EXPLORING BRANCHED SILICONE POLYMERS TO TAILOR THE PROPERTIES OF GELS

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A Thesis
Submitted to the School of Graduate Studies
In Partial Fulfillment of the Requirements
For the Degree of
Master of Science

McMaster University Master of Science (2017) Hamilton, Ontario (Department of Chemistry and Chemical Biology)

TITLE: Exploring Branched Silicone Polymers to Tailor the Properties of Gels

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NUMBER OF PAGES: xii, 84

Abstract

Silicones are useful in a variety of applications due to their diverse properties. The materials gain additional value when the basic constituents, oils and elastomers, are combined to create silicone gels. These materials possess excellent tunable properties such as moldability, tack, and adhesion, which are useful in certain circumstances. Only linear oils are currently used to make commercial silicone gels. While the materials initially possess desirable properties, over time the linear silicone oil can bleed out, and naturally, this is problematic for a variety of reasons. Among other things, the physical properties of the gel change and the oil that leaches out can be problematic. We test in this thesis the hypothesis that the use of branched silicone oils, as opposed to linear materials, in a gel could lead to lower levels of bleed (or slower release). There is currently very little research in the literature on the effect of adding branches to linear silicone polymers.

This thesis explores the synthesis of branched structures (dendrons) synthesized using the Piers Rubinsztajn reaction. These compounds were subsequently grafted onto linear SiH bearing silicone polymers at different frequencies through a hydrosilylation reaction. The branched silicones were characterized by NMR and the viscosity of the various oils was measured; the latter property correlated with the frequency of branching. The viscosity increased in a linear fashion until a maximum viscosity was observed, at which point further branching led to a slight decrease in viscosity; this trend was observed with silicone backbones at three molecular weights.

The branched silicone oils, capped with vinylpentamethyldisiloxane to remove remaining SiH sites, were then incorporated into gels. The Young's modulus was measured and bleed measurements were collected twice over a ten-day period. Both measurements demonstrated that branching silicone polymers influenced the properties relative to linear silicone oils of comparable molecular weight. We discuss the possible origins of these differences.

Acknowledgements

I would like to start by thanking my supervisor, Dr. Michael A. Brook, for providing me with the opportunity to work in his lab and be a part of his group. I am extremely grateful for the experience I have had over the past few years. Mike has always been willing to answer my endless lists of questions, and the many discussions have helped guide me throughout this process. His advice and assistance have always been appreciated and helpful. Mike's enthusiasm and encouraging words have not only been uplifting when the results were unexpected, but have also been critical to building my confidence as a scientist. I have learnt a lot about silicone chemistry and working in a lab and I am thankful that Mike provided me with the opportunity and time to do so. He has helped to shape me as a scientist and encouraged me to think beyond the project. Mike has been a great supervisor and mentor and I am truly so thankful for everything he has done. Thank you!

I would also like to thank my committee members, Dr. Todd Hoare and Dr. Harald Stöver for their suggestions and thought-provoking questions throughout the degree, allowing me to look at my project from different perspectives.

Thank you to everyone in the Brook group for making me feel like part of the team. I appreciate all of the scientific discussions we have had and the different outlooks on challenges I have had to overcome. Thank you as well for the other, lighter conversations and laughter in between the research and lab work. Many of you have helped me to understand and better grasp various topics, which has been beneficial on numerous occasions. I'd like to especially thank Dan for all of the endless hours he has spent answering my never-ending list of questions and all of the time he has taken to

show me different reactions and procedures. Your insight has always been valued and extremely helpful. Thank you!

I would also like to thank the friends I have made in the Brook lab, for not only welcoming me into the group, but putting up with my constant chatter and keeping me sane. While I'd love to thank everyone by name, I will keep the list short for the sake of space: Alyssa, Talena, and Marlena, I am happy to have met you. Thank you for always being there to listen, letting me be my weird self, and for making grad school fun. I'd also like to thank my best friend, Portia, for listening to countless, often pointless rants on the frustrations of grad school and research, and constantly reminding me to stress less.

Thank you to my parents for their love and support throughout my life, and of course throughout my school career.

Last, but certainly not least, I would like to thank my husband, Aaron, for his constant support and encouragement, despite not understanding a word of the science I am often describing. While you might not have the answers to my chemistry problems, the sentiment of your help is, and always has been appreciated. Thank you for being so understanding for all of my late nights studying and always believing in me, no matter how many times I say, and have said, 'nothing is working'.

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Chapter 1 : Introduction

1.1 Overview

Silicones are a versatile group of polymers that find use in a variety of different applications, due to their many interesting properties, including their resistance to heat, low Tg (glass transition temperature), and biocompatibility.[1, 2] Typical silicones, poly(dimethylsiloxane) (PDMS), mostly contain two methyl groups attached to the silicon atoms catentated with oxygen. This basic structure is augmented with functional groups, either pendant or terminal, including crosslinks, to give higher value materials. Once created, these functional materials can interact either through chemical or physical interactions to give elastomers or gels with interesting properties.

1.2 Silicone Elastomers

Silicone elastomers are usually prepared through crosslinking reactions between PDMS chains. The length of the chains between crosslinks must be considered when considering desired properties. Furthermore, the method of crosslinking should be carefully chosen. High energy radiation, for example, has been shown to be a crude, uncontrollable method that can result in a mixture of crosslinks and unreacted chains.[3, 4] Other methods such as hydrosilylation or room temperature vulcanization, for example, make use of functional groups (vinyl/hydride and hydroxyl groups, respectively) on the silicones in known locations to covalently add the chains together.[5] These methods are therefore able to provide a higher level of control and synthesize reproducible material properties based on the stoichiometry of the functional groups involved.

1.3 Silicone Gels

Elastomeric properties can be tuned to fit specific requirements by incorporating an oil within the network. One way to achieve this is by strategically adjusting the stoichiometric ratio of the network reagents to purposely leave unreacted oil within the network.[6] Alternatively, elastomers can be swollen with a non-functional linear oil, to give a gel whose properties can be precisely tuned.[7, 8] Such materials find use as pressure sensitive adhesives[9], in sealants for windows and HEPA filters[10], intraocular devices[11], and breast implants[12], for example. Depending on the desired properties, the oil content varies from a few percent up to 85% in the case of breast implants.[13, 14]

Over time, the untethered oils can begin to leach out (termed ‘bleed’), altering the properties of the gel as it returns to a more rigid, elastomeric state. For example, as silicone oil bleeds from a sealant, the material may begin to lose adhesion and no longer function efficiently as a seal. In addition, migration of the bleed into the surrounding environment has been suggested to be particularly problematic for materials that have been implanted in living organisms.[11, 13, 14]

The effect of bleed can, in some cases, be mitigated by placing the silicone gel within another material in which the oil is less soluble (i.e., enveloping a dimethylsilicone gel with a fluorosilicone envelope[14]). While this can be appropriate in certain circumstances, it takes away surface applications from the gel. In addition, the ‘fix’ adds extra thickness to the material, and can also alter the other desirable properties of the initial gel, such as texture or hardness. For these reasons, there would be a benefit to exploring how the swelling silicone oils could be modified in the first place to prevent, reduce or at least retard the rate of bleed at the source.[14] This would reduce the need for a containment system and lower the risk of silicone oils leeching from the device, particularly in a biological systems, in the case of implantable materials.

While it is obvious that physical incorporation is insufficient to constrain silicone oil bleed, it is also clear that these oils cannot be tethered into the network without reverting back to an elastomeric material and thus elastomeric properties. Therefore, to reduce bleed, the silicone oil needs to be better captured and retained in a different physical way. One way to achieve this could be increasing the viscosity of the oil, thus slowing the bleed process. Such changes will also impact the physical properties of the gel, however.

Several studies have shown that the modulus of a gel can change due to the presence of a swelling agent.[6, 15-17] The quantity and type of swelling agent naturally alters the modulus further, depending on the interactions of the polymer chain. The presence of more swelling agent, either in volume, or density, causes the network to expand, decreasing entanglement and therefore weakening the overall gel.[15, 16] Additionally, Mrozek et al.[16] showed that the entanglement limit of the swelling agent influenced gel properties; when the swelling agent had a molecular weight greater than the entanglement limit and, thus, presumably more viscous, the impact on the modulus was less drastic. Bibbo and Valles[18] observed that moduli were lower in the case of swelling agents containing pendant chains, if the chains were able to collapse easily. By contrast, however, where the chains were unable to collapse Vega et al.[19] showed that harder, stronger gels resulted. Overall, these studies of branched materials clearly demonstrate that branched swelling agents should not be expected to provide the same changes to polymer behavior as unbranched swelling agents and that the type and frequency of branching heavily influences properties, for example, the modulus of a gel.[18-20] As a consequence, one should also expect that gels formed with branched oil structures should exhibit different bleed rates than linear polymers.

Polymer chains are able to move past each other through reputation, a process that is more difficult with linear polymers with rigid backbones than flexible backbones, and for branched than linear polymers.[20, 21] Note that, somewhat surprisingly, tubular polymers – bottlebrush polymers – can also migrate with relative efficiency. The process of leaching of untethered fluids from gels would be expected to correlate directly with the ability of the free polymers to reptate. Other factors also contribute to the rate and quantity of bleed. Naturally, as the weight percentage of oils is increased in gels, there is unsurprisingly a corresponding increase in the total bleed. However, the rate of bleed decreases with increasing molecular weight of the oil; in the case of polymer greases, cothickeners have been used to reduce oil bleed.[22]

A different strategy to change the degree of entrainment of silicone oils would be to modify the structure from linear to branched structures, which could alter the degree of oil entanglement in the network. Unfortunately, very little is known in the literature about the effects of branching on linear silicone polymer backbones.

1.4 Effects of Branching on Polymer Properties

It is well known that linear silicone polymers are required to have a high molecular weight, greater than 15,000 Da (Figure 1.1), to reach the entanglement limit – the chain length where entanglement manifests in different polymer properties; at this point, a rapid increase in viscosity occurs.[23, 24] The entanglement limit is related to specific polymer structures.[24-27] Silicone polymers exhibit increases in viscosity as the backbone lengths increase, but not rapidly until they surpass the entanglement limit.[28, 29]

These properties are observed for linear structures but naturally, changes are expected for branched or partially gelled materials.

The impact of branching on polymer properties, including viscosity, at a given molecular weight has not been extensively studied (see below). Many of the studies of the effect of polymer branching on properties were carried out on low density polyethylene (LDPE) with long chain branching (LCB). Bersted[30] and Bersted et al.[31] found that the low shear viscosity (the plateau observed in a plot of Stress vs. Viscosity) increased with increasing branching due to an increased amount of viscous branched molecules. Eventually, however, this number reached a maximum because the increasing number of branches decreased the polymer radius of gyration and, as a result, the low shear viscosity values began to decrease as the branching continued to increase.[31]

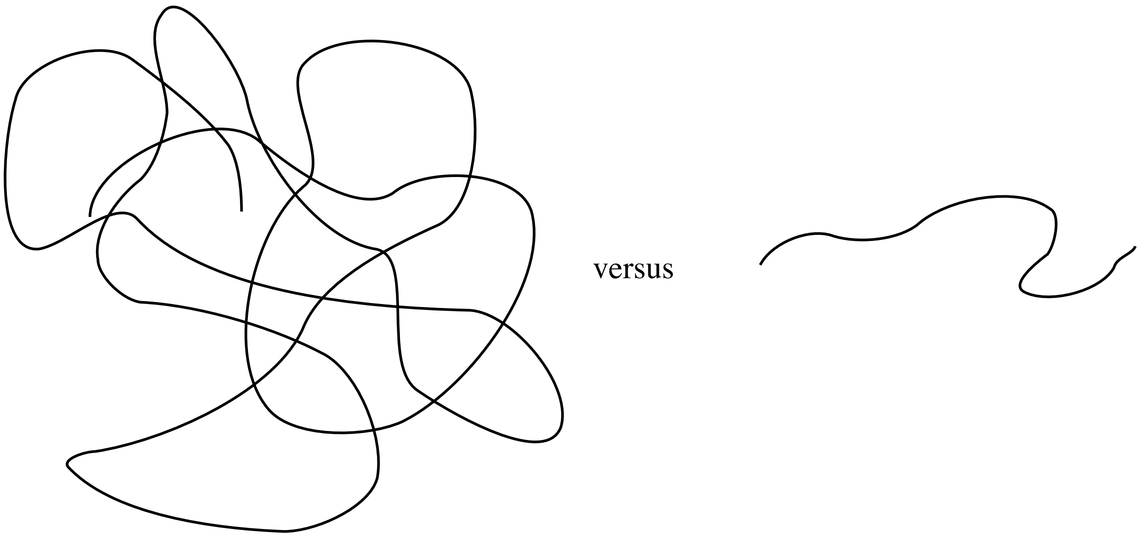

Figure 1.1:Scheme depicting a longer, higher molecular weight linear polymer with entanglement versus a shorter linear polymer chain that has not reached the critical molecular weight required for entanglement.

While these properties alone are very interesting and imply that the viscosity of a linear material can be enhanced through the use of branching to an extent, Liu et al.[32] considered how long chain branching (LCB) on a polyethylene (PE) backbone would affect the shear thinning properties and studied this while comparing the differences in shear thinning characteristics between linear, comb-branched, and star-branched materials. Their research focused on synthesizing linear and comb-branched structures through a graft-onto approach where a polybutadiene backbone was modified to contain polybutadiene branches; the entire polymer was then converted into branched PE through hydrogenation or residual C=C bonds. The linear PE behaved, as expected, like a Newtonian fluid and the comb and star-branched counterparts were shear thinning, with the comb material exhibiting the highest degree of shear thinning. While there was not a direct correlation between viscosity and degree of branching, it is evident that the frequency of branching in addition to the 3D structure of molecule influences the rheological characteristics of a polymer.

As noted by Yan et al.[33], LCB polyethylenes behave rheologically as if different chains have randomly been incorporated onto the backbone. To better understand the effect of branching, they instead used a constrained geometry catalyst to generate their own LCB polyethylene structures, which permitted more regular branching both with respect to frequency and length of branch. As with other studies, increased branching led to higher viscosities when compared the linear counterpart and the polymers underwent shear thinning more readily. Unlike other studies, however, there was no apparent decrease in viscosity at higher branching, which suggests that the method of preparing the polymers, and thus the final arrangement of branches, might also play a role in the final properties. It further suggests that large branches can have a larger impact on the point at which polymers undergo the transition to a globular shaped material (see below). This observation emphasizes the importance of controlling the synthetic process to minimize the PDI when studying branched materials.

Other interesting branched materials that have been prepared with varying properties include bottlebrush polymers (Figure 1.2). Bottlebrush polymers differ from a typical branched species in that their entire backbone is saturated with side chains and branches, typically including just one type of branch. The high branch density leads to these structures adopting extended, rigid, essentially linear configurations: they appear more as a cylinder as opposed to a mobile, sterically unhindered chain.

Dalsin et al.[34] studied the viscosity changes in polypropylene bottlebrush polymers and found that they behaved rather similarly to linear polymers; a short bottlebrush polymer chain compared to a longer bottlebrush polymer chain (of comparable grafting density and frequency) resulted in a viscosity increase; the viscosity of a bottlebrush polymer of a given molecular weight was lower than that of an unbranched polymer of the same molecular weight. Due to the high branching, these polymers do not tangle in the same manner as a linear polymer would, even though the critical molecular weight required for entanglement may have been reached. Viscosity increases are enhanced when the polymer backbone length exceeds that of the branches; shorter bottlebrush polymers resemble a globular dendrimer whereas longer chains are what force the configuration into a cylindrical structure.

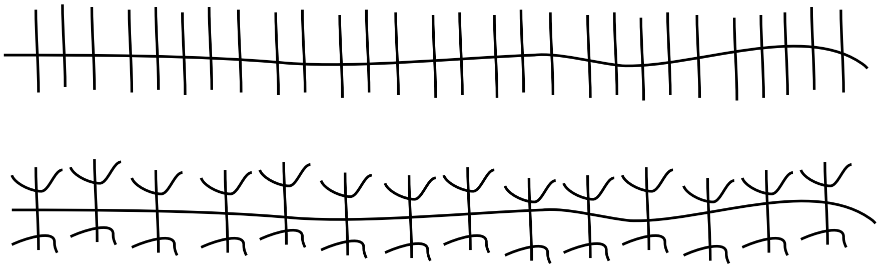

Figure 1.2: Scheme giving two examples of bottlebrush polymers (polymer backbones with a high frequency of branching).

The Rzayev group has looked extensively at the synthesis of bottlebrush polymers and their utilization in various applications. They have taken advantage of the cylindrical properties and extended configurations of the polymers and, additionally, the customizability of the properties using different monomers and branches.[35] Several of their studies revolve around branches that are able to self-assemble into various cylindrical shapes: they utilized a mixture of different branches to achieve the desired interactions.[36-39] Fenyves et al.[36] found that the final shape was largely influenced by the interactions of the various segments; more highly branched side chains could create an asymmetry in the structure, causing it to curve. Similarly, the size and amount of branches influences how these bottlebrush polymers pack into their cylindrical conformations; extra side-chain bulk can cause the resulting structures to pack less efficiently, while more uniform materials can easily fit together.[36, 37] In the case of these bottlebrush polymers the resulting packing arrangement affects the stability of the resulting cylindrical micelles.

Other researchers have also taken advantage of multiple branches within bottlebrush structures to tune the properties for use as thin-films that are sensitive to different environments.[40] While Dalsin et al.[34] focused on studying the differences between analogous bottlebrush polymers, Zhang et al.[41] compared the differences of branched substituents along the bottlebrush backbone. They synthesized polyisoprene compounds that had dendrons essentially built onto backbones of different molecular weights. The first generation branches consisted only of linear branches on the backbone, causing the viscosity to increase. However subsequent generations, which began to resemble more dense, dendrimer branches, led to lower viscosities, in almost all cases. Their explanation for this is related to the formation of dendrimers; as a dendrimer forms, the weight and hydrodynamic radius do not increase proportionally, causing the 3D structure to collapse on itself in higher generations, and this collapse in 3D size (density) is what leads to a drop in viscosity. Therefore, depending on the type of branch incorporated onto a silicone backbone, a similar phenomenon could be observed; the 3D density could play a crucial role in the viscosity properties of the products, independent of the nature of the branch prior to being grafted onto a silicone backbone. For example, while the branched, bulky sidechains are expected to increase entanglement and thus the viscosity, if branches along the backbone cause the structure to collapse, a viscosity decrease would therefore be expected. These experiments demonstrate that different types of branches can be successfully incorporated to yield similarly shaped materials that provide a wider array of properties or potentially even additional functional groups for later utilization.

Other studies have looked at changes in viscosity associated with the growth in generation of dendrimers (rather than as branches on a linear chain, Figure 1.3), that is, how the 3D orientation of the material results in a change in density. Mourey et al.[42] was interested, in particular, in studying the onset and effect of the structural collapse that occurs as the polymers convert to globular, compacted spherical materials with higher degrees of dendronization. The viscosity changes in polyether dendrimers were compared with polyamidoamine (PAMAM) dendrons and tert-butyloxycarbonylpoly(α, ε-L-lysine) monodendrons. It was found that certain dendrimers (PAMAM and polyether) displayed increasing viscosity values, to a maximum, with increasing generations (and increasing hydrodynamic radius), at which point the viscosity would then decrease as the structure collapsed into a globular configuration. By contrast, *tert*-butyloxycarbonylpoly(α, ε-L-lysine) dendrons displayed a constant viscosity, regardless of generation increases due to their constant globular shape.

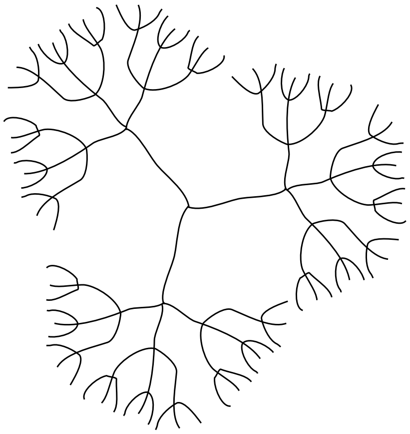

Figure 1.3: Scheme of the spherical shape a dendrimer structure conforms to at higher generations.

The 3D assembly of polymer branches also affects the efficiency of polymer interactions, as judged using viscosity as a surrogate for these effects. Graessley[43] showed that star-shaped polymers, with branches originating from a single core (as opposed to dispersed branches along a backbone) were lower in viscosity than a linear compound of comparable molecular weight. While he also found that an increased number of branches originating from the central core resulted in a further decrease in viscosity, these star polymers did not have a maximum viscosity as the molecular weight increased. At very high molecular weights (>1,000,000 g/mol), the star polymers interestingly enough eventually surpass the viscosity of the linear counterpart. Moore,[44] who summarized the findings of several different viscosity experiments, reasoned that 3D branched species might have lower viscosities due to more efficient dispersion of the branched structures, which can move easily into a ‘comfortable,’ nonsterically hindering configuration. In the case of these star polymers, the branches are sterically unhindered. This helps to further support the theories discussed above where one must take into consideration both the density of given branches and the frequency of the branching that leads to the characteristic maximum viscosity, as opposed to just the molecular weight of the materials.

1.5 Branched Silicones

In an early study, Charlesby[3] attempted to study the effects that branching would have on a silicone backbone by irradiating a polydimethylsiloxane (PDMS) polymer mixture to induce chain branching; this study is closely analogous to the study of long branched polyethylene noted above. Their method may have produced some lightly branched materials, but they also recognized that, due to their crude synthetic method, their materials likely included crosslinked or uncontrollably branched components in addition to strict linear branches. This was especially found to be the case at higher levels of ‘branching’ where their materials began to gel as an elastomeric network was formed. Fortunately, their results were still able to provide some insight into potential effects of branching. Their results showed that branching led to a decrease in viscosity when compared to an unbranched structure of comparable molecular weight; further increases in the molecular weight of the ‘branched’ structures led to decreases in the viscosity. This study suggests that the structure of the silicone, or more importantly the branching on a silicone, can change the viscosity properties as we predicted above, but more research would need to be considered to explore how explicit branching affects the properties when crosslinking is not occurring.

1.6 Very Highly Branched Silicones: MQ Resins

Very, very highly reticulated silicones can also affect viscoelastic properties of elastomers. Greater control over elastomer and gel properties can be attained by the addition of siloxane-based excipients, including MQ resins ($M = SiMe_3$, $Q = SiO_{4/2}$), which are used as tackifiers and reinforcing agents.[9, 45, 46] MQ resins typically exhibit useful properties in the 5,000-10,000 g/mol range.[47-49] They are more effective than silica in this regard. However, the preparative routes for these compounds are typically based on hydrolysis and condensation, which lack precision and lead to materials with broad dispersities *Đ* (formerly, polydispersity index PDI).[50]

1.7 Hypothesis and Goals

We propose that controlled branching, with different shapes and molecular weights, of a silicone polymer backbone can lead to programmed changes in properties of the polymers themselves and the elastomers into which they are placed. To test this, the type of branch and the degree of branching were varied to give materials of approximately the same molecular weight, which facilitated comparison of the effects of branching on physical properties. Once these materials were prepared, it was possible to establish gel properties as a function of branch frequency and type (varied by branch density), and then to the migratory aptitude of such polymers when used as oils in silicone gels. Subsequently, different polymer chain lengths were used to compare how the molecular mass influences the polymer properties. The bleed rates from gels of the different molecular weight structures were also compared, and related to the branching profile. The purpose of this research was therefore to synthesize an array of branched silicone oils that when incorporated into gels will, it is hypothesized, impede or retard bleed from the material (Figure 1.4). We elected to use the Piers-Rubinsztajn (PR) reaction to make the materials.[51]

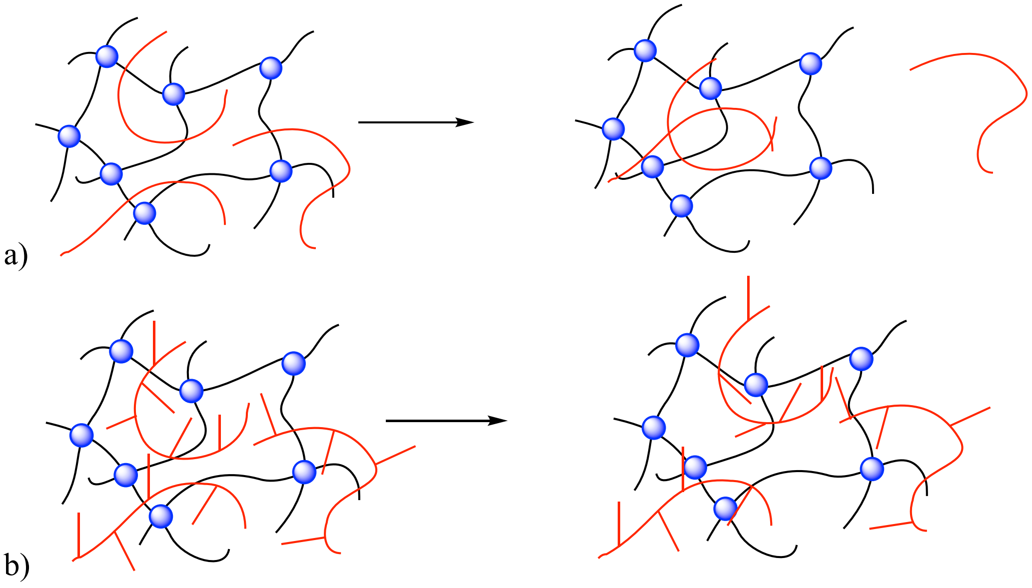

Figure 1.4: This cartoon depicts a silicone gel in which the silicone oil (in red) is physically entangled within a silicone elastomer (in black and blue); a) models how a linear, unbranched oil will bleed out of the system efficiently, while b) suggests how a desired branched structure should become entangled within the elastomer, reducing or retarding bleed.

1.8 Chemistry to be Exploited

1.8.1 Piers-Rubinsztajn (PR) Reaction

The PR reaction utilizes a boron catalyst, tris(pentafluorophenyl)borane ($B(C_6F_5)_3$; (BCF)), which is a strong Lewis acid,[52] capable of interacting with SiH bonds allowing for a variety of reactions to occur.[53] With respect to the PR reactions, siloxane bonds can be formed by reacting a hydrosilane with an alkoxysilane in the presence of BCF.[54, 55] Previous studies have shown that these reactions can be controlled by varying the geometry of the starting reagents, which can lead to different architectures of the final material (Figure 1.5) and, depending on the reagents, the by-product is often gaseous and easily removed.[51, 55] Furthermore, if excess hydrosilane is used, all of the alkoxysilane sites can be converted to siloxanes, allowing for predictable product formation.[54] The PR reaction is excellent for synthesizing well-defined, branched, silicone structures because of the ready availability of appropriately functional starting materials that can optionally contain a pendant vinyl or allyl group; the presence of BCF does not interfere with typical organic functional groups.[54] Additionally, this reaction is relatively quick and requires less catalyst than related Sn-catalyzed reactions.[51] This reaction was therefore used to facilitate the preparation of the branches in which we were interested. Previously, this process has been used to assemble dendrimeric silicones.[55, 56]

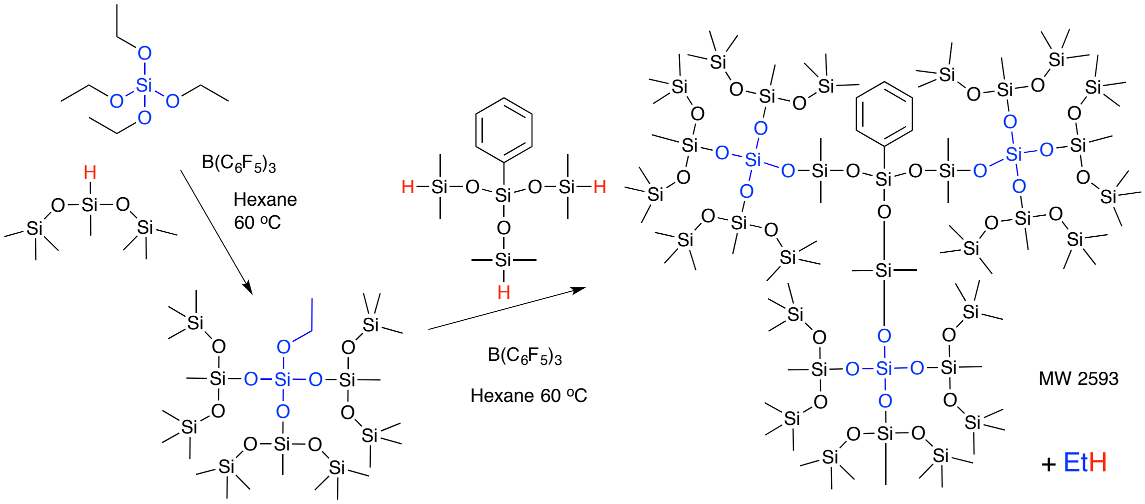

Figure 1.5: Examples of the PR reaction leading to branched structures.[55]

1.8.2 Silicone Polymer Backbones

It was initially necessary to create a linear silicone that has appropriate degrees of SiH functionality. Some examples of this material are commercially available. For others, uniform molecular weight silicone polymer backbones were synthesized through an equilibration reaction to provide polymers with a known number of SiH sites to which the branches can be attached (Figure 1.6A). It was proposed that simply varying the amount of the vinyl- or allyl-terminated branch added to the reaction would easily alter the degree of branching (Figure 1.6B). Figure 1.7 summarizes the synthesis plan and depicts what some of these structures should look like. With the backbone in place, it was necessary to assemble the branches and then to attach the branches to the backbone.

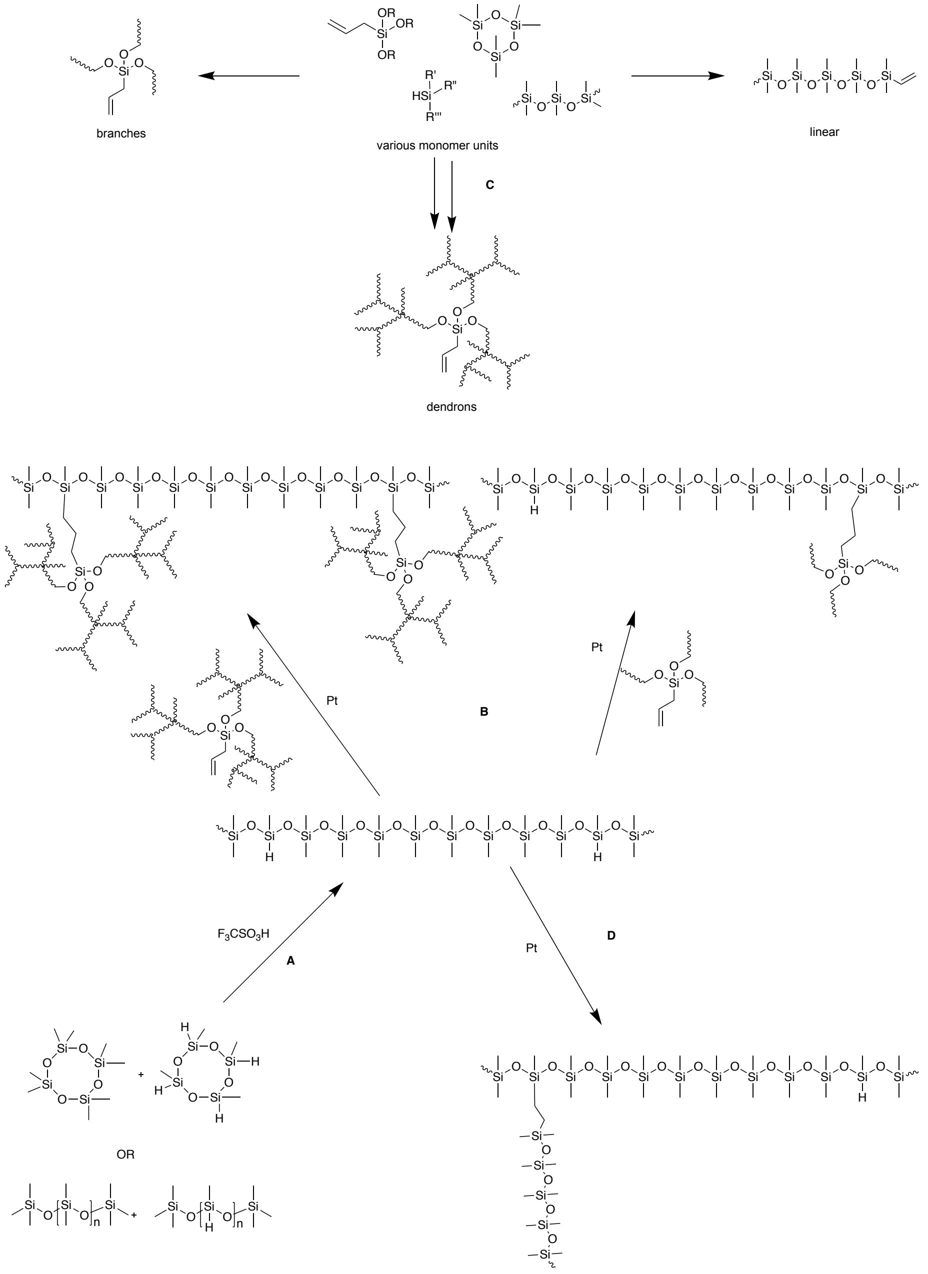

Figure 1.6: This figure summarizes the types of reactions and some of the final products we aimed to synthesize. A) Equilibration reaction to synthesize linear, functional silicone polymer backbones of 2,200 and 3,700 g/mol (n=1, m=10); A third linear, functional silicone backbone of 25,200 g/mol (n=1, m=17) was purchased from Gelest. B) Hydrosilylation reactions with branches to generate branched silicones. C) Reactions to generate branched materials. D) Potential crosslinking that can occur between SiH functional silicone backbones in the presence of the platinum catalyst.

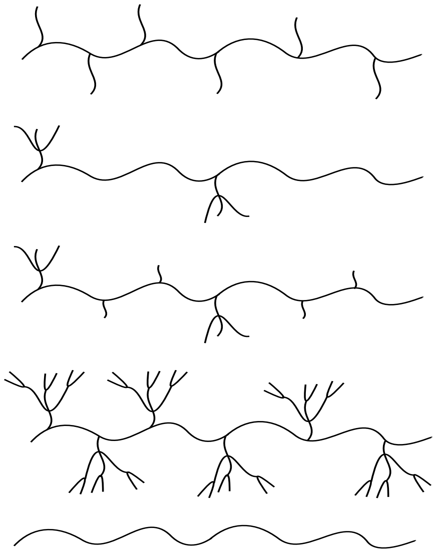

Figure 1.7: These cartoons depict some examples of different branching possibilities that can be achieved through the use of different branches and modifying the degree of branching.

Through the use of PR reactions and hydrosilylation, it will be possible to prepare a suite of different silicone oils.

1.8.3 Kinetically Controlled Ring-opening Polymerization: Linear Branches

A linear branch served a crucial control reaction to better understand whether any changes in oil or gel properties would result from the weight of a specific branch or the degree of branching it possesses. Thus, it was necessary to create narrow molecular weight linear polymers terminated with an alkene as a control branch. The most efficient reaction for this process is a kinetically controlled ring-opening polymerization; such reactions allow for chain length control and specific end groups can be chosen.[57] Peters et al.[57] chose to use living polymerization to synthesize an anionic polymer chain end, which was then terminated through the use of a chlorosilane. They utilized D_3 with sec-butyllithium to propagate a polymer chain in which a functionalized chlorosilane was used as the terminating agent (Figure 1.8). This reaction allowed us to functionalize a small polymer chain with our desired allyl or vinyl group.

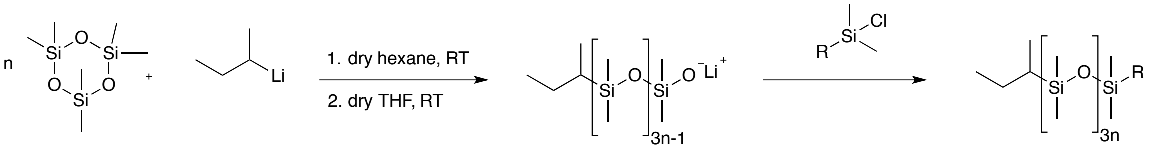

Figure 1.8: Example of a generic kinetically controlled ring-opening polymerization using D_3.[57]

The PR reaction used in conjunction with alternating hydrosilylation reactions can be used to synthesize larger, more elaborate branches that will begin to resemble dendrimer structures but will contain the necessary terminal allyl group to graft onto the polymer backbone. Full silicone dendrimers of this nature, but lacking a single allyl- or vinyl- terminated functionality have been prepared in the past using this method with great success (Figure 1.9).[56]

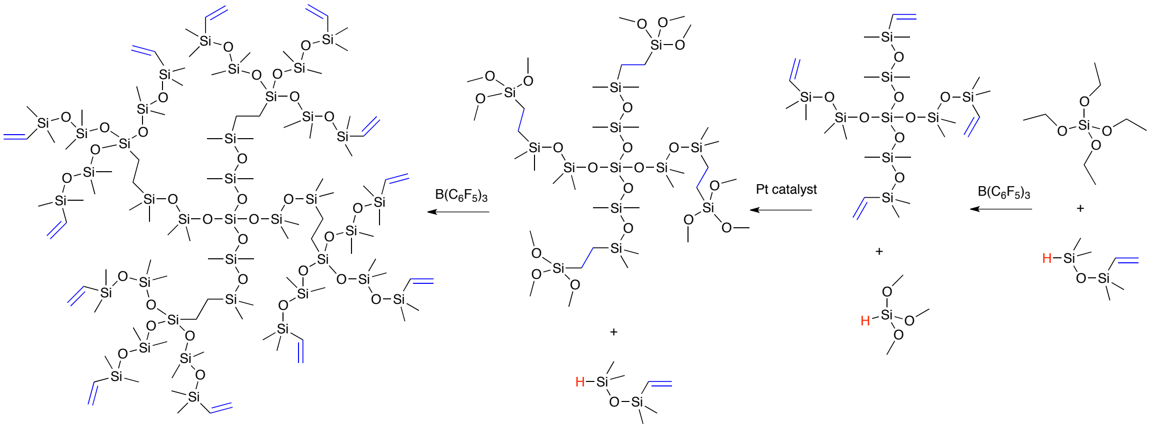

Figure 1.9: Examples of alternating PR and hydrosilylation reactions leading to dendrimeric structures.[56]

1.8.4 Hydrosilylation

The reaction that will be used to link the branches to the linear backbone is hydrosilylation (Figure 1.6B).[13] In some cases, the BCF catalyst can been used for these reactions, but relatively high quantities of catalyst are required.[58, 59] Instead, these reactions, carried out with Karstedt's platinum catalyst, were effective at adding an alkene to an SiH group with a relatively high product yield and no by-products (Figure

1.10).[14, 56, 60] Platinum-catalzyed hydrosilylation reactions are commonly used in commerce to form elastomers or crosslinked materials.[61] This reaction also allows for the synthesis of functionalized silicones, or in our case, the connection of two different materials. Hydrosilylation could be used to link the branches to the backbone (Figure 1.6).

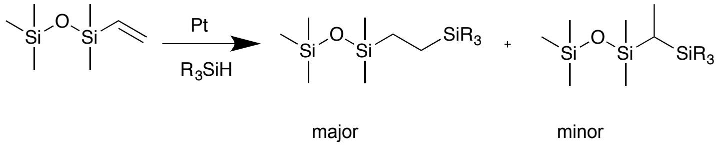

Figure 1.10: Example of a hydrosilylation reaction from Grande et al.[56]

1.9 Thesis Focus I: Viscosity Changes in Branched Silicone

In Chapter 2, the synthesis of a suite of branched silicones and their resulting viscosity properties are discussed. Our hypothesis was, given that viscosity of linear polymers increased with the addition of linear branches on the backbone, more elaborate branches would therefore more effectively contribute to viscosity and other property changes.[34, 62] The molecular weight of the backbone was varied from ~2,000-25,000 g/mol. This range of materials was chosen because to the intrinsic interest in materials at the lower end of the molecular weight range (such compounds are of particular commercial interest): they could be considered to be more flexible analogues of MQ resins, discussed above (Figure 1.11). Three different branch types were also compared and the frequency of branching along the chain was varied.

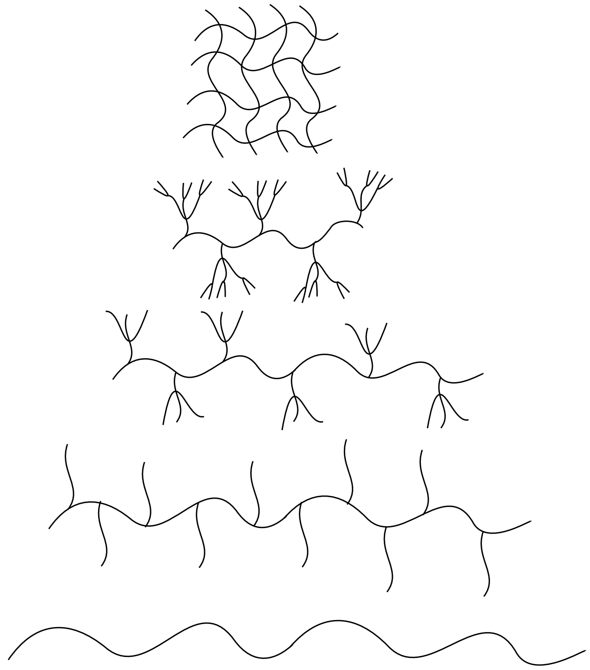

Figure 1.11: Scheme depicting different types of branched structures that are all of comparable molecular weights.

1.10 Thesis Focus II: Branched Silicones in Gels

Once an analysis of the effect of branching in silicone polymers influences polymer properties is complete, the next logical step would be to incorporate these branched silicones into silicone gels. The branched silicones will be used to swell silicone elastomer networks into gels and changes that result will be observed. This will include Young's modulus and the magnitude of bleed of branched silicone oils from gels compared to that of linear silicones with a comparable molecular weight

1.11 References

1. The Freedonia Group In *World Silicones Industry Study with Forescasts for 2015 and 2020*, Cleveland, Cleveland, 2011.
2. Rahimi, A.; Shokrolahi, P., Application of inorganic polymeric materials. *The International Journal of Inorganic Materials* **2001,** *3*, 843-847.
3. Charlesby, A., Viscosity measurements in branched silicones. *Journal of Polymer Science* **1955,** *17*, 379-390.
4. Mark, J. E., Molecular aspects of rubberlike elasticity. *Accounts of Chemical Research* **1985,** *18* (7), 202-206.
5. Clarson, S. J.; Semlyen, J. A., *Siloxane Polymers*. Prentice Hall: Englewood Cliffs, NJ, 1993.

6. Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W., Equilibrium modulus of model poly(dimethylsiloxane) networks. *Macromolecules* **1981,** *14* (4), 1039-1046.

7. LeVier, R. R.; Harrison, M. C.; Cook, R. R.; Lane, T. H., What Is Silicone? *Plastic and reconstructive surgery* **1993,** *92* (1), 12-167.

8. Naim, J. O.; Ippolito, K. M. L.; Lanzafame, R. J.; van Oss, C. J., The Effect of Molecular Weight and Gel Preparation on Humoral Adjuvancy of Silicone Oils and Silicone Gels. *Immunological Investigations* **1995,** *24* (3), 537-547.

9. Pocius, A. V., Adhesives. In *Physical Properties of Polymers Handbook*, Second Edi ed.; Mark, J. E., Ed. Springer Science and Business Media: New York, 2007; pp 470-486.

10. Alvarez, K. E.; Berry, P. A.; Stanga, M. A.; Strong, M. R., Silicone gel composition and silicone gel produced therefrom. **2001**.

11. Gruber, A. D.; Widenhouse, C. W.; Mathes, S.; Gruber, R. P., Exhaustive soxhlet extraction for the complete removal of residual compounds to provide a nonleaching silicone elastomer. *Journal of Biomedical Materials Research* **2000,** *53*, 445-448.

12. Zambacos, G.; Molnar, C.; Mandrekas, A., Silicone Lymphadenopathy After Breast Augmentation: Case Reports, Review of the Literature, and Current Thoughts. *Aesthetic Plastic Surgery* **2013,** *37*, 278-289.

13. Brook, M. A., *Silicon in Organic, Organometallic and Polymer Chemistry*. John Wiley & Sons, Inc.: New York, 2000.

14. Brook, M. A., Platinum in silicone breast implants. *Biomaterials* **2006,** *27*, 3274-3286.

15. Kalcioglu, Z. I.; Mrozek, R. A.; Mahmoodian, R.; VanLandingham, M. R.; Lenhart, J. L.; Van Vliet, K. J., Tunable mechanical behavior of synthetic organogels as biofidelic tissue simulants. *Journal of Biomechanics* **2013,** *46* (9), 1583-1591.

16. Mrozek, R. A.; Cole, P. J.; Otim, K. J.; Shull, K. R.; Lenhart, J. L., Influence of solvent size on the mechanical properties and rheology of polydimethylsiloxane-based polymeric gels. *Polymer* **2011,** *52* (15), 3422-3430.

17. Mrozek, R. A.; Knorr, D. B.; Spangler, S. W.; Cole, P. J.; Lenhart, J. L., Impact of precursor size on the chain structure and mechanical properties of solvent-swollen epoxy gels. *Soft Matter* **2012,** *8* (43), 11185-11192.

18. Bibbo, M. A.; Valles, E. M., Influence of pendant chains on the loss modulus of model networks. *Macromolecules* **1984,** *17* (3), 360-365.

19. Vega, D. A.; Villar, M. A.; Alessandrini, J. L.; Vallés, E. M., Terminal Relaxation of Model Poly(dimethylsiloxane) Networks with Pendant Chains. *Macromolecules* **2001,** *34* (13), 4591-4596.

20. Villar, M. A.; Vallés, E. M., Influence of Pendant Chains on Mechanical Properties of Model Poly(dimethylsiloxane) Networks. 2. Viscoelastic Properties. *Macromolecules* **1996,** *29* (11), 4081-4089.

21. Gennes, P.-G. d., *Scaling Concepts in Polymer Physics*. Cornell University: Ithaca, New York, 1979.

22. Gonçalves, D.; Marques, R.; Graça, B.; Campos, A. V.; Seabra, J. H. O.; Leckner, J.; Westbroek, R., Formulation, rheology and thermal aging of polymer greases—Part II: Influence of the co-thickener content. *Tribology International* **2015,** *87* (Supplement C), 171-177.

23. Dvornic, P. R.; Jovanovic, J. D.; Govedarica, M. N., On the critical molecular chain length of polydimethylsiloxane. *Journal of Applied Polymer Science* **1993,** *49*, 1497-1507.

24. Kataoka, T.; Ueda, S., Viscosity–molecular weight relationship for polydimethylsiloxane. *Journal of Polymer Science Part B: Polymer Letters* **1966,** *4*, 317-322.

25. Heymans, N., A Novel Look at Models for Polymer Entanglement. *Macromolecules* **2000,** *33* (11), 4226-4234.

26. Wu, S., Chain structure and entanglement. *Journal of Polymer Science Part B: Polymer Physics* **1989,** *27* (4), 723-741.

27. Wu, S., Predicting chain conformation and entanglement of polymers from chemical structure. *Polymer Engineering & Science* **1992,** *32* (12), 823-830.

28. Gelest, Silicone Fluids: Stable, Inert Media. **2012**.

29. Barry, A. J., Viscometric Investigation of Dimethylsiloxane Polymers. *Journal of Applied Physics* **1946,** *17*.

30. Bersted, B. H., On the effects of very low levels of long chain branching on rheological behavior in polyethylene. *Journal of Applied Polymer Science* **1985,** *30*, 3751-3765.

31. Bersted, B. H.; Slee, J. D.; Richter, C. A., Prediction of rheological behavior of branched polyethylene from molecular structure. *Journal of Applied Polymer Science* **1981,** *26*, 1001-1014.

32. Liu, F.; Wang, L.; Zhang, G.-c.; Zheng, J.; Tang, T., Synthesis of well-defined long chain branched polyethylene via anionic polymerization combined with graft-onto method. *Chemical Research in Chinese Universities* **2013,** *29*, 589-595.

33. Yan, D.; Wang, W.-J.; Zhu, S., Effect of long chain branching on rheological properties of metallocene polyethylene. *Polymer* **1999,** *40*, 1737-1744.

34. Dalsin, S. J.; Hillmyer, M. A.; Bates, F. S., Molecular Weight Dependence of Zero-Shear Viscosity in Atactic Polypropylene Bottlebrush Polymers. *ACS Macro Letters* **2014,** *3*, 423-427.

35. Rzayev, J., Molecular Bottlebrushes: New Opportunities in Nanomaterials Fabrication. *ACS Macro Letters* **2012,** *1*, 1146-1149.

36. Fenyves, R.; Schmutz, M.; Horner, I. J.; Bright, F. V.; Rzayev, J., Aqueous Self-Assembly of Giant Bottlebrush Block Copolymer Surfactants as Shape-Tunable Building Blocks. *Journal of the American Chemical Society* **2014,** *136*, 7762-7770.

37. Bolton, J.; Bailey, T. S.; Rzayev, J., Large Pore Size Nanoporous Materials from the Self-Assembly of Asymmetric Bottlebrush Block Copolymers. *Nano Letters* **2011,** *11*, 998-1001.

38. Bolton, J.; Rzayev, J., Synthesis and Melt Self-Assembly of PS–PMMA–PLA Triblock Bottlebrush Copolymers. *Macromolecules* **2014,** *47*, 2864-2874.

39. Bolton, J.; Rzayev, J., Tandem RAFT-ATRP Synthesis of Polystyrene–Poly(Methyl Methacrylate) Bottlebrush Block Copolymers and Their Self-Assembly into Cylindrical Nanostructures. *ACS Macro Letters* **2012,** *1*, 15-18.

40. Li, X.; Prukop, S. L.; Biswal, S. L.; Verduzco, R., Surface Properties of Bottlebrush Polymer Thin Films. *Macromolecules* **2012,** *45*, 7118-7127.

41. Zhang, H.; Qu, C.; He, J., Cylindrical polymer brushes with dendritic side chains by iterative anionic reactions. *Polymer* **2015,** *64*, 240-248.

42. Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Hawker, C. J.; Wooley, K. L., Unique behavior of dendritic macromolecules: intrinsic viscosity of polyether dendrimers. *Macromolecules* **1992,** *25*, 2401-2406.

43. Graessley, W. W., Effect of long branches on the flow properties of polymers. *Accounts of Chemical Research* **1977,** *10*, 332-339.

44. Moore, L. D., Relations among melt viscosity, solution viscosity, molecular weight, and long-chain branching in polyethylene. *Journal of Polymer Science* **1959,** *36*, 155-172.

45. Amouroux, N.; Restagno, F.; Léger, L., Adhesion at Poly(Butylacrylate)–Poly(Dimethylsiloxane) Interfaces. *The Journal of Adhesion* **2007,** *83*, 741-760.

46. Xu, X.; Wu, C.; Zhang, B.; Dong, H., Preparation, structure characterization, and thermal performance of phenyl-modified MQ silicone resins. *Journal of Applied Polymer Science* **2013,** *128*, 4189-4200.

47. Lin, S. B.; Durfree, L. D.; Knott, A. A.; Schalau II, G. K., Silicone Pressure-Sensitive Adhesives. In *Technology of Pressure-Sensitive Adhesives and Products*, Benedek, I.; Feldstein, M. M., Eds. Taylor & Francis Group, LLC: 2009.

48. Arkles, B., Commercial Applications of Sol-Gel-Derived Hybrid Materials. *MRS Bulletin* **2001,** *25* (5), 402-408.

49. Lewis, L. N.; Wengrovius, J. H.; Burnell, T. B.; Rich, J. D., Powdered MQ Resin−Platinum Complexes and Their Use as Silicone-Soluble Hydrosilylation Cure Catalysts. *Chemistry of Materials* **1997,** *9* (3), 761-765.

50. Stepto, R. F. T.; Gilbert, R. G.; Hess, M.; Jenkins, A. D.; Jones, R. G.; Kratochvíl, P., Dispersity in Polymer Science. *Pure Appl. Chem.* **2009,** *81*, 351-353.

51. Fawcett, A. S.; Grande, J. B.; Brook, M. A., Rapid, metal-free room temperature vulcanization produces silicone elastomers. *Journal of Polymer Science Part A: Polymer Chemistry* **2013,** *51*, 644-652.

52. Piers, W. E., The chemistry of perfluoroaryl boranes. *Advances in Organometallic Chemistry* **2005,** *52*, 1-77.

53. Brook, M. A.; Grande, J. B.; Ganachaud, F., New Synthetic Strategies for Structured Silicones Using $B(C_6F_5)_3$. *Advances in Polymer Science* **2011,** *235*, 161–183.

54. Grande, J. B.; Thompson, D. B.; Gonzaga, F.; Brook, M. A., Testing the functional tolerance of the Piers-Rubinsztajn reaction: a new strategy for functional silicones. *Chem. Commun.* **2010,** *46*, 4988-4990.

55. Thompson, D. B.; Brook*, a. M. A., Rapid Assembly of Complex 3D Siloxane Architectures. *Journal of the American Chemical Society* **2008,** *130*, 32-33.

56. Grande, J. B.; Urlich, T.; Dickie, T.; Brook, M. A., Silicone dendrons and dendrimers from orthogonal SiH coupling reactions. *Polym. Chem.* **2014,** *5*, 6728-6739.

57. Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M., Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers. *Journal of the American Chemical Society* **1995,** *117*, 3380-3388.

58. Rubin, M.; Schwier, T.; Gevorgyan, V., Highly Efficient B(C6F5)3-Catalyzed Hydrosilylation of Olefins. *The Journal of Organic Chemistry* **2002,** *67* (6), 1936-1940.

59. Xunjun, C.; Yingde, C.; Guoqiang, Y.; Liewen, L., Synthesis of vinyl substitute poly(silphenylene-siloxane) via silyl hydride-dialkoxysilane process. *Journal of Applied Polymer Science* **2007,** *106* (2), 1007-1013.

60. Putzien, S.; Nuyken, O.; Kühn, F. E., Functionalized polysilalkylene siloxanes (polycarbosiloxanes) by hydrosilylation—Catalysis and synthesis. *Progress in Polymer Science* **2010,** *35*, 687-713.
61. Fawcett, A. S.; Hughes, T. C.; Zepeda-Velazquez, L.; Brook, M. A., Phototunable Cross-Linked Polysiloxanes. *Macromolecules* **2015,** *48*, 6499-6507.
62. Das, C.; Inkson, N. J.; Read, D. J.; Kelmanson, M. A.; McLeish, T. C. B., Computational linear rheology of general branch-on-branch polymers. *Journal of Rheology* **2006,** *50*.

Chapter 2 : Facile Synthesis of Dendron-Branched Silicone Polymers*

2.1 Abstract

Monofunctional dendritic silicone branches were created from hydro- and alkoxysilanes using the Piers-Rubinsztajn reaction. Platinum-catalyzed hydrosilylation of the dendrons onto functional (MeHSiO) silicone backbones at various frequencies led to a library of branched silicones. Viscosities of the polymers increased with branch frequency to a maximum beyond which the viscosity decreased, as a consequence of a globular transition.

2.2 Introduction

Silicones possess a variety of interesting bulk properties including gas permeability, thermal and electrical stability and, in many applications biocompatibility.[1, 2] However, many of their applications are derived from their useful interfacial properties, which in turn are affected by their viscoelastic behaviour;[3] viscoelasticity is typically controlled through crosslink density, network structure including fillers and, for gels, the quantity and type of oils contained in the network.

The vast majority of silicone polymers, typically polydimethylsiloxanes, are linear in nature, and exhibit shear thinning behavior once their molecular weight reaches the entanglement limit of about 15,000 g/mol.[4] Compared to organic polymers,

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* This chapter is reproduced by permission of The Royal Society of Chemistry (RSC) from Jennifer Morgan, Tong Chen, Robin Hayes, Tara Dickie, Tomas Urlich and Michael A. Brook, in Polymer Chemistry, 2017, 8, 2743-2746. http://pubs.rsc.org/is/content/articlelanding/2017/py/c7py00260b/unauth#!divAbstract. Morgan synthesized the starting materials (**1**, **2**, **3**, **4**, **5**) and Chen produced additional amounts of **2**, **3**, **4**, and **5**. Morgan synthesized 48 of the 55 branched oils (**7-9**); Chen synthesized the remaining 7 branched oils (**7**,**8**). Viscosity measurements were performed simultaneously by Morgan and Chen. Morgan was responsible for the initial write-up and it was adapted for this paper with guidance, editing and additions provided by Dr. Brook.

viscosities of silicone oils change little with temperature or pressure. Little, however, is known about the behavior of branched silicones. They have not been studied mostly because effective methods for their synthesis do not exist, including the preparation of monofunctional silicones.

The behaviour of branched polymers, when compared to linear analogues, is well understood. Long chain branches, on polyethylene for example, exhibit lower viscosities in the melt than polymers with regular, shorter chain branching, for example, on linear low density polyethylene.[5] The controlled addition of branches on a linear backbone allows one to tailor Tg, viscoelastic properties and the self-assembly of polymers. With high density branching, as with bottlebrush polymers (molecular brushes with branching at every monomer), viscosities similarly decrease because intermolecular chain interactions become disfavored.[6]

What about silicones? The key (but now dated) study in this area involved the radiation-induced grafting of silicones to give random branching and random branch lengths (possibly mixed with gels).[7] The study showed that as the molecular weight of the polymers increased, the viscosity decreased.

The Piers-Rubinsztajn (PR) reaction is a facile process for the preparation of siloxane structures in which hydrosiloxanes are converted to siloxanes with alkane byproducts in the presence of BCF ($B(C_6F_5)_3$, Figure 2.12B).[8, 9] We have previously shown that both dendrons, including monofunctional moieties, and dendrimers are readily prepared in high yields in a few steps.[10] Given the potentially useful properties that could be associated with branched structures, we report below a PR approach to highly branched silicone polymers created from monofunctional silicone dendrons.

2.3 Results and Discussion

Three different branch structures were prepared: linear chains, and lightly or more densely packed dendritic branches. A linear silicone terminated with an alkene **1** was prepared by ring-opening polymerization of D_3 ($(Me_2SiO)_3$), using BuLi as the initiator and chlorodimethylvinylsilane to cap the reaction (Figure 2.12A).[11] The medium **2** and dense 3D branch **3** structures were prepared in a one-step PR reaction from allyltrimethoxysilane (Figure 2.12B). The branches were comprised of between 7-10 siloxane units and, thus, had comparable molecular weights of 810, 558 and 780 g/mol for **1**, **2** and **3**, respectively. In all cases, the linear, branched or highly branched dendrons possessed a single functional group.

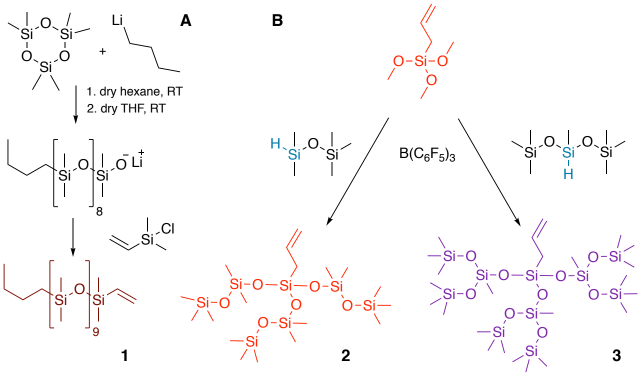

Figure 2.12: Preparation of three distinct branch types.

Si-H rich linear polymers – the functional backbones – were prepared by the acid-catalyzed equilibration of D_4, D^H_4 and $Me_3SiOSiMe_3$ (Figure 2.13A).[12] Three different backbone molecular weights were prepared or purchased providing **4**, **5** and **6** at 2,200, 3,700 and 25,200 g/mol, respectively. The fraction of functional MeSiHO vs Me_2SiO monomers in the polymers ranged from ~5-10%, calculated from the ^1H and ^{29}Si NMR integrations of MeSiHO vs Me_2SiO.

Libraries of branched silicones were prepared by the simple, efficient, and expedient reaction of the Si-H rich polymers **4**, **5**, **6**, using platinum-catalyzed hydrosilylation, with different concentrations of vinyl-terminated sidechains **1**, **2**, and **3** to give **7-1**, **7-2**, **7-3**, **8-1**, **8-2**, **8-3** and **9-1**, **9-2**, **9-3** (Figure 2.13). The number of branches/polymer was systematically varied. Thus, the products varied in branch type (**1-3**, Figure 2.13B vs C vs D), branch frequency (Figure 2.13E vs F), and overall molecular weight (Figure 2.13E, F, and G). These reactions were monitored by ^{1}H NMR; the disappearance of the vinyl peaks, reduction of the SiH peak intensity and peak formation ~0.5 ppm provided information on the percentage of branched monomers. In cases where not all SiH groups were consumed by hydrosilylation we note that care needs to be taken to avoid basic conditions, as under such conditions any residual SiH groups are subject to hydrolysis and condensation[13] which, in one early experiment, led to gelation.

In no case was it possible to react all of the SiH groups on the backbone even when a stoichiometric excess of branches was present during the reaction. It was proposed that steric constraints were responsible for the inability of all SiH groups to react. To test this hypothesis, a stoichiometric excess (compared to [SiH]) of branches **1-3**, respectively, was added to PHMS ($Me_3Si(OSiMeH)_nOSiMe_3$) **10-1**, **10-2**, **10-3** with which every monomer bears an SiH group (n~30, m=0, Figure 2.13B) using the same hydrosilylation conditions. For all branch types, the maximum efficiency of incorporation was about 60% (Table 2.1 and ESI[‡]). Thus, irrespective of SiH monomer concentration on the silicone backbone it was not possible to modify all the available SiH groups. This demonstrates that the SiH groups are not homogeneously distributed along the linear polymer backbone on polymers **4-6**; there must be always be clusters of SiH-containing monomers present that, for steric reasons, can only undergo partial branching.

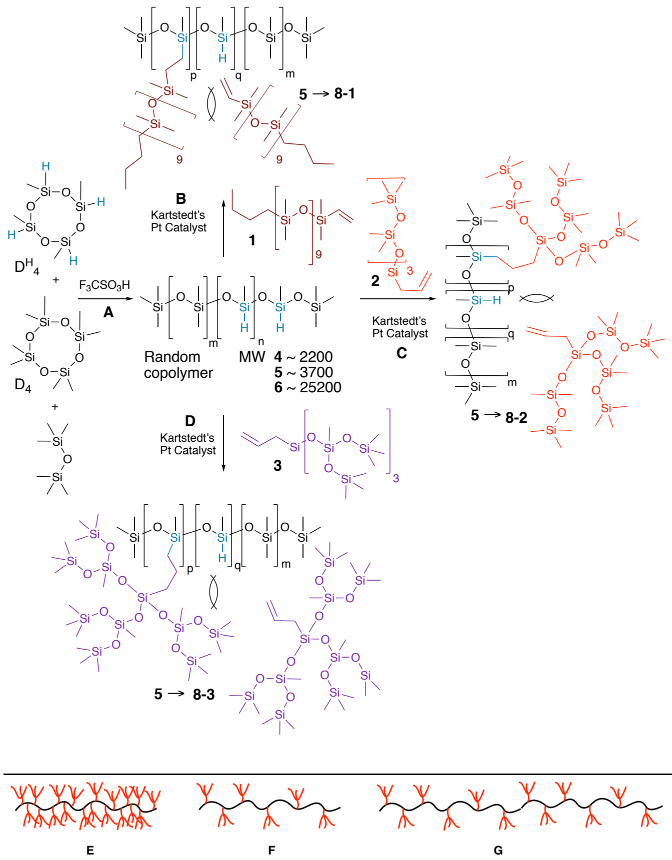

Figure 2.13: Preparation of branched silicones with varying branch frequency, varying branch type and backbone molecular weight (Mn in g/mol) shown for **5→8-1** < **8-2** < **8-3**. The same process leads **4→7-1**, **7-2**, **7-3** and **6→9-1**, **9-2**, **9-3.** Compound **4** ~2200 g/mol, n=1 m=10; Compound **5** ~3700 g/mol, n=1 m=10; Compound **6** ~25,200 g/mol n=1 m=17 (Table 2.1).

Rheological behavior was used to better understand the effect of both branch frequency and the density of individual branches on polymer properties. Unsurprisingly, only a small increase in dynamic viscosity was noted with increasing frequency of type **1** branches. By contrast, the more dense type **2** and **3** branches led to higher viscosities at the same branch frequency. The viscosities of any branch frequency followed the pattern **8-1** < **8-2** < **8-3** (Figure 2.14A).

The correlation between increased viscosity and increased frequency of branching failed at higher branch frequencies. The graph shows a slight decrease in viscosity for type **1** branches (**8-1**) at the highest branch frequency (9%) **7-2-9** This change was not distinguishable from error, but the same trend was noted, and was more pronounced, when more dense type **8-2** and most dense type **8-3** branched materials were added to the same backbone (Figure 2.14A). In all cases, there was a clear maximum in viscosity between 3-6% branching and then a reduction in viscosity at higher branching levels.

Table 2.1 Partial Table of Branched Polymers Prepared[a]

Compound	Branching %[b]	Mn g/mol	Viscosity Pa·s
7-2	1.6	2140	0.05
	1.9	2480	0.04
	3.3	2490	0.06
	3.4	2670	0.05
	5.6	2850	0.10
	6.5	3300	0.10
	8.2	3490	0.09
7-2-9	8.5	3140	0.08
8-2	1.5	4590	0.12
	1.7	5950	0.22
	3.0	4860	0.26
	3.3	4760	0.24
	4.9	5300	0.21
	5.3	5960	0.23
	5.9	5580	0.80
	9.1	7620	0.64
9-2	1.1	26840	1.08
	1.9	25860	0.98
	2.6	26220	3.14
	3.4	27700	2.53
	5.5	32680	2.07

[a] see also Supporting Information for series **7-1**, **7-3, 8-1**, **8-3**, **9-1**, **9-3** [b] ratio of [branchMeSiO]/[Me_2SiO+residual MeHSiO]x100.

More confidence in this observation followed experiments with higher molecular weight backbones **9-2**, **9-2**, **9-3** (25200 MW); the changes in viscosity both before and after the maximum were more pronounced (Figure 2.14B,C, Table 2.1, ESI[‡]). When plotted against type **2** branch frequency, it can be seen that the maximum in viscosity occurs at lower branch frequency for the higher molecular weight backbone (Figure 2.14B vs A), and an increase in molecular weight amplifies the change in viscosity as a function of branch frequency (Figure 2.14C). That is, the impact of branching on viscosity is more significant once the branched polymer approaches or exceeds the entanglement chain length.[14]

It is well understood that viscoelastic properties of polymers are significantly affected by the presence of branches. The relative lack of control of branching in low density polyethylene (PE), for example, drove development of linear low density PE in which comonomer incorporation is controlled, leading to better materials with well-defined properties including rheological behaviour. Increasing the degree of long chain branching (LCB) initially leads to an increase in low shear viscosity. Eventually, however, this number reaches a limit because the increasing number of branches decreases the polymer radius of gyration and, as a result, the low shear viscosity values will decrease.[15, 16] Note that the magnitude of these effects depends on polydispersity of the branches and the polymer backbone.[17] In the one study of silicone branching, which involved poorly controlled molecular weight and frequency of introduction of long branches, similar effects on viscosity were observed.[7]

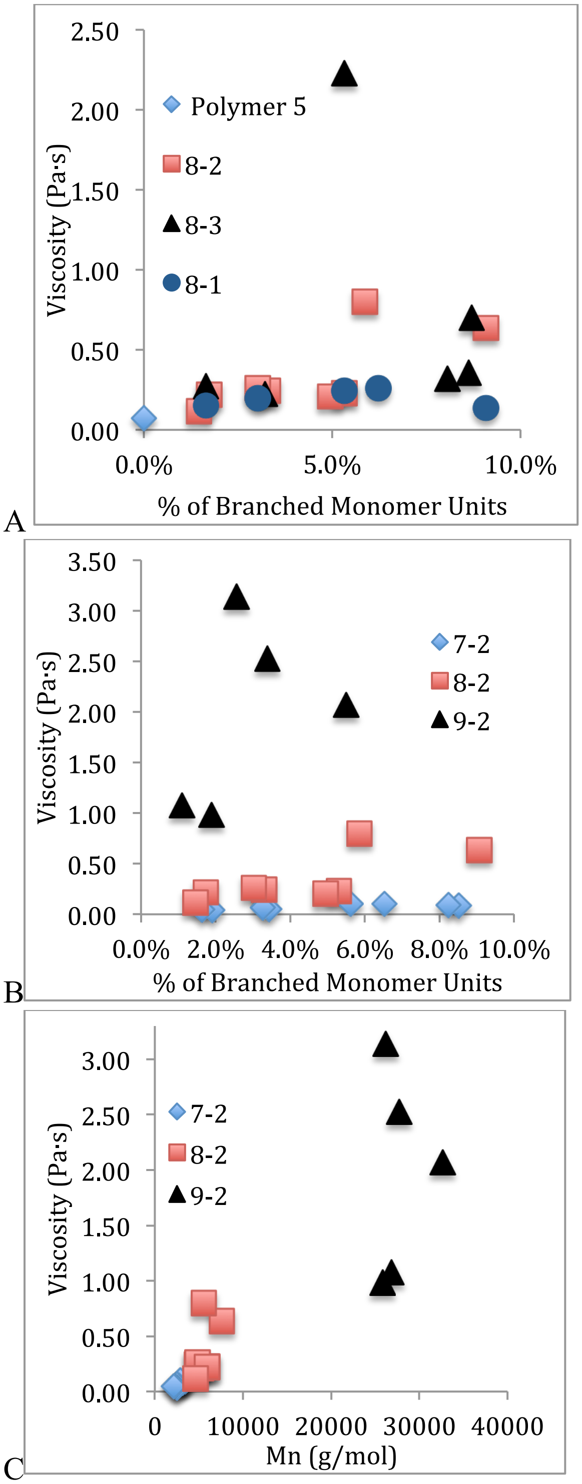

Figure 2.14 A: Effect of branch type **1-3** on viscosity of polymers derived from **5** (**8-1**, **8-2**, **8-3**) as a function of branch frequency; Effect of starting backbone molecular weight on viscosity as a function of B: by branch frequency and C: gross molecular weight for type **2** branches, **7-2**, **8-2**, **9-2**.

At the other end of the spectrum, bottlebrush polymers that bear long chains on every backbone monomer typically have lower viscosities than their unbranched backbone precursors and more lightly branched analogues[18] because the side chains on very dense brushes do not easily entangle; the products are cylindrical.[19]

A similar trend is observed with dendrimers. Viscosities increase with dendrimer molecular weight as generations are sequentially assembled. However, at higher generations, the 3D space occupied by the growing chains consume most of the available free volume, adjacent dendrimeric structures interact less effectively and there a shift to lower viscosities after this transition to a globular structure is reached.[20]

The library of silicones we prepared from low molecular weight branches varied with respect to both branch frequency and branch density. Irrespective of branch types, an increase in branch frequency led initially to increases in silicone viscosity as would be expected from precedent with other polymers. Enhanced polymer entanglement/interaction reduces flow under shear. Those branches that are less mobile, including those derived from **2** and particularly **3** led to higher viscosities at comparable branching frequencies, than those derived from more flexible linear branches **1**. Since all three branch types have approximately the same molecular weight – e.g., the MW of **8-1** ~ **8-2** ~ **8-3** – differences in viscosity are not associated with the molecular weight of polymers at a given branch frequency, but rather branch mobility: more rigid branches entangle more easily **7-1** < **7-2** < **7-3**, **8-1** < **8-2** < **8-3**, and **9-1** < **9-2** < **9-3**.

The maximum in viscosity that was observed with all branch types and backbone molecular weights follows the trend exhibited by bottlebrush polymers and high generation dendrimers. As the polymers pack more and more space filling groups on the backbone, they increasingly adopt a dense ball like structure. Once they reach the globular transition point, the intermolecular interactions that drive viscosity effects become less important and, as a consequence, a trend to lower viscosities with increasing branch frequency was observed.

2.4 Conclusions

The Piers-Rubinsztajn reaction lends itself to the preparation of small, highly branched dendrons **1**-**3** in good yield. This permitted the preparation of a library of silicones that varied in molecular weight from about 2,200 to 30,000 g/mol with branch frequencies of up to 9%. In all series, initial increases in branch frequency led to viscosity increases. However, at higher branch frequencies this trend reversed and the viscosity decreased with increasing branching. This is ascribed to a globular transition that leads to less efficient interpolymer interactions.

2.5 Acknowledgements

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC). We also thank Dr. P. Whiting of Mirexus for providing access to their rheometer.

2.6 References

1. Noll, W. J., *Chemistry and Technology of Silicones*. Academic Press: New York, 1968.
2. Clarson, S. J.; Semlyen, J. A., *Siloxane Polymers*. Prentice Hall: Englewood Cliffs, NJ, 1993.
3. Wrobel, D., Structure and Properties of Hot-Vulcanized Silicone Rubbers. In *Silicones chemistry and Technology*, CRC Press: Boca Raton, 1991; pp 61-73.
4. Kataoka, T.; Ueda, S., Viscosity–molecular weight relationship for polydimethylsiloxane. *J. Polym. Sci. B, Polym. Lett.* **1966,** *4* (5), 317-322.
5. Read, D. J., From reactor to rheology in industrial polymers. *J. Polym. Sci. B, Polym. Phys.* **2015,** *53* (2), 123-141.
6. Verduzco, R.; Li, X.; Pesek, S. L.; Stein, G. E., Structure, function, self-assembly, and applications of bottlebrush copolymers. *Chem. Soc. Rev.* **2015,** *44* (8), 2405-2420.

7. Charlesby, A., Viscosity measurements in branched silicones. *Journal of Polymer Science* **1955,** *17*, 379-390.
8. Brook, M. A.; Grande, J. B.; Ganachaud, F., New Synthetic Strategies for Structured Silicones Using $B(C_6F_5)_3$. *Advances in Polymer Science* **2011,** *235*, 161–183.
9. Piers, W. E., The chemistry of perfluoroaryl boranes. *Advances in Organometallic Chemistry* **2005,** *52*, 1-77.
10. Grande, J. B.; Urlich, T.; Dickie, T.; Brook, M. A., Silicone dendrons and dendrimers from orthogonal SiH coupling reactions. *Polym. Chem.* **2014,** *5* (23), 6728-6739.
11. Peters, M. A.; Belu, A. M.; Linton, R. W.; Dupray, L.; Meyer, T. J.; DeSimone, J. M., Termination of Living Anionic Polymerizations Using Chlorosilane Derivatives: A General Synthetic Methodology for the Synthesis of End-Functionalized Polymers. *J. Am. Chem. Soc.* **1995,** *117*, 3380-3388.
12. Brook, M. A., Silicones. In *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley: New York, 2000; pp 256-308.
13. Lewis, L. N., On the mechanism of metal colloid catalyzed hydrosilylation: proposed explanations for electronic effects and oxygen cocatalysis. *J. Am. Chem. Soc.* **1990,** *112*, 5998-6004.
14. Flagg, D. H.; McCarthy, T. J., Rediscovering Silicones: MQ Copolymers. *Macromolecules* **2016,** *49* (22), 8581-8592.
15. Bersted, B. H., On the effects of very low levels of long chain branching on rheological behavior in polyethylene. *Journal of Applied Polymer Science* **1985,** *30*, 3751-3765.
16. Bersted, B. H.; Slee, J. D.; Richter, C. A., Prediction of rheological behavior of branched polyethylene from molecular structure. *Journal of Applied Polymer Science* **1981,** *26*, 1001-1014.
17. Yan, D.; Wang, W.-J.; Zhu, S., Effect of long chain branching on rheological properties of metallocene polyethylene. *Polymer* **1999,** *40*, 1737-1744.
18. Dalsin, S. J.; Hillmyer, M. A.; Bates, F. S., Molecular Weight Dependence of Zero-Shear Viscosity in Atactic Polypropylene Bottlebrush Polymers. *ACS Macro Letters* **2014,** *3*, 423-427.
19. Rzayev, J., Molecular Bottlebrushes: New Opportunities in Nanomaterials Fabrication. *ACS Macro Letters* **2012,** *1*, 1146-1149.
20. Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Hawker, C. J.; Wooley, K. L., Unique behavior of dendritic macromolecules: intrinsic viscosity of polyether dendrimers. *Macromolecules* **1992,** *25* (9), 2401-2406.

Chapter 3 : Lower Bleed from Silicone Gels Containing Branched Silicone Oils[†]

3.1 Abstract

Silicone gels – elastomers filled with linear silicone oils – are widely used due to their special adhesive and other properties. However, over time, the untethered oils will leach (“bleed”) from the gel altering properties of the gel and, in some cases, leading to undesirable side effects. We describe the preparation of silicone gels containing branched silicone oils, in which both branch frequency and branch density of the oils were systematically varied. The relatively low molecular weight oils (5000-8500 g mol^{-1}) were entrained in an elastomer at loadings ranging from 15-50 wt%. Subtle changes were noted in the Young’s modulus of gels prepared with branched rather than linear oils. In general, increases in free volume led to slightly lower values of Young’s moduli at 15wt% loadings, but all the oils affected the gels to a similar degree at higher loadings. The rate of bleed was significantly reduced, by up to an order of magnitude, when branched oils were used instead of linear oils of comparable molecular weight. The trends relating structure to bleed rates showed that molecular weight of the oil, degree of branching, and the wt% of oil in the gel all played roles.

3.2 Introduction

Silicone gel materials are used in a variety of applications due to their interesting and unusual properties that include strong adhesion, ability to form and seal interfaces efficiently, and their biocompatibility. Thus, for example, they are used as sealants for

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[†] This chapter was initially prepared by Jennifer Morgan and Dr. Brook provided guidance, editing and additions. Morgan synthesized 4 of the 7 branched (capped) oils. Morgan was also responsible for the synthesis of the gels and extracted elastomers, and Young’s modulus measurements. Cody Gale measured the bleed from the gels.

HEPA filters and fillers for implantable biodevices.[1, 2] Silicone gels are typically formed in situ by the curing of functional silicone oils, typically via platinum-catalyzed hydrosilylation of SiH and Si-vinyl groups, in the presence of non-functional linear silicone oils.[3, 4] In some cases, as with silicone gel breast implants, the loading of oil in the matrix can be very high; up to 85wt%.

One disadvantage of silicone gels is the tendency of the oils to leach out of the body – 'bleed' – over time into the surrounding environment.[5-8] This can lead to issues ranging from undesired aesthetic outcomes, as when the oil attracts dirt adjacent to junctions between pre-stressed concrete panels sealed with silicone gels, to concerns about ultimate in vivo location of oils that bleed from breast implants and related devices.[9-11] In some cases, bleed can be mitigated by enveloping the silicone gel in another material, for example, a phenylsilicone envelope.[10] However it would be beneficial to find alternative strategies to reduce the rate and magnitude bleed from unrestrained gels, particularly for sealants. One such strategy could include the modification of the entrained silicone oils.

The incorporation of a solvent or other fluids into an elastomer to form a gel can dramatically change physical properties. Kalcioglu et al.[12] demonstrated that the modulus of a silicone elastomer decreased when a solvent or swelling agent (1100 MW silicone oil, in their case) was incorporated to form a gel because the network chains are better spread out by the solvent and less network entanglement can occur – the oil acts as a plasticizer; the effects track with the concentration of the swelling agent. Gong et al.[13] found that, to a degree, this effect could be overcome by incorporating a secondary network within the gel.

The molecular weight (MW) of the swelling solvent also plays a role in manipulating the physical parameters of a gel. Mrozek et al. demonstrated that higher oil loading in a gel resulted in lower storage modulus values.[14] However, higher MW oils led to increases in the moduli at given loading, when compared to low MW oils. The effect was particularly pronounced above the entanglement limit. This observation was ascribed to better entanglement of the large swelling oils within the network. The proposal was substantiated by changing the frequency of the rheological measurements. Oils with molecular weights above the entanglement limit acted as hardening agents (reinforcing structures) because they were unable to undergo reptation on the time scale of the experiment. By contrast, oils in gels with MW below the entanglement limit reduced reinforcement of the network, that is, led to lower storage moduli, essentially irrespective of MW at a given loading.[14]

We have previously developed methods to reliably introduce branches along linear silicone backbones.[15] The viscosities of the oils were found to increase with both the branch density and frequency. However, at higher branching frequencies the trend was reversed and the viscosity began to decrease, likely due to a globular collapse of the expanding structure, as has been observed with dendrimers.[16]

We reasoned that the changes in entanglement of branched polymers leading to viscosity rise could be alternatively employed, for example, to modify the rate of bleed from a gel. Branched polymers were prepared that varied in both the 3D density of a given branch, and branch frequency from 1-9% of the available monomers along the initially 3700 g mol^{-1} backbone. The preparation of silicone gels containing either linear or branched silicone oils in loadings up to 50wt%, the resulting impact on Young's modulus of the gels, and the efficiency of bleed over 10 days are reported below.

3.3 Results

Gels were prepared by adding a linear or branched silicone oil to a pre-elastomer mixture comprised of a 1:1 ratio of vinylSi:SiH-containing pre-elastomer without mineral fillers, and then curing the mixture using a platinum-catalyzed hydrosilylation crosslinking reaction between the hydride- and vinyl-functional silicones. Branched silicone oils were derived from a linear 3700 g mol^{-1} polymer **1** to which dendrons were added at different frequencies using a **PA Branch** or **BA Branch** (Figure 3.15A); any unreacted SiH sites in polymers **2**, **3** were capped with vinylpentamethyldisiloxane giving **PA**, **BA** (Figure 3.15B) to prevent chemical grafting of the oil into the elastomer and to minimize the possibility of subsequent hydrolysis and condensation of the oil within the elastomer (e.g., to give **4**, Figure 3.15C).[17, 18] The molecular weights of the branched polymers ranged from 5000 to 8500 g mol^{-1}. This molecular weight range was chosen because MQ resins (M = Me_3Si, Q = $SiO_{4/2}$) in the same range are used as silicone elastomer reinforcing agents and could be used as comparators for the branched oils.[19]

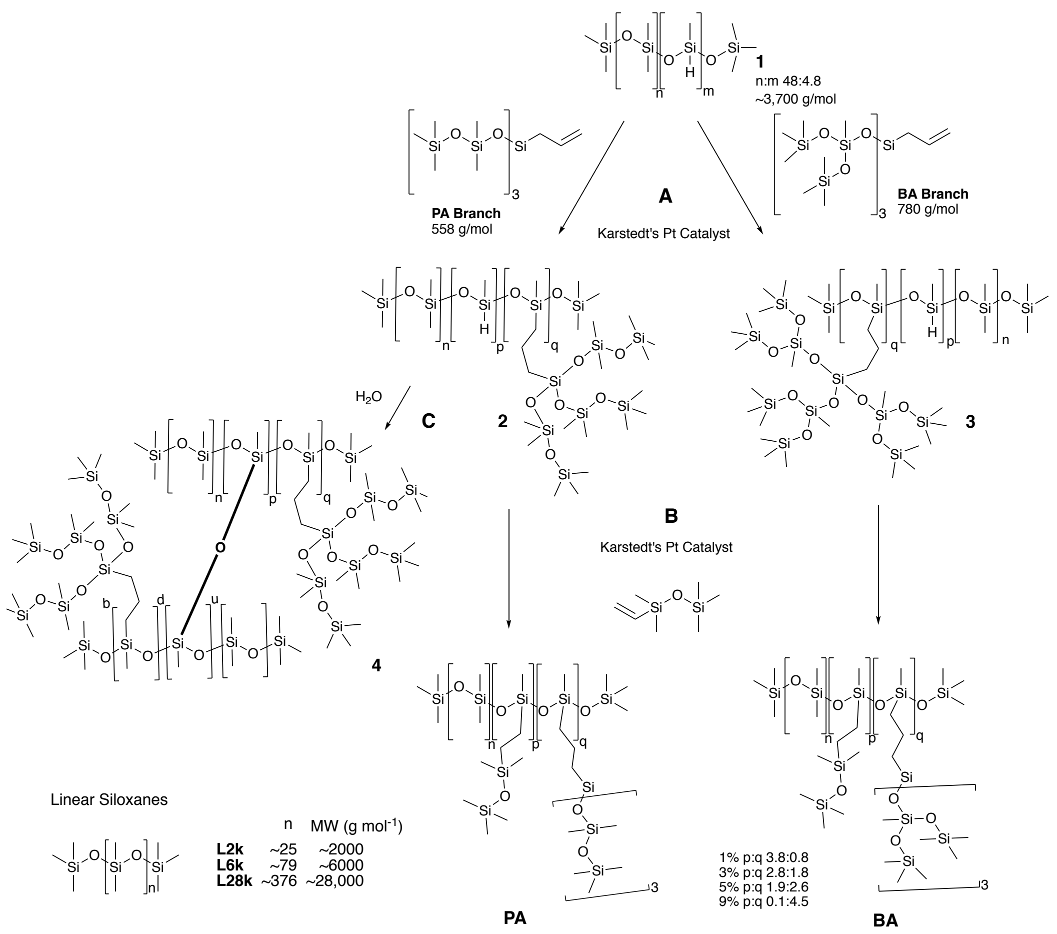


Figure 3.15: A) Preparation of branched silicone polymers PA and BA by hydrosilylation with dendrons. B) Capping of any residual Si-H groups. C) Hydrolytic cleavage and condensation of SiH groups. TMS-terminated linear silicones: L2k, L6k, L28k, n = ~25, ~79, ~376 and MW= ~2,000, ~6,000, ~28,000 g mol^{-1}, respectively.[15]

To compare the effects of branched vs linear oils, Me_3SiO-terminated silicones in three molecular weights ~2,000 **L2k**, ~6,000 **L6k**, ~28,000 g/mol **L28k** (Figure 3.15) were incorporated, respectively, into separate gels prepared by mixing them with functional silicones – vinyl-terminated + MeHSiO – and then curing by hydrosilylation in the presence of the non-functional oil (Figure 3.16). The oil was incorporated at loadings of 15, 30, or 50%, respectively, by weight. Analogous gels were prepared using **PA** and **BA**, respectively. The gels were prepared in triplicate in a 96-well plate (Note: nomenclature of gels = oil, branch frequency, loading. Thus, **PA3-30** is a gel containing the 3% frequency branched **PA** polymer at 30wt%; **L2k-15** is a gel containing 15wt% of the 2000 MW linear oil).

3.3.1 Young's Modulus

After curing, the plates of gels were left for two weeks at room temperature prior to measuring Young's modulus (Figure 3.17, see also Supporting Information). The base elastomer without any added oil unsurprisingly had the highest Young's modulus. As the oil weight fraction was increased in a gel, the materials became softer, with either linear and branched oil constituents (Figure 3.17A,B). There were subtle differences in the impact of oil MW at a given loading. Branching type and frequency played a role in the way in which the moduli were affected. However, this could only be seen at lower oil loadings; all the oils had comparable impact on Young's modulus at 50% loading.

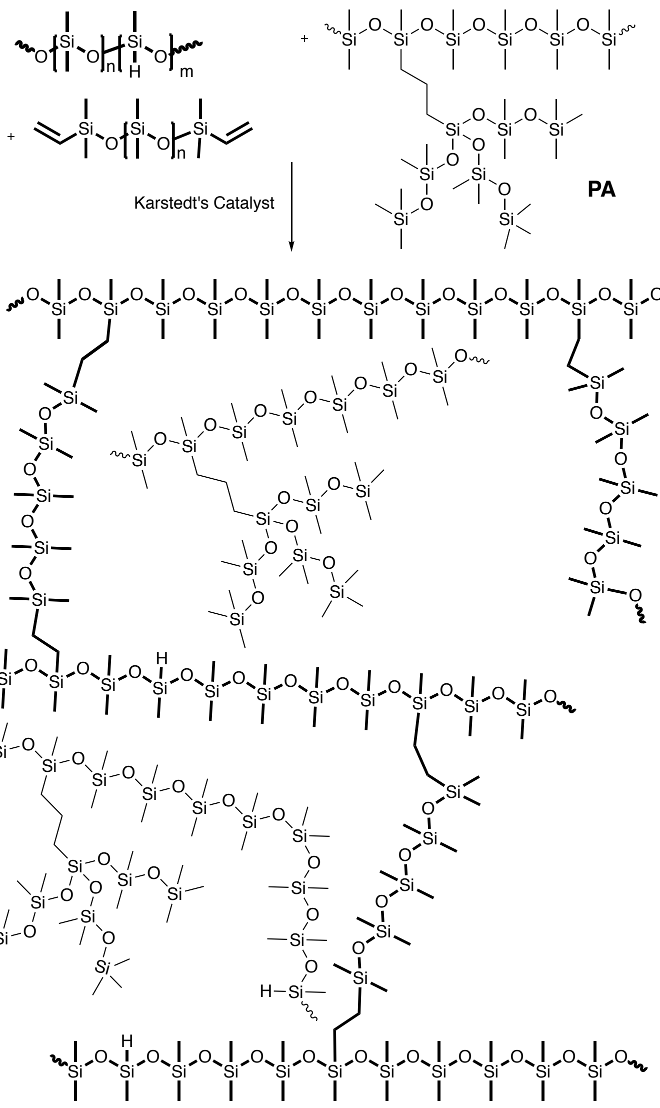


Figure 3.16: Formation the gel by forming an crosslinked network around a non-functional silicone oil, shown for PA.

An examination (made with caution – these are subtle differences) of the Young's moduli of **PA** oils of comparable MW at 15% loading shows the best 'diluents' – leading most effectively to lower moduli – followed the order **PA3** > **PA9** > **PA5 > L6k** (Figure 3.17C), PA branches. By contrast, for the **BA** oils at 15% loading, the most effective diluents have higher branch frequencies **BA8** > **BA5** > **BA3** (Figure 3.17D). That is, at lower (15%) loadings, the oils with the less dense **PA branches** are reinforcing the network more, at a given concentration, than oils with **BA branches**. The **BA3-15** oil reinforced the network better than comparable molecular weight linear oils, or oils with lower density **PA** branches. These effects were essentially lost at higher loadings of oil.

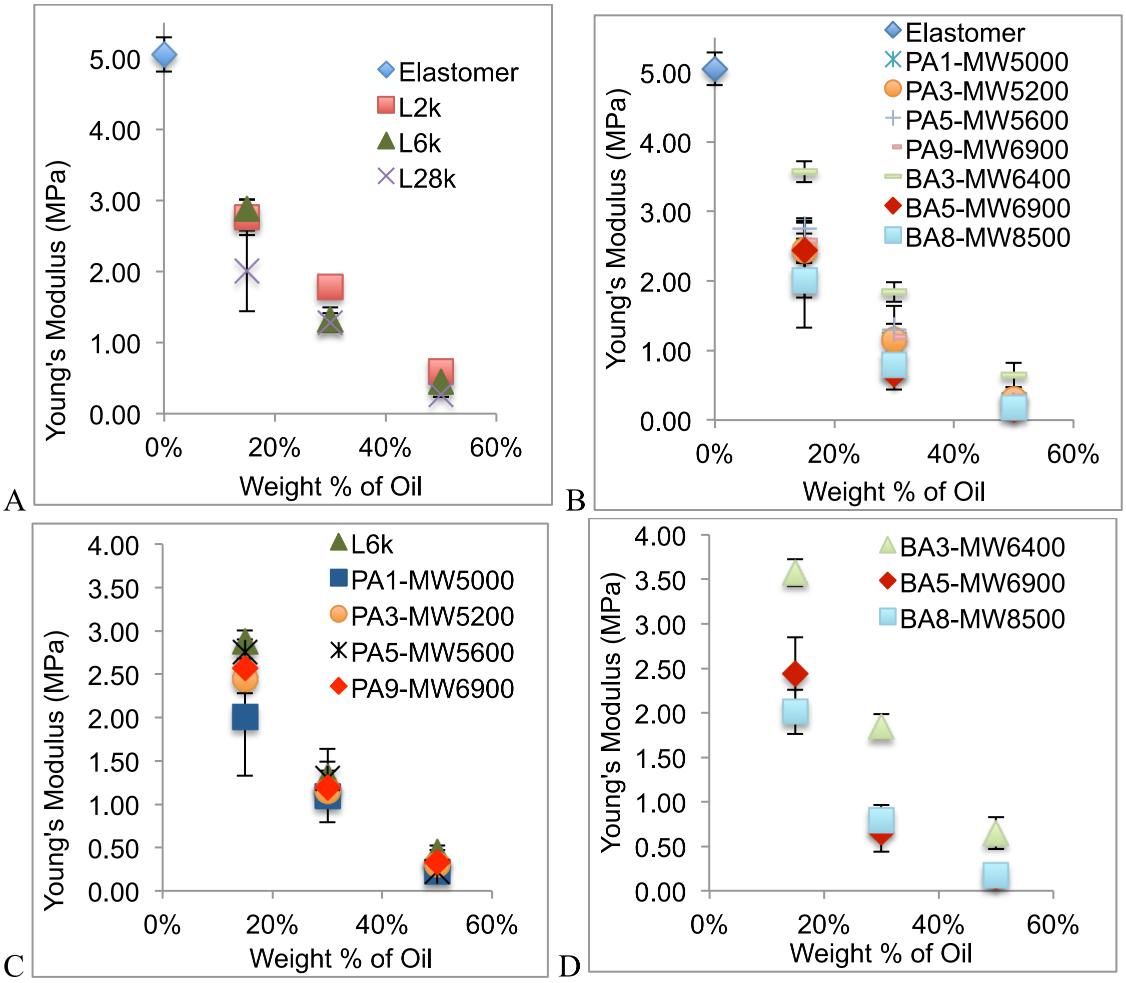


Figure 3.17: Effect of branch type and frequency on the Young's modulus of gels. A: linear silicone oils; B: branched silicone oils. Expansion of plot B for gels prepared with C: PA, and D: BA oils, respectively. An additional expansion can be found in Supporting Information (Figure S24) as well as a comparison between Young's modulus and the degree of branching on the backbone (Figure S25). Reported values are the average of 9 measurements; three comparable samples were measured thrice.

3.3.2 Bleed

The presence of branches on the oils was expected to change the rate of oil migration (bleed) from the gels. Bleed was measured by allowing oil to flow from a gel to an oil-free, unfilled elastomer. Oil-free recipient silicone elastomers were prepared by hydrosilylation cure of a commercial silicone elastomer that contained no filler (Note:

silicone elastomers are often reinforced with silica, but gels are not.[20]). The 5mm thick elastomer sheets were extracted exhaustively with dichloromethane and then dried. The extracted elastomer had a Young's modulus of 5.05 MPa (Figure 3.17). Small circular coupons were punched from the elastomer sheets and then pre-weighed coupons were placed on selected gels containing different loadings of linear or branched oils. Bleed weights were measured gravimetrically after 5 days: the contact surface areas between gel and elastomer were identical for all samples. Fresh, oil-free pre-weighed coupons were placed on the same gels for a second 5-day period. Weight differences – the amount of oil that transferred (bled) from the gel to the extracted elastomers – are shown in Figure 3.18. In all cases, the rate of bleed decreased in the second 5-day period (Figure 3.18B). Such decreases in release rate are typical of first order processes.[21]

Bleed from the unextracted base elastomer is shown as a control; small quantities of an uncharacterized oil bled from this material into the extracted elastomer (untethered oils are commonly found in concentrations up to 10wt% in silicone 'elastomers'). Bleed from the gels tracked with the quantity of oil they contained (Figure 3.18A, for a normalized plot of bleed, see Supporting Information). Lower molecular weight linear oil **L2k** MW 2000 bled much more rapidly than the 6000 MW oil **L6k**, and the linear oils exhibited higher bleed rates than any of the branched oils. Although small differences in molecular weight of the oils are observed – 6000 MW for **L6k** and 5200-8500 g mol^{-1} for the **PA** and **BA** oils, all branched oils were better retained by the elastomeric network in the gel than linear oils (Figure 3.18A).

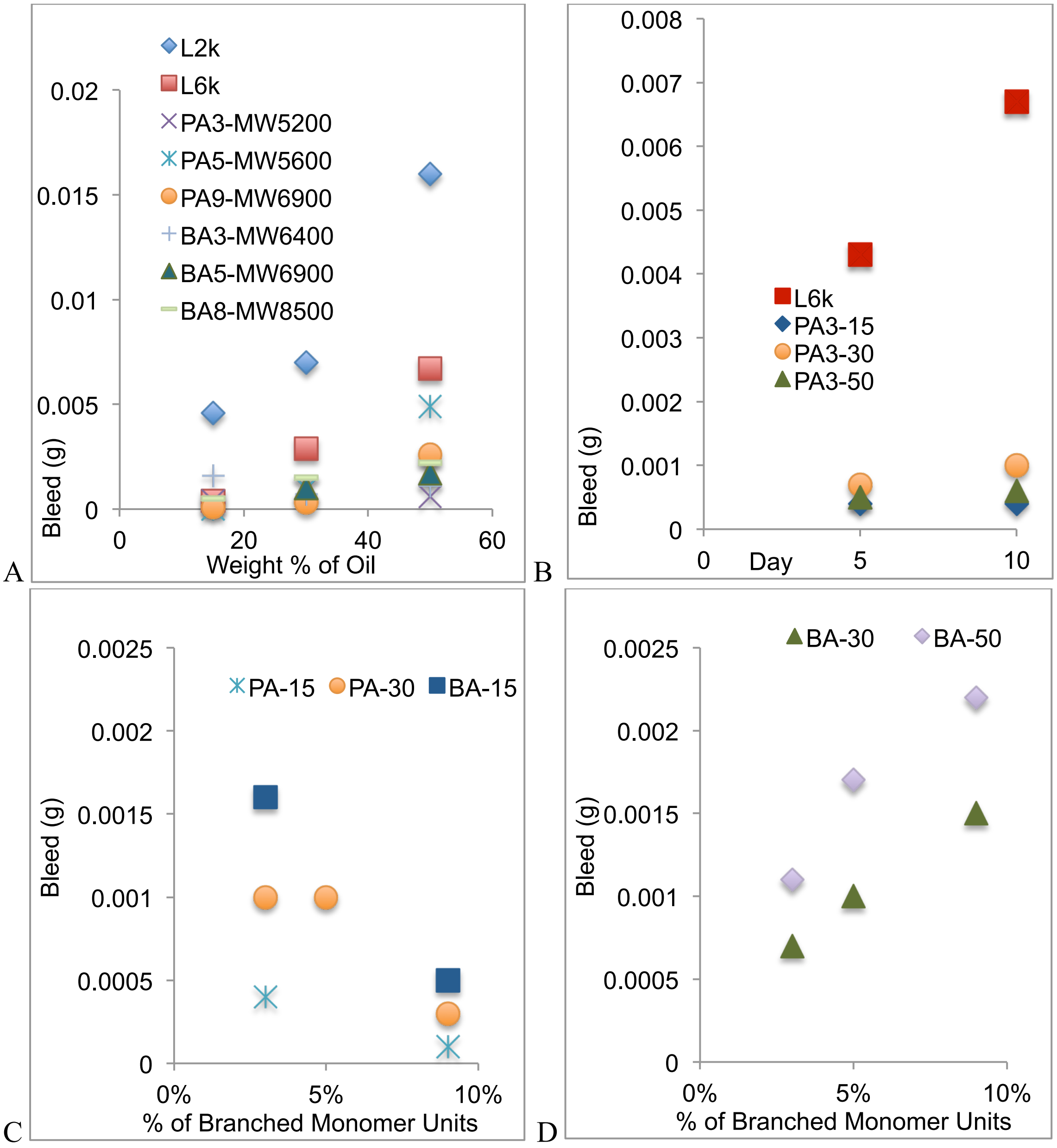


Figure 3.18 Effect of branch type and frequency on the amount of bleed from the gels for: A) the total amount of bleed collected over 10 days; B) PA3 at 5 and 10 days (the entire series, over 10 days, can be found in Figure S27, in Supporting Information). Plots of bleed as a function of branch frequency. C: PA-15,30 and BA-15 and D: BA-30,50. Note: not shown on the graph is PA1-50, value 0.18 g (Figure S26 in Supporting Information).

As the quantity of oil was increased in the gel, the rate of release was expected to increase, as a larger fraction of oil is expected to be located at or near an external surface from which bleed can occur. While all oils exhibited this trend, the increase in rate of release for the branched polymers was much smaller than for the linear polymers (Figure

3.18A). That is, the presence of branches reduces the ability of the oils to migrate to, and bleed from, the external interface.

Care must be taken not to overinterpret small differences in bleed rates. Additional confidence in making such interpretations, however, comes from previous studies on oil viscosity[22] and the Young's moduli data above. The effect of branch frequency on the bleed rate followed two different trends. Oils bearing the lower density **PA branch** at any loading and **BA-15** polymer (15% loading) showed a noticeable *decrease* in the rate of bleed with increased branching (Figure 3.18C). By contrast, the **BA-30** and **BA-50** gel showed a small increase in bleed rate (Figure 3.18D) with increased branching.

3.4 Discussion

3.4.1 Young's Moduli

Silicone (and other) polymers bearing long side chain branches exhibit very different properties than their linear counterparts both as oils, or after crosslinking. Bibbo and Valles[23] used their study relating the effect of pendant chains to loss modulus to conclude that both pendant chains and free fluids of low molecular weight structures allow the materials to more readily collapse, thus leading to softer structures. Gottlieb et al.[24] similarly found that when the reagents making up an elastomer network were not entirely consumed, unreacted untethered oils (and also partly grafted oils) acted as swelling agents, that is, to give a gel, leading to a decrease in the modulus. However, the free and bound chains can contribute differently to the physical properties of the gel.

Villar and Valles[25] looked at the effects of pendant chains in PDMS networks and found that pendant chains caused a decrease in the elastic modulus. This change was attributed to the ability of chains to relax differently than their linear, non-branched counterparts,[25] similar to the way in which branches have been shown to cause changes in viscosity behaviour.[22] They also found that when measurements were taken at higher frequencies, the elastic modulus increased, due to reduced mobility of chains during the time of the experiment. That is, at higher frequencies the linear branches are effectively more stiff, strengthening the material.[25] Vega et al.[26] similarly demonstrated that pendant groups are less likely to collapse than untethered oils because it would be entropically less favourable to do so. The resulting materials were harder when compared to gels filled with untethered fluids.[26]

The addition of untethered silicone oils to an elastomer to form a silicone gel leads to a reduction in the Young's modulus. Under stress, unbound chains are able to migrate through the network through reptation. The facility with which they are able to reptate depends on the network crosslink density, the loading of the oil (which affects crosslinking density) and the molecular weight of the oil. The latter effect was clearly shown through frequency dependent response.[12, 14] At low frequencies, long and short chains can both efficiently reptate and, at the same loading, relatively small differences are observed in Young's moduli as a function of oil MW. Those effects are dramatically different at higher frequencies, where the less mobile chains (particularly those above the entanglement limit) are unable to readily respond in the time of the experiment and 'harder' materials are observed.

All the oils examined in this report are well below the entanglement limit. Increased loading of any of the oils in the silicone gels led to reductions in the Young's moduli (Figure 3.17A,B). At a given loading level of oil incorporation into the network, particularly the lower 15% loading, the gels containing branched oil structures (MW

5200-8900 g mol^{-1}) exhibited slightly lower modulus values than the linear, unbranched structure of comparable molecular weight, **L6k**. To the degree these trends are viable (some are very close to the observed error), one can attribute lower moduli to the higher free volume created by the branched materials, which interferes with the network structure. That is, more chain ends allow for the branches to deform and rearrange more readily when faced with an external force, therefore leading to softer gels and the branches also reduce the efficiency of internal interactions of the network.[23] The exception to this, **BA3-15**, was less effective at lowering the Young's moduli. These subtle differences were only seen at low oil loadings.

One interpretation that explains these data involves the degree to which branching facilitates self-association of the oils, ultimately leading to a globular transition.[16] We previously reported the viscosity of both **PA** and **BA** polymers as a function of branch frequency (Figure 3.19A).[22] There was an increase in oil MW with increased branching, and an accompanying increase in viscosity. This was interpreted to be a consequence of increasing interchain interactions with increasing branch frequency that led to higher viscosities. However, there was a clear break point above 5% branch frequency where, with further increases in branching, the viscosity starts to drop. This was interpreted to be a consequence better internal packing of the chains, lower free volumes of a given chain, fewer interactions with branches on adjacent chains, and a consequential drop in viscosity as the molecules approach or pass through a globular transition.

A chart showing the Young's moduli of gels as a function of oil branching follows a very similar pattern (Figure 3.19B). While higher loadings lead to lower Young's moduli as expected **PA-30** > **PA-50** and **BA-30 > BA-50**, the **PA** chains at a given loading lead to an increase in Young's moduli with branching frequency until about 5% branching, and then fall. The more densely branched **BA** polymers just exhibit a fall in Young's moduli with increased branching.

These data demonstrate that the observed physical properties of gels containing branched oils are primarily affected by the oil fraction, with the biggest drop in Young's modulus found in gels with the highest oil concentrations. However, the branch type and frequency play a subordinate role. **PA** branches interact effectively with each other (chain/chain) and with the network (chain/elastomer) to better reinforce the gel (Figure 3.20A), until the branching frequency is too high – near 5% – and interchain interactions become more important than the chain/network interactions (Figure 3.20B). In the case of the **BA** polymers, self-association already becomes more important than chain/elastomer interactions at a 3% branch frequency (Figure 3.20C→D); the oils are already self-associating, interweaving less with the network, and having a better diluting effect on the network.

3.4.2 Bleed

Traditionally, the only controlling factors for gel bleed that could be applied were total loading and molecular weight of the oil; more rapid bleed is expected for oils of lower molecular weight at higher loadings. Bleed is a consequence of polymer reptation through a network.[25, 27] The higher the loading, the more dilute the network, the lower is the resistance to bleed. Once the molecular weight of the solvent oils exceeds the entanglement limit of about 29000 g mol^{-1} however, reptation is much more difficult and the rate of bleed will drop (in the literature, the weight for entanglement ranges from about 15000-35000; here we use data from the seminal study of Mrozek et al.[14]). The comprehensive study of silicone gels noted the difficulty of extracting high molecular weight materials (>308,000 g/mol) from a gel even when using low viscosity organic solvents.[14] But below the entanglement limit, bleed should track with molecular weight, as was shown for **L2k** vs **L6k** (Figure 3.18A).

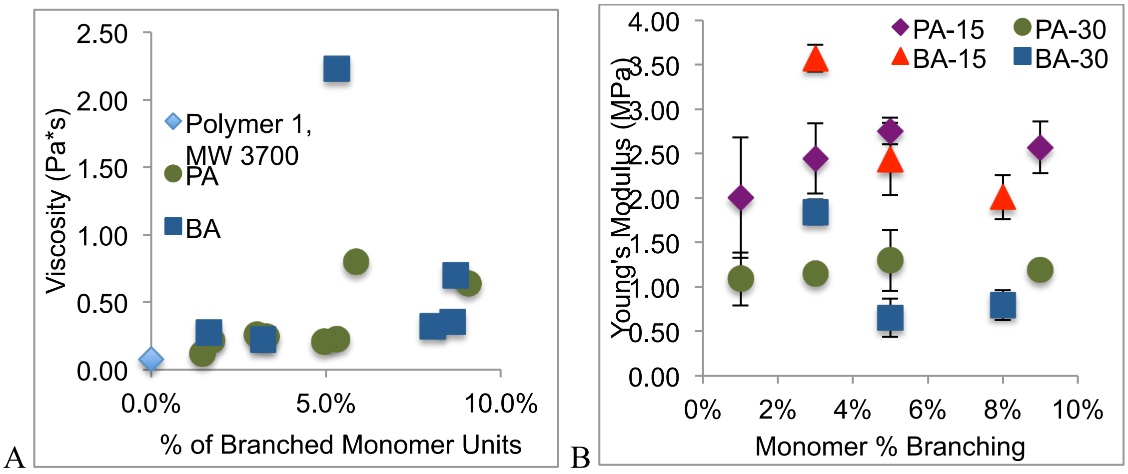


Figure 3.19 A: Viscosity of PA and BA polymers, as a function of branch frequency. Adapted from reference 22 and B: Young's modulus for gels containing PA and BA oils at higher loadings.

While the release of linear oils in this study was found to correlate with molecular weight, bleed of the branched oils from gels were found to correspond more closely with branch frequency and branch density (Figure 3.18B). Initially, this is unsurprising. Polymer chains move past one another through reptation.[25, 27] Branching will decrease the ability of a polymer to reptate through an existing elastomeric network. Even though localized interchain interactions between branched oil and network may be less effective than with linear oils, the migratory aptitude of the branched polymer will be intrinsically lower due to lower mobility.

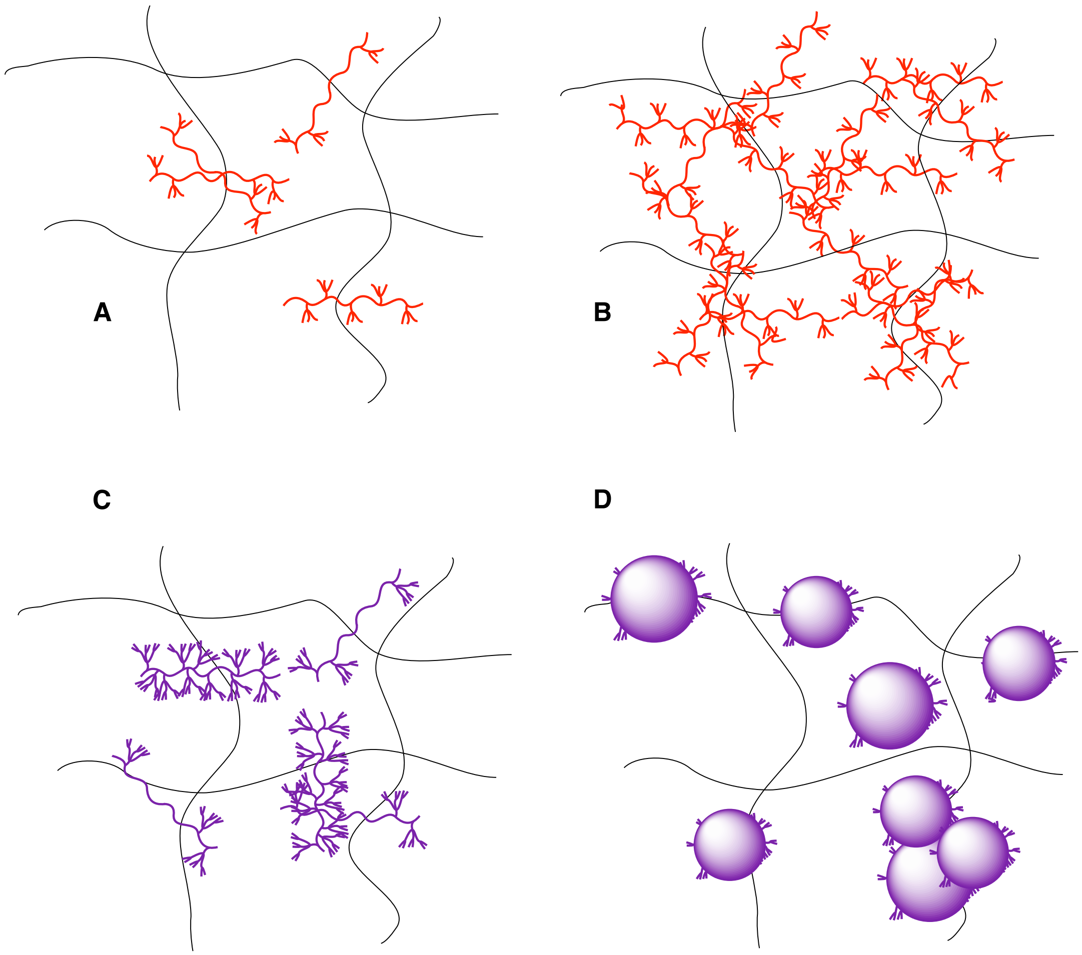


Figure 3.20: Models of chain/chain and chain/network interactions A: PA low loading; B: PA high loading; C: BA low loading; D: BA high loading.

The observed bleed rates are also consistent with the previously reported viscosity data.[22] At higher branch frequencies, and with higher loadings of the **BA** oils in the gel, more chain/chain and fewer chain/network interactions lead to small increases in bleed with loading (Figure 3.19A,D, Figure 3.20D). By contrast, **PA** oils undergo more efficient chain/chain and chain/network interactions and higher loading leads to reduced bleed (Figure 3.19A,C, Figure 3.20A,B). We note that the oils are distinguished from the network structure in that they have a higher alkyl fraction, arising from the allyl groups that are used to graft the branches to the backbone. Thus, it could be inferred that the different χ parameter for the oil than a pure silicone lead to incompatibility with the network. That proposition, however, is contradicted by the **PA** oils, which have a higher alkyl loading than **BA** oils, yet are less efficient at bleeding from the gel. It is important to reiterate that these are minor variations in bleed rates as a function of small differences in branching; bleed from gels made from all the branched polymers was notably lower than for linear polymers of comparable molecular weight.

Silicone oils commonly bleed from elastomers and particularly from gels. This can be used, in commerce, as an advantage. For example, it is possible to buy 'self-lubricating' silicone elastomers from which oil slowly leaches. The release of silicone oils from gels has have previously been used, for example, to reduce fouling of surfaces.[28-31] The particularly elegant work of Aizenberg et al. demonstrates the high degree of control over lubrication that can result from controlled release of silicone oils from controlled porosity materials – SLIPs – including for biofouling applications.[32, 33]

However, release of oils from silicone gels is not always beneficial. Regulatory agencies require manufacturers of silicone gel breast implants to quantify gel bleed as a precaution in case a link between bleed and systemic physiological changes is found in the future.[34] Manufacturers of HEPA filters have expressed concern about oils that may leak from silicone gel sealants; silicone manufacturers provide guidance on how to remove silicone oils from various substrates, including concrete. Obviously, in addition to any detriments caused by the release of oil, the remaining gel will undergo dynamic mechanical changes as oil is lost.

These experiments demonstrate that, even with low molecular weight oils, the addition of branches can significantly reduce the rate of bleed from silicone gels, even at loadings of 50wt% oil. Several factors contribute to this observation. At low frequency, branched oils interact more effectively with the network and with each other. The less densely branched **PA** oils show decreasing bleed with increasing branch frequency, suggesting the efficiency of both chain/elastomer and chain/chain interactions increases. The more densely branched **BA** oils exhibit the same behavior at low loading and low branch frequency. At higher branch frequencies, and high loadings the **BA** chain/chain interactions become more important at the expense of chain/elastomer interactions, and the bleed starts to increase (and the Young's modulus decreases). The observation of the effects with such low molecular weight oils, nearly an order of magnitude below the entanglement limit, suggests that a balance between better physical properties and lower bleed can be met by using these and higher molecular weight analogues in silicone gels, an hypothesis that is currently being tested.

3.5 Conclusions

The replacement of linear oils by branched oils, of comparable molecular weight, in silicone gels changes the physical behaviour of the gel. At high loadings (>30%), the Young's moduli of gels containing branched or linear oils were comparable, and lower than the starting elastomer. At lower oil loadings, subtle differences were observed between the impact of the branched vs linear oil on the Young's moduli, with more highly branched oils leading to lower moduli. More significant differences were seen with gel bleed. Lower bleed was observed with any of the branched oils, when compared to linear oils; the differences were particularly evident at higher loadings. This is ascribed to inhibited reptation though the gel of branched materials, when compared to the linear counterparts. The frequency and density of branches contributed to the specific bleed profiles. The less dense **PA** branches effectively interacted both with the network and other chains; as branch frequency increased, bleed decreased. The more densely branched

BA polymers exhibited higher degrees of self-association leading to lower bleed than linear polymers (reptation is still important), but slightly higher degrees of bleed were observed with **BA** than the **PA** polymers. These observations suggest that both the physical properties of gels and gel bleed can be readily tuned by controlling oil MW, loading, branch density and branch frequency.

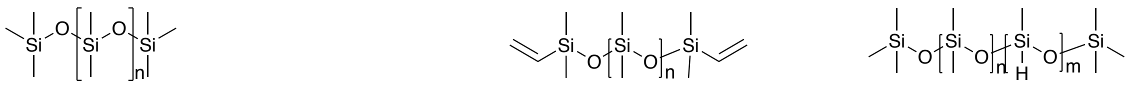
3.6 Acknowledgements

We gratefully acknowledge the financial support of the Natural Sciences and Engineering Research Council of Canada (NSERC) and Siltech Corp. for providing CR13-46 elastomer. We also thank Prof. Todd Hoare for both the use of his modulus instrument and for helpful discussions.

3.7 Experimental

3.7.1 Materials

Siltech CR13-46A and Siltech CR13-46B (which, upon mixing in a 1:1 ratio and heating lead to a silicone elastomer), were used as received from Siltech. Me_3Si-capped PDMS (~2,000 g/mol, 100% Me_2SiO, **L2k**; ~6,000 g/mol, 100% Me_2SiO, **L6k**), DMS-T31 (~28,000 g/mol, 100% Me_2SiO, **L28k**), DMS-V31 (~28,000 g/mol, 0.18-0.26% $OSi(CH_3)_2CHCH_2$), HMS-301 (~2,000 g/mol, mole %: 20-35% MeHSiO), and vinylpentamethyldisiloxane were purchased from Gelest and used as received (Figure 3.21). Platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's Catalyst) solution (0.1M in poly(dimethylsiloxane), vinyl-terminated) was purchased from Sigma-Aldrich and used as received. The Me_3Si-capped MeHSiO/Me_2SiO linear silicone polymer **5**, was previously synthesized and used as received. **PA Branch**, and **BA Branch** were prepared as previously reported[15] using a Piers-Rubinsztajn reaction between allyltriethoxysilane and $HSiMe_2OSiMe_3$, or $HMeSi(OSiMe_3)_2$, respectively in the presence of B(C_6F_5)$_3$. Commercial solvents were purchased from Caledon Laboratory Chemicals including hexane, toluene, and dichloromethane were dried prior to use over activated alumina.



DMS-T12, DMS-T21
DMS-T31 n = ~25, ~79, ~376
MW= ~2,000, ~6,000, ~28,000 g mol^{-1}

DMS-V31
n=~378
MW=~28,000 g mol^{-1}

HMS-301
n=~7, m=~21
MW=~2,000 g mol^{-1}

Figure 3.21 Functional polymers from Gelest.

3.7.2 Methods

Young's modulus measurements were made using a BioMomentum Mach-1 Mechanical Testing System. Mach-1 Motion software was used to control the machine with the following sequence of commands: Scan, Move Absolute, Zero Load, Find Contact, Stress Relaxation, Move Absolute, Wait. This sequence was repeated for each row of the 96-well plate (12 wells at a time). Each well was measured three times. The stress relaxation data was saved and analyzed using the Mach-1 Analysis software where Force (in the z direction) was plotted against Position (in the z direction). The radius of the probe on the Mach-1 instrument has a radius of 0.5mm. The sample thickness was measured for each sample and adjusted accordingly. The Poisson ratio was set to 0.3.

3.7.3 General Procedure for the Preparation of Branched, Capped Silicones (shown for PA5)

Polymer **1** (3.8285 g, 5.76 mmol SiH) was weighed out into a 25 mL round-bottomed flask before capping and stirring under nitrogen for 5 min. **PA Branch** (1.6043 g, 2.8751 mmol) was added to the flask using a syringe and needle and left stirring for 10 min prior to adding of Karstedt's catalyst (109 μL of 0.011 g/mL of toluene, 6.29 x10^{-5}

mmol) through the septum. The reaction was left overnight at room temperature; ^{1}H NMR confirmed that **PA Branch** had been consumed. A fraction (~1 mL) of the reaction mixture was out by syringe and added to an activated carbon (~0.1 g) in dry hexanes (~10 mL) to be quenched. The extracted mixture was stirred overnight and then filtered through Celite packed with dry hexanes. Hexanes were removed under reduced pressure to yield 0.6562 g of **PA5i**.

To the remaining reaction mixture was added vinylpentamethyldisiloxane (MM^H, 0.4349 g, 2.4938 mmol) and additional Karstedt's catalyst (200 µL of 0.011 g/mL of toluene, 1.15 x10^{-4} mmol). The reaction was heated to 50 °C for 6 d. Activated carbon (~0.1 g) was added to the reaction to quench the catalyst and this was stirred for 3 h prior to adding ~10 mL of dry hexanes. This was left overnight prior and then filtered through Celite packed with dry hexanes. Hexanes and excess vinylpentamethyldisiloxane were removed under reduced pressure. The yield of **PA5** was 2.4641 g (~50% yield).

PA5i: ^{1}H NMR (CDCl$_3$, 600MHz): d 4.68 (s, 0.85H), 1.47-1.41 (m, 2H), 0.59-0.56 (t, 4H), 0.19-(-), 0.3 (m, 170H).

PA5: ^{1}H NMR (CDCl$_3$, 600MHz): d 6.07-5.91 (d, 0.18H), 5.81-5.77 (t, 0.09H), 4.7 (s, 0.02H), 1.46-1.40 (m, 2H), 0.60-0.56 (t, 4H), 0.46-0.37 (m, 2.7H), 0.17-(-), 0.3 (m, 183H).

Table 3.2: Grafting of branches to the backbone shown for ~5g reactions.

Reaction Label[a]	% of Branched Monomer Units	Backbone (g)	mmol SiH	Branch (g)	Branch mmol
PA3i	3.4	3.8369	5.7799	1.6112	2.8875
PA9i	9.0	3.0051	4.5233	2.5189	4.5142
PA5i	5.0	3.8285	5.7600	1.6043	2.8751
PA1i	1.0	4.2129	6.3413	1.0617	1.9027
BA5i	5.0	3.9989	6.0192	3.0101	3.0100
BA3i	3.0	3.8533	5.8000	1.3544	1.7364
BA8i	8.0%	3.0018	4.5183	3.5262	4.5208

[a] where PA and BA in the reaction label refer to the branch type and i refers to a reaction that does *not* contain vinylpentamethyldisiloxane as a capping agent.

Table 3.3: Capping reactions

Reaction Label[a]	Amount of reaction used for capping[b]	MM^H (g)	MM^H mmol	NMR MW	Viscosity (Pa*s)
PA1	~80%	0.7744	4.4406	4977	0.3808
PA3	100%	0.4962	2.8453	5229	0.3083
PA5	~80%	0.4349	2.4938	5601	0.423
PA9	100%	0.0740	0.4243	6889	0.4224
BA3	~80%	0.7030	4.0310	6418	1.09
BA5	100%	0.4603	2.6393	6888	2.072
BA8	100%	0.0730	0.4186	8514	-

[a] **PA** and **BA** in the reaction label refer to the branch type.

[b] In select cases, part of the reaction mixture was removed prior to introducing vinylpentamethyldisiloxane as a capping agent and therefore, only a percentage of the reaction was used for the capping procedure.

3.7.4 Gel Preparation and Young's Modulus Measurements

The base elastomer mixture was prepared by hand-mixing Siltech CR13-46A and Siltech CR13-46B in a 1:1 ratio in a large Petri dish (10 cm diameter). For Plate A, this consisted of CR13-46A (8.6813 g) and CR13-46B (8.7293 g); for Plate B CR13-46A (4.0221 g) and CR13-46B (4.0134 g). The formulations were prepared for 12 wells at a time in 96-well plates; the pre-elastomer mixture was added, followed by the desired oil, to Plate A or Plate B (Table S5 and Table S6 in Supporting Information). The wells were mixed thoroughly by hand. After all wells were prepared, the plate was placed in a desiccator under vacuum (~50 Torr) for 1 h to remove any bubbles formed through mixing. The plates were then placed in a 60 °C oven for ~2 h to complete cure. The plates were then left at RT for two weeks prior to measuring Young's Modulus (Table S7 and Table S8 in Supporting Information) and were left at RT throughout the bleed measurements, which extended over longer periods of time, as described below.

3.7.5 General Procedure for the Preparation of the Extracted Elastomers

DMS-V31 (21.8787 g, 1.56 mmol of $SiCH=CH_2$) and HMS-301 (0.4186 g, 1.71 mmol of $Si\mathit{H}(CH_3)O$) were weighed into a "Max 40" FlackTek cup and the lid was tightly closed. The cup was put into the FlackTek using a "Max 40 Holder" at 3,000 rpm for 2 min. The cup was removed and Karstedt's catalyst (30 µL of 0.005 /mL in toluene, ~10 ppm) was added before resealing the cup. The cup was put back into the FlackTek using a "Max 4 Holder" at 3,000 rpm for an additional 2 min. The contents were then transferred to the bottom of a large Petri dish (diameter), which was put into a 60 °C oven for 2 h. The thickness of the prepared film was ~5 mm. This process was repeated four additional times and the quantities of oil used can be found in the Supporting Information (Table S5).

The prepared elastomers were extracted to remove unreacted silicone oil by placing the elastomer sheet 1/tube into 50 mL Falcon tubes with dichloromethane (~30 mL) and placed on a VWR Rocking Platform (Model 100) on the highest setting for 8 h; the solvent was changed every 2 h. The samples were removed from the solvent and left on the bench top at RT for 24 h before being punched used a ¼ inch metal puncher. The extracted elastomer coupons **D** were stored in a sealed vial at RT.

3.7.6 Bleed Measurements

At both one week and two weeks after Young's Modulus measurements were made on Plate A and Plate B, respectively, coupons **D** were individually weighed prior to placing one on selected wells in the plates. The plates were left untouched at RT for 5 days before the coupons **D** were removed and reweighed. A new set of coupons **D** were individually weighed and placed on the same wells in Plate A. The plate was again left untouched at RT for 5 days before removing the second set of **D** and reweighing. The differences in weights at 5 and 10 days was recorded (Table S10 and Table S11 in Supporting Information). It should be noted that several of the coupons underwent varying degrees of cohesive failure during attempted removal, leading to 'negative amounts of bleed'.

3.8 References

1. Natale, A. Disposable HEPA filtration device. US4613348 A, 1986.
2. Lantada, A. D., Hydroactive Materials for Biodevices. In *Handbook of Active Materials for Medical Devices: Advances and Applications*, Lantada, A. D., Ed. Pan Stanford Publishing Pte. Ltd.: Singapore, 2012; pp 369-397.
3. LeVier, R. R.; Harrison, M. C.; Cook, R. R.; Lane, T. H., What Is Silicone? *Plastic and reconstructive surgery* **1993,** *92* (1), 12-167.
4. Naim, J. O.; Ippolito, K. M. L.; Lanzafame, R. J.; van Oss, C. J., The Effect of Molecular Weight and Gel Preparation on Humoral Adjuvancy of Silicone Oils and Silicone Gels. *Immunological Investigations* **1995,** *24* (3), 537-547.
5. Noll, W., *Chemistry and Technology of Silicones*. Academic Press: New York, 1968.
6. Clarson, S. J.; Semlyen, J. A., *Siloxane Polymers*. Prentice Hall: Englewood Cliffs, NJ, 1993.
7. Alvarez, K. E.; Berry, P. A.; Stanga, M. A.; Strong, M. R., Silicone gel composition and silicone gel produced therefrom. **2001**.
8. Zambacos, G.; Molnar, C.; Mandrekas, A., Silicone Lymphadenopathy After Breast Augmentation: Case Reports, Review of the Literature, and Current Thoughts. *Aesthetic Plastic Surgery* **2013,** *37*, 278-289.
9. Gruber, A. D.; Widenhouse, C. W.; Mathes, S.; Gruber, R. P., Exhaustive soxhlet extraction for the complete removal of residual compounds to provide a nonleaching silicone elastomer. *Journal of Biomedical Materials Research* **2000,** *53*, 445-448.
10. Brook, M. A., Platinum in silicone breast implants. *Biomaterials* **2006,** *27*, 3274-3286.

11. Brook, M. A., *Silicon in Organic, Organometallic and Polymer Chemistry*. John Wiley & Sons, Inc.: New York, 2000.

12. Kalcioglu, Z. I.; Mrozek, R. A.; Mahmoodian, R.; VanLandingham, M. R.; Lenhart, J. L.; Van Vliet, K. J., Tunable mechanical behavior of synthetic organogels as biofidelic tissue simulants. *Journal of Biomechanics* **2013,** *46* (9), 1583-1591.

13. Gong, J. P.; Katsuyama, Y.; Kurokawa, T.; Osada, Y., Double-Network Hydrogels with Extremely High Mechanical Strength. *Advanced Materials* **2003,** *15* (14), 1155-1158.

14. Mrozek, R. A.; Cole, P. J.; Otim, K. J.; Shull, K. R.; Lenhart, J. L., Influence of solvent size on the mechanical properties and rheology of polydimethylsiloxane-based polymeric gels. *Polymer* **2011,** *52* (15), 3422-3430.

15. Morgan, J.; Chen, T.; Hayes, R.; Dickie, T.; Urlich, T.; Brook, M. A., Facile synthesis of dendron-branched silicone polymers. *Polymer Chemistry* **2017,** *8* (18), 2743-2746.

16. Mourey, T. H.; Turner, S. R.; Rubinstein, M.; Frechet, J. M. J.; Hawker, C. J.; Wooley, K. L., Unique behavior of dendritic macromolecules: intrinsic viscosity of polyether dendrimers. *Macromolecules* **1992,** *25*, 2401-2406.

17. Lewis, L. N.; Lewis, N., Platinum-catalyzed hydrosilylation - colloid formation as the essential step. *Journal of the American Chemical Society* **1986,** *108*, 7228-7231.

18. Karlsson, A.; Singh, S. K.; Albertsson, A. C., Controlled destruction of residual crosslinker in a silicone elastomer for drug delivery. *J. Appl. Polym. Sci.* **2002,** *84* (12), 2254-2264.

19. Flagg, D. H.; McCarthy, T. J., Rediscovering Silicones: MQ Copolymers. *Macromolecules* **2016,** *49* (22), 8581-8592.

20. Ulman, K. L.; Thomas, X., Silicone Pressure Sensitive Adhesives For Healthcare Applications. In *Handbook of Pressure Sensitive Adhesive Technology* Satas, D., Ed. Satas & Associates: Warwick RI, 1999; Vol. 3, pp 724–747.

21. Fu, Y.; Kao, W. J., Drug Release Kinetics and Transport Mechanisms of Non-degradable and Degradable Polymeric Delivery Systems. *Expert Opin. Drug Deliv.* **2010,** *7* (4), 429-444.

22. Morgan, J.; Chen, T.; Hayes, R.; Dickie, T.; Urlich, T.; Brook, M. A., Facile synthesis of dendron-branched silicone polymers. *Polym. Chem.* **2017**.

23. Bibbo, M. A.; Valles, E. M., Influence of pendant chains on the loss modulus of model networks. *Macromolecules* **1984,** *17* (3), 360-365.

24. Gottlieb, M.; Macosko, C. W.; Benjamin, G. S.; Meyers, K. O.; Merrill, E. W., Equilibrium modulus of model poly(dimethylsiloxane) networks. *Macromolecules* **1981,** *14* (4), 1039-1046.

25. Villar, M. A.; Vallés, E. M., Influence of Pendant Chains on Mechanical Properties of Model Poly(dimethylsiloxane) Networks. 2. Viscoelastic Properties. *Macromolecules* **1996,** *29* (11), 4081-4089.

26. Vega, D. A.; Villar, M. A.; Alessandrini, J. L.; Vallés, E. M., Terminal Relaxation of Model Poly(dimethylsiloxane) Networks with Pendant Chains. *Macromolecules* **2001,** *34* (13), 4591-4596.

27. Gennes, P.-G. d., *Scaling Concepts in Polymer Physics*. Cornell University: Ithaca, New York, 1979.

28. Shivapooja, P.; Cao, C. Y.; Orihuela, B.; Levering, V.; Zhao, X. H.; Rittschof, D.; Lopez, G. P., Incorporation of silicone oil into elastomers enhances barnacle detachment by active surface strain. *Biofouling* **2016,** *32* (9), 1017-1028.
29. Stein, J.; Truby, K.; Wood, C. D.; Stein, J.; Gardner, M.; Swain, G.; Kavanagh, C.; Kovach, B.; Schultz, M.; Wiebe, D.; Holm, E.; Montemarano, J.; Wendt, D.; Smith, C.; Meyer, A., Silicone foul release coatings: Effect of the interaction of oil and coating functionalities on the magnitude of macrofouling attachment strengths. *Biofouling* **2003,** *19*, 71-82.
30. Truby, K.; Wood, C.; Stein, J.; Cella, J.; Carpenter, J.; Kavanagh, C.; Swain, G.; Wiebe, D.; Lapota, D.; Meyer, A.; Holm, E.; Wendt, D.; Smith, C.; Montemarano, J., Evaluation of the performance enhancement of silicone biofouling-release coatings by oil incorporation. *Biofouling* **2000,** *15* (1-3), 141-+.
31. Galhenage, T. P.; Hoffman, D.; Silbert, S. D.; Stafslien, S. J.; Daniels, J.; Miljkovic, T.; Finlay, J. A.; Franco, S. C.; Clare, A. S.; Nedved, B. T.; Hadfield, M. G.; Wendt, D. E.; Waltz, G.; Brewer, L.; Teo, S. L. M.; Lim, C.-S.; Webster, D. C., Fouling-Release Performance of Silicone Oil-Modified Siloxane-Polyurethane Coatings. *ACS Appl. Mater. Interfaces* **2016,** *8* (42), 29025-29036.
32. MacCallum, N.; Howell, C.; Kim, P.; Sun, D.; Friedlander, R.; Ranisau, J.; Ahanotu, O.; Lin, J. J.; Vena, A.; Hatton, B.; Wong, T. S.; Aizenberg, J., Liquid-Infused Silicone As a Biofouling-Free Medical Material. *Acs Biomaterials Science & Engineering* **2015,** *1* (1), 43-51.
33. Howell, C.; Vu, T. L.; Lin, J. J.; Kolle, S.; Juthani, N.; Watson, E.; Weaver, J. C.; Alvarenga, J.; Aizenberg, J., Self-Replenishing Vascularized Fouling-Release Surfaces. *ACS Appl. Mater. Interfaces* **2014,** *6* (15), 13299-13307.
34. Guidance for Industry and FDA Staff - Saline, Silicone Gel, and Alternative Breast Implants. FDA: http://www.fda.gov/MedicalDevices/ucm071228.htm; pp November 17, 2006.

Chapter 4 : General Conclusions

The interfacial properties of silicones have allowed them to be used in a variety of applications; specific structures are linked to specific applications. Silicone gels have been shown to be advantageous as sealants that bridge interfaces, among other uses, but bleed of the linear oil from the material can be problematic. In this thesis, we posed the question, "Would bleed be different with branched, rather than linear, oils in silicone gels?" While there are many existing studies of non-silicone branched polymers and dendrimeric silicones, little research has been done on the effect of introducing branches onto a silicone backbone. Through existing methods of preparing silicone dendron and dendrimer structures, a suite of branched silicones polymers were prepared and later incorporated into silicone gels.

Chapter 2 introduced the idea of preparing branched silicone polymers using existing, popular silicone chemical reactions; the Piers Rubinsztajn reaction was combined with hydrosilylation. The Piers Rubinsztajn reaction is known to produce functional, controlled branched structures, and these structures could be easily grafted onto a silicone backbone by selecting appropriate functional groups both in the branched product, and on the silicone backbone. For example, by synthesizing branches that were allyl- or vinyl-terminated and working with silicones backbone bearing SiH functional groups, hydrosilylation could readily practiced in the presence of Karstedt's catalyst, which grafted the branches onto the backbone. The branched silicones were characterized using NMR spectroscopy and the viscosities of these branched oils were found to depend on branch frequency; this was shown using three different molecular weight silicone backbones. Larger, more elaborate branches resulted in more viscous oils when introduced at the same density on a backbone, than smaller, less dense branches. Furthermore, as the degree of branching increased, there was an increase in viscosity until a maximum was achieved at which point further branching led to a decrease in viscosity. This trend likely occurred due to a globular collapse at higher degrees of branching, an effect that is common in dendrimers (silicone and otherwise). Overall, this data clearly demonstrated that branching influenced the silicone properties and further showed that the viscosity could be tailored by selecting a particular branch and/or controlling the branch frequency along a silicone backbone.

After the successful synthesis and characterization of the resulting property changes of the branched silicones structures, Chapter 3 explored the outcome of incorporating these oils into gels. The base for the silicone elastomers (and subsequent gels) was prepared through a hydrosilylation reaction between two commercially available (Siltech) elastomer components. The silicone oils were physically incorporated into the gels prior to the elastomer curing and the system was formulated such there were no remaining SiH functional sites on the polymer. This was achieved by use of a second capping step in their synthesis in which vinylpentamethyldisiloxane was reacted with residual SiH groups. The resulting branched, non-functional polymers could not graft into the silicone network.

Each gel was prepared with a single type of silicone oil and the incorporation was varied by weight. The gels were characterized using a Mach1 mechanical tester and the Young's modulus values were measured. The modulus measurements demonstrated a similar trend as the viscosity data. The values increased with degree of branching to a maximum, at which point the modulus decreased with further branching. This supports the theory that lower levels of branching results in oils which occupy more space, strengthening the gel, whereas larger degree of branching gives oils that undergo a globular collapse. The resulting polymers occupy less space, interact less with the network and therefore acts as a poorer reinforcing agents.

Branching also affect gel bleed. Pre-extracted elastomer coupons were placed on top of the gels and left for five days and then replaced with a new set of coupons that were removed after an additional five days. The amount of collected bleed was plotted, demonstrating a correlation between the weight percentage incorporated and overall amount of bleed. While the quantity of oil bleeding out decreased with time, the more important outcome was the magnitude of bleed of linear vs branched oils. When the branched oils were compared to linear unbranched silicone oils of a similar molecular weight, it is clear that higher degrees of branching decreased the amount of bleed in a given time period.

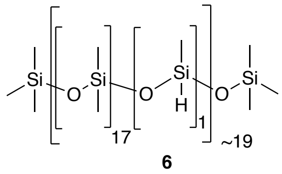
In conclusion, this thesis demonstrates a successful method to prepare branched silicone structures in a controlled manner and selectively incorporate them into gels. The original hypothesis was that branching would lead to profound changes in the properties of silicones oils, and this has been shown to be correct. The branched oils themselves exhibit very different, and tuneable, viscosity properties than linear oils. When placed in elastomers, the branched polymers change the Young's modulus values in a different way than linear oils. More importantly, the bleed of branched polymers is lower than that of linear oils. These observations provide a strategy to improve silicone gels; branched materials can be structurally optimized for a specific application using the strategies developed in this thesis.

Appendix 1: Supporting Information for Chapter 2

A1.1 Experimental

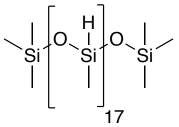
A1.1.1 Materials

n-Butyllithium (nominally 2.5 M) was purchased from Sigma Aldrich was shown by titration before use to have a concentration of 1.725 M. Chlorodimethylvinylsilane, triflic acid and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex solution (Karstedt's catalyst) in xylene (Pt ~2%) were purchased from Sigma Aldrich and used as received. Chromium (III) acetylacetonate was purchased from Sigma Aldrich and was used as received as a relaxation agent for ^{29}Si NMR experiments. Tris(pentafluorophenyl)borane ($B(C_6F_5)_3$, BCF catalyst) was purchased from Alpha Aesar and used as received. Allyltrimethoxysilane, bis(trimethylsilylsiloxy)methylsilane, pentamethyldisiloxane, octamethylcyclotetrasiloxane (D_4), 1,3,5,7-tetramethylcyclotetrasiloxane (D^H_4), hexamethylcyclotrisiloxane (D_3) and hexamethyldisiloxane, HMS-053 **6** (25,200 g/mol, 5.6% MeHSiO) and HMS-992 **10** (~2,000 g/mol, mole %: 100% MeHSiO) were purchased from Gelest and used as received (Figure S22). Commercial solvents including hexane, toluene and tetrahydrofuran were dried using an activated alumina column prior to use.



6

HMS-053



10

HMS-992

Figure S22: Functional polymers from Gelest. HMS-053 6 and HMS-992 10.

A1.1.2 Methods

^{1}H NMR, ^{13}C NMR and ^{29}Si NMR experiments (at 600, 150 and 119 MHz, respectively) were recorded at room temperature on a Bruker Avance 600MHz nuclear magnetic resonance spectrometer.

GPC data was collected on a Viscotek GPC Max (VE 2001 GPC Solvent/Sample Module) using a Viscotek VE 3580 RI Detector and a Viscotek 270 Dual Detector using a PolyAnalytik SupeRes

PAS-101 (8mmx30cm) column with a single pore, 6nm particle size, a plate count >18,000, and an exclusion limit of 1.5K. The column was packed with hard styrene-divinylbenzene gel. The samples were run in toluene.

FTIR data was collected on a Nicolet 6700 FTIR using Thermo Electron's OMNIC software.

Viscosity measurements were performed on two rheometers. A cone-and-plate Stresstech Rheometer by ATS RheoSystems was used for the majority of the measurements. The stress range was set between 0.1 and 150Pa for a logarithmic sample set, with a 1s delay time between 70 measurements. Select measurements were made on a TA Instruments Discovery HR-3 Hybrid Rheometer with a 40mm steel Peltier plate. The shear rate was set between 0.1 and 500 s^{-1} for a logarithmic sample set with 5 points per decade.

A1.1.3 n-BuMe$_2$SiD$_8$SiMe$_2$HC=CH$_2$[§] 1

D$_3$ (44.3892 g, 199.538 mmol) was weighed into a 1 L three-neck round-bottomed flask that was then flushed with nitrogen before capping and leaving under a slow nitrogen flow. Dry hexane (120 mL) was added with a syringe and the solution was left to stir for ~15 min, until all of the D$_3$ had dissolved. n-BuLi was added dropwise (18 mL of 1.73 M and 13 mL of 2.2 M in cyclohexanes, 59.7 mmol) over the course of ~30 min. The reaction was left to stir for 2 h at room temperature. Dry THF (16 mL) was added to the reaction, which was left stirring for 48 h. Chlorodimethylvinylsilane in excess (12 mL, 87.0 mmol) was added dropwise. The reaction was left stirring overnight. The reaction was transferred to a clean, one-neck 1 L round-bottomed flask and hexane, THF and excess chlorodimethylvinylsilane were removed under reduced pressure. The solution was then filtered through Celite packed with dry hexane and then excess hexane was removed from the filtrate under reduced pressure. Any impurities or excess cyclics were distilled off at 150 °C for 45 min and the final yield of **1** was 36.66 g (75% yield).

[§] Silicone nomenclature: M = OSiMe$_3$; D = OSiMe$_2$.

^{1}H NMR (CDCl$_3$, 600MHz): d 6.16-6.10 (dd, 1H, *J*=15.15 Hz, *J*=21.6 Hz), 5.95-5.92 (dd, 1H, *J* =4.3 Hz, *J*=15.15 Hz), 5.76-5.72 (dd, 1H, *J*=4.3 Hz, *J*=21.1 Hz), 1.35-1.28 (m, 4.5H), 0.90-0.87 (t, 3H, *J* = 7.0 Hz), 0.54-0.52 (t, 2H, *J* = 9.2 Hz), 0.16 (s, 6H), 0.07 (m, 65H) ppm.

A1.1.4 Allyltris(pentamethyldisilxoanyl)silane 2

Allyltrimethoxysilane (5.0328 g, 31.017 mmol) was added to a 250 mL round-bottomed flask. Dry hexanes (~10 mL) were added to the reaction and the flask was capped and flushed with nitrogen. BCF catalyst solution (110 mL, 0.0365 g/mL toluene, 7.84 x 10^{-3} mmol) was added before slowly adding in excess pentamethyldisiloxane (22.7582 g, 153.401 mmol). In between additions of pentamethyldisiloxane, four additional 10 mL amounts of BCF catalyst solution were added. After ~45 min the reaction was shown to be complete by ^{1}H NMR and ~1.5 g of neutral alumina was added to the flask to remove the BCF. The solution was left to stir for ~1 h before gravity filtering the product and rinsing with hexane. Hexanes were removed under reduced pressure, yielding 14.6443 g of **2** (85% yield).

^{1}H NMR (CDCl$_3$, 600 MHz): d 6.13 (dd, 1H, *J* = 14.8, 20.4 Hz), 5.93 (dd, 1H, *J* = 3.8, 14.8 Hz), 5.74 (dd, 1H, *J* = 3.8, 20.4 Hz), 1.57 (d, 2H, *J* = 7.9 Hz), 0.19-0.05 (m, 46H) ppm. ^{13}C NMR (CDCl$_3$, 150 MHz): d 133.86-133.73, 114.4, 22.32, 2.04, 1.31 ppm. ^{29}Si NMR (CDCl$_3$, 119 MHz, Cr(acac)$_3$): d 6.99, -20.91 to -21.72, -72.99 to -74.66 ppm. ES+ MS m/z for $[M + NH_4]^+$ = 576.4 (impurity at 632.4 and 824.4).

A1.1.5 Allyltris(bis(trimethysiloxyl)methylsilyl)silane 3

Allyltrimethoxysilane (5.0087 g, 30.868 mmol) was added to a 250 mL round-bottomed flask. Dry hexanes (~10 mL) were added to the reaction and the flask was capped and flushed with nitrogen. BCF catalyst solution (600 mL, 0.0400g/mL toluene, 4.68 x 10^{-2} mmol) was added before slowly adding excess bis(trimethylsiloxy)methylsilane (34.4652 g, 154.900 mmol). In between additions of bis(trimethylsiloxy)methylsilane, four additional 200 mL amounts of BCF catalyst solution were added. The reaction was left under nitrogen overnight. Neutral alumina (~1 g) was added to the flask. The solution was left to stir for ~1 h before gravity filtering the product and rinsing with hexane. Hexanes were removed under reduced pressure. Excess bis(trimethylsiloxy)methylsilane was removed by distillation at 120 °C for ~45 min yielding 19.4302 g of **3** (81% yield).

^{1}H NMR ($CDCl_3$, 600MHz): d 6.13 (dd, 1H, *J* = 14.8, 20.4 Hz), 5.93 (dd, 1H, *J* = 3.8, 14.8 Hz), 5.74 (dd, 1H, *J* = 3.8, 20.4 Hz), 1.57 (d, 2H, *J* = 7.9 Hz), 0.20-0.02 (m, 70H) ppm. ^{13}C NMR ($CDCl_3$, 150MHz): d 133.69, 114.51, 22.09, 1.96, -1.88 ppm. ^{29}Si NMR ($CDCl_3$, 119MHz, $Cr(acac)_3$): d 7.89, -66.28 ppm. ES+ MS m/z for $[M + NH_4]^+$ = 798.4 (impurity at 854.5).

A1.1.6 $Me_3SiO[(Me_2SiO)_n(MeHSiO)_m]_zSiMe_3$, n = 10, m = 1 z~2.5 MW = 2200 g/mol 4

D_4 (92.15 g, 310.669 mmol), $D^H{}_4$ (7.47 g, 31.047 mmol), and hexamethyldisiloxane (7.60 g, 46.817 mmol) were weighed into a 1 L round-bottomed flask and stirred for 10 min. Triflic acid (400 mL, 4.52 mmol) was added to the reaction. The reaction was left for 48 h at room temperature. Magnesium oxide (~4 g) was added to quench the acid and this was left to stir overnight. Dry hexane (~75 mL) was added and the reaction was left stirring for ~3 h. The reaction was filtered through Celite packed with hexane before removing hexanes from the filtrate under reduced pressure. This reaction was heated at 160 °C under high vacuum (1 mmHg) in three separate batches to remove excess cyclics and smaller polymers, yielding 91 g of product (85% yield).

^{1}H NMR ($CDCl_3$, 600MHz): d 4.69 (m, 1H), 0.17-0.08 (m, 70H). ^{13}C NMR ($CDCl_3$, 150MHz): d 2.00, 1.25 ppm. ^{29}Si NMR ($CDCl_3$, 119MHz, $Cr(acac)_3$): d 7.26, -21.64, -37.57 ppm. GPC Mn: 2270, Mw: 5000, PDI: 2.21.

Note that this reaction was duplicated at a later date to generate a similar polymer that was mostly used in these experiments. ^{1}H NMR ($CDCl_3$, 600MHz): d 4.68 (s, 1H), 0.17 to -0.01 (m, 70H). Mn (GPC) is ~2200 g/mol.

A1.1.7 $Me_3SiO[(Me_2SiO)_n(MeHSiO)_m]_zSiMe_3$, n = 10, m = 1 z~4.4 MW = 3700 g/mol 5

D_4 (92.2668 g, 311.061 mmol), $D^H{}_4$ (7.4142 g, 24.996 mmol), and hexamethyldisiloxane (2.9140 g, 17.9456 mmol) were weighed into a 1 L round-bottomed flask and stirred for 10 min. Triflic acid

(400 mL, 4.52 mmol) was added to the reaction. The reaction was left for 48 h at room temperature. Magnesium oxide (~4 g) was added to quench the acid and this was left to stir for ~2 h. Dry hexane (~75 mL) was added and the reaction was left stirring overnight. The reaction was filtered through Celite packed with hexane before removing the hexanes from the filtrate under reduced pressure. This reaction was heated at 180 °C under high vacuum (1 mmHg) in three separate batches to remove excess cyclics and smaller polymers, yielding 86.5818 g of product in the stillpot (84% yield).

^{1}H NMR ($CDCl_3$, 600MHz): d 4.68 (m, 1H), 0.24-0.01 (m, 70H). ^{13}C NMR ($CDCl_3$, 150MHz): d1.27, -0.84 ppm. ^{29}Si NMR ($CDCl_3$, 119MHz, $Cr(acac)_3$): d 7.69, -21.65, -36.49 ppm. MALDI m/z = 3753. GPC Mn: 3700, Mw: 7300, PDI: 1.95.

A1.1.8 $Me_3SiO(Me_2SiO)_n(MeHSiO)_m]_zSiMe_3$, n = 17, m = 1 z~ 20 MW = 25200 g/mol 6

^{1}H NMR ($CDCl_3$, 600MHz): d 4.69 (m, 1H), 0.17-0.08 (m, 101.7H) ppm. ^{29}Si NMR ($CDCl_3$, 119MHz, $Cr(acac)_3$): d 7.26, -21.64, -37.57 ppm. GPC Mn: 25188, Mw: 36538, PDI: 1.45.

A1.1.9 General Procedure for the Preparation of Branched Silicones 7-9 (shown for 8-2-5')

5 (3.8285 g, 5.76 mmol SiH) was weighed out into a 25 mL round-bottomed flask before capping and stirring under nitrogen for 5 min. The **2** branch (1.6043 g, 2.8751 mmol) was added to the flask using a syringe and needle and left stirring for 10 min prior to adding of Karstedt's catalyst (109 mL of 0.011 g/mL of toluene, 6.29 x10^{-5} mmol) through the septum. The reaction was left for overnight at room temperature (this reaction has been shown to finish to completion within 24 h); ^{1}H NMR confirmed that **2** had been consumed and therefore this reaction was shown to be complete. Activated carbon (~0.1 g) was added to the reaction to quench the catalyst and this was stirred for 3 h prior to adding ~10 mL of hexanes. The mixture was left overnight and filtered through Celite packed with hexanes. Hexanes were removed under reduced pressure to yield 1.5 g of **8-2-5'** (28 % yield).

^{1}H NMR (CDCl$_3$, 600MHz): d 4.68 (s, 0.85H), 1.47-1.41 (m, 2H), 0.59-0.56 (m, 4H), 0.19 to -0.3 (m, 170H) ppm. ^{13}C NMR (CDCl$_3$, 150MHz): d 22.60, 19.43, 17.32, 2.04, 1.24, -0.28 ppm. ^{29}Si NMR (CDCl$_3$, 119MHz, Cr(acac)$_3$): d 7.25-6.96, -20.56 to -22.91, -37.58, -69.22 ppm.

NOTE: The ^{1}H NMR given is for a polymer with a type **2** branch. The ^{1}H NMR data for polymers modified with branch type **1** vs **2** vs **3** were virtually identical, differing only in the integration of residual SiH and the large SiMe peaks near 0 ppm. We provide representative data for polymers bearing each of the branch types. A full listing of reaction formulations is provided in Table S4.

Type **1** branch polymer

^{1}H, ^{13}C and ^{29}Si NMR for **8-1-5** (polymer **5** to bearing 5.3% linear type **1** branches):

^{1}H NMR (CDCl$_3$, 600MHz): d 4.68 (m, 0.8H), 1.32-1.29 (m, 4H), 0.89-0.87 (t, 3H, *J*=6.65 Hz), 0.55-0.52 (t, 2H, 8.6 Hz), 0.46-0.40 (m, 4H), 0.18-0.07 (m, 191H) ppm. ^{13}C NMR (CDCl$_3$, 150MHz): d 26.64-25.67, 18.19, 14.02, 9.55, 8.95, 1.27-0.43, -0.37 ppm. ^{29}Si NMR (CDCl$_3$, 119MHz, Cr(acac)$_3$) d 8.29-7.26, -20.55 to -22.13, -37.57 ppm.

Type **3** branch polymer

^{1}H, ^{13}C and ^{29}Si NMR for **8-3-5** (polymer **5** to bearing 5.3% linear type **3** branches):

^{1}H NMR (CDCl$_3$, 600MHz): d 4.68 (m, 1H), 1.45-1.44 (m, 2H), 0.62-0.58 (m, 4H), 0.10-0.07 (m, 187H) ppm. ^{13}C NMR (CDCl$_3$, 150MHz): d 22.81, 19.43, 16.89, 2.32, 1.48, -1.69 ppm. ^{29}Si NMR (CDCl$_3$, 119MHz, Cr(acac)$_3$): d 7.60-7.12, -20.56 to -22.77, -37.58, -65.92 to -66.42 ppm.

Table S4: Recipes for Branched Silicone Polymers and Viscosity [a]

Backbone	Type of Branch	Back-bone (g)	mmol SiH	Branch (g)	Branch mmol	Branched Monomers %	Yield g (%)	NMR MW	GPC MW	Viscosity (Pa·s)[b]
4[c]	N/A									0.04
7-1-9	**1**	2.4001	3.6154	3.9612	4.8921	9.0	4.7 (88)	14490		0.05
7-1-5		3.3092	4.9849	2.0162	2.4901	5.1	4.6 (86)	3610		0.06
7-1-3		3.9056	5.8833	1.4371	1.7749	3.2	4.6 (86)	2550		0.04
7-1-2		4.3718	6.5856	0.8302	1.0253	1.6	4.4 (85)	2810		0.04
7-2-8	**2**	3.5523	5.3511	2.9850	5.3495	8.5	5.5 (84)	3140		0.08
7-2-8'		3.3594	5.0606	2.9082	5.2118	8.2	4.3 (59)	3490	5630	0.09
7-2-7		3.8069	5.7347	1.6240	2.9103	6.5	2.7 (50)	3300		0.10
7-2-6		3.9995	6.1154	1.6845	3.0188	5.6	2.1 (37)	2850		0.10
7-2-3		4.1740	6.2877	1.0800	1.9355	3.4	4.1 (78)	2670		0.05
7-2-3'		4.5025	6.885	1.1045	1.979	3.3	0.64 (64)	2490		0.06
7-2-2		4.5934	6.9194	0.6505	1.1658	1.9	4.0 (76)	2480		0.04
7-2-2'		5.0021	7.6	0.6224	1.1154	1.6	0.60 (60)	2140		0.05
7-3-8	**3**	3.1481	4.7423	4.1601	5.3335	8.4	5.4 (66)	5060		0.21
7-3-8'		2.9994	4.5183	3.5244	4.5185	8.2	2.86 (44)	3990		0.13
7-3-6		3.5400	5.3326	2.2086	2.8315	5.8	5.0 (87)	3340		0.15
7-3-3		3.8475	5.7958	1.3545	1.7365	3.3	4.5 (87)	2880		0.09
7-3-2		4.2348	6.3792	0.7451	0.9552	1.8	4.4 (88)	2570		0.05
5[c]	N/A									0.07
8-1-9	**1**	2.4001	3.6155	4.0273	4.9738	9.1	4.1 (53)	12620	10580	0.14
8-1-6		3.3119	4.9890	2.3776	2.9364	6.2	5.1 (90)	7290	5460	0.26
8-1-5		3.3183	4.9986	2.0183	2.4927	5.3	4.4 (82)	7060	11100	0.25
8-1-3		3.9086	5.8879	1.4217	1.7558	3.0	3.9 g (73)	5670	5250	0.20
8-1-2		4.3010	6.4790	0.7912	0.9772	1.6	4.0 (78)	5720	12170	0.15
8-2-9	**2**	3.3045	4.9779	3.0142	5.5408	9.1	3.1 (51)	7620	11020	0.64
8-2-6		3.8265	5.7642	1.5925	2.8539	5.9	1.5 (28)	5580	36600	0.80
8-2-5		15.2271	22.9669	6.3109	11.3099	5.3	16.48 (77)	5960	5350	0.23
8-2-5'		3.8285	5.76	1.6043	2.8751	4.9	(60)	5300		0.21
8-2-3		4.2707	6.4333	1.0224	1.8323	3.3	2.8 (53)	4760	5450	0.24
8-2-3'		4.2129	6.3413	1.0617	1.9027	3.0	0.73 (70)	4860		0.26
8-2-2		4.6210	6.9610	0.5821	1.0432	1.7	.4 (85)	5950	6700	0.22
8-2-2'		4.5918	6.9116	0.5808	1.0408	1.5	0.73 (70)	4590		0.12
8-3-9	**3**	3.0298	4.5641	4.1502	5.3208	8.7	4.0 (62)	8950	6470	0.70
8-3-9'		3.0018	4.5183	3.5262	4.5208	8.6	5.78 (88)	8470		0.36
8-3-8		3.0057	4.5242	4.0060	5.1359	8.1	6.25 (95)	9080		0.32
8-3-5		3.5092	5.2862	2.0601	2.6411	5.3	3.2 (57)	5930	7640	2.23
8-3-3		3.8722	5.833	1.3623	1.7465	3.2	4.5 (86)	5290	4660	0.22
8-3-2		4.2626	6.4211	0.7491	9.6038	1.6	4.4 (88)	5710	4240	0.27

6[c]	N/A							25200	0.40
9-1-5	1	4.9953	3.7900	1.9781	2.4430	4.6	4.99 (72)	49210	0.65[d]
9-1-3		5.0031	3.7960	1.1242	1.3884	2.6	5.14 (84)	42360	0.52[d]
9-1-1		4.5750	3.4712	0.4991	0.6164	0.8	1.51 (75)	32070	0.33[d]
9-2-6	**2**	4.9891	3.7854	2.2520	4.0358	5.5	3.96 (50)	32680	1.38[d]
9-2-5		5.0781	3.8529	1.7794	3.1889	4.6	4.87 (71)	30940	4.78[d]
9-2-4		5.0772	3.8522	1.3645	2.4453	3.5	4.99 (77)	29280	1.85[d]
9-2-3		5.0648	3.8428	0.7669	1.3744	2.6	3.87 (66)	38550	0.71[d]
9-2-1		5.0099	3.8011	0.3809	0.6826	1.1	4.96 (92)	30340	0.60[d]
6[cd]	N/A								0.74[d]
9-2-5”	**2**	4.9891	3.7854	2.2520	4.0358	5.5	3.96 (50)	32680	2.07
9-2-3”		5.0288	3.8155	1.4210	2.5466	3.4	0.54 (54)	27700	2.53
9-2-3’”		4.5337	3.4398	0.9888	1.7720	2.6	4.32 (80)	26220	3.14
9-2-2”		5.0244	3.8121	0.7760	1.3907	1.9	0.64 (64)	25860	0.98
9-2-1”		5.0252	3.8127	0.4132	0.7405	1.1	0.81 (81)	26840	1.08
9-3-5	**3**	4.9226	3.7349	3.2247	4.1342	5.2	5.99 (74)	38770	0.80[d]
9-3-5’		4.9958	3.7904	2.9967	3.8419	4.8	6.63 (83)	35880	0.91[d]
9-3-3		5.0047,	3.7972	1.9478	2.4972	3.2	4.130 (59)	30970	0.88[d]
9-3-2		5.0537	3.8344	1.0668	1.3677	1.9	4.64 (76)	26210	0.66[d]
9-3-1		5.0145	3.8046	0.5234	0.6710	0.9	3.83 (69)	28110	0.49[d]
PHMS									
10-1	**1**	0.0970	1.6167	1.3645	1.6581	60.0			N/A
10-2	**2**	0.0962	1.6033	0.9292	1.6652	61.0			N/A
10-3	**3**	0.0965	1.6083	1.3679	1.7537	60.0			N/A

[a] The concentration of Karstedt’s catalyst was set to ~20 ppm, relative to the available SiH content. Depending on the specific reaction different concentrations of Karstedt’s catalyst in toluene were used (e.g., 0.0171, 0.0058, 0.0123 g/mL in toluene.

[b] Except for polymers noted by footnote d, viscosity measurements were performed using a cone-and-plate Stresstech Rheometer by ATS RheoSystems.

[c] The Mn of the backbone silicone polymers was **7** 2200 g/mol; **8** 3700 g/mol, and **9** 25200 g/mol

[d] Viscosity of theses samples we obtained using a TA Instruments Discovery HR-3 Hybrid Rheometer.

A1.1.10 General Procedure for Control Reactions – Branching an HPDMS Backbone

The following NMR survey experiments were carried out to simply follow the conversion of SiH to SiC with compound **10**. Conversion was shown in ^{1}H NMR spectra by analyzing the SiH resonances (1H, 4.68 ppm) relative to the Si-CH_2CH_2-Si bond formation (4H, ~0.6 ppm). Conversions of ~60% were observed from the crude ^{1}H NMR spectra; note, the NMR spectra contained residual vinyl groups from unreacted starting branch materials, presumably for steric reasons. These signals are not included in the listings below.

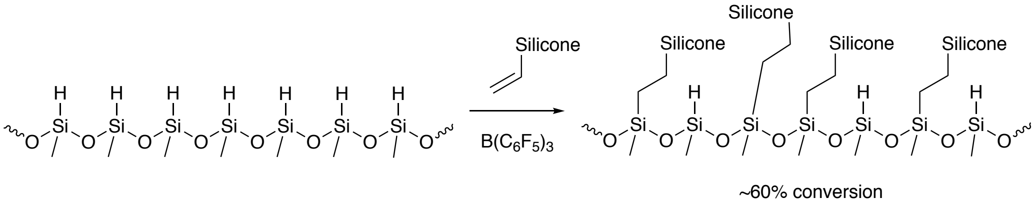


Figure S23: Branching of poly(hydromethylsiloxane) 10.

A1.1.10.1 Addition of 1 to 10 HMS-992

HMS-992 (0.0970 g, 1.6167 mmol of SiH); **1** (1.3645 g, 1.6851 mmol); Karstedt's catalyst (26 mL of 0.0110 g/mL of toluene, 1.50 x10^{-5} mmol). The reaction was left stirring overnight until completion.

^{1}H NMR ($CDCl_3$, 600MHz): d 4.71 (s, 0.68H), 1.33-1.29 (m, 4H), 0.89-0.87 (m, 3H), 0.56-0.52 (m, 2H), 0.46 (bs, 4H), 0.15-0.05 (m, 29`0H) ppm.

A1.1.10.2 Addition of 2 to 10 HMS-992

10 (0.0962 g, 1.6033 mmol of SiH) was added to a round-bottomed flask and capped. Compound **2** (0.9292 g, 1.6652 mmol, excess) was added by syringe through a septum. The mixture was left to stir under nitrogen for 5 min before adding Karstedt's catalyst (26 mL of 0.0110 g/mL of toluene, 1.50 x10^{-5} mmol). The reaction was left stirring for 2 d and no further changes were observed using ^{1}H NMR. Activated carbon (~0.1 g) was added to quench the catalyst. This was stirred for several hours before adding ~2 mL of dry hexanes. The mixture was left overnight prior to filtering through Celite packed with dry hexane. Hexanes were removed under reduced pressure.

^{1}H NMR (CDCl$_3$, 600MHz): d 4.68 (s, 0.64H), 1.53-1.41 (m, 2H), 0.62-0.51 (m, 4H), 0.21 to -0.1 (m, 80H) ppm.

A1.1.10.3 Addition of 3 to 10 HMS-992

10 (0.0965 g, 1.6083 mmol of SiH); **3** branch (1.3679 g, 1.7537 mmol); Karstedt's catalyst (26 mL of 0.0110 g/mL of toluene, 1.50 x10^{-5} mmol). The reaction was left stirring overnight until completion.

^{1}H NMR (CDCl$_3$, 600MHz): d 4.68 (s, 0.74H), 1.46-1.42 (m, 2H), 0.61-0.54 (m, 4H), 0.19 to -0.1 (m, 125H) ppm.

Appendix 2: Supporting Information for Chapter 3

In the main document, the effect of oil loading and branching of oils was explored in regards to the effects on Young's modulus. In Figure S1 below, the weight percentage of oil incorporated into the gels was compared to the Young's modulus values, excluding the elastomer at 5.0 MPa to better demonstrate the changes occurring in the branched oils.

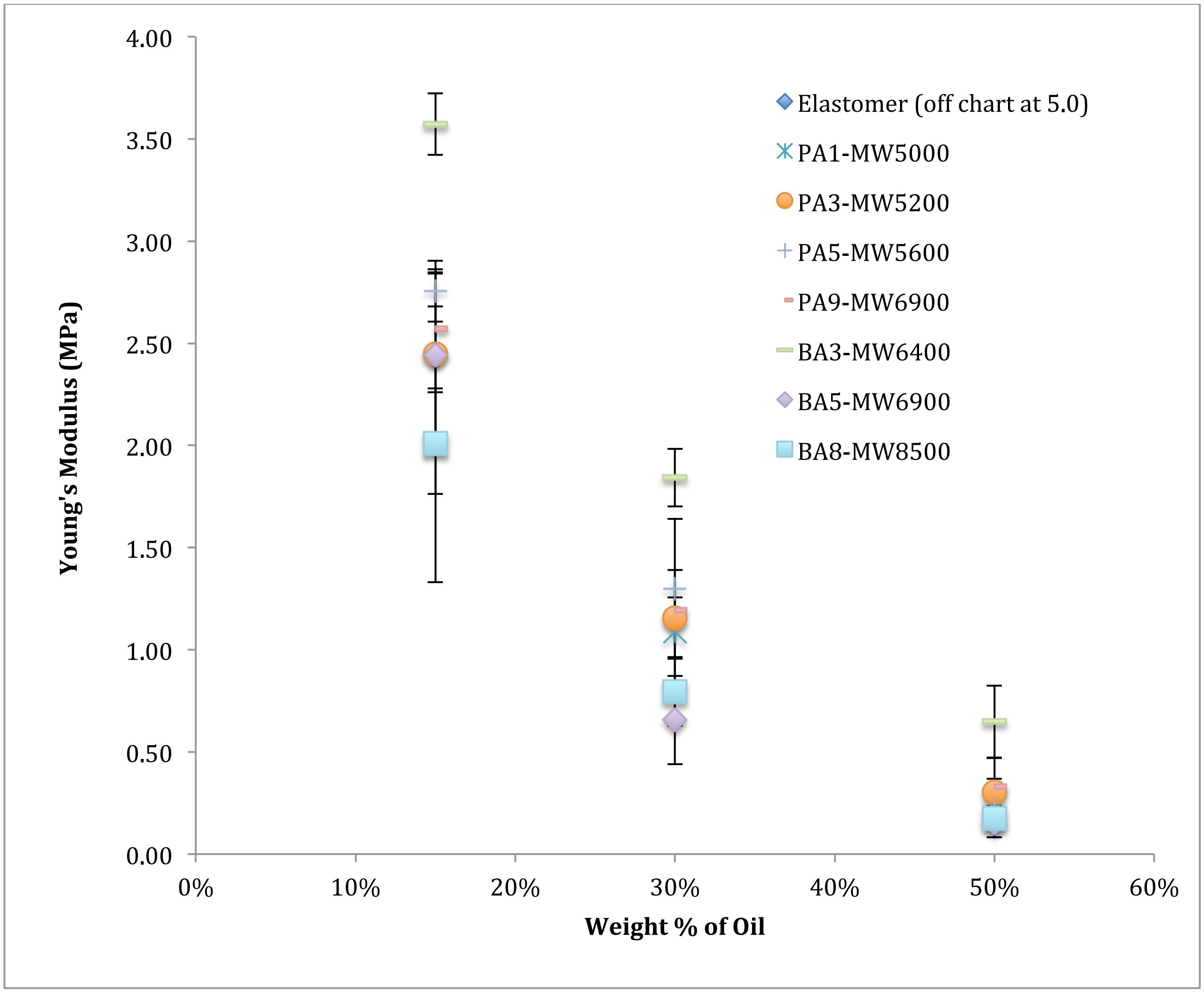


Figure S24: Expanded version of Figure 3.17 (main document), to better show the differences between branched oils.

While the loading content of oil demonstrates a set of trends, the data can alternatively be compared by exploring the effects of branching in relation to Young's modulus. This can be seen below in Figure S25.

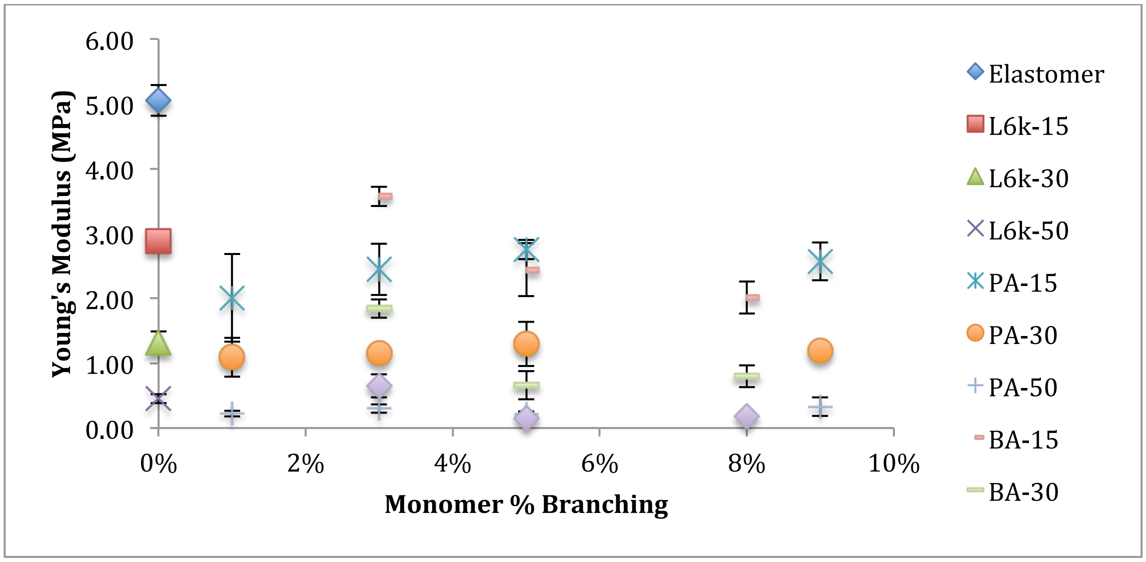


Figure S25: Effects of monomer branching on Young's modulus of gels with PA and BA loaded into the gels at various concentrations.

In the main document, the amount of bleed observed from the gels is depicted quantitatively and excludes any raw data consisting of negative values; as discussed in the main document, this was observed due to cohesive failure between the gel and the elastomer used to collect bleed. A more inclusive plot including the raw data can be found below in Figure S26.

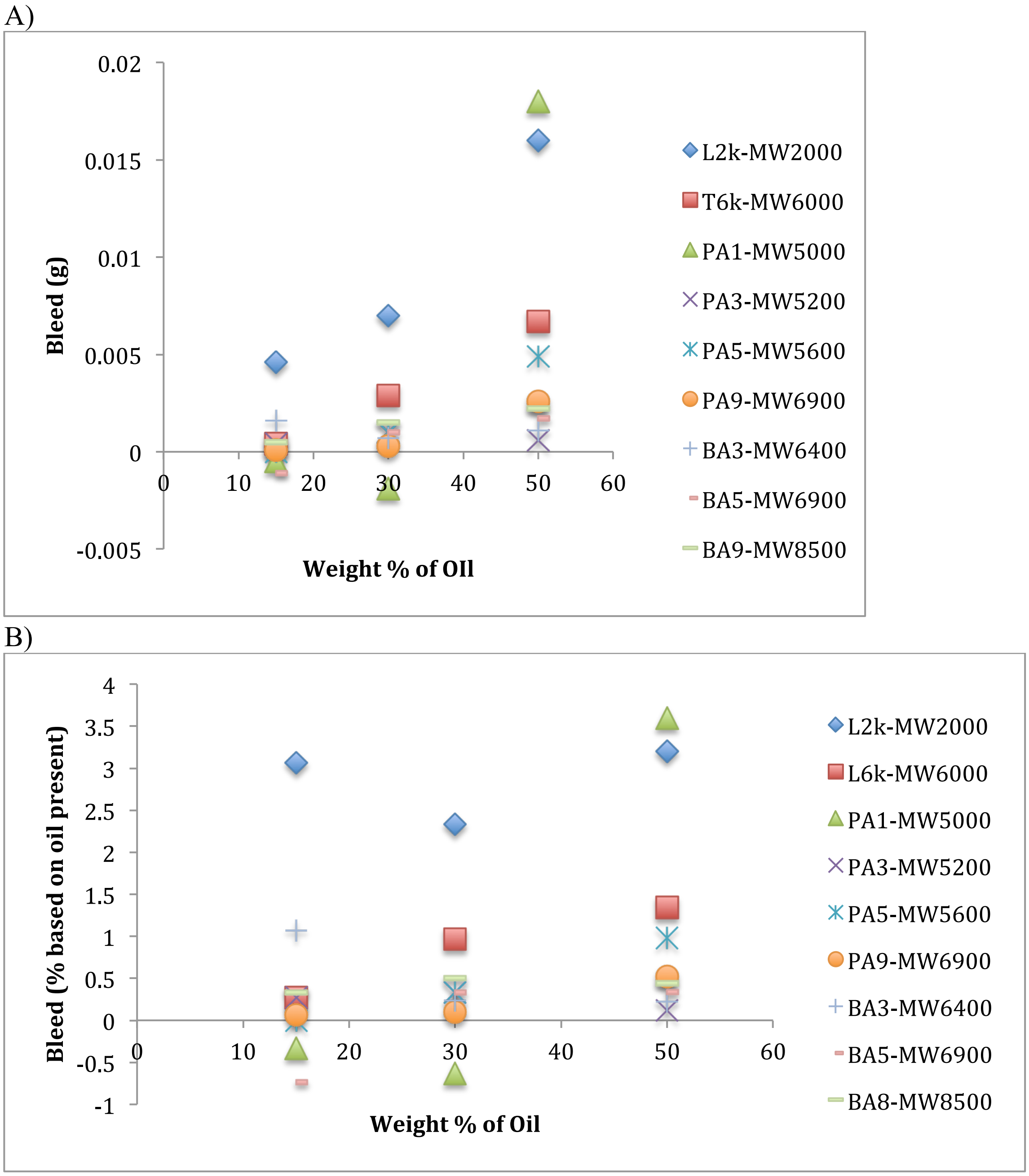
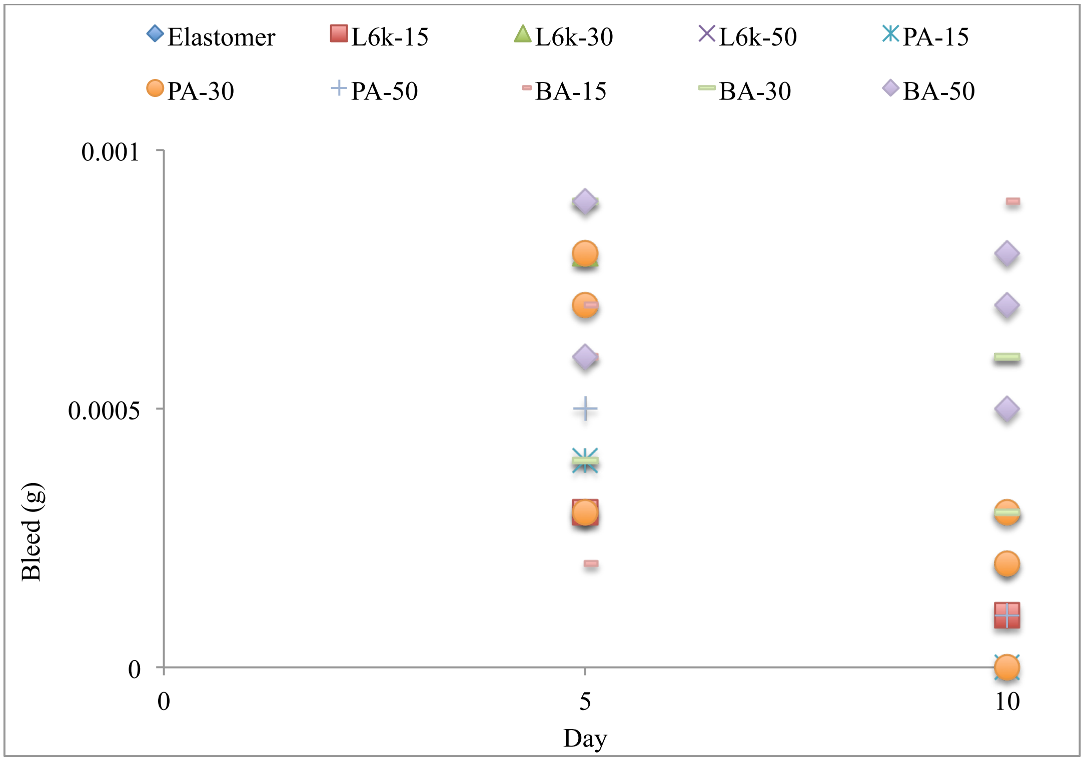


Figure S26: Effect of branch type and frequency on the amount of bleed from the gels for A) the total amount of bleed collected over 10 days and B) normalized bleed amount of oil released as a % of the available oil present in the gel (only L2k is different).

In addition to comparing the total bleed collected over ten days, the gels can also be compared on day 5 and day 10; more oil was collected in the first measurement on day 5. Figure S27A demonstrates the amount of bleed collected independently on day 5 and day 10 whereas Figure S27B compares the total bleed over ten days to the initial collection on day 5.

A)



B)

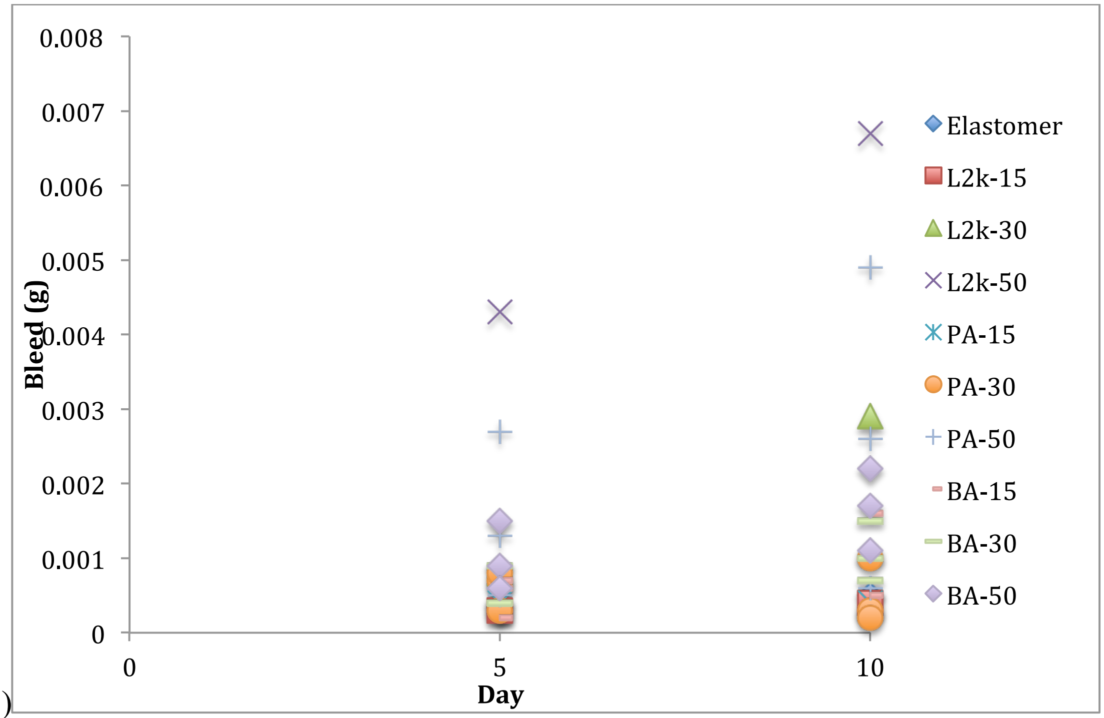


Figure S27:A) Bleed observed over ten days, where day ten represents the total amount of bleed collected and B) bleed observed over ten days, expanded to better show the differences between PA3 samples and the correlation between loading volume.

The gels were synthesized in two 96-well plates by incorporating the elastomer mixture (combination of Siltech CR13-46A and Siltech CR13-46B) with a specific silicone oil (branched and linear oils), by weight %. The exact quantities are laid out below in Table S5 and Table S6.

Table S5: Reagents used to make up the elastomers and gels in Plate A[a]

Row Column	A	B	C	D	E	F	G	H
1		0.1442 Elastomer	0.1562 **L6k-15** (0.0263g)	0.1607 **L28k-30** (0.0634)	0.1438 **PA3-50** (0.1470)	0.1548 **PA5-15** (0.0255)	0.1512 **PA1-30** (0.0638)	0.1513 **BA5-30** (0.0854)
2		0.1706 Elastomer	0.1668 **L6k-15** (0.0294)	0.1617 **L28k-30** (0.0698)	0.1500 **PA3-50** (0.1480)	0.1563 **PA5-15** (0.0283)	0.1557 **PA1-30** (0.0701)	0.1479 **BA5-50** (0.1530)
3		0.1538 Elastomer	0.1673 **L6k-15** (0.0261)	0.1545 **L28k-30** (0.0610)	0.1632 **PA3-50** (0.1560)	0.1504 **PA5-15** (0.0275)	0.1583 **BA5-50** (0.0636)	0.1632 **BA5-50** (0.1438)
4		0.1579 **L2k-15** (0.0264)	0.1568 **L6k-30** (0.0618)	0.1538 **L28k-50** (0.1520)	0.1476 **PA9-15** (0.0293)	0.1598 **PA5-30** (0.0635)	0.1673 **PA1-50** (0.1551)	0.1531 **BA5-50** (0.1561)
5		0.1561 **L2k-15** (0.0290)	0.1638 **L6k-30** (0.0695)	0.1596 **L28k-50** (0.1639)	0.1896 **PA9-15** (0.0394)	0.1603 **PA5-30** (0.0635)	0.1665 **PA1-50** (0.1621)	
6		0.1599 **L2k-15** (0.0301)	0.1503 **L6k-30** (0.0675)	0.1678 **L28k-50** (0.1603)	0.1564 **PA9-15** (0.0240)	0.1643 **PA5-30** (0.0635)	0.1641 **PA1-50** (0.1616)	
7		0.1638 **L2k-30** (0.0664)	0.1738 **L6k-50** (0.1517)	0.1679 **PA3-15** (0.0278)	0.1622 **PA9-30** (0.0636)	0.1898 **PA5-50** (0.1582)	0.1513 **BA5-15** (0.0268)	
8		0.1504 **L2k-30** (0.0634)	0.1864 **L6k-50** (0.1519)	0.1548 **PA3-15** (0.0272)	0.1531 **PA9-30** (0.0629)	0.1785 **PA5-50** (0.1475)	0.1693 **BA5-15** (0.0213)	
9		0.1511 **L2k-30** (0.0631)	0.1684 **L6k-50** (0.1531)	0.1791 **PA3-15** (0.0235)	0.1598 **PA9-30** (0.0601)	0.1512 **PA5-50** (0.1601)	0.1601 **BA5-15** (0.0513)	
10		0.1689 **L2k-50** (0.1512)	0.1491 **L28k-15** (0.0261)	0.1489 **PA3-30** (0.0751)	0.1630 **PA9-50** (0.1441)	0.1553 **PA1-15** (0.0251)	0.1577 **BA5-30** (0.0631)	
11		0.1600 **L2k-50** (0.1669)	0.1621 **L28k-15** (0.0234)	0.1503 **PA3-30** (0.0613)	0.1801 **PA9-50** (0.1515)	0.1672 **PA1-15** (0.0226)	0.1519 **BA5-30** (0.0701)	
12		0.1504 **L2k-50** (0.1669)	0.1623 **L28k-15** (0.0251)	0.1504 **PA3-30** (0.0632)	0.1563 **PA9-50** (0.1561)	0.1600 **PA1-15** (0.0227)	0.1608 **BA5-30** (0.0637)	

[a] First number = quantity of the pre-elastomer mixture added to the well in g; **bold L%**, **PA%** or **BA%**, respectively = the approximate weight percentage of oil incorporated (g of oil added to the well). Wells in A and H5-12 were not filled.

Table S6: Reagents used to make up the elastomers and gels in Plate B.[a]

Row Column	A	B
1		
2		
3		
4	0.1631 **BA3-15** (0.0335)	0.1549 **BA8-15** (0.0279)
5	0.1538 **BA3-15** (0.0209)	0.1573 **BA8-15** (0.0318)
6	0.1731 **BA3-15** (0.0307)	0.1602 **BA8-15** (0.0341)
7	0.1648 **BA3-30** (0.0634)	0.1526 **BA8-30** (0.0701)
8	0.1551 **BA3-30** (0.0635)	0.1510 **BA8-30** (0.0690)
9	0.1501 **BA3-30** (0.0633)	0.1531 **BA8-30** (0.0758)
10	0.1563 **BA3-50** (0.1683)	0.1618 **BA8-50** (0.1587)
11	0.1678 **BA3-50** (0.1453)	0.1830 **BA8-50** (0.1548)
12	0.1531 **BA3-50** (0.1589)	0.1560 **BA8-50** (0.1774)

[a] First number = quantity of the pre-elastomer mixture added to the well in g; **PA** or **BA**, respectively = the approximate weight percentage of oil incorporated (g of oil added to the well). Wells in A1-A3, B1-B3 and C-H were not filled.

The tables above show that each sample was prepared thrice; the Young's modulus was measured three times for each sample, and the combined average of these nine measurements can be found in Table S7 and Table S8 below.

Table S7: Average Young’s Modulus measurements and the standard deviation for Plate A.

Contents	Monomer % Branching	% by weight oil	Average Young's Modulus (MPa)	Standard Deviation
Elastomer	0	0	5.05	0.24
L2k-15	0	15	2.77	0.26
L2k-30	0	30	1.78	0.10
L2k-50	0	50	0.59	0.05
L6k-15	0	15	2.88	0.13
L6k-30	0	30	1.32	0.17
L6k-50	0	50	0.45	0.07
L28k-15	0	15	2.01	0.57
L28k-30	0	30	1.28	0.13
L28k-50	0	50	0.27	0.03
PA3-15	3	15	2.45	0.39
PA3-30	3	30	1.15	0.03
PA3-50	3	50	0.30	0.07
PA9-15	9	15	2.57	0.29
PA9-30	9	30	1.19	0.06
PA9-50	9	50	0.33	0.14
PA5-15	5	15	2.75	0.15
PA5-30	5	30	1.30	0.34
PA5-50	5	50	0.22	0.04
PA1-15	1	15	2.01	0.68
PA1-30	1	30	1.09	0.30
PA1-50	1	50	0.22	0.04
BA5-15	5	15	2.44	0.41
BA5-30	5	30	0.66	0.22
BA5-50	5	50	0.15	0.07

Table S8: Average Young’s Modulus measurements and the standard deviation for Plate B.

Contents	Monomer % Branching	% by weight oil	Average Young's Modulus (MPa)	Standard Deviation
Elastomer	0	0	5.53	0.21
BA3	3	15	3.57	0.15
BA3	3	30	1.84	0.14
BA3	3	50	0.65	0.18
BA8	8	15	2.01	0.25
BA8	8	30	0.80	0.17
BA8	8	50	0.18	0.02

In order to collect bleed, five elastomers were prepared, extracted, and punched into coupons. The preparation for the first elastomer is described in detail in the main document. In Table S9, additional measurements to synthesize the remaining three elastomers are recorded. Bleed measurements were not recorded for all of the synthesized gels but the raw data for those measured can be found in Table S10 and Table S11.

Table S9: Additional elastomer batch preparation

Batch #	DMS-V31 g (mmol of $SiCHCH_2$)	HMS-301 g (mmol of $SiH(CH_3)O$)
2	22.0715 (1.58)	0.4107 (1.68)
3	22.4580 (1.60)	0.3859 (1.58)
4	22.0853 (1.58)	0.3840 (1.58)

Table S10: Raw data for bleed measurements for Plate A.

Well #	Contents	% By Weight Oil	Bleed - Day 5 (g)	Bleed - Day 10 (g)	Total Bleed (g)
B3	Elastomer	0	0.0003	0.0002	0.0005
B4	**L2k-15**	15	0.0045	0.0001	0.0046
B9	**L2k-30**	30	0.0052	0.0018	0.007
B12	**L2k-50**	50	0.0139	0.0021	0.016
C1	**L6k-15**	15	0.0003	0.0001	0.0004
C5	**L6k-30**	30	0.0008	0.0021	0.0029
C9	**L6k-50**	50	0.0043	0.0024	0.0067
D9	**PA3-15**	15	0.0004	0	0.0004
D12	**PA3-30**	30	0.0007	0.0003	0.001
E1	**PA3-50**	50	0.0005	0.0001	0.0006
E4	**PA9-15**	15	0.0006	-0.0005	1E-04
E7	**PA9-30**	30	0.0003	0	0.0003
E12	**PA9-50**	50	0.0013	0.0013	0.0026
F1	**PA5-15**	15	-0.0011	0.0005	-0.0006
F4	**PA5-30**	30	0.0008	0.0002	0.001
F9	**PA5-50**	50	0.0027	0.0022	0.0049
F11	**PA1-15**	15	-0.001	0.0005	-0.0005
G1	**PA1-30**	30	0.0005	-0.0024	-0.0019
G5	**PA1-50**	50	0.0121	0.0059	0.018
G9	**BA5-15**	15	0.0006	-0.0017	-0.0011
G10	**BA5-30**	30	0.0004	0.0006	0.001
H2	**BA5-50**	50	0.0009	0.0008	0.0017

[a] NOTE: Although reported here, we consider the data from PA1% to be unreliable. The elastomer did not disengage cleanly from the gel leading to false "negative" bleed data. In addition, the data for L2k-15% seems unreasonably high, and constitutes an outlier. We therefore relied on the other experiments when undertaking our analysis.

Table S11: Raw data for bleed measurements for Plate B.

Well #	Contents	% By Weight Oil	Bleed - Day 5 (g)	Bleed - Day 10 (g)	Total Bleed (g)
B2	Elastomer	NA	0.0002	0	0.0002
A4	**BA3-15**	15	0.0007	0.0009	0.0016
A9	**BA3-30**	30	0.0004	0.0003	0.0007
A11	**BA3-50**	50	0.0006	0.0005	0.0011
B6	**BA8-15**	15	0.0002	0.0003	0.0005
B7	**BA8-30**	30	0.0009	0.0006	0.0015
B10	**BA8-50**	50	0.0015	0.0007	0.0022