)</u>

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.05 (s, 1 H, **g**), 4.49 (t, 2H, **d,** *J* = 6.0 Hz), 4.36 (t, 2H, **c,** *J* = 8.6 Hz), 3.81 (t, 2H, **e**, *J* = 6.0 Hz), 3.58-3.68 (m, ~ 176H, -OC**H$_2$**C**H$_2$**O-), 3.52 (m, 2H, **f**), 3.35 (s, 3H, OC**H$_3$**), 1.90-1.95 (m, 2H, **b**), 0.40-0.44 (m, 2H, **a**), 0.07 ppm (s, 27H, **h**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 160.82, 139.82, 127.46, 72.03, 70.66 (PEO), 69.05, 64.19, 59.12, 53.04, 24.81, 11.31, 1.83 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 8.45 (M), -67.56 ppm (T). HRMS (ES Positive mode): m/z $[M+3H]^{3+}$ calc. = 877.8098, found = 877.8420. 3D HLB value = % Hydrophillic = (2013.15/2444.94)*100 = 82.33%/5 = 16.46. % Oil = (137.151/2444.94)*100 = 5.60%/5 = 1.12)

Minor Isomer 1,5 (~25%)

^{1}H NMR ($CDCl_3$, 600 MHz): δ 8.13 (s, 1 H, **g'**), 4.66 (t, 2H, **c',** *J* = 7.9 Hz), 4.44 (t, 2H, **d',** *J* = 6.0 Hz), 3.79 (t, 2H, **e'**, *J* = 6.0 Hz), 3.58-3.68 (m, ~ 176H, -OC**H₂**C**H₂**O-), 3.50 (m, 2H, **f**), 3.35 (s, 3H, OC**H₃**), 1.86-1.90 (m, 2H, **b'**), 0.40-0.44 (m, 2H, **a'**), 0.05 ppm (s, 27H, **h'**). ^{13}C NMR ($CDCl_3$ 150 MHz): δ 158.46, 138.20, 127.46, 72.03, 70.66 (PEO), 68.85, 64.64, 59.12, 52.92, 24.73, 11.31, 1.813 ppm. ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 7.99 (M), -67.23 ppm (T). HRMS (ES Positive mode): m/z $[M+3H]^{3+}$ calc. = 877.8098, found = 877.8420. HLB value = 20*(2012.15/2444.94) = 16.4.

9.2 Appendix II - Supporting information for Chapter 4: Amphiphilic Silicone Architectures via Anaerobic Thiol-Ene Chemistry

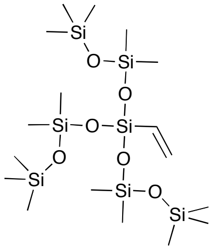
Experimental Section

Materials

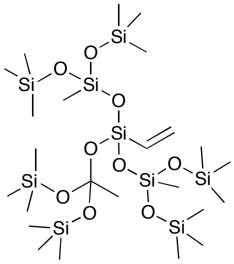
Triethylene glycol methyl ether, poly(ethylene glycol) 350 methyl ether, poly(ethylene glycol) 750 methyl ether, tetra(ethylene glycol), *p*-toluenesulfonyl chloride, potassium thioacetate and 2,2-dimethoxy-2-phenylacetophenone were purchased from Sigma-Aldrich and used as received. α,ω-Divinyl-terminated polydimethylsiloxane, vinyltetramethyldisiloxane, vinyltriethoxysilane, vinyltrimethoxysilane, phenyldimethylsilane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, and pentamethyldisiloxane were purchased from Gelest and used as received.

Characterization

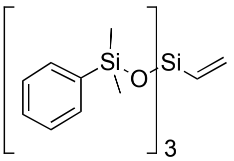
Nuclear magnetic resonance (NMR) spectra obtained on a Bruker Avance 500 MHz spectrometer (^{1}H 500 MHz, ^{13}C 125 MHz, ^{29}Si 99 MHz). High-resolution mass spectrometry was performed using a Waters Quattro Ultima Global quadrupole time-of-flight mass spectrometer under electrospray ionization mode. A UV reactor at 254 nm (low pressure mercury lamp, 220W) was used to generate radicals.



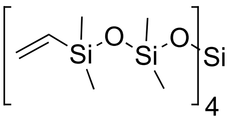
Tris(pentamethyldisiloxy)vinylsilane 1: To a solution of vinyltriethoxysilane (2 g, 10.5 mmol) in dry hexane (15 ml), was added pentamethyldisiloxane (7.01 g, 47 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (50 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9 x 10^{-3} mmol). After a 5 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (2.5 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure tris(pentamethyldisiloxy)vinylsilane (5.06 g, 9.3 mmol, 89% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.86-6.0 (m, 3 H's, $O_3SiC\mathbf{H}C\mathbf{H_2}$), 0.09 (s, 27 H's ($\mathbf{H_3}C)_3SiO$), 0.07 ppm (s, 18 H's ($C\mathbf{H_3})_2SiO_2$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 133.97 (CH vinyl), 133.53 (CH_2 vinyl), 1.95 (Si(**C**H_3)$_3$), 1.24 ppm (O_2Si(**C**H_3)$_2$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.0 (M), -21.6 (D), -82.2 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 562.2180, found = 562.2153.



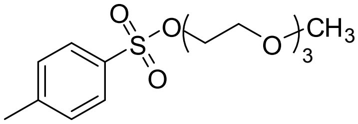
Tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)vinylsilane 2: To a solution of vinyltrimethoxysilane (0.513 g, 3.5 mmol) in dry hexane (10 ml) was added 1,1,1,3,5,5,5-heptamethyltrisiloxane (3.85 g, 17.3 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (40 μl of a prepared solution containing 40 mg dissolved in 1 ml of toluene, 3.1 x 10^{-3} mmol). After a 3 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)vinylsilane (2.40 g, 3.13 mmol, 89.5% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 5.89-5.98 (m, 3 H's, O_3SiC**H**C**H$_2$**), 0.09 (s, 54 H's (**H$_3$**C)$_3$SiO), 0.05 ppm (s, 9 H's (C**H$_3$**)SiO_3); ^{13}C NMR: δ ($CDCl_3$ 125 MHz) 134.75 (CH vinyl), 133.74 (CH_2 vinyl), 2.48 (Si(**C**H_3)$_3$), -1.33 ppm (O_3Si**C**H_3); ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.16 (M), -66.43 (D), -84.02 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 784.2743, found = 784.2771.



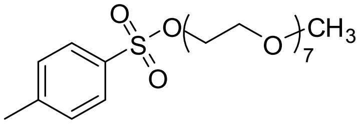
Tris(phenyldimethylsilyloxy)vinylsilane 3: To a solution of vinyltrimethoxysilane (0.250 g, 1.68 mmol) in dry hexane (10 ml) and dichloromethane (5 ml) was added dimethylphenylsilane (0.919g, 6.74 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (15 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 1.2 x 10^{-3} mmol). After a 40 s induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed in vacuo, affording pure tris(phenyldimethylsilyloxy)vinylsilane (0.79 g, 1.55 mmol, 92%). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 7.50-7.52 (m, 6 H's, phenyl), 7.34-7.37 (m, 3 H's, phenyl), 7.28-7.31 (m, 6 H's, phenyl), 5.78-5.92 (m, 3 H's, vinyl), 0.29 ppm (s, 18 H's, $(C_6H_6)(\mathbf{H_3}C)_2SiO$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.45, 134.46, 133.30, 133.21, 129.37, 127.76, 0.71 ppm. ^{29}Si NMR (99 MHz 1 % w/v Cr(acac)$_3$): δ -1.58 (M), -78.86 (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 526.2085, found = 526.2051.



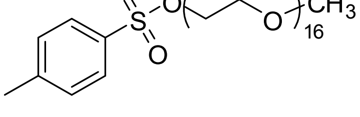
Tetrakis(vinyltetramethyldisiloxy)silane 4: To a solution of tetraethyl orthosilicate (0.200 g, 0.96 mmol) in dry hexane (5 ml), was added vinyltetramethyldisiloxane (0.85 g, 5.28 mmol). The mixture was stirred at room temperature for 5 min before the addition of tris(pentafluorophenyl)borane (10 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 7.81×10^{-4} mmol). After a 2 min induction time, rapid evolution of gas and heat from the solution occurred. The mixture was allowed to cool to room temperature before the addition of neutral alumina (1 g). The resulting solution was filtered and concentrated under reduced pressure. The remaining solvent and excess reagents were removed *in vacuo,* affording pure tetrakis(vinyltetramethyldisiloxy)silane (0.520 g, 0.72 mmol, 75% yield). ^{1}H NMR ($CDCl_3$, 500 MHz): δ 6.13 (dd, 4 H's, $R_3SiC\mathbf{H}CHH$, $J = 15.0$, 20.5 Hz), 5.93 (dd, 4 H's, $R_3SiCHCH\mathbf{H}$, $J = 4.0$, 15.0 Hz), 5.74 (dd, 4 H's, $R_3SiCHC\mathbf{H}H$, $J = 4.0$, 20.5 Hz), 0.166 (s, 24H's $O(\mathbf{H_3}C)_2Si(CHCH_2)$), 0.09 ppm (s, 24 H's $(C\mathbf{H_3})_2SiO_2$)). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.47 (CH vinyl), 131.82 (CH_2 vinyl), 1.17 ($SiCH_3$), 0.45 ppm ($SiCH_3$). ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -4.34 (M), -20.95 (D), -110.18 ppm (Q). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 746.2555, found = 746.2564.



***p*-Toluenesulfonyl triethyleneglycol methyl ether 5**: Triethylene glycol monomethyl ether (5.47 g, 5.22 mL, 33.3 mmol) and *p*-toluenesulfonyl chloride (6.5 g, 34.1 mmol, 1.02 equiv) were dissolved in DCM (dichloromethane, 35 mL). The solution was cooled to 0 °C and KOH (7.5 g, 133 mmol, 4 equiv) was added slowly. The reaction was left to stir at RT for 16 h, the reaction mixture was poured onto ice/water and extracted with DCM (3 × 100 mL). The organic phase was washed with H_2O (3 × 100 mL) and the aqueous washings back extracted with DCM (2 × 100 mL). The combined organic phases were dried (Na_2SO_4) and the solvent removed under reduced pressure to give *p*-toluenesulfonyl triethylene glycol methyl ether **5** (9.66 g, 30.3 mmol, 91 %); ^{1}H NMR (500 MHz): 2.40 (s, 3 H's, $C\mathbf{H_3}$), 3.32 (s, 3 H's, $OC\mathbf{H_3}$), 3.46-3.50 (m, 2 H's, $OC\mathbf{H_2}$), 3.52-3.58 (m, 6 H's, OC**H**$_2$), 3.62-3.66 (m, 2 H's, OC**H**$_2$), 4.10-4.13 (m, 2 H's, C**H**$_2$OS), 7.30 (d, 4 H's, *J* = 7.8 Hz, ArC**H**), 7.75 (d, 4 H's, *J* = 7.8 Hz, ArC**H**); ^{13}C NMR (125 MHz): 22.4, 59.7, 69.4, 70.0, 71.3, 71.3, 71.5, 72.6, 128.7, 130.6, 133.7, 145.6.; +ESI MS found $(M+NH_4)^+$ 336.3 (100 %), $(M+H)^+$ 319.2 (10).

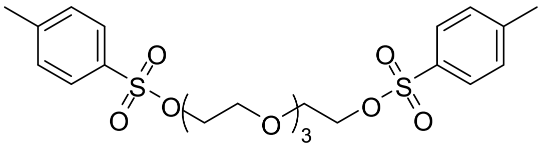


***p*-Toluenesulfonyl poly(ethylene glycol) 350 methyl ether 6**: Poly(ethylene glycol) 350 monomethyl ether (11.6 g, 33.3 mmol) and *p*-toluenesulfonyl chloride (6.5 g, 34.1 mmol, 1.02 equiv) were dissolved in DCM (35 mL). The solution was cooled to 0 °C to which KOH (7.5 g, 133 mmol, 4 equiv) added slowly. The reaction was left to stir at RT for 16 h, the reaction mixture was poured onto ice/water and extracted with DCM (3 × 100 mL). The organic phase was washed with H_2O (3 × 100 mL) and the aqueous washings back extracted with DCM (2 × 100 mL). The combined organic phases were dried (Na_2SO_4) and the solvent removed under reduced pressure to give *p*-toluenesulfonyl poly(ethylene glycol) 350 methyl ether **6** (15.0 g, 30.3 mmol, 91 %); ^{1}H NMR (500 MHz): 2.40 (s, 3 H's, C**H**$_3$), 3.32 (s 3 H's, OC**H**$_3$), 3.47-3.66 (m, 26 H's, OC**H**$_2$), 4.08-4.13 (m, 2 H's, C**H**$_2$OS), 7.30 (d, 4 H's, ArC**H**, *J* = 7.8 Hz), 7.74 (d, 4 H's, ArC**H**, *J* = 7.8 Hz); ^{13}C NMR (125 MHz): 22.3, 59.7, 69.3, 70.0, 71.2, 71.3, 71.3, 71.4, 72.6, 128.7, 130.6, 133.7, 145.5.; +ESI MS found $(M+Na)^+$ 473.3 (42 %), 517.4 (65), 561.4 (100), 605.4 (77), 649.4 (52).



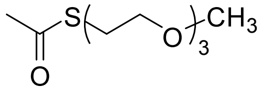
***p*-Toluenesulfonyl poly(ethylene glycol) 750 methyl ether 7**: Poly(ethylene glycol) 750 monomethyl ether (12.4 g, 16.7 mmol) and *p*-toluenesulfonyl chloride

(4.9 g, 25.6 mmol, 1.5 equiv) were dissolved in DCM (25 mL). The solution was cooled to 0 °C and had KOH (5.6 g, 100 mmol, 6 equiv) added slowly. The reaction was left to stir at RT for 16 h, after which the reaction mixture was poured onto ice/water and extracted with DCM (3 × 100 mL). The organic phase was washed with H_2O (3 × 100 mL) and the aqueous washings back extracted with DCM (2 × 100 mL). The combined organic phases were dried (Na_2SO_4) and the solvent removed under reduced pressure to give *p*-toluenesulfonyl poly(ethylene glycol) 750 methyl ether **7** (13.1 g, 14.7 mmol, 88 %); ^{1}H NMR (500 MHz): 2.42 (s, 3 H's, C**H₃**), 3.35 (s, 3 H's, OC**H₃**), 3.44-3.78 (m, 62 H's, OC**H₂**), 4.10-4.14 (m, 2 H's, C**H₂**OS), 7.31 (d, 4 H's, ArC**H**, *J* = 7.8 Hz), 7.76 (d, 4 H's, ArC**H**, *J* = 7.8 Hz); ^{13}C NMR (125 MHz): 22.4, 59.7, 69.4, 70.0, 71.2, 71.3, 71.3, 71.5, 72.7, 128.7, 130.6, 133.8, 145.5.; +ESI MS found $(M+Na)^+$ 737.5 (80 %), 781.5 (98), 825.5 (100), 869.5 (98), 913.6 (82), 957.7 (64), 1001.6 (42).

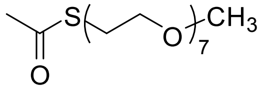


Ditosylate 8: Tetraethylene glycol (12.1 g, 62 mmol) and *p*-toluenesulfonyl chloride (24.4 g, 128 mmol, 2.06 equiv.) were dissolved in DCM (62.5 mL). The solution was cooled to 0 °C and KOH (28.1 g, 500 mmol, 8 equiv) was added slowly. The reaction was left to stir at RT for 16 h and which the reaction mixture was poured onto ice/water and extracted with DCM (3 × 100 mL). The organic phase was washed with H_2O (3 × 50 mL) and the aqueous washings back extracted with DCM (2 × 50 mL). The combined organic phases were dried (Na_2SO_4) and the solvent was removed under reduced pressure to give bis-*p*-toluenesulfonyl tetraethyleneglycol **8** (28.2 g, 56 mmol, 90 %); ^{1}H NMR: 2.43 (6H, s, C*H*₃), 3.55 (8H, s, OC*H*₂C*H*₂O), 3.67 (4H, t, *J* = 4.1 Hz, OC*H*₂CH₂O), 4.14 (4H, t, *J* = 4.1 Hz, OCH₂C*H*₂OS), 7.33 (4H, d, *J* = 7.6 Hz, ArCH), 7.78 (4H, d, *J* = 7.6

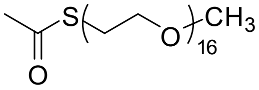
Hz, ArCH); ^{13}C NMR (125 MHz): 21.6, 68.6, 69.3, 70.4, 70.6, 127.9, 129.8, 132.9, 144.8; +ESI MS found $(M+NH_4)^+$ 520.3 (100 %), $(M+H)^+$ 503.3 (15); HRMS +ESI found 503.1372, expected 503.1404 ($C_{22}H_{31}O_9S_2^+$).



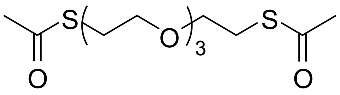
Tri(ethylene glycol) methyl ether thioacetate 9: *p*-Toluenesulfonyl tri(ethylene glycol) methyl ether **5** (12.0 g, 37 mmol) and potassium thioacetate (14.0 g, 120 mmol, 3.2 equiv) were dissolved in dry DMF (120 mL) and heated at 90 °C under N_2 for 16 h. The reaction mixture was cooled and diluted with DCM (400 mL). The resulting solution was washed with H_2O (5 × 250 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the crude product (8.95 g). The isolated residue was purified by column chromatography (SiO_2, eluent: 25 % EtOAc/75 % *n*-hexane) to give Triethylene glycol methyl ether thioacetate **9** as an orange colored liquid (3.31 g, 14.9 mmol, 40 %); ^{1}H NMR: 2.32 (s, 3 H's, SCOC**H$_3$**), 3.08 (t, 2 H's, C**H$_2$**S, *J* = 6.5 Hz), 3.37 (s, 3 H's, OC**H$_3$**), 3.52-3.66 (m, 10 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR (125 MHz): 29.6, 31.3, 59.8, 70.5, 71.1, 71.3, 71.3, 72.7, 196.3; +ESI MS found $(M+NH_4)^+$ 240.1 (100 %), $(M+H)^+$ 223.0 (10).



Poly(ethylene glycol) 350 methyl ether thioacetate 10: *p*-Toluenesulfonyl poly(ethylene glycol) 350 methyl ether **6** (15.3 g, 30.9 mmol) and potassium thioacetate (11.6 g, 99 mmol, 3.2 equiv) were dissolved in dry DMF (100 mL) and heated at 90 °C under N_2 for 16 h. The reaction mixture was cooled and then DCM (400 mL) was added. The resulting solution was washed with brine (5 × 250 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the crude product. The isolated residue was purified by column chromatography (SiO_2, eluent: 50 % EtOAc/50 % *n*-hexane) to give poly(ethylene glycol) 350 methyl ether thioacetate **10** as an orange colored viscous liquid (4.36 g, 10.9 mmol, 35 %); ^{1}H NMR: 2.28 (s, 3 H's, SCOC**H$_3$**), 3.03 (t, 2 H's, C**H$_2$**S, *J* = 6.6 Hz), 3.32 (s, 3 H's, OC**H$_3$**), 3.46-3.65 (m, 26 H's, m, OC**H$_2$**C**H$_2$**O); ^{13}C NMR (125 MHz): 29.5, 31.3, 59.7, 70.5, 71.0, 71.2, 71.3, 72.6, 196.2; +ESI MS found $(M+Na)^+$ 333.2 (30 %), 377.3 (80), 421.3 (100), 465.3 (78), 509.4 (62), 553.4 (40).

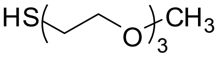


Poly(ethylene glycol) 750 methyl ether thioacetate 11: *p*-Toluenesulfonyl poly(ethylene glycol) 750 methyl ether **7** (28 g, 31.4 mmol) and potassium thioacetate (14.6 g, 127 mmol, 4 equiv) were dissolved in dry DMF (100 mL) and heated at 90 °C under N_2 for 16 h. The reaction mixture was cooled and had DCM (400 mL) added. The resulting solution was washed with brine (5 × 250 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the crude product. The isolated residue was purified by column chromatography (SiO_2, eluent: 100 % EtOAc) to give poly(ethylene glycol) 750 methyl ether thioacetate **11** as an orange colored amorphous solid (7.97 g, 10.0 mmol, 32 %); ^{1}H NMR: 2.30 (3H, s, SCOC**H$_3$**), 3.06 (2H, t, *J* = 6.6 Hz, C**H$_2$**S), 3.35 (3H, s, OC**H$_3$**), 3.49-3.66 (62H, m, OC**H$_2$**C**H$_2$**O); ^{13}C NMR (125 MHz): 29.6, 31.3, 59.8, 70.5, 71.0, 71.2, 71.3, 72.7, 196.3; +ESI MS found $(M+NH_4)^+$ 548.5 (50 %), 592.5 (72), 636.5 (96), 680.5 (90), 724.6 (100), 768.6 (70), 812.6 (66), 856.6 (50).

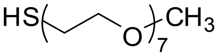


Dithioacetate **12**: Ditosylate **8** (20.0 g, 40 mmol) and potassium thioacetate (29.2 g, 250 mmol, 6.25 equiv) were dissolved in dry DMF (150 mL) and heated at 90 °C under N_2 for 16 h. The reaction mixture was cooled and had DCM (400 mL) added. The resulting solution was washed with H_2O (5 × 250 mL), dried (Na_2SO_4) and the solvent was removed under reduced pressure to give the crude product

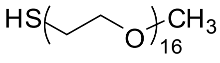
(8.95 g). The isolated residue was purified by column chromatography (SiO_2, eluant: 25 % EtOAc/75 % *n*-hexane then SiO_2, eluant: 100 % DCM) to give tetraethyleneglycol dithioacetate **12** as an orange colored liquid (4.44 g, 14.3 mmol, 36 %); ^{1}H NMR: 2.33 (6H, s, CH_3), 3.08 (4H, t, *J* = 6.3 Hz, SCH_2), 3.56-3.67 (16H, m, OCH_2); ^{13}C NMR (125 MHz): 29.6, 31.3, 70.5, 71.1, 71.3, 196.3; +ESI MS found $(M+NH_4)^+$ 328.3 (26 %), $(M+Na)^+$ 333.2 (60); HRMS +ESI found 333.0795, expected 333.0801 ($C_{12}H_{22}O_5S_2Na^+$).



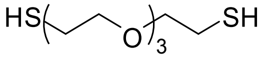
Tri(ethylene glycol) methyl ether thiol 13: Tri(ethylene glycol) methyl ether thioacetate **9** (3.3 g, 13.9 mmol) was heated at 100 °C in MeOH (20 mL)/aq. HCl (10%, 20 mL) for 2.5 h. The reaction mixture was cooled and DCM (100 mL) was added. The solution was washed with H_2O (3 × 50 mL) and sat. $NaHCO_3$ (3 × 50 mL), dried (Na_2SO_4) and the solvent removed under reduced pressure to give the crude product (2.35 g). The product was further purified by vacuum distillation to give triethylene glycol methyl ether thiol **13** as a pale yellow liquid (2.03 g, 11.3 mmol, 81 %); ^{1}H NMR: 1.56 (1H, t, *J* = 8.2 Hz, S**H**), 2.67 (2H, dt, *J* = 6.3 and 8.2 Hz, SC$\mathbf{H_2}$), 3.35 (3H, s, OC$\mathbf{H_3}$), 3.50-3.66 (10H, m, OC$\mathbf{H_2}$C$\mathbf{H_2}$O); ^{13}C NMR (125 MHz): 25.0, 59.8, 71.0, 71.3, 72.7, 73.7; +ESI MS found $(M+NH_4)^+$ 198.0 (100 %), $(M+H)^+$ 181.0 (15), $(M+Na)^+$ 203.0 (88).



Poly(ethylene glycol) 350 methyl ether thiol 14: Poly(ethylene glycol) 350 methyl ether thioacetate **10** (4.1 g, 10.3 mmol) was heated at 100 °C in MeOH (13 mL)/aq. HCl (10%, 13 mL) for 2.5 h. The reaction mixture was cooled and DCM (100 mL) was added. The solution was washed with H_2O (3 × 50 mL) and sat. $NaHCO_3$ (3 × 50 mL), dried (Na_2SO_4) and the solvent removed under reduced pressure to give poly(ethylene glycol) 350 methyl ether thiol **14** as an orange viscous liquid (3.25 g, 9.1 mmol, 88 %); ^{1}H NMR: 1.55 (1H, t, *J* = 8.2 Hz, S**H**), 2.65 (2H, dt, *J* = 6.3 and 8.2 Hz, SC$\mathbf{H_2}$), 3.33 (3H, s, OC$\mathbf{H_3}$), 3.47-3.66 (26H, m, OC$\mathbf{H_2}$C$\mathbf{H_2}$O); ^{13}C NMR (125 MHz): 25.0, 59.8, 71.0, 71.3, 71.3, 71.3, 71.4, 72.7, 73.6; +ESI MS found (M+Na)$^+$ 335.3 (48 %), 379.3 (93), 423.3 (100), 467.4 (70), 511.4 (50).



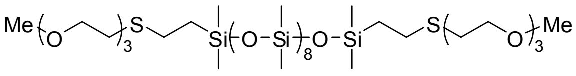
Poly(ethylene glycol) 750 methyl ether thiol 15: Poly(ethylene glycol) 750 methyl ether thioacetate **11** (7.97 g, 10.0 mmol) was heated at 100 °C in MeOH (12 mL)/aq. HCl (10%, 12 mL) for 2.5 h. The reaction mixture was cooled and DCM (100 mL) was added. The solution was washed with H_2O (3 × 50 mL) and sat. $NaHCO_3$ (3 × 50 mL), dried (Na_2SO_4) and the solvent removed under reduced pressure to give poly(ethylene glycol) 750 methyl ether thiol **15** as an orange viscous liquid (7.24 g, 9.6 mmol, 96 %); ^{1}H NMR: 1.54 (1H, t, *J* = 8.2 Hz, S**H**), 2.64 (2H, dt, *J* = 6.3 and 8.2 Hz, SC$\mathbf{H_2}$), 3.32 (3H, s, OC$\mathbf{H_3}$), 3.40-3.77 (62H, m, OC$\mathbf{H_2}$C$\mathbf{H_2}$O); ^{13}C NMR (125 MHz): 25.0, 59.8, 71.0, 71.2, 71.3, 71.3, 71.4, 72.7, 73.6; +ESI MS found (M+NH$_4$)$^+$ 550.6 (65 %), 594.5 (72), 638.5 (82), 682.6, (100), 726.6 (80), 770.6 (81), 814.7 (56), 858.7 (45).



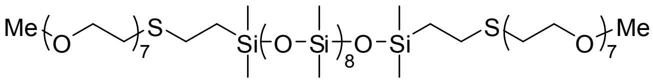
Dithiol 16: Tetraethyleneglycol dithioacetate **12** (3.2 g, 10.3 mmol) was heated at 100 °C in MeOH (15 mL)/aq. HCl (10%, 15 mL) for 2.5 h. The reaction mixture was cooled and DCM (100 mL) was added. The solution was washed with H_2O (3 × 50 mL) and sat. $NaHCO_3$ (3 × 50 mL), dried (Na_2SO_4) and the solvent removed under reduced pressure to give the crude product (1.82 g). The product was further purified by vacuum distillation to give tetraethyleneglycol dithiol **16** as a pale yellow liquid (1.45 g, 6.4 mmol, 62 %); ^{1}H NMR: 1.56 (2H, t, *J* 8.2 Hz, S*H*), 2.67 (4H, dt, *J* 6.3 and 8.2 Hz, SCH_2), 3.53-3.66 (12H, m, OCH_2CH_2O); ^{13}C NMR

(125 MHz): 25.0, 71.0, 71.3, 73.6; HRMS (ES Positive mode): m/z $[M+H]^+$ calculated = 225.0619, found = 225.0635.

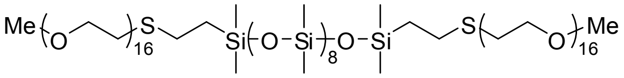
Thiol-ene coupling of PEGs and silicones: Linear silicones



18: a,w-Divinyl-terminated polydimethylsiloxane **17** (200 mg, M_n = 780, 0.25 mmol), triethylene glycol methyl ether thiol **13** (90 mg, 0.50 mmol, 2 equiv) and 2,2-dimethoxy-2-phenylacetophenone (26 mg, 0.1 mmol, 0.4 equiv) were placed in a vial and sealed with a rubber septum before being dissolved in degassed, dry THF (3 mL). The resulting reaction mixture was purged with N_2 gas for 5 min and subsequently irradiated with UV light for 2 h. The solvent was removed under reduced pressure and the resultant residue purified by column chromatography (SiO_2, eluent: 25 % EtOAc/75 % *n*-hexane) to give the triethylene glycol PDMS copolymer **18** as a colorless liquid (188 mg, 0.164 mmol, 66 %); ^{1}H NMR: 0.01-0.11 (m, 60 H's, $SiC\mathbf{H_3}$), 0.89 (m, 4 H's, $SiC\mathbf{H_2}$), 2.59 (m, 4 H's, $SC\mathbf{H_2}CH_2Si$), 2.71 (t, 4 H's, $SC\mathbf{H_2}CH_2O$, *J* = 7.2 Hz), 3.37 (s, 6 H's, $OC\mathbf{H_3}$), 3.52-3.66 (m, 20 H's, $OC\mathbf{H_2}C\mathbf{H_2}O$); ^{13}C NMR (125 MHz): 1.0, 1.8, 1.9, 19.9, 28.1, 31.9, 59.8, 71.0, 71.3, 71.4, 71.7, 72.7; ^{29}Si NMR (99 MHz, 1 % w/v $Cr(acac)_3$): 5.4 (M), -21.5 (D), -22.4 (D). +ESI MS found $(M+NH_4)^+$ 1084.6, 1010.5, 936.4 861.4.



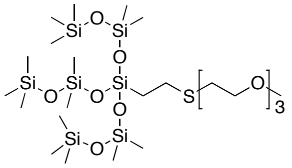
19: a,w-Divinyl-terminated polydimethylsiloxane (200 mg, M_n = 780, 0.25 mmol), poly(ethylene glycol) 350 methyl ether thiol **14** (180 mg, 0.50 mmol, 2 equiv) and 2,2-dimethoxy-2-phenylacetophenone (26 mg, 0.1 mmol, 0.4 equiv) were placed in a vial and sealed with a rubber septum before being dissolved in degassed, dry THF (3 mL). The resulting reaction mixture was purged with N_2 gas for 5 min and subsequently irradiated with UV light for 2 h. The solvent was removed under reduced pressure and the resultant residue purified by column chromatography (SiO$_2$, eluent: 25 % EtOAc/75 % *n*-hexane then 100 % EtOAc) to give the poly(ethylene glycol) 350 PDMS copolymer **19** as a colorless viscous liquid (259 mg, 0.174 mmol, 70 %); ^{1}H NMR: 0.01-0.14 (m, 60 H's, SiC**H$_3$**), 0.89 (m, 4 H's, SiC**H$_2$**), 2.58 (m, 4 H's, SC**H$_2$**CH$_2$Si), 2.70 (t, 4 H's, SC**H$_2$**CH$_2$O, J = 7.2 Hz), 3.36 (s, 6 H's, OC**H$_3$**), 3.50-3.67 (m, 52 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR (125 MHz): 1.0, 1.8, 1.9, 19.9, 28.1, 31.9, 59.8, 71.0, 71.3, 71.3, 71.7, 72.7; ^{29}Si NMR (99 MHz, 1 % w/v Cr(acac)$_3$): 5.4 (M), 21.5 (D), -22.4 (D). +ESI MS found (M+NH$_4$)$^+$ 1422.15 (100 %), 1437.24 (60%), 1465.25 (45%), 1480.28 (55%) 1511.30 (40%).



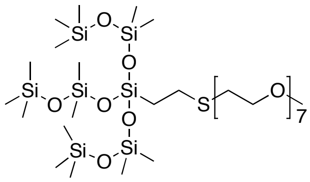
20: a,w-Divinyl-terminated polydimethylsiloxane (200 mg, M$_n$ = 780, 0.25 mmol), poly(ethylene glycol) 750 methyl ether thiol **15** (380 mg, 0.50 mmol, 2 equiv) and 2,2-dimethoxy-2-phenylacetophenone (26 mg, 0.1 mmol, 0.4 equiv) were placed in a vial and sealed with a rubber septum before being dissolved in degassed, dry THF (3 mL). The resulting reaction mixture was purged with N$_2$ gas for 5 min and subsequently irradiated with UV light for 2 h. The solvent was removed under reduced pressure and the resultant residue purified by column chromatography (SiO$_2$, eluent: 50 % EtOAc/50 % *n*-hexane then 10 % MeOH/90 % EtOAc) to give the poly(ethylene glycol) 750 PDMS copolymer **20** as a colorless liquid (450 mg, 0.197 mmol, 79 %); ^{1}H NMR: 0.01-0.16 (m, 60 H's, SiC**H$_3$**), 0.89 (m, 4 H's, SiC**H$_2$**), 2.59 (m, 4 H's, SC**H$_2$**CH$_2$Si), 2.70 (t, 4 H's, SC**H$_2$**CH$_2$O, J = 7.2 Hz), 3.36 (s, 6 H's, OC**H$_3$**), 3.50-3.68 (m, 124 H's, OCH$_2$C**H$_2$**O); ^{13}C NMR (125 MHz): 1.0, 1.8, 1.9, 19.9, 28.1, 31.9, 59.8, 71.0, 71.3, 71.7, 72.7; ^{29}Si NMR (99 MHz, 1 % w/v Cr(acac)$_3$): 5.4 (M), 21.5 (D), -22.4 (D). +ESI MS found (M+NH$_4$)$^{2+}$ 1123.89 (100%), 1086.99 (95 %), 1101.89 (85 %), 1164.94 (95%), 1209.06 (85%), 1253.06 (65%).

Thiol-ene coupling of PEGs and silicones: Branched silicones

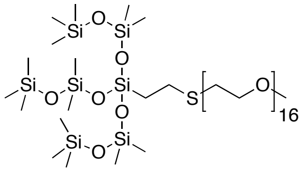
The following experimental is a general procedure for the following syntheses of thiol-ene clicked materials. Additional details and spectroscopic characterizations are provided below.



Thiol-ene click produc 21: Tris(pentamethyldisiloxy)vinylsilane **1** (500 mg, 0.92 mmol), tri(ethylene glycol) methyl ether thiol **13** (248 mg, 1.38 mmol, 1.5 eq) and 2,2-dimethoxy-2-phenylacetophenone (47 mg, 0.18 mmol) were placed in a vial and sealed with a rubber septum before being dissolved in degassed, dry THF (1 mL). The resulting reaction mixture was purged with N_2 gas for 5 min and subsequently irradiated with UV light for 2 h. The solvent was removed under reduced pressure and the resultant residue purified by kugelrohr distillation at 165 degrees centigrade for 1 hour. Yield = quantitative before kugelrohr purification, after purification = 0.603 g, 91 %, of a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.05 (s, 18 H's, $OSi(C\mathbf{H}_3)_2O$), 0.07 (s, 27 H's, $OSi(C\mathbf{H}_3)_3$), 0.84-0.87 (m, 2 H's, $R_3SiC\mathbf{H}_2CH_2S$), 2.58-2.61 (m, 2 H's, $R_3SiCH_2C\mathbf{H}_2S$), 2.71 (t, 2 H's, $SC\mathbf{H}_2CH_2O$, *J* = 7.3 Hz), 3.36 (s, 3 H's, $OC\mathbf{H}_3$), 3.52-3.54 (m, 2 H's, $SCH_2C\mathbf{H}_2O$), 3.60-3.64 ppm (m, 8 H's, $OC\mathbf{H}_2C\mathbf{H}_2O$); ^{13}C NMR: ($CDCl_3$ 125 MHz): δ 1.21, 1.92, 15.77, 27.28, 31.25, 59.10, 70.39, 70.67, 70.85, 72.05 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ 7.12 (M), -21.77 (D), -72.38 ppm (T). HRMS (ES Positive mode): m/z $[M+Na]^+$ calculated = 747.2554, found = 747.2527.

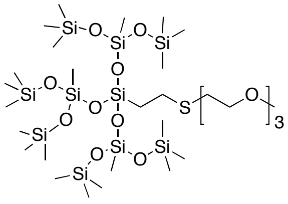


22: Thiol-ene click product **22** was prepared according to the general procedure above from tris(pentamethyldisiloxy)vinylsilane **1** (128 mg, 0.23 mmol), poly(ethylene glycol) methyl ether thiol **14** (125 mg, 0.35 mmol, 1.5 eq) and 2,2-dimethoxy-2-phenylacetophenone (12 mg, 0.05 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.184 g, 87 %, of a pale yellow oil. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.06 (s, 18 H's, OSi(C**H**$_3$)$_2$O), 0.09 (s, 27 H's, OSi(C**H$_3$**)$_3$), 0.85-0.88 (m, 2 H's, R$_3$SiC**H$_2$**CH$_2$S), 2.59-2.62 (m, 2 H's, R$_3$SiCH$_2$C**H$_2$**S), 2.72 (t, 2 H's, SC**H$_2$**CH$_2$O, *J* = 6.3 Hz), 3.38 (s, 3 H's, OC**H$_3$**), 3.54-3.55 (m, 2 H's, SCH$_2$C**H$_2$**O), 3.61-3.65 ppm (m, ~26 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR: (CDCl$_3$ 125 MHz): δ 1.26, 1.97, 15.77, 27.30, 31.24, 59.18, 69.77, 70.39, 70.66, 70.84, 72.06 ppm; ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.16 (M), -21.73 (D), -72.40 ppm (T). HRMS (ES Positive mode): m/z [M+NH$_4$]$^+$ calculated = 918.4048, found = 918.4024.

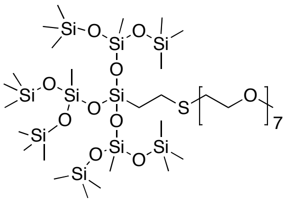


23: Thiol-ene click product **23** was prepared according to the general procedure above from tris(pentamethyldisiloxy)vinylsilane **1** (150 mg, 0.28 mmol) and poly(ethylene glycol) methyl ether thiol **15** (310 mg, 0.412 mmol, 1.5 eq) and 2,2-dimethoxy-2-phenylacetophenone (14 mg, 0.28 mmol). In addition to purification through kugelrohr distillation, **23** was subjected to a hexane wash (3 x 1.5 ml) and concentrated under reduced pressure to yield a pale yellow oil. Yield = quantitative before kugelrohr purification, after purification = 0.294 g, 82 %. ^{1}H

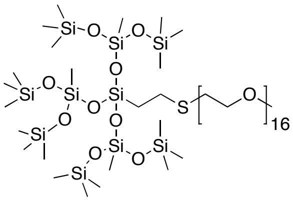
NMR ($CDCl_3$, 500 MHz): δ 0.06 (s, 18 H's, OSi(C**H**$_3$)$_2$O), 0.08 (s, 27 H's, OSi(C**H$_3$**)$_3$), 0.84- 0.88 (m, 2 H's, R_3SiC**H$_2$**CH$_2$S), 2.58-2.62 (m, 2 H's, R_3SiCH$_2$C**H$_2$**S), 2.71 (t, 2 H's, SC**H$_2$**CH$_2$O, *J* = 7.5 Hz), 3.37 (s, 3 H's, OC**H$_3$**), 3.53-3.55 (m, 2 H's, SCH$_2$C**H$_2$**O), 3.62-3.65 ppm (m, ~62 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR: ($CDCl_3$ 125 MHz): δ 1.26, 1.97, 15.79, 27.32, 31.28, 59.16, 70.40, 70.71, 72.08 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.19 (M), -21.70 (D), -72.37 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 1226.5825, found = 1226.5823.



24: Thiol-ene click product **24** was prepared according to the general procedure above from tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)vinylsilane **2** (500 mg, 0.65 mmol) and tri(ethylene glycol) methyl ether thiol **13** (152 mg, 0.84 mmol, 1.3 eq) and 2,2-dimethoxy-2-phenylacetophenone (33 mg, 0.13 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.586 g, 95 %, of a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.05 (s, 9 H's, O$_3$Si(C**H$_3$**)), 0.10 (s, 54 H's, OSi(C**H$_3$**)$_3$), 0.87-0.91 (m, 2 H's, R_3SiC**H$_2$**CH$_2$S), 2.61-2.65 (m, 2 H's, R_3SiCH$_2$C**H$_2$**S), 2.72 (t, 2 H's, SC**H$_2$**CH$_2$O, *J* = 7.3 Hz), 3.37 (s, 3 H's, OC**H$_3$**), 3.54-3.55 (m, 2 H's, SCH$_2$C**H$_2$**O), 3.60-3.65 ppm (m, 8 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR: ($CDCl_3$ 125 MHz): δ -1.94, 1.88, 15.69, 27.17, 31.34, 59.16, 70.40, 70.67, 70.71, 70.84, 72.07 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.42 (M), -66.43 (D), -73.92 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 964.3564, found = 964.3576.

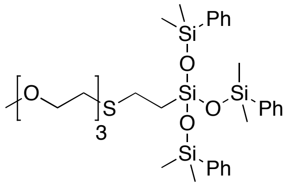


25: Thiol-ene click product **25** was prepared according to the general procedure above from tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)vinylsilane **2** (150 mg, 0.20 mmol) and poly(ethylene glycol) methyl ether thiol **14** (104 mg, 0.29 mmol, 1.5 eq) and 2,2-dimethoxy-2-phenylacetophenone (10 mg, 0.04 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.194 g, 88.5 %, of a pale yellow oil. ^{1}H NMR (CDCl$_3$, 500 MHz): δ 0.03 (s, 9 H's, O$_3$Si(C**H**$_3$)), 0.09 (s, 54 H's, OSi(C**H$_3$**)$_3$), 0.86-0.90 (m, 2 H's, R$_3$SiC**H$_2$**CH$_2$S), 2.60-2.64 (m, 2 H's, R$_3$SiCH$_2$C**H$_2$**S), 2.70 (t, 2 H's, SC**H$_2$**CH$_2$O, *J* = 7.5 Hz), 3.36 (s, 3 H's, OC**H$_3$**), 3.52-3.54 (m, 2 H's, SCH$_2$C**H$_2$**O), 3.59-3.64 ppm (m, ~26 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR: (CDCl$_3$ 125 MHz): δ -1.96, 1.87, 15.69, 27.16, 31.34, 59.13, 70.38, 70.64, 70.70, 70.84, 72.06 ppm; ^{29}Si NMR (CDCl$_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ 7.41 (M), -66.43 (D), -73.90 ppm (T). HRMS (ES Positive mode): m/z [M+NH$_4$]$^+$ calculated = 1140.4612, found = 1140.4620.



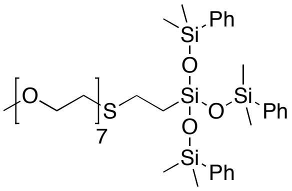
26: Thiol-ene click product **26** was prepared according to the general procedure above from tris(1,1,1,3,5,5,5-heptamethyltrisiloxy)vinylsilane **2** (250 mg, 0.33 mmol) and poly(ethylene glycol) methyl ether thiol **15** (368 mg, 0.48 mmol, 1.5 eq) and 2,2-dimethoxy-2-phenylacetophenone (17 mg, 0.07 mmol). In addition to purification through kugelrohr distillation, **26** was subjected to a hexane wash (3 x 1.5 ml) and concentrated under reduced pressure to yield a pale yellow oil. Yield

= quantitative before kugelrohr purification, after purification = 0.413 g, 84%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.03 (s, 9 H's, $O_3Si(C\mathbf{H}_3)$), 0.09 (s, 54 H's, $OSi(C\mathbf{H_3})_3$), 0.86-0.90 (m, 2 H's, $R_3SiC\mathbf{H_2}CH_2S$), 2.60-2.64 (m, 2 H's, $R_3SiCH_2C\mathbf{H_2}S$), 2.70 (t, 2 H's, $SC\mathbf{H_2}CH_2O$, *J* = 7.8 Hz), 3.36 (s, 3 H's, $OC\mathbf{H_3}$), 3.52-3.54 (m, 2 H's, $SCH_2C\mathbf{H_2}O$), 3.59-3.64 ppm (m, ~ 66 H's, $OC\mathbf{H_2}C\mathbf{H_2}O$); ^{13}C NMR: ($CDCl_3$ 125 MHz): δ -1.96, 1.86, 15.67, 27.15, 31.32, 59.13, 70.36, 70.68, 70.83, 72.05 ppm; ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ 7.83 (M), -66.01 (D), -73.50 ppm (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 1580.7234, found = 1580.7302.

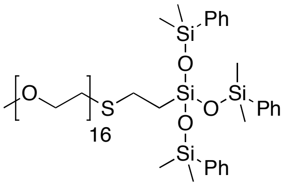


27: Tris(dimethylphenylsiloxy)vinylsilane **3** (500 mg, 0.98 mmol), tri(ethylene glycol) methyl ether thiol **13** (265 mg, 1.47 mmol, 1.5 equiv) and 2,2-dimethoxy-2-phenylacetophenone (45 mg, 0.19 mmol) were placed in a vial and sealed with a rubber septum before being dissolved in degassed, dry THF (1 mL). The resulting reaction mixture was purged with N_2 gas for 5 min and subsequently irradiated with UV light for 2 h. The solvent was removed under reduced pressure and the resultant residue purified by kugelrohr distillation at 165 °C for 1 h. Complete conversion by NMR; after kugelrohr purification = 0.53 g, 77% of a pale yellow liquid. ^{1}H NMR ($CDCl_3$, 200 MHz): δ 0.31 (s, 18 H's, $OSi(C\mathbf{H}_3)_2(C_6H_5)$), 0.78-0.87 (m, 2 H's, $R_3SiC\mathbf{H_2}CH_2S$), 2.37-2.50 (m, 2 H's, $R_3SiCH_2C\mathbf{H_2}S$), 2.57 (t, 2 H's $SC\mathbf{H_2}CH_2O$, *J* = 4.0 Hz), 3.39 (s, 3 H's, $OC\mathbf{H_3}$), 3.48- 3.66 (m, 12 H's, $OC\mathbf{H_2}C\mathbf{H_2}O$), 7.26- 7.52 ppm (m, 15 H's, $OSi(CH_3)_2(C_6\mathbf{H_5})$); ^{13}C NMR: ($CDCl_3$ 50 MHz): δ 0.63, 15.82, 27.22, 31.20, 59.17, 70.37, 70.70, 72.06, 127.86, 129.53, 133.10, 139.18 ppm ; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v Cr(acac)$_3$): δ -1.74 (M),

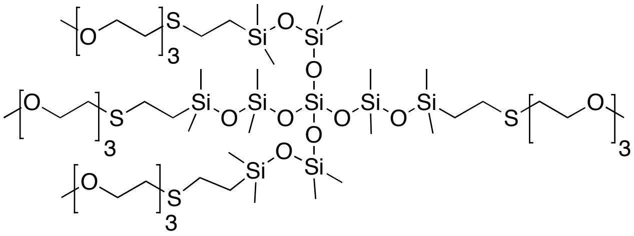
-69.06 (T). HRMS (ES Positive mode): m/z $[M+Na]^+$ calculated = 711.2459, found = 711.2449.



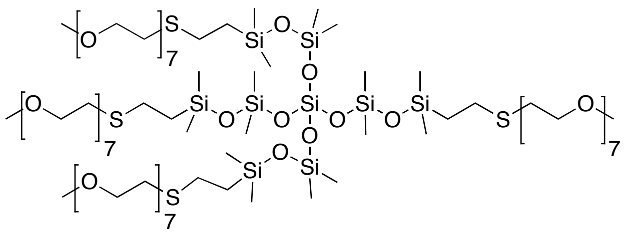
28: Thiol-ene click product **28** was prepared according to the general procedure above from tris(dimethylphenylsilyloxy)vinylsilane **3** (100 mg, 0.20 mmol), poly(ethylene glycol) methyl ether thiol **14** (105 mg, 0.29 mmol, 1.5 equiv) and 2,2-dimethoxy-2-phenylacetophenone (10 mg, 0.04 mmol). Yield = quantitative before kugelrohr purification; after purification = 0.169 g, 78 % of pale yellow liquid. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.30 (s, 18 H's, $OSi(C\mathbf{H}_3)_2(C_6H_5)$), 0.79-0.83 (m, 2 H's, $R_3SiC\mathbf{H_2}CH_2S$), 2.39-2.43 (m, 2 H's, $R_3SiCH_2C\mathbf{H_2}S$), 2.56 (t, 2 H's $SC\mathbf{H_2}CH_2O$, *J* = 7.0 Hz), 3.38 (s, 3 H's, $OC\mathbf{H_3}$), 3.49- 3.51 (m, 2 H's, $SCH_2C\mathbf{H_2}O$), 3.53-3.73 (m, ~ 26 H's, $OC\mathbf{H_2}C\mathbf{H_2}O$) 7.29-7.50 ppm (m, 15 H's, $OSi(CH_3)_2(C_6\mathbf{H_5})$); ^{13}C NMR: ($CDCl_3$ 150 MHz): δ 0.61, 15.81, 27.22, 31.20, 59.15, 70.35, 70.65, 72.06, 127.85, 129.51, 133.09, 139.18 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -1.76 (M), -69.12 (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 882.3954, found = 882.3964.



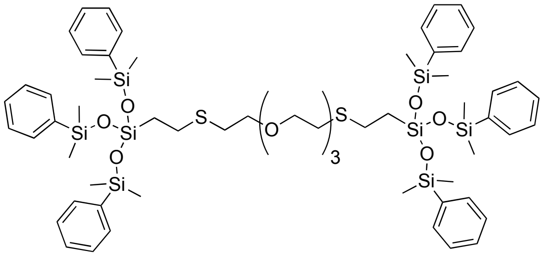
29: Thiol-ene click product **29** was prepared according to the general procedure above from tris(dimethylphenylsilyloxy)vinylsilane **3** (150 mg, 0.29 mmol), poly(ethylene glycol) methyl ether thiol **15** (217 mg, 0.28 mmol, 0.95 equiv) and 2,2-dimethoxy-2-phenylacetophenone (15.1 mg, 0.05 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.300 g, 81% of a pale yellow oil. ^{1}H NMR (CDCl$_3$, 600 MHz): δ 0.29 (s, 18 H's, OSi(C**H**$_3$)$_2$(C$_6$H$_5$)), 0.79-0.82 (m, 2 H's, R$_3$SiC**H$_2$**CH$_2$S), 2.38-2.41 (m, 2 H's, R$_3$SiCH$_2$C**H$_2$**S), 2.55 (t, 2 H's SC**H$_2$**CH$_2$O, *J* = 7.0 Hz), 3.37 (s, 3 H's, OC**H$_3$**), 3.49 (t, 2 H's, *J* = 6.0 Hz), 3.54-3.57 (m, 4 H's) 3.60-3.65 (m, ~ 66 H's, OC**H$_2$**C**H$_2$**O) 7.29-7.49 ppm (m, 15 H's, OSi(CH$_3$)$_2$(C$_6$**H$_5$**)); ^{13}C NMR: (CDCl$_3$ 150 MHz): δ 0.63, 15.82, 27.23, 31.21, 59.16, 70.36, 70.70, 72.07, 127.86, 129.53, 133.10, 139.19 ppm; ^{29}Si NMR (CDCl$_3$, 119 MHz, 1 % w/v Cr(acac)$_3$): δ -1.36 (M), -68.68 (T). HRMS (ES Positive mode): m/z [M+Na]$^+$ calculated = 1278.6313, found = 1278.6317.



30: Thiol-ene click product **30** was prepared according to the general procedure above from tetrakis(vinyltetramethyldisiloxy)silane **4** (500 mg, 0.69 mmol) and tri(ethylene glycol) methyl ether thiol **13** (741 mg, 4.1 mmol, 6 eq) and 2,2-dimethoxy-2-phenylacetophenone (52 mg, 0.13 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.81 g, 82%. ^{1}H NMR (CDCl$_3$, 200 MHz): δ 0.06 (s, 24 H's, O$_2$Si(C**H$_3$**)$_2$), 0.160 (s, 24 H's, OSi(C**H$_3$**)$_2$(CH$_2$CH$_2$S), 0.84-0.92 (m, 8 H's, R$_3$SiC**H$_2$**CH$_2$S), 2.53-2.57 (m, 8 H's, R$_3$SiCH$_2$C**H$_2$**S), 2.70 (t, 2 H's, SC**H$_2$**CH$_2$O, *J* = 7.0 Hz), 3.36 (s, 12 H's, OC**H$_3$**), 3.51-3.72 (m, 36 H's, OC**H$_2$**C**H$_2$**O); ^{13}C NMR: (CDCl$_3$ 50 MHz): δ -0.39, 1.18, 19.15, 27.46, 31.28, 59.16, 70.39, 70.70, 71.02, 72.04 ppm; HRMS (ES Positive mode): m/z [M+Na]$^+$ calculated = 1466.5836, found = 1466.576.



31: Thiol-ene click product **31** was prepared according to the general procedure above from tetrakis(vinyltetramethyldisiloxy)silane **4** (51 mg, 0.07 mmol) and poly(ethylene glycol) methyl ether thiol **14** (150 mg, 0.42 mmol, 6 eq) and 2,2-dimethoxy-2-phenylacetophenone (3.5 mg, 0.014 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.11g, 72%. NMR ($CDCl_3$, 500 MHz): δ 0.7 (s, 24 H's, $O_2Si(C\mathbf{H}_3)_2$), 0.10 (s, 24 H's, $OSi(C\mathbf{H_3})_2(CH_2CH_2S)$, 0.87-0.91 (m, 8 H's, $R_3SiC\mathbf{H_2}CH_2S$), 2.56-2.59 (m, 8 H's, $R_3SiCH_2C\mathbf{H_2}S$), 2.71 (t, 2 H's, $SC\mathbf{H_2}CH_2O$, *J* = 7.5 Hz), 3.37 (s, 12 H's, $OC\mathbf{H_3}$), 3.53-3.64 (m, ~ 105 H's, $OC\mathbf{H_2}C\mathbf{H_2}O$); ^{13}C NMR: ($CDCl_3$ 125 MHz): δ 0.42, 1.21, 19.19, 27.50, 31.34, 59.17, 70.41, 70.54, 70.66, 72.08 ppm; ^{29}Si NMR ($CDCl_3$, 119 MHz, 1 % w/v $Cr(acac)_3$): δ 6.23 (D), -20.59 (D), -109.6 ppm (Q). Repeated attempts to obtain a high resolution mass spectrum of this compound were unsuccessful. However, it was possible to acquire a low resolution MS. The presence of more than one ethylene oxide oligomer in the product was readily apparent: LRMS (ES Positive mode): m/z 1007.9 (M+2 x NH_4^+, doubly charged, $(CH_2CH_2O)_{24}$); and higher ethylene oxide homologues, 1029.9 $(CH_2CH_2O)_{25}$, 1051.9 $(CH_2CH_2O)_{26}$, 1073.9 $(CH_2CH_2O)_{27}$, 1095.4 $(CH_2CH_2O)_{28}$.



32: Thiol-ene click product **32** was prepared according to the general procedure above from tris(dimethylphenyl)vinylsilane **3** (200 mg, 0.39 mmol), tetraethyleneglycol dithiol (44 mg, 0.196 mmol, 1 eq) and 2,2-dimethoxy-2-phenylacetophenone (20 mg, 0.08 mmol). Yield = quantitative before kugelrohr purification, after purification = 0.216 g, 89%. ^{1}H NMR ($CDCl_3$, 500 MHz): δ 0.31 (s, 36 H's, $OSi(C\mathbf{H}_3)_2(C_6H_5)$), 0.81-0.85 (m, 4 H's, $R_3SiC\mathbf{H_2}CH_2S$), 2.41-2.44 (m, 4 H's, $R_3SiCH_2C\mathbf{H_2}S$), 2.58 (t, 4 H's $SC\mathbf{H_2}CH_2O$, *J* = 7.0 Hz), 3.51 (t , 4 H's, *J* = 7.1 Hz), 3.57- 3.64 (m, 8 H's, $OC\mathbf{H_2}C\mathbf{H_2}O$), 7.30- 7.52 ppm (m, 30 H's, $OSi(CH_3)_2(C_6\mathbf{H_5})$); ^{13}C NMR: ($CDCl_3$, 125 MHz): δ 0.64, 15.85, 27.25, 31.24, 70.38, 70.71, 70.78, 127.87, 129.54, 133.12, 139.21 ppm; ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -1.74 (M), -69.10 (T). HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calculated = 1260.4524, found = 1260.4497.

9.3 Appendix III: Supporting information for Chapter 5: Silicone Dendrons and Dendrimers Using Orthogonal SiH Coupling Reactions

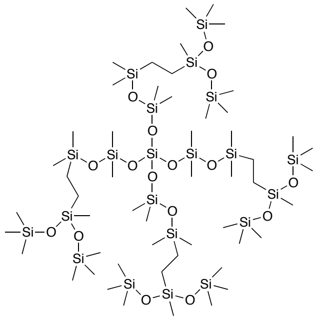
Materials and Methods

Vinyltetramethyldisiloxane, triethoxysilane, tetraethylorthosilicate (TEOS), were purchased from Gelest and distilled prior to use. Phenyldimethylsilane, pentamethyldisiloxane, 1,1,1,3,5,5,5-heptamethyltrisiloxane, and vinyl(trimethylsiloxy)silane, were purchased from Gelest and used as received. Chloropropyltriethoxysilane, and chloropropyltrimethoxysilane, chromium (III) acetylacetonate and tris(pentafluorophenyl)borane (95%) were purchased from Sigma-Aldrich and used as received.

Commercial solvents: hexane, dichloromethane and toluene were dried over activated alumina prior to use.

^{1}H NMR, ^{13}C NMR and ^{29}Si NMR experiments were recorded at room temperature and performed on Bruker Avance 500 and 600 MHz nuclear magnetic resonance spectrometers. High-resolution mass Spectrometry was performed with a Hi-Res Waters/Micromass Quattro Global Ultima (Q-TOF mass spectrometer). GPC Data was collected on a Viscotek VE 2001 GPC solvent/sample module.

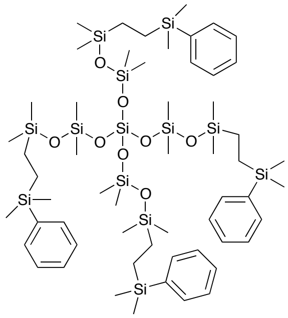
Synthesis of compound 6



To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.053 g, 0.073 mmol) in and oven dried 25 mL round bottom flask was added 1,1,1,3,5,5,5-heptamethytrisiloxane **3** (0.086 g, 0.386 mmol, ~ 5 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2 % by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **6**. (Isolated Yield – 0.075 g, 67%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.42 (m, 8 H, -$SiC\mathbf{H_2}CH_2Si(CH_3)_2$), 0.33 (m, 8 H, $SiCH_2C\mathbf{H_2}Si(CH_3)_2$), 0.08 (M, 72 H, $((Si(C\mathbf{H_3})_3O)_2SiCH_3)_3$), 0.07 (s, 24 H, CH_2 $Si(C\mathbf{H_3})_2OSi(CH_3)_2O$), 0.06 (s, 24 H, $CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2O$), -0.02 (m, 12 H, $((Si(CH_3)_3O)_2SiC\mathbf{H_3})_3$) ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 9.49, 8.99, 1.99, 1.20, -0.4, -1.06 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.49 (M), 6.82 (M), -20.75 (D), -21.34 (D), -109.51 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1632.6226; found = 1634.6277.

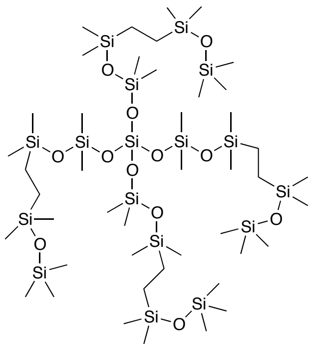
Synthesis of compound 7



To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.076g, 0.104 mmol) in and oven dried 25 mL round bottom flask was added phenyldimethylsilne **4** (0.071g, 0.521 mmol ~ 5 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **7**. (Isolated Yield – 0.086 g, 65%)

^{1}H-NMR (CDCl$_3$, 600 MHz): δ = 7.50 (m, 8 H, C_6H_5), 7.34 (m, 12 H, C_6H_5), 0.64 (m, 8 H, $SiC\mathbf{H_2}CH_2Si(CH_3)_2$), 0.44 (m, 8 H, $SiCH_2C\mathbf{H_2}Si(CH_3)_2$), 0.24 (s, 24 H, $Si(C\mathbf{H_3})_2(C_6H_5)$), 0.05 (s, 24 H $OSi(CH_3)_2$ $OSi(C\mathbf{H_3})_2CH_2$), 0.03 (s, 24 H $OSi(C\mathbf{H_3})_2$ $OSi(CH_3)_2CH_2$)ppm. ^{13}C-NMR (CDCl$_3$, 150 MHz): δ = 139.65, 133.76, 128.88, 127.82, 10.28, 7.20, 1.22, -0.34, -3.46 ppm. ^{29}Si-NMR (CDCl$_3$, 119MHz, 1% w/v Cr(acac)$_3$): δ = 8.31(M), -1.33 (M), -21.27 (D), -109.52 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1290.5389; found = 1290.5430.

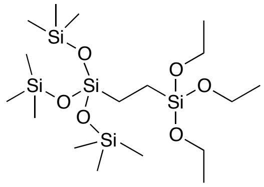
Synthesis of compound 8



To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.054 g, 0.073 mmol) in and oven dried 25 mL round bottom flask was added pentamethyldisiloxane **5** (0.054 g, 0.37 mmol, 5 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **8** (Isolated Yield – 0.067 g, 70 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.39-0.41 (m, 16 H, -OSiC**H**$_2$C**H**$_2$SiO-), 0.07 (s, 24 H, O Si(C**H**$_3$)$_2$CH$_2$CH$_2$), 0.08 (s, 24 H, CH$_2$OSi(C**H**$_3$)$_2$OSi(CH$_3$)$_3$), 0.05 (m, 36 H, OSi(C**H**$_3$)$_3$), 0.03 (s, 24H, OSi(C**H**$_3$)$_2$O Si(CH$_3$)$_2$) ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 9.74, 9.63, 2.13, 1.23, -0.26, -0.36 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v Cr(acac)$_3$): δ = 8.47 (M), 6.99 (M), -21.36 (D), -109.60 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1338.5514; found = 1338.5526.

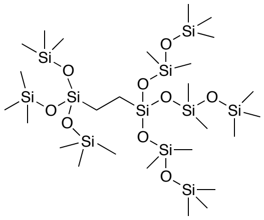
Synthesis of Asymmetrical Ethoxy compound 9



To a solution of vinyl(trimethylsiloxy)silane (0.313 g, 0.97 mmol) in and oven dried 25 mL round bottom flask was added triethoxysilane (0.241 g, 1.47 mmol, 1.5 equiv) and 5 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 60 °C under nitrogen atmosphere and monitored via NMR until all vinylic peaks were consumed (~ 24 hours). The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 75 degrees centigrade under high vacuum for 10 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **9**. (Isolated Yield – 0.252 g, 59%).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 3.84 (q, 6 H, -OSiC**H₂**CH₃, *J* = 5.85 Hz), 0.09 (t, 9 H, -OSiCH₂C**H₃**, *J* = 5.85 Hz), 0.55-0.59 (m, 2 H, -SiC**H₂**CH₂Si-), 0.43-0.47 (m, 2 H, -SiC**H₂**CH₂Si-), 0.09 (s, 27 H, -OSi(CH₃)₃) ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 58.50, 18.45, 5.84, 2.21, 1.88 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ = 6.35 (M), -44.85 (T), -65.89 (T) ppm. HRMS (ES Positive mode): m/z $[M+H]^+$ calc. = 487.2219; found = 487.2240

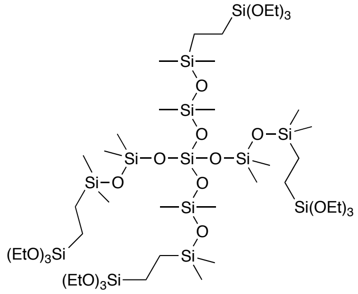
Synthesis of Asymetrical compound 10



To a solution of unsymmetrical triethoxy **9** (0.050 g, 0.115 mmol) in and oven dried 25 mL round bottom flask was added pentamethyldisiloxane (0.073 g, 0.49 mmol ~ 4.2 eq) and 5 mL of dry hexane. The mixture was stirred at room temperature for 1 min before the addition of tris(pentafluorophenyl)borane (50 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9 x 10^{-3} mmol). After a ~ 30 second induction time, moderate evolution of gas and heat from the solution occurred. The mixture was heated to 60 degrees centigrade for 15 minutes to ensure complete reaction. The mixture was then allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was gravity filtered and concentrated under reduced pressure. The mixture was then subject to Kugelhohr distillation under high vacuum (1 mmHg, 170 degrees centigrade), to remove excess starting materials, yielding colorless **10**. Yield (0.074 g, 85.6 %).

^{1}H-NMR ($CDCl_3$, 500 MHz): δ = 0.414-0.479 (m, 4 H, -OSiC**H$_2$**C**H$_2$**SiO-), 0.09 (s, 54 H, $OSi(C\mathbf{H_3})_3CH_2CH_2Si(OSi(CH_3)_2OSi(C\mathbf{H_3})_3)_3)$, 0.06 (s, 18 H, $OSi(CH_3)_3CH_2CH_2Si(OSi(C\mathbf{H_3})_2OSi(CH_3)_3)_3)$ ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 6.26, 6.19, 1.97, 1.86, 1.23 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ = 6.82 (M), 6.86 (M), -22.36 (D), -66.32 (T), -68.49 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 858.3295; found = 858.3320.

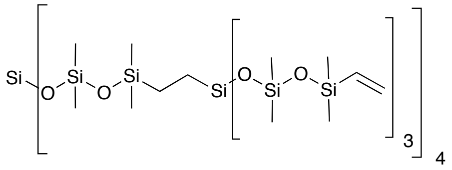
Synthesis of Compound 11



To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.250 g, 0.34 mmol) in and oven dried 25 mL round bottom flask was added triethoxysilane (0.242 g, 1.47 mmol, 4.3 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **11**. (Yield – 0.410 g, 86.3 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 3.80 (q, 24 H, $Si(OC\mathbf{H_2}CH_3)_3$, *J* = 10 Hz), 1.21 (t, 2 H, $Si(OCH_2C\mathbf{H_3})_3$, *J* = 7.5 Hz), 0.54 (s, 16 H, $O_3SiC\mathbf{H_2}C\mathbf{H_2}Si(OCH_2CH_3)_3$), 0.07 (s, 24 H, $SiOSi(CH_3)_2OSi(C\mathbf{H_3})_2CH_2$), 0.06 (s, 24 H, $SiOSi(C\mathbf{H_3})_2OSi(CH_3)_2CH_2$-). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ 58.39, 18.35, 9.11, 1.82, 1.07, -0.52 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.44 (M), -21.10 (D), -44.49 (T), -109.5 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1402.6030; found = 1402.6062.

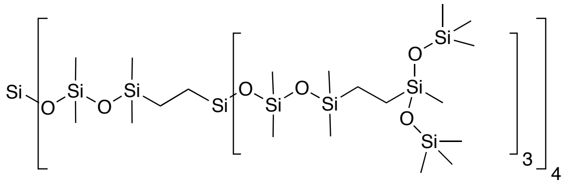
Syntheis of compound 12:



To a solution of compound **11** (0.100 g, 0.072 mmol) in and oven dried 25 mL round bottom flask was added vinyltetramethyldisiloxane **1** (0.185 g, 1.15 mmol, 16 equiv) and 5 mL of dry hexane. The mixture was stirred at room temperature The mixture was stirred at room temperature for 1 min before the addition of tris(pentafluorophenyl)borane (50 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9 x 10^{-3} mmol). After a ~30 second induction time, moderate evolution of gas and heat from the solution occurred. The mixture was heated to 60 degrees centigrade for 15 minutes to ensure complete reaction. The mixture was then allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was gravity filtered and concentrated under reduced pressure. The mixture was then subject to Kugelhohr distillation under high vacuum (1 mmHg, 170 degrees centigrade), to remove excess starting materials, yielding colorless **12**. Yield (0.164 g, 77.9 %).

^{1}H NMR ($CDCl_3$, 600 MHz): δ 6.11 (dd, 4 H's, $R_3SiC\mathbf{H}CHH$, *J* = 15.0, 20 Hz), 5.91 (dd, 4 H's, $R_3SiCHCH\mathbf{H}$, *J* = 4.0, 15.0 Hz), 5.74 (dd, 4 H's, $R_3SiCHC\mathbf{H}H$, *J* = 4.0, 20 Hz), 0.48-0.51 (m, 8 H, $O(H_3C)_2Si(CH_2C\mathbf{H_2}SiO(CH_3)_2)$), 0.36-0.39 (m, 8 H $O(H_3C)_2Si(C\mathbf{H_2}CH_2SiO(CH_3)_2)$ 0.13 (s 72 H, $OSi(C\mathbf{H_3})_2CH_2CH_2$), 0.04 ppm (s, 120 H, $OSi(CH_3)_2O$). ^{13}C NMR ($CDCl_3$ 125 MHz): δ 139.48 (CH vinyl), 131.77 (CH_2 vinyl), 9.78, 5.87, 1.30, 1.20, 0.45, -0.39 ppm. ^{29}Si NMR ($CDCl_3$, 99 MHz, 1 % w/v $Cr(acac)_3$): δ -8.39 (M), -4.125 (M), -21.33 (D), -67.88 (T), -109.56 ppm (Q). MALDI MS (ES Positive mode): m/z $[M+Na]^+$= 2,972.956, $[M+CH_3CN+Na]^+$ = 3012.888

Synthesis of compound 13

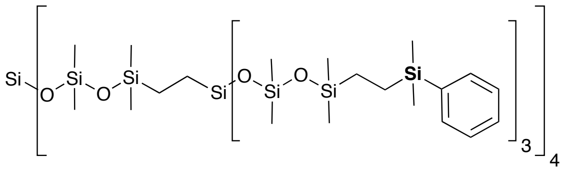


SiRR'R" = $SiMe(OSiMe_3)_2$

To a solution of compound **12** (0.025 g, 0.008 mmol) in and oven dried 25 mL round bottom flask was added 1,1,1,3,5,5,5-heptamethyltrisiloxysilane **3** (0.034 g, 0.154 mmol ~ 20 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **13** (Isolated Yield – 0.027 g, 86 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.32-0.45 (m, 64 H, $[(Si(OSi(CH_3)_3)_2(CH_3)C\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2O)_3SiC\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2O]_4$), 0.08 (s, 216 H, $[(Si(OSi(C\mathbf{H_3})_3)_2(CH_3)CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_4$), 0.06 (s, 192 H, $[(Si(OSi(CH_3)_3)_2(CH_3)CH_2CH_2Si(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2O)_3SiCH_2CH_2Si(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2O]_4$), -0.01 (s, 36 H, $[(Si(OSi(CH_3)_3)_2(C\mathbf{H_3})CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_4$),. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 10.01, 9.72, 6.04, 2.20, 1.54, -0.18, -0.84 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.25 (M), 6.76 (M), -20.856 (D), -21.41 (D), -22.20 (D), -67.95 (T), -77.90, -108.9 (Q) ppm. MALDI m/z for $[M+Na]^+$ = 5,643.584

Synthesis of Compound 14



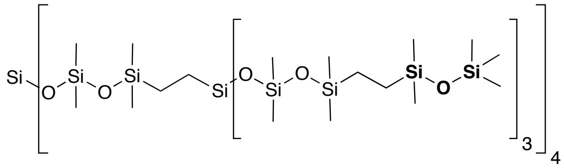
14

SiRR'R" = $SiMe_2Ph$

To a solution of compound **12** (0.020 g, 0.0068 mmol) in and oven dried 25 mL round bottom flask was added phenyldimethylsilne **4** (0.013 g, 0.095 mmol ~ 14 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **14**. (Isolated Yield – 0.025 g, 81 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR (CDCl$_3$, 600 MHz): δ = 7.47-7.49 (m, 24 H, C_6H_5, *meta*), 7.31-7.32 (m, 36 H, C_6H_5, *ortho, para*), 0.62-0.65 (m, 24 H, $-SiCH_2C\mathbf{H_2}Si(CH_3)_2C_6H_5$), 0.47-0.51 (m, 8 H, $-OSi(CH_3)_2SiCH_2C\mathbf{H_2}SiO_3-$), 0.40-0.44 (m, 24 H, $-SiC\mathbf{H_2}CH_2Si(CH_3)_2C_6H_5$), 0.35-0.39 (m, 8 H, $-OSi(CH_3)_2SiC\mathbf{H_2}CH_2SiO_3-$), 0.24 (s, 72 H, $-SiCH_2CH_2Si(C\mathbf{H_3})_2C_6H_5$), 0.03-0.06 (combination of singlets, 192 H, $Si(OSi(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2CH_2CH_2Si(OSi(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2CH_2-)_3)_4$) ppm. ^{13}C-NMR (CDCl$_3$, 150 MHz): δ = 139.58, 133.72, 128.85, 127.80, 10.27, 9.79, 7.18, 5.84, 1.32, -0.36, -3.47 ppm. ^{29}Si-NMR (CDCl$_3$, 119 MHz, 1% w/v Cr(acac)$_3$): δ = 8.43 (M), -8.14 (M), -1.37 (M), -21.32 (D), -22.09 (D), -67.93 (T), -109.52 (Q) ppm.

Synthesis of compound 15



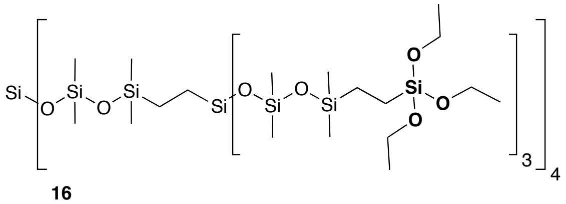
15

SiRR'R'' = $SiMe_2OSiMe_3$

To a solution of compound **12** (0.020 g, 0.0068 mmol) in and oven dried 25 mL round bottom flask was added pentamethyldisiloxane **5** (0.014 g, 0.095 mmol ~ 14 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **15**. (Isolated Yield – 0.027 g, 86 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.48-0.52 (m, 8 H, -OSi(CH_3)$_2$C**H**$_2$CH$_2$SiO$_3$-), 0.37-0.44 (m + s, 56 H, -OSi(CH_3)$_2$CH$_2$C**H**$_2$SiO$_3$-, -OSi(CH_3)$_2$C**H**$_2$C**H**$_2$Si(CH_3)$_2$O-), 0.01-0.07 ppm (combination of singlets, 372 H, all CH_3 groups.). ^{13}C-NMR ($CDCl_3$, 125 MHz): δ = 9.74, 9.64, 5.86, 5.85, 2.12, 1.57, 1.35, 1.17, -0.26, -0.37 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v Cr(acac)$_3$): δ = 8.38 (M), 8.26 (M),7.93 (M), 6.95 (M), -21.38 (D), -22.18 (D), -67.93 (T), -109.56 (Q) ppm.

Synthesis of compound 16



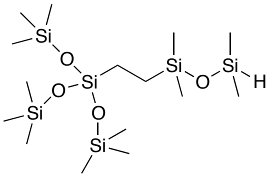
16

SiRR'R" = S(OEt)$_3$

To a solution of compound **12** (0.06 g, 0.02 mmol) in and oven dried 25 mL round bottom flask was added triethoxysilane (0.047 g, 0.284 mmol ~ 14 equiv) and 5 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 90 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess triethoxysilane, yielding colorless liquid **16**. (Isolated Yield – 0.082 g, 82 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 500 MHz): δ 3.81 (q, 72 H, $-OC\mathbf{H_2}CH_3$, *J = 10 Hz*) 1.21 (t, 109 H, $-OCH_2C\mathbf{H_3}$, *J* = 10 Hz), 0.53 (s, 48 H, 0.01 (s, 36 H, $(CH_3CH_2O)_3SiC\mathbf{H_2}C\mathbf{H_2}$-), 0.47-0.66 (m, 8 H, $-O_3SiC\mathbf{H_2}CH_2Si(CH_3)_2O$-), 0.38-0.41 (m, 8 H, $-O_3SiCH_2C\mathbf{H_2}Si(CH_3)_2O$-), 0.06, 0.05, 0.048 ppm (three overlapping singlet's, 192 H, $(-CH_2Si(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2O)_3SiCH_2CH_2Si(C\mathbf{H_3})_2OSI(C\mathbf{H_3})_2O)_4Si$ ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 58.49, 18.45, 9.80, 9.22, 5.87, 1.94, 1.32, -0.43 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.36 (M), 8.11 (M), -21.35 (D), -22.02 (D), -44.63 (T), -67.89 (T), -109.37 (Q).

Synthesis of monohydride dendron 17

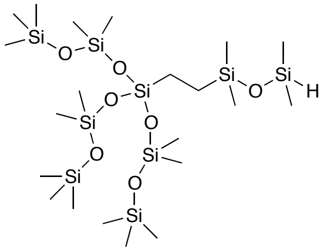


Vinyltris(trimethylsiloxy)silane (2 g, 6.2 mmol) was added to a solution of tetramethyldisiloxane (8.33 g, 62.0 mmol) in 15 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for 3 hours. The solvent was then removed in vacuo and the remaining liquid was distilled under high vacuum (1 mmHg) at 125 °C yielding pure **17** (2.48 g, 87% yield). Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 4.68-4.71 (m, 1 H, $Si(CH_3)_2\mathbf{H}$), 0.44-.47 (m, 2 H, $SiC\mathbf{H_2}CH_2Si(CH_3)_2$), 0.33-0.36 (m, 2 H, $SiCH_2C\mathbf{H_2}Si(CH_3)_2$), 0.18 (d, *J* = 2.72

Hz, 6 H, Si(C**H$_3$**)$_2$H), 0.07 (s, 33 H, (Si(C**H$_3$**)$_3$O)$_3$, SiCH$_2$CH$_2$Si(C**H$_3$**)$_2$). ^{13}C-NMR (CDCl$_3$, 150 MHz): δ 9.88, 5.91, 1.90, 1.06, -0.77 pp. ^{29}Si-NMR (CDCl$_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ 10.27 (M), 6.77 (M), -7.25 (M), -65.25 (T) ppm. HRMS (ES Positive mode): m/z [M+NH$_4$]$^+$ calc. = 474.2199; found = 474.2220

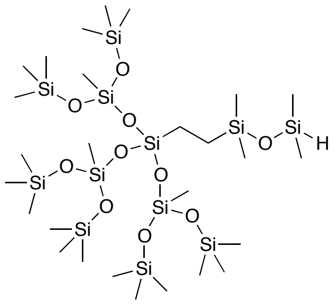
Synthesis of monohydride dendron 18



Vinyltris(pentamethyldisiloxy)silane (1.58 g, 2.81 mmol) was added to a solution of tetramethyldisiloxane (5.36 g, 39.9 mmol) in 15 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for 3 hours. The solvent was then removed in vacuo and the remaining liquid was distilled under high vacuum (1 mmHg) at 160 °C yielding pure **18** (1.08 g, 57% yield). Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR (CDCl$_3$, 600 MHz): δ 4.70 (m, 1 H, Si(CH$_3$)$_2$**H**), 0.52-0.54 (m, 2 H, SiC**H$_2$**CH$_2$Si(CH$_3$)$_2$), 0.41-0.44 (m, 2 H, O$_3$SiCH$_2$C**H$_2$**Si(CH$_3$)$_2$O), 0.16 (d, 6 H, *J* = 2.56 Hz, Si(C**H$_3$**)$_2$H), 0.10 (s, 27 H, [Si(C**H$_3$**)$_3$OSi(CH$_3$)$_2$O]$_3$), 0.07 (s, 24 H, [Si(CH$_3$)$_3$OSi(**CH$_3$**)$_2$O]$_3$).^{13}C-NMR (CDCl$_3$, 150 MHz): δ 9.76, 5.91, 1.99, 1.28, 1.07, -0.55 ppm. ^{29}Si-NMR (CDCl$_3$, 99 MHz, 1% w/v Cr(acac)$_3$): δ 10.15 (M), 6.80 (M), -7.29 (M), -22.28 (D), -68.38 (T) ppm. HRMS (ES Positive mode): m/z [M+Na]$^+$ calc. = 696.2763; found = 696.2782.

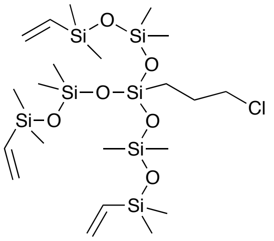
Synthesis of monohydride dendron 19



Vinyltris(1,1,1,3,5,5,5-heptamethyltrisiloxy)silane (1.52 g, 1.98 mmol) was added to a solution of tetramethyldisiloxane (3.53 g, 26.3 mmol) in 15 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for 3 hours. The solvent was then removed in vacuo and the remaining liquid was distilled under high vacuum (1 mmHg) at 160 °C yielding pure **19** (1.05g, 60% yield). Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 4.68-4.72 (m, 1H, $Si(CH_3)_2\mathbf{H}$), 0.55-57 (m, 2 H, $SiC\mathbf{H_2}CH_2Si(CH_3)_2$), 0.43-0.46 (m, 2 H, $SiCH_2C\mathbf{H_2}Si(CH_3)_2$), 0.15 (d, *J* = 2.86 Hz, 6 H, $Si(C\mathbf{H_3})_2H$), 0.10 (s, 60 H, $[(Si(\mathbf{CH_3})_3O)_2SiCH_3O]_3$), 0.05 (s, 16 H, $[(Si(CH_3)_3O)_2Si\mathbf{CH_3}O]_3$, $O_3SiCH_2CH_2Si(\mathbf{CH_3})_2$). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 7.67, 3.88, 0.05, -0.85, -2.46, -3.82 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 10.07 (M), 6.96 (M), -7.43 (M), -66.65 (T), -70.03 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 918.3327; found = 918.3304.

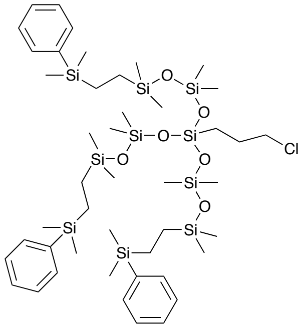
Synthesis of compound 20



To a solution of 3-chloropropyltrimethoxysilane (1.00 g, 5.03 mmol) in and oven dried 25 mL round bottom flask was added vinyltetramethyldisiloxane **1** (4.04 g, 25.15 mmol ~ 5 eq) and 10 mL of dry hexane. The mixture was stirred at room temperature for 1 min before the addition of tris(pentafluorophenyl)borane (50 μl of a solution containing 40 mg dissolved in 1 ml of toluene, 3.9 x 10^{-3} mmol). After a ~ 30 second induction time, moderate evolution of gas and heat from the solution occurred. The mixture was then allowed to cool to room temperature before the addition of neutral alumina (1.5 g). The resulting solution was gravity filtered and concentrated under reduced pressure. The mixture was then subject to Kugelhohr distillation under high vacuum (1 mmHg, 162 degrees centigrade), to ensure completely pure **20**. Isolated Yield: (After distillation, 1.98 g, 62%).

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 6.12 (dd, 3 H, *J* = 14.5, 20.4 Hz), 5.94 (dd, 3 H, *J* = 3.9, 14.5 Hz), 5.73 (dd, 3 H, *J* = 3.6, 20.4 Hz), 3.50 (t, 2 H, $CH_2C\mathbf{H_2}Cl$), 1.82-1.89 (m, 2 H, $CH_2C\mathbf{H_2}CH_2Cl$), 0.62-0.65 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2$), 0.16 (s, 18 H, $[CH_2CHSi(CH_3)_2OSi(C\mathbf{H_3})_2O]_3$), 0.08 (s, 18 H, $[CH_2CHSi(C\mathbf{H_3})_2OSi(CH_3)_2O]_3$) ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 139.58, 132.11, 47.93, 27.24, 12.28, 1.49, 0.61 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ -3.84 (M), -20.87 (D), -69.68 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 648.2103; found = 648.2109.

Synthesis of compound 21

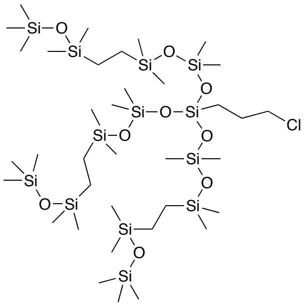


To a solution of chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.250 g, 0.395 mmol) in and oven dried 25 mL round bottom flask was added phenyldimethylsilane **4** (0.242 g, 1.78 mmol, 4.5 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **21**. (isolated Yield – 0.29 g, 70%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 7.49-7.51 (m, 6 H, [$(C_6H_5)^{\boldsymbol{o}}$ $Si(CH_3)_2$-), 7.34-7.35 (m, 9 H, [$(C_6H_5)^{\boldsymbol{m,p}}Si(CH_3)_2$-), 3.42 (t, 2 H, *J* = 6.93 Hz, $O_3SiCH_2CH_2C\mathbf{H_2}Cl$), 1.78-1.83 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2Cl$), 0.57-0.60 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2Cl$), 0.62-0.66 (m, 6 H, [$(C_6H_5)Si(CH_3)_2C\mathbf{H_2}CH_2Si(CH_3)_2O$-), 0.42-0.45 (m, 6 H, [$(C_6H_5)Si(CH_3)_2CH_2C\mathbf{H_2}Si(CH_3)_2O$-), 0.25 (s, 18 H,

$[(C_6H_5)Si(C\mathbf{H_3})_2CH_2CH_2SiO(CH_3)_2\text{-})$, 0.05 (s, 18 H, $[(C_6H_5)Si(CH_3)_2CH_2CH_2Si(C\mathbf{H_3})_2OSi(CH_3)_2O]_3Si\text{-})$, 0.04 (s, 18 H, $[(C_6H_5)Si(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2O]_3Si\text{-})$. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 139.78, 133.97, 129.11, 128.04, 47.82, 27.28, 12.28, 10.51, 7.45, 1.54, -0.16, -3.26 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.40 (M), -1.33 (M), -21.63 (D), -69.67 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1056.4228; found = 1056.4220.

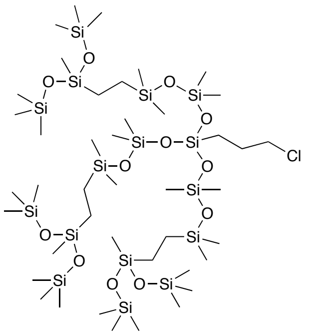
Synthesis of compound 22



To a solution of chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.250 g, 0.395 mmol) in and oven dried 25 mL round bottom flask was added pentamethyldisiloxane **5** (0.264 g, 1.78 mmol, 4.5 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2 % by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **22**. (Yield – 0.398, 86%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 3.50 (t, 2 H, *J* = 6.9 Hz, $R_3SiCH_2CH_2C\mathbf{H_2}Cl$), 1.83-1.88 (m, 2 H, $R_3SiCH_2C\mathbf{H_2}CH_2Cl$), 0.62-0.65 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2Cl$), 0.38-0.45 (m, 12 H, $-OSi(CH_3)_2C\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2O-$), 0.07 (s, 36 H, $[(CH_3)_3SiOSi(C\mathbf{H_3})_2CH_2CH_2Si(C\mathbf{H_3})_2OSi(CH_3)_2O]_3$), 0.06 (s, 27 H, $[(C\mathbf{H_3})_3SiOSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3SiCH_2-$), 0.04 (s, 18 H, $[(CH_3)_3SiOSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2O]_3SiCH_2-$). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 47.84, 27.33, 12.32, 9.96, 9.86, 2.34, 1.55, -0.04, -0.17 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.56 (M), 8.35 (M), 7.03 (M), -21.72 (D), -69.71 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1092.4322; found = 1092.4318.

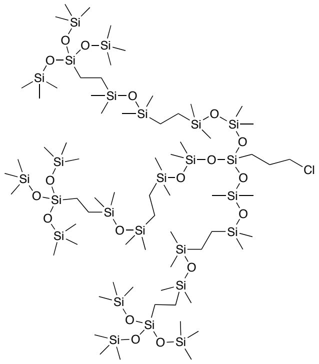
Synthesis of compound 23



To a solution of chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.250 g, 0.395 mmol) in and oven dried 25 mL round bottom flask was added 1,1,1,3,5,5,5-heptamethyltrisiloxane **3** (0.396 g, 1.78 mmol, 4.5 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **23**. (Yield – 0.483 g, 94%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 3.50 (t, 2 H, *J* = 6.93 Hz, $SiCH_2CH_2C\mathbf{H_2}Cl$), 1.83-1.88 (m, 2 H, $O_3SiCH_2C\mathbf{H_2}CH_2Cl$), 0.62-0.65 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2CH_2Cl$), 0.33-0.46 (m, 12 H, $[CH_3((CH_3)_3SiO)_2SiC\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2O$-), 0.09 (s, 54 H, $[CH_3((C\mathbf{H_3})_3SiO)_2SiCH_2CH_2Si(CH_3)_2O$-), 0.07 (s, 18 H, $[CH_3((CH_3)_3SiO)_2SiCH_2CH_2Si(C\mathbf{H_3})_2O$-), 0.07 (s, 18 H, $[CH_3((CH_3)_3SiO)_2SiCH_2CH_2Si(CH_3)_2O$-), 0.00 (s, 9 H, $[C\mathbf{H_3}((CH_3)_3SiO)_2SiCH_2CH_2Si(CH_3)$-.). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 47.82, 27.31, 12.28, 9.73, 9.23, 2.21, 1.54, -0.19, -0.82 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.16 (M), 6.43 (M), -21.31 (D), -22.13 (D), -70.19 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 1314.4886; found = 1314.4889.

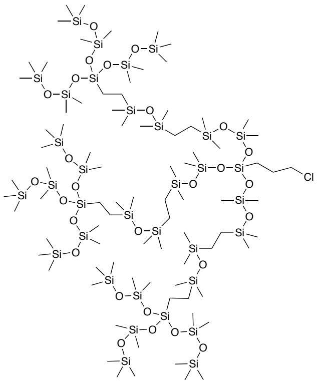
Synthesis of compound 24



To a solution of chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.110 g, 0.166 mmol) in and oven dried 25 mL round bottom flask was added mono Si-H dendron **17** (0.331 g, 0.747 mmol) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 150 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal solvent/starting materials, yielding colorless liquid **24**. (Isolated Yield – 0.283 g, 81 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 3.50 (t, 2 H, *J* = 6.90 Hz, $CH_2C\mathbf{H_2}Cl$), 1.74-1.77 (m, 2 H, $CH_2C\mathbf{H_2}CH_2Cl$), 0.52-0.55 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2$), 0.31-0.37 (m, 18 H, $[(Si(CH_3)_3O)_3SiCH_2C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2C\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.22-0.25 (m, 6 H, $[(Si(CH_3)_3O)_3SiC\mathbf{H_2}CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), -0.01 (s, 81 H, $[(Si(C\mathbf{H_3})_3O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), -0.03 (s, 36 H, $[(Si(CH_3)_3O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2O]_3$), -0.05 (s, 18 H, $[(Si(CH_3)_3O)_3SiCH_2CH_2Si(C\mathbf{H_3})_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), -0.05 (s, 18 H, $[(Si(CH_3)_3O)_3SiCH_2CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 47.63, 27.14, 12.12, 10.09, 9.76, 9.66, 6.00, 1.90, 1.34, -0.23, -0.26, -0.38 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ 8.57 (M), 8.18 (M), 8.13 (M), 7.12 (M), -21.73 (D), -64.62 (T), -69.72 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 2016.7687; found = 2016.7669.

Synthesis of compound 25

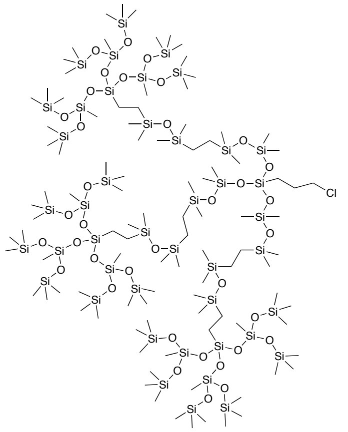


To a solution of chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.026 g, 0.042 mmol) in and oven dried 25 mL round bottom flask was added mono Si-H dendron **19** (0.086 g, 0.126 mmol) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 150 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal solvent/starting materials, yielding colorless liquid **25**. (Isolated Yield – 0.0684 g, 61 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 3.49 (t, 2 H, *J* = 6.90 Hz, $CH_2C\mathbf{H_2}Cl$), 1.82-1.87 (m, 2 H, $CH_2C\mathbf{H_2}CH_2Cl$), 0.61-0.64 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2$), 0.49-0.56 (m, 6 H, $[(Si(CH_3)_3OSi(CH_3)_2O)_3SiC\mathbf{H_2}CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.39-0.46 (m, 18 H, $[(Si(CH_3)_3OSi(CH_3)_2O)_3SiCH_2C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2C\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.09 (s, 81 H,

$[(Si(C\mathbf{H_3})_3OSi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.07 (s, 36 H, $[(Si(CH_3)_3OSi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2O]_3$), 0.06 (s, 54 H, $[(Si(CH_3)_3OSi(C\mathbf{H_3})_2O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.04 (s, 18 H, $[(Si(CH_3)_3OSi(CH_3)_2O)_3SiCH_2CH_2Si(C\mathbf{H_3})_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.03 (s, 36 H, $[(Si(CH_3)_3OSi(CH_3)_2O)_3SiCH_2CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$). ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 47.78, 27.32, 12.31, 10.14, 9.95, 9.86, 6.16, 2.19, 1.53, 1.48, -0.04, -0.18 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.24 (M), 7.72 (M), 7.57 (M), 6.78 (M), -22.16 (D), -22.33 (D), -68.30 (T), -70.15 (T) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 2682.9360; found = 2682.9324

Synthesis of compound 26

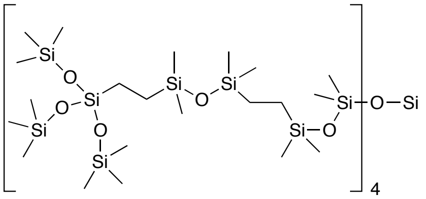


To a solution of chloropropyltris(vinyltetramethyldisiloxy)silane **20** (0.023 g, 0.037 mmol) in and oven dried 25 mL round bottom flask was added mono Si-H dendron **18** (0.100 g, 0.111 mmol) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 150 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal solvent/starting materials, yielding colorless liquid **26**. (Isolated Yield – 0.0763 g, 62%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 3.49 (t, 2 H, *J* = 6.90 Hz, $CH_2C\mathbf{H_2}Cl$), 1.82-1.87 (m, 2 H, $CH_2C\mathbf{H_2}CH_2Cl$), 0.61-0.64 (m, 2 H, $O_3SiC\mathbf{H_2}CH_2$), 0.54-0.57 (m, 6 H, $[(Si(OSi(CH_3)_3)_2(CH_3)O)_3SiC\mathbf{H_2}CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.40-0.46 (m, 18 H, $[(Si(OSi(CH_3)_3)_2(CH_3)O)_3SiCH_2C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2C\mathbf{H_2}C\mathbf{H_2}Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.10 (s, 162 H, $[(Si(OSi(C\mathbf{H_3})_3)_2(CH_3)O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.06 (s, 36 H, $[(Si(OSi(CH_3)_3)_2(CH_3)O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(C\mathbf{H_3})_2OSi(C\mathbf{H_3})_2O]_3$), 0.05 (s, 27 H, $[(Si(OSi(CH_3)_3)_2(CH_3)O)_3SiCH_2CH_2Si(CH_3)_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.033 (s, 18 H, $[(Si(OSi(CH_3)_3)_2(CH_3)O)_3SiCH_2CH_2Si(C\mathbf{H_3})_2OSi(CH_3)_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$), 0.028 (s, 18 H, $[(Si(OSi(CH_3)_3)_2(CH_3)O)_3SiCH_2CH_2Si(CH_3)_2OSi(C\mathbf{H_3})_2CH_2CH_2Si(CH_3)_2OSi(CH_3)_2O]_3$),. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 47.77, 27.33, 12.32, 9.96, 9.88, 6.08, 2.12, 1.53, -0.02, -0.19, -1.69 ppm. ^{29}Si-NMR ($CDCl_3$, 99 MHz, 1% w/v $Cr(acac)_3$): δ 8.15 (M), 7.70 (M), 7.66 (M), 6.95 (M), -22.18 (D), -66.66 (T), -67.74 (T), -69.99

(T) ppm. HRMS (ES Positive mode): m/z $[M+2NH_4]^+/2$ calc. = 1686.0691; found = 1686.0885.

Synthesis of compound 27

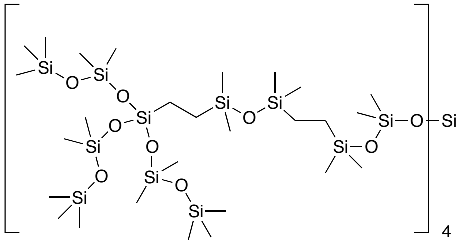


To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.297 g, 0.041 mmol) in and oven dried 25 mL round bottom flask was added small monohydride dendron **17** (0.075 g, 0.164 mmol, 4 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10ml of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **27** (Yield 0.086 g, 82%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.39-0.45 (m, 24 H, $SiCH_2\mathbf{CH_2}Si(CH_3)_2$, $Si(CH_3)_2\mathbf{CH_2CH_2}Si(CH_3)_2$), 0.31-0.34 (m, 8 H, $Si(CH_3)_3OSi(CH_3)_2O)3Si\mathbf{CH2}$), 0.09 (s, 108 H, $(Si(\mathbf{CH_3})_3O)_3$, 0.07 (s, 48 H, $Si(\mathbf{CH_3})_2OSi(\mathbf{CH_3})_2CH_2CH_2Si(CH_3)_2$), 0.029-0.03 (s, s, 48 H, $CH_2Si(\mathbf{CH_3})_2OSi(\mathbf{CH_3})_2OSi$) ppm.^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 10.07, 9.74, 9.64, 5.97, 1.88, 1.20, -0.25, -0.28, -0.38 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.44 (M), 8.17 (M), 8.11 (M), 7.11 (M), -

21.42 (D), -64.61 (T), -109.54 (Q) ppm. HRMS (ES Positive mode): m/z $[M+NH_4]^+$ calc. = 2570.9977; found = 2571.0056

Synthesis of compound 28

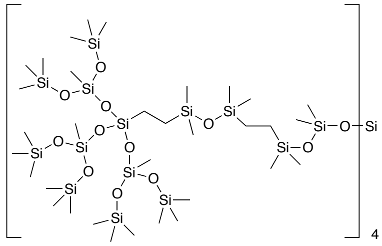


To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.260 g, 0.036 mmol) in and oven dried 25 mL round bottom flask was added linear mono hydride dendron **18** (0.098 g, 0.144 mmol, 4 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 ml of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **28** (Yield – 0.099g, 79%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.49-0.52 (m, 8 H, $(Si(CH_3)_3OSi(CH_3)_2O)_3SiCH_2$), 0.39-0.42 (m, 24 H, $SiCH_2\mathbf{CH_2}Si(CH_3)_2$, $Si(CH_3)_2\mathbf{CH_2CH_2}Si(CH_3)_2$), 0.08 (s, 108 H, $(Si(\mathbf{CH_3})_3OSi(CH_3)_2O)_3$), 0.07-0.06 (s,s, 48 H, $Si(\mathbf{CH_3})_2OSi(\mathbf{CH_3})_2CH_2CH_2Si(CH_3)_2$), 0.05 (s, 72 H, $(Si(CH_3)_3OSi(\mathbf{CH_3})_2O)_3$), 0.02 (s, 24 H, $CH_2Si(CH_3)_2OSi(\mathbf{CH_3})_2Si$), 0.02 (s, 24 H, $CH_2Si(\mathbf{CH_3})_2OSi(CH_3)_2Si$)

ppm.^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 9.93, 9.73, 9.64, 5.94, 1.97, 1.27, 1.19, -1.26, -0.38 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.43 (M), 8.19 (M), 8.02 (M), 7.18 (M), -21.43 (D), -21.91 (D), -67.86 (T), -109.55 (Q) ppm. MALDI m/z: for $[M+Na]^+$ = 3,470.333

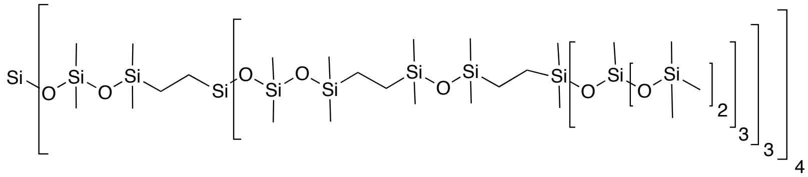
Synthesis of compound 29



To a solution of tetrakis(vinyltetramethyldisiloxy)silane **2** (0.260 g, 0.036 mmol) in and oven dried 25 mL round bottom flask was added monohydride dendron **19** (0.130 g, 0.144 mmol, 4 equiv) and 5 mL of dry hexane. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 ml of a 2 % by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 100 degrees centigrade under high vacuum (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless liquid **29** (Yield –0.136g, 87%) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ = 0.54-0.57 (m, 8 H, $(Si(CH_3)_3OSi(CH_3)_2O)_3SiCH_2$), 0.40-0.45 (m, 24 H, $SiCH_2\mathbf{CH_2}Si(CH_3)_2$, $Si(CH_3)_2\mathbf{CH_2CH_2}Si(CH_3)_2$), 0.10 (s, 216 H, $(Si(\mathbf{CH_3})_3OSi(CH_3)_2O)_3$), 0.06-0.07 (s,s, 48 H, $Si(\mathbf{CH_3})_2OSi(\mathbf{CH_3})_2CH_2CH_2Si(CH_3)_2$), 0.05 (s, 36 H, $((Si(CH_3)_3O)_2Si\mathbf{CH_3})_3$), 0.03 (s, 24 H, $CH_2Si(CH_3)_2OSi(\mathbf{CH_3})_2Si$), 0.02 (s, 24 H, $CH_2Si(\mathbf{CH_3})_2OSi(CH_3)_2Si$) ppm. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ = 9.75, 9.73, 9.65, 5.86, 1.90, 1.18, -0.25, -0.40, -1.92 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ = 8.44 (M), 8.19 (M), 8.02 (M), 7.40 (M), -21.42 (D), -66.24 (T), -69.55 (T), -109.53 (Q) ppm. MALDI m/z: for $[M+ Na]^+$ = 4,359.605

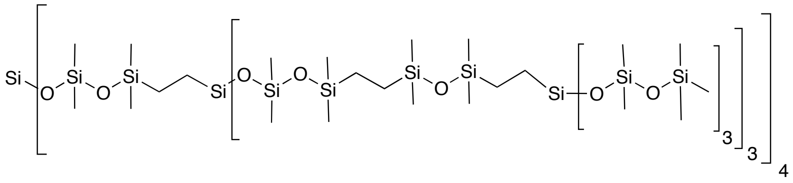
Synthesis of compound 30



To a solution of compound **12** (0.013 g, 0.004 mmol) in and oven dried 25 mL round bottom flask was added mono Si-H dendron **18** (0.046 g, 0.051 mmol 12 equiv) and 5 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10μl of a 2% by wt. in xylenes solution, 2.24×10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless viscous liquid **30**. (Isolated Yield – 0.045 g, 76 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR ($CDCl_3$, 600 MHz): δ 0.39-0.44 (m + m, 32 H, $–CH_2$-) 0.29-0.38 (m + m, 80 H, CH_2-), -0.08-0.01 (multiple singlet's, 1092 H $Si(CH_3)_2$ + $SI(CH_3)_3$),. ^{13}C-NMR ($CDCl_3$, 150 MHz): δ 9.71, 9.70, 9.68, 9.61, 5.82, 2.09, 1.85, 1.26, 1.06, -0.31, -0.45, -1.60, -1.97 ppm. ^{29}Si-NMR ($CDCl_3$, 119 MHz, 1% w/v $Cr(acac)_3$): δ 8.23 (M), 8.12 (M), 8.00 (M), 7.35 (M), 6.94 (M), -21.43 (D), -22.28 (D), -66.25 (T), -67.33 (T), -69.55 (T), -109.59 (Q) ppm. GPC PDI – 1.08.

Synthesis of compound 31



To a solution of compound **12** (0.018 g, 0.006 mmol) in and oven dried 25 mL round bottom flask was added mono Si-H dendron **19** (0.05 g, 0.075 mmol, 12 equiv) and 5 mL of dry toluene. A drop of Platinum (0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane catalyst (10 μl of a 2% by wt. in xylenes solution, 2.24 x 10^{-2} mmol) was then added. The mixture was then heated to 40 °C under nitrogen atmosphere for approx 4 hours, or when all vinylic peaks were shown as consumed via proton NMR. The mixture was then treated with activated charcoal and allowed to stir for 1 hour. The solution was then gravity filtered and concentrated in vacuo. The remaining solution was then heated to 170 degrees centigrade under high vacuum for 30 minutes (1 mmHg) to ensure complete removal of excess starting materials, yielding colorless viscous liquid **31**. (Isolated Yield –0.058 g, 84 %) Note – Only the major hydrosilylation isomer is reported, typically comprising roughly 90 % of the product.

^{1}H-NMR (CDCl$_3$, 600 MHz): δ 0.41-0.43 (m + m, 32 H, –CH$_2$-) 0.30-0.33 (m + m, 80 H, CH$_2$-), -0.10-0.01 (multiple singlet's 876 H Si(CH$_3$)$_2$ + SI(CH$_3$)$_3$),. ^{13}C-NMR (CDCl$_3$, 150 MHz): δ 9.93, 9.82, 9.73, 9.65, 5.94, 5.86, 1.97, 1.47, 1.32, 1.26, 1.12, -0.27, -0.38, -0.43 ppm. ^{29}Si-NMR (CDCl$_3$, 119 MHz, 1% w/v Cr(acac)$_3$): δ 8.24 (M), 8.15 (M), 8.01 (M), 7.17 (M), 6.72 (M), -22.24 (D), -22.77 (D), -22.99 (D), -67.85 (T), -68.05 (T), -109.58 (Q) ppm.

9.4 Appendix IV: Supporting information for Chapter 6: Rapid, Metal-Free Room Temperature Vulcanization Produces Silicone Elastomers

Table S - Experimental elastomer data

ENTRY #	EXP # In Paper	Silane MW (g)^{a}	x-linker (g)^{b}	Ratio^{c}	Catalyst (µL/ppm)^{d}	Hexane (mL)	Rubber (Y/N)	Shore A	Shore OO
				Solvent					
1		28000 (5.0)	Me (0.021)	1|1	30/238	THF 5.0	N	-	-
2		28000 (5.0)	Me (0.021)	1|1	30/238	Hexane 5.0	Y	21	67
3		28000 (5.0)	Me (0.021)	1|1	30/238	Hexane 10.0	Y	10	55
4		28000 (5.0)	Me (0.021)	1|1	30/238	DCM 5.0	Y	10	55
5		28000 (5.0)	Me (0.021)	1|1	30/238	D$_4$ 5.0	Y	9	51
6		28000 (5.0)	Me(0.021)	1|1	30/238	D$_4$ 1.0	N	-	-
				0.5:1					
7	**10**	28000 (2.5)	Me (0.005)	0.5|1	15/239	2.0	Y	20	78
8		28000 (2.5)	TM (0.003)	0.5|1	15/239	2.0	Y	14	66
9		28000 (2.5)	TE (0.005)	0.5|1	15/239	2.0	Y	17	66
10		28000 (2.5)	TP (0.006)	0.5|1	15/239	2.0	Y	16	66
11		16000 (2.5)	Me (0.009)	0.5|1	15/239	2.0	N		
12		16000 (2.5)	TM (0.006)	0.5|1	15/239	2.0	N		
13	**12**	16000 (2.5)	TE (0.008)	0.5|1	15/239	2.0	N		
14		16000 (2.5)	TP (0.010)	0.5|1	15/239	2.0	N		
15		5900 (2.5)	Me (0.025)	0.5|1	15/238	2.0	Y	20	70

ENTRY #	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (μL/ppm)[d]	Hexane (mL)	Rubber (Y/N)	Shore A	Shore OO
16	**22**	5900 (2.5)	TM (0.016)	0.5|1	15/238	2.0	N		
17	**23**	5900 (2.5)	TM (0.016)	0.5|1	9/143	5.0	Y		11
18	**11**	5900 (2.5)	TE (0.022)	0.5|1	15/237	2.0	N		
19		5900 (2.5)	TP (0.028)	0.5|1	15/237	2.0	N		
				1:1					
20	**13**	28000 (2.5)	Me (0.0011)	1|1	15/239	2.0	Y	21	67
21		28000 (2.5)	TM (0.007)	1|1	15/239	2.0	Y	18	67
22	**6**	28000 (2.5)	TE (0.009)	1|1	15/239	2.0	Y	18	67
10	**29**	28000 (2.5)	TE (0.009)	1:1	30ppm[e]	2.0	Y	12	62
11	**30**	28000 (2.5)	TE (0.009)	1:1	30ppm[f]	2.0	Y	12	62
23		28000 (2.5)	TP (0.012)	1|1	15/238	2.0	Y	20	66
24		16000 (2.5)	Me (0.0018)	1|1	15/238	2.0	Y	22	67
25		16000 (2.5)	TM (0.012)	1|1	15/238	2.0	N	-	-
26		16000 (2.5)	TE (0.016)	1|1	15/238	2.0	Y	20	68
27		16000 (2.5)	TP (0.020)	1|1	15/238	2.0	Y	28	71
28		5900 (2.5)	Me (0.050)	1|1	15/236	2.0	N	-	-
29	**26, 1-5**[g]	5900 (2.5)	TM (0.032)	1|1	15/236	2.0	Y	22	75
30	**27**	5900 (2.5)	TM (0.032)	1|1	1.9/30	2.0	Y	22	78
31		5900 (2.5)	TE (0.044)	1|1	15/236	2.0	Y	11	47
32		5900 (2.5)	TP (0.056)	1|1	15/235	2.0	Y	22	61

ENTRY #	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Rubber (Y/N)	Shore A	Shore OO
				1.5:1					
33	**14**	28000 (2.5)	Me (0.016)	1.5l1	15/238	2.0	Y	18	62
34		28000 (2.5)	TM (0.010)	1.5l1	15/239	2.0	Y	8	58
35	**7**	28000 (2.5)	TE (0.014)	1.5l1	15/238	2.0	Y	13	63
36		28000 (2.5)	TP (0.018)	1.5l1	15/238	2.0	Y	16	61
37	**19**	16000 (2.5)	Me (0.028)	1.5l1	15/238	2.0	Y	18	65
38	**16**	16000 (2.5)	TM (0.018)	1.5l1	15/238	2.0	Y	23	70
39	**8**	16000 (2.5)	TE (0.024)	1.5l1	15/238	2.0	Y	21	70
40	**18**	16000 (2.5)	TP (0.031)	1.5l1	15/237	2.0	Y	18	63
41	**25**	5900 (2.5)	Me (0.075)	1.5l1	15/235	2.0	Y	30	80
42		5900 (2.5)	TM (0.048)	1.5l1	15/235	2.0	Y	25	69
43	**9**	5900 (2.5)	TE (0.066)	1.5l1	15/234	2.0	Y	25	68
44		5900 (2.5)	TP (0.084)	1.5l1	15/232	2.0	Y	22	71
				2:1					
45	**15**	28000 (2.5)	Me (0.021)	2l1	15/238	2.0	Y	10	53
46		28000 (2.5)	TM (0.013)	2l1	15/238	2.0	Y	22	68
47		28000 (2.5)	TE (0.018)	2l1	15/238	2.0	Y	20	68
48		28000 (2.5)	TP (0.024)	2l1	15/238	2.0	Y	5	49
49		16000 (2.5)	Me (0.037)	2l1	15/237	2.0	Y	8	52
50	**17**	16000 (2.5)	TM (0.023)	2l1	15/238	2.0	Y	14	51
51		16000 (2.5)	TE (0.032)	2l1	15/237	2.0	Y	21	71

ENTRY #	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Rubber (Y/N)	Shore A	Shore OO
52	**24**	16000 (2.5)	TP (0.041)	2l1	15/236	2.0	Y	-	15
53	**12**	5900 (2.5)	Me (0.100)	2l1	15/233	2.0	Y	13	51
54		5900 (2.5)	TM (0.064)	2l1	15/234	2.0	Y	18	67
55		5900 (2.5)	TE (0.088)	2l1	15/232	2.0	Y	22	54
56		5900 (2.5)	TP (0.112)	2l1	15/229	2.0	Y		
Functional Elastomers									
57	**21**	5900 (2.5)	IT (0.163)	2l1	15/225	2.0	Y	21	66
58	**20**	5900 (2.5)	VT (0.083)	2l1	15/232	2.0	Y	15	68
59	**28**	28000 (2.5)	TM (0.009)	1.5l1	15/239	2.0[h]	Y	8	60

[a] Hydride-terminated PDMS: 7-10 cSt (1,190 g mol-1), 2-3 cSt (730 g mol-1).[b] Me: Methyltriethoxysilane, TM: Tetramethyl orthosilicate, TE: Tetraethyl orthosilicate, TP: Tetrapropyl orthosilicate.[c] ratio = alkoxysilane groups : PDMS hydride groups. [d] Catalyst solution: 40 mg of $B(C_5F_5)_3$ in 1 mL of dry toluene. [e] A 30ppm Pt solution was prepared by taking 10 mL of Karstedt's Catalyst (2.5% Pt in xylenes) and diluting in 1 mL of hexanes. 0.33 mL of this stock solution was placed added to a vial containing the TEOS and 1.67 mL of hexanes, this solution was then quickly added to the silane, stirred, and poured into a Petri dish to cure. [f] Same conditions as e, but performed at 50 °C. [g] Table 1 in paper, varying solvent volumes from 0 – 2 mL. [h] 1.4 m L hexane with 0.6 mL toluene + 1-pyrenemethanol (0.001 g).

9.5 Appendix V: Supporting Information For Chapter 7: Anhydrous Formation of Foamed Silicone Elastomers using the Piers-Rubinsztajn Reaction

Experimental foam data

ENT#	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (μL/ppm)[d]	Hexane (mL)	Induction Time (s)	Total time (s)	Density (g/cm^3)	Hardness[e] Shore 00
				1:0.5						
F1		730 (1.0)	TM (0.052)	1l0.5	10/380	1.0	-			
F2		730 (1.0)	TE (0.071)	1l0.5	10/373	1.0	-			
F3		730 (1.0)	TP (0.091)	1l0.5	10/366	1.0	-			
F4		1190 (2.0)	TM (0.063)	1l0.5	20/387	1.0	-			
F5		1190 (2.0)	TE (0.087)	1l0.5	20/383	1.0	-			
F6		1190 (2.0)	TP (0.110)	1l0.5	20/379	1.0	-			
F7		5000 (2.0)	TM (0.012)	1l0.5	20/397	1.0	-			
F8		5000 (2.0)	TE (0.017)	1l0.5	20/396	1.0	-			
F9		5000 (2.0)	TP (0.022)	1l0.5	20/395	1.0	-			
				1:1						
F10	**5**	730 (1.0)	TM (0.104)	1l1	10/362	1.0	5.5 ± 2.2	15.9 ± 0.5	0.13 ± 0.03	0
F11	**6**	730 (1.0)	TE (0.143)	1l1	10/349	1.0	8.1 ± 2.1	25.4 ± 5.9	0.11 ± 0.01	0
F12	**7**	730 (1.0)	TP (0.182)	1l1	10/338	1.0	42.9 ± 5.9	75.7 ± 7.9	0.09 ± 0.01	0
F13	**8**	1190 (2.0)	TM (0.127)	1l1	20/376	1.0	10.3 ± 3.4	23.7 ± 1.6	0.17 ± 0.02	0
F14	**16**	1190 (2.0)	TE (0.174)	1l1	20/367	1.0	12.0 ± 1.1	35.1 ± 2.8	0.13 ± 0.01	0
F15	**17**	1190 (2.0)	TP (0.222)	1l1	20/360	1.0	27 ± 11	68.7 ± 5.7	0.15 ± 0.03	0

ENT#	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Induction Time (s)	Total time (s)	Density (g/cm^3)	Hardness[e]	Shore 00
F16	**9**	2570 (2.0)	TM (0.059)	1l1	20/388	1.0	11.3 ± 2.6	14.9 ± 1.4	0.46 ± 0.04	3	51
F17		2570 (2.0)	TE (0.081)	1l1	20/384	1.0	22.3 ± 6.8	38.0 ± 1.6	0.33 ± 0.07	3	55
F18		2570 (2.0)	TP (0.103)	1l1	20/380	1.0	42.7 ± 9.1	69 ± 30	0.27	2	25
F19		5000 (2.0)	TM (0.024)	1l1	20/395	1.0	-	-	-		
F20		5000 (2.0)	TE (0.036)	1l1	20/393	1.0	-	-	-		
F21		5000 (2.0)	TP (0.044)	1l1	20/391	1.0	-	-	-		
				1:1.5							
F22	**1**	730 (1.0)	TM (0.157)	1l1.5	10/345	1.0	13.1 ± 1.2	33.6 ± 0.9	0.23 ± 0.03	0	
F23		730 (1.0)	TE (0.215)	1l1.5	10/329	1.0	52.9 ± 4.1	73.6 ± 6.1	0.16 ± 0.02	0	
F24		730 (1.0)	TP (0.274)	1l1.5	10/314	1.0	194.9 ± 6.3	211 ± 11	0.15 ± 0.04	0	
F25	**2**	1190 (2.0)	TM (0.191)	1l1.5	20/365	1.0	21.6 ± 5.7	32.2 ± 2.8	0.17 ± 0.02	0	
F26		1190 (2.0)	TE (0.262)	1l1.5	20/353	1.0	26 ± 18	39 ± 23	0.18 ± 0.01	1	7
F27		1190 (2.0)	TP (0.333)	1l1.5	20/342	1.0	73 ± 33	155 ± 22	0.20 ± 0.02	0	
F28	**3**	2570 (2.0)	TM (0.089)	1l1.5	20/382	1.0	16.1 ± 0.71	18.1 ± 1.9	0.32 ± 0.04	3	50
F29		2570 (2.0)	TE (0.121)	1l1.5	20/377	1.0	32.2	47.2	0.41 ± 0.01	3	49
F30		2570 (2.0)	TP (0.154)	1l1.5	20/371	1.0	144 ± 29	215 ± 27	0.29 ± 0.02	3	49
F31	**4**	5000 (2.0)	TM (0.094)	1l1.5	20/382	1.0	N	-	-		
F32		5000 (2.0)	TE (0.129)	1l1.5	20/375	1.0	N	-	-		
F33		5000 (2.0)	TP (0.170)	1l1.5	20/368	1.0	N	-	-		
				1:2							
F34	**10**	730 (1.0)	TM (0.201)	1l2	10/333	1.0	31.8 ± 5.1	37.5 ± 4.2	0.14 ± 0.02	0	
F35		730 (1.0)	TE (0.287)	1l2	10/310	1.0	49.2 ± 5.3	79.9 ± 3.1	0.15 ± 0.01	0	

ENT#	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Induction Time (s)	Total time (s)	Density (g/cm^3)	Hardness[e]	Shore 00
F36		730 (1.0)	TP (0.364)	1l2	10/293	1.0	155	316	0.12	0	
F37		1192 (2.0)	TM (0.256)	1l2	20/354	1.0	50.9 ± 4.1	60.4 ± 8.0	0.23 ± 0.03	3	60
F38		1190 (2.0)	TE (0.350)	1l2	20/340	1.0	57 ± 10	74.1 ± 3.5	0.18 ± 0.01	0	
F39		1190 (2.0)	TP (0.444)	1l2	20/327	1.0	152.9	243.2	0.27	0	
F40		2570 (2.0)	TM (0.118)	1l2	20/377	1.0	13.6 ± 0.8	18.3 ± 1.2	0.25 ± 0.03	2	28
F41	**11**	2570 (2.0)	TE (0.162)	1l2	20/370	1.0	37 ± 10	69 ± 12	0.30 ± 0.03	2	31
F42	**12**	2570 (2.0)	TP (0.205)	1l2	20/362	1.0	186 ± 95	453 ± 220	0.25 ± 0.07	2	35
F43		5000 (2.0)	TM (0.052)	1l2	20/389	1.0	N	-	-		
F44		5000 (2.0)	TE (0.070)	1l2	20/386	1.0	N	-	-		
F45		5000 (2.0)	TP (0.090)	1l2	20/382	1.0	N	-	-		
			Solvent Free								
F46	**13n**	1190 (2.0)	TM (0.127)	1l1	20/376	-	13.6 ± 1.8	19.6 ± 1.9	0.34 ± 0.03	0	
F47	**14n**	1190 (2.0)	TE (0.174)	1l1	20/367	-	34.5 ± 8.4	43.6 ± 7.7	0.31 ± 0.01	0	
F48	**15n**	1190 (2.0)	TP (0.222)	1l1	20/360	-	170 ± 21	204 ± 34	0.21 ± 0.01	1	7
F49		1190 (2.0)	TM (0.191)	1l1.5	20/365	-	20.6	45.1	0.46	3	56
F50		1190 (2.0)	TE (0.262)	1l1.5	20/353	-	25.6	115	0.28	0	
F51		1190 (2.0)	TP (0.333)	1l1.5	20/342	-	39.1	556	0.24	0	
F52		1190 (2.0)	TM (0.256)	1l2	20/354	-	23.2	72.9	0.33	2	28
F53		1190 (2.0)	TE (0.349)	1l2	20/340	-	42.9	171	0.32	1	
F54		1190 (2.0)	TP (0.444)	1l2	20/327	-	115	759	0.30	1	

ENT#	EXP # In Paper	Silane MW (g)[a]	x-linker (g)[b]	Ratio[c]	Catalyst (µL/ppm)[d]	Hexane (mL)	Induction Time (s)	Total time (s)	Density (g/cm^3)	Hardness[e]	Shore 00
Half the solvent											
F55	**18**	1190 (2.0)	TM (0.127)	1|1	20/376	0.5	15.5 ± 1.2	19.3 ± ±2.7	0.19 ± 0.01	1	3
F56		1190 (2.0)	TE (0.174)	1|1	20/367	0.5	28.3	33.4	0.27	2	24
F57		1190 (2.0)	TP (0.222)	1|1	20/360	0.5	79.0	148	0.22	0	
Double the solvent											
F58	**19**	1190 (2.0)	TM (0.127)	1|1	20/376	2.0	21.2 ± 1.2	24.0 ± 1.6	0.08 ± 0.01	0	
F59		1190 (2.0)	TE (0.174)	1|1	20/367	2.0	N	-	-		
F60		1190 (2.0)	TP (0.222)	1|1	20/360	2.0	N	-	-		

[a] Hydride-terminated PDMS: 7-10 cSt (1,190 g mol-1), 2-3 cSt (730 g mol-1).[b] TM: Tetramethyl orthosilicate, TE: Tetraethyl orthosilicate, TP: Tetrapropyl orthosilicate. [c] ratio = PDMS hydride groups : alkoxysilane groups. [d] Catalyst solution: 40 mg of $B(C_5F_5)_3$ in 1 mL of dry toluene. [e] Hardness scale: In general, foam hardness tracked with density, but was also affected by bubble size and friability. For those samples for which a Shore 00 hardness could not be obtained we provide an empirical scale clarifying a range of hardness 0 = too soft to measure with Shore 00, 1 = Shore 00 values: 0-20, 2 = Shore 00 values – 20-40, 3 = Shore 00 values – 40-65. Many of the harder foams cracked during measureme