Exploring Sustainable Silicone Crosslinking Motifs

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Abstract

Silicone elastomers are highly versatile and used in everyday life for their thermal and chemical stability, oxygen permeability, hydrophobicity, and relative biocompatibility. Many of these properties are a result of the stable siloxane (Si-O) backbone that can possess different functionalities (e.g., hydrosilanes, aminopropylsilicones, vinylsilicones, etc.). However, along with the obvious advantages and convenience these materials provide, there are concerns regarding their sustainability in the environment. Some of their sustainability issues involve their synthetic process which requires high temperatures for their formation (2000 °C), and their resistance to degradation in the environment due to the nature of their covalent crosslinks which is not as well understood as the degradation of linear silicone oils. Additionally, traditional crosslinking methods (i.e., hydrosilylation, RTV) use expensive, endangered, or poisonous metal catalysts like platinum and tin that are consumed and entrapped within the cured silicone rubbers. Despite these drawbacks, it is difficult to find materials that possess the same advantages that silicones provide, so it is therefore important to research methods that can improve their sustainability. These issues can be mitigated by exploring alternate crosslinking motifs that bypass the consumption of metal catalysts.

Nature is a great source of chemical inspiration; it has had eons of evolutionary advantage to shape its biosynthetic processes. Oxidative phenolic coupling is a process that occurs readily; trees employ this process in the production of lignin. The idea is to incorporate this biomimetic process into silicone materials to create covalent crosslinks through the radical coupling of phenols. Eugenol – a naturally occurring phenolic compound found abundantly

in clove oil – was used to functionalize telechelic and pendent silicone copolymers. While nature uses enzymes, this process mimicked the coupling by employing di-t-butyl peroxide as a radical initiator to initiate the phenolic coupling of eugenol moieties. Through this process, dark brown elastomers of varying hardnesses and crosslink densities were created using the pendent eugenol-modified silicones. These physical properties were able to be easily manipulated by adjusting the loading of the radical initiator used. Additionally, eugenol possesses radical scavenging properties which allow for the formation of silicone oils with antioxidant activity. These properties were expected to wane with the consumption of the eugenol groups for crosslinking. Still, interestingly, the elastomers retained antioxidant activity although to a lower degree than the eugenol-modified silicone oils.

The incorporation of eugenol introduced new properties (antioxidant activity) to silicone elastomers and provided an alternate route to create robust, covalent crosslinks. There was interest in creating silicone materials using dynamic crosslinks to allow for the potential of easier end-of-life or reprocessing. Boronic esters are a class of dynamic covalent bonds that are formed between a boronic acid and a 1,2- or 1,3- diol – they a specifically known to bind to different types of sugars. These exist in an equilibrium that is affected by the presence of water and the structural orientation of the diol they are bound to. Boronic acid-modified silicones and glucose-modified aminosilicones were both able to be synthesized in relatively mild conditions at room temperature. These two silicones were later combined to create libraries of translucent, colourless elastomers that possessed a range of viscoelastic properties. These properties were affected by the ratio of glucose to boronic acid residues as well as the nature of the boronic ester linkages (i.e., chain extension vs. crosslinking). Their viscoelasticity could be further modified by introducing a dative B-N bond, which increased the stability of the boronic ester bond and improved the robustness of the materials.

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M.A.B. developed the hypothesis that drove the project. K.S., A.P. and E.D-B. did the preparation and characterization of silicone materials. K.S. and E.D-B. wrote the first draft of the manuscript. M.A.B. edited and contributed to the final draft, supervised the with and obtained funding. A.L. was responsible for the collection of Young’s Modulus data.

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1 Introduction

1.1 Silicone material overview

1.1.1 Properties

Silicones (polydimethylsiloxanes) are polymers that are made primarily of strong siloxane (Si-O) bonds which are responsible for their unique properties. Silicone materials are industrially popular for their resistance to thermal and chemical degradation when compared to their carbon analogues,[1] and are therefore used in a wide range of applications. Medical devices are often made from silicones because they are also permeable to oxygen, flexible, and relatively biocompatible.[2–5] Silicones are also hydrophobic and can act as insulators. Their resistance to degradation by light leads to the use of silicones as encapsulating coatings for LEDs (light emitting diodes).[6–8] Despite their popularity and wide range of applications, there have been concerns regarding the sustainability of silicone materials both during manufacture and end of life. Their synthesis involves an energy-intensive synthetic process and, for elastomers at least, the rates of their degradability in nature are unknown. Given that elastomers are highly crosslinked, the rate is likely to be low. Traditional crosslinking methods, although convenient, also contribute to their lack of sustainability because of the metal catalysts used. To better understand the sustainability issues of these materials, their synthetic process and degradation must first be explained.

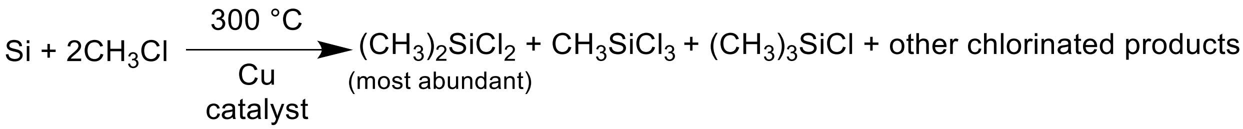
1.1.2 Synthesis of silicone

The synthesis of silicone polymers begins by performing a thermally induced carbon-based reduction of raw materials containing SiO_2 (sand or quartz) to produce elemental silicon. This is an energy-intensive process which typically requires temperatures above 1800 °C (Figure 1-1).[9,10]

$$SiO_2 + C \xrightarrow{2000\ ^\circ C} Si + CO_2$$

Figure 1-1 - Conversion of silicon dioxide to elemental silicon.

The resulting silicon undergoes the Rochow or Direct Process with methyl chloride at temperatures around 300 °C with copper catalysts to form various chlorosilane building blocks (Figure 1-2);[9] dimethyldichlorosilane is the most abundant monomer. Hydrolysis and condensation of the units produce short linear siloxane chains and, concomitantly, small cyclic structures in which D_4 dominates (D = Me_2SiO, therefore D_4 = octamethylcyclotetrasiloxane = $(Me_2SiO)_4$); D_5 is formed in lower quantities.[1] The by-product of the hydrolysis, HCl, is used to make MeCl from methanol for the Direct Process, closing the chloride loop.



$$Si + 2CH_3Cl \xrightarrow[\text{Cu catalyst}]{300\ ^\circ C} \underset{\text{(most abundant)}}{(CH_3)_2SiCl_2} + CH_3SiCl_3 + (CH_3)_3SiCl + \text{other chlorinated products}$$

Figure 1-2 - Direct process to chlorosilanes from elemental silicon.

Acid/base catalyzed ring-opening polymerization (ROP) of D_4/ D_5 can also be employed to yield high molecular weight siloxane polymers with desired functionalities based on the monomer units (Figure 1-3). An equilibrium exists between linear siloxane units and their cyclic structures that is affected largely by entropic contributions, its value is near 1. The molecular weight is affected by the ring-chain equilibrium and to control this, many factors need to be considered including the dilution of silicone in the reaction mixture (which lowers molar mass), the types of catalysts employed, and the ratio of backbone monomers vs end groups (e.g., hexamethyldisiloxane $Me_3SiOSiMe_3$). End groups and cyclic silicone oligomers that contain functional groups can be added to the reaction to introduce functionality (Figure 1-3a,b). This process is flexible and functionality can also be introduced through addition reactions (i.e. hydrosilylation) (Figure 1-3c).

Through this process, two classes of silicone polymers are easily produced; telechelic silicones have functional groups on either end of the backbone while pendent silicones have functional groups built into the backbone of the polymer (Figure 1-3a vs b).

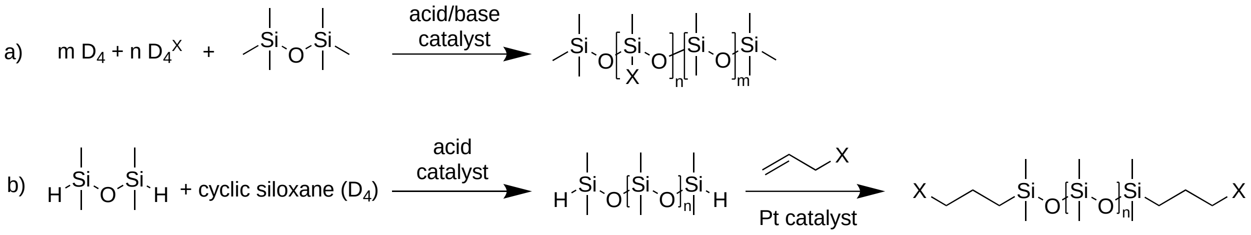


Figure 1-3 - Silicone functionalization to make a) telechelic polymers through hydrosilylation and b) pendent SiH polymers through acid-catalyzed ROP of functional cyclic oligomers. Other functional silicones can be processed using base catalysis.

As shown in Figure 1-3c, it is straightforward to introduce organofunctional groups onto silicone polymers using hydrosilylation. This is a relatively facile way to create functional polymers that can be used in a variety of applications. For instance, amine-functionalized silicones have the potential to participate in Schiff-base chemistry with aromatic carbonyls like vanillin to form imine linkages and this process has been used to create thermoplastic elastomers.[11]

1.1.3 Degradation and sustainability

Contrary to common misconceptions based on thermoplastics in the environment, linear PDMS fluids can degrade in environmental soil through hydrolysis to reform small cyclic siloxanes and small siloxane units like dimethylsilanediol.[12] This biodegradation is catalyzed by constituents of the soil, including clay minerals.[13,14] The rate of depolymerization, however, depends on several factors including the pH, level of moisture, and level of oxygen in the soil and can range from weeks to months. Degradation in soil can result in dimethylsilanediol (DMSD), an initial product of degradation that can undergo oxidation to eventually form silica and CO_2; this degradation is often mediated by hydroxy radicals (Figure 1-4). While acids and bases are used to facilitate the polymerization of silicones (as noted above, the process is an equilibrium), they can also catalyze the conversion of silicone oils back to small cyclic oligomeric structures that are volatile and evaporate into the air where they can undergo oxidative degradation.

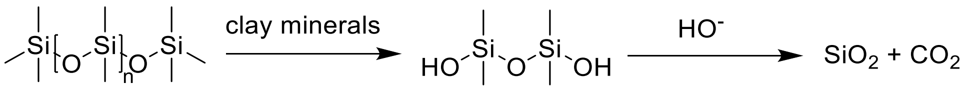


Figure 1-4 - Depolymerization of linear silicones to DMSD then silica and carbon dioxide through oxidizing agents.

Despite the reasonable degradation rate of linear silicone oils, there are concerns regarding the degradability of crosslinked thermoset silicone materials; processes to degrade elastomers are less well understood. Silicone rubber is designed to be thermally and chemically stable, which brings their end-of-life sustainability into question. There is currently no known timeline for the degradation of thermoset silicone elastomers. To begin improving the sustainability of silicone materials, it is important to first understand the types of curing processes used and how they affect the properties of the material.

1.2 Silicone curing processes

Crosslinking of linear silicone oils is required to produce industrially relevant thermoset silicone elastomers. The most common curing methods used industrially include hydrosilylation, room-temperature vulcanization, and radical cure. These processes yield robust silicone materials that can be used in various applications, but each process has its own drawback.

1.2.1 Room-temperature vulcanization (RTV)

Silicon is electron deficient and susceptible to nucleophilic attack – particularly by oxygen nucleophiles to form stable Si-O bonds.[15] RTV (room temperature vulcanization) exploits this bonding interaction to form siloxane crosslinks between silicone chains typically using tri- or tetrafunctional silanes as crosslinkers. The condensation reaction occurs between the hydroxy groups on a polymer and the silicon of the crosslinker. Like its name, this reaction occurs at room temperature, requires the presence of water (to activate the catalyst)[16] and usually requires an acid, base, or tin catalyst (Figure 1-5)

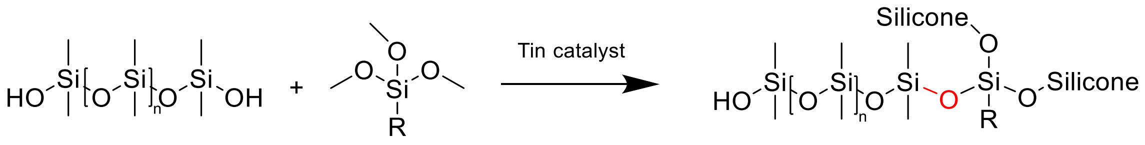


Figure 1-5 - Tin-catalyzed room-temperature vulcanization to form siloxane crosslinks.

Acid catalysts can activate alkoxy groups by protonating the electrophilic oxygen to enhance leaving group activity. Base catalysts lead to better nucleophiles. Tin catalysts (esters), on the other hand, are activated by water to form a tin-alkoxysilane that acts as an excellent leaving group that is susceptible to a nucleophilic attack by another silanol group (Figure 1-6). This allows the tin catalyst to reform and facilitate numerous polymerization reactions.[16]

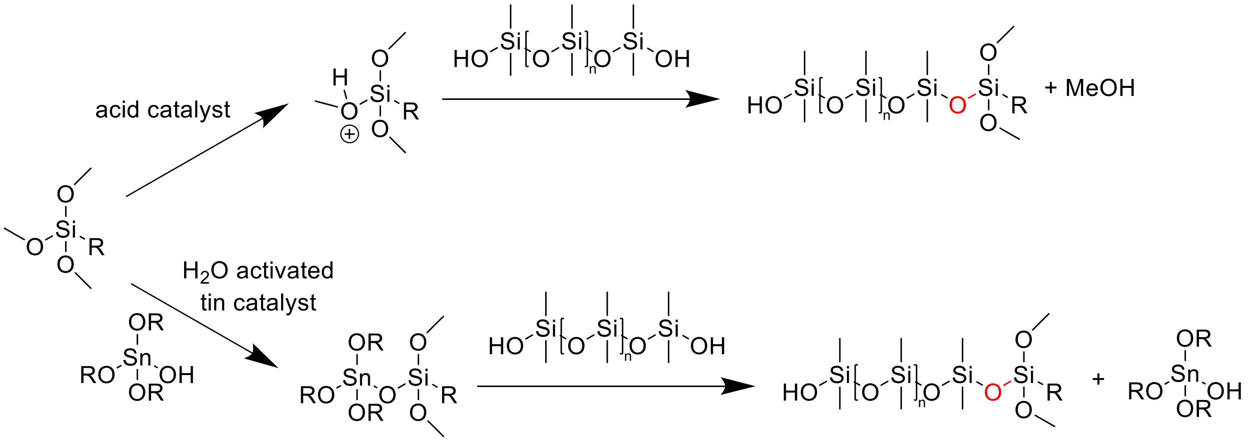


Figure 1-6 - Acid versus water-activated tin catalyzed (to form better leaving groups) RTV reactions.

These condensation reactions result in thermally and chemically stable rubbers that, for example, are often used as bathroom sealants due to reasonably fast cure times and the ability to effectively cure in the presence of water. However, the downside is that the types of catalysts used for this are typically trapped within the cured material and are normally unretrievable. Tin catalysts can be toxic to humans and animals which means that even if there was a way to design the silicone rubbers to (bio)degrade, the tin catalyst could leach into the environment and cause harm to its living organisms.[17] This is the motivation for exploring alternatives to this curing method.

1.2.2 Hydrosilylation

Another route to fabricating silicone materials is through hydrosilylation, which is an addition reaction that occurs in the presence of an appropriate transition metal, typically platinum (e.g. Karstedt's catalyst) or palladium catalyst in small amounts (ppm).[15] This involves the reaction between a hydrosilane (Si-H) and a silicone bearing a carbon-carbon unsaturated bond (typically $Si-CH=CH_2$). The process is analogous to hydrogenation – the Si-H group is added across the double bond to generate a new Si-C bond (rather than H_2, Figure 1-7). This reaction can occur at room temperature, but the rate increases with elevated temperatures; overall reaction conditions are mild.

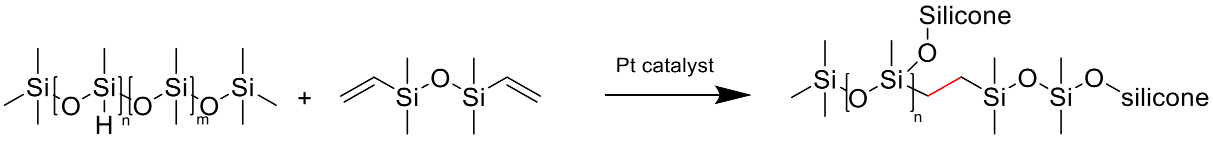


Figure 1-7 – Platinum-catalyzed hydrosilylation of pendent silicone polymers using vinyl silicone crosslinkers.

The resulting elastomers are quite robust and can possess a range of desired physical properties that can be tuned by adjusting the degree of crosslinking through control of the amount of vinyl and Si-H groups present in the pre-elastomer. Silica fillers are often used to improve the mechanical robustness of these elastomers. In fact, the popular commercialized product, Sylgard™ 184,[6] uses this exact process to create elastomers. There are limitations to this reaction – amines, for instance, tend to bind the platinum catalyst which effectively poisons it.[18] Additionally, like

RTV silicones, the platinum catalysts are trapped within the material and left unretrievable – although they are catalysts, they are consumed rather than retrieved and reused. Noble metals are expensive, ‘endangered’ (they are rare), and lack cost-effectiveness and sustainability – it is imperative to undertake research to find other versatile routes to creating elastomeric materials.

1.2.3 High-temperature vulcanization/radical cure (HTV)

HTV (otherwise known as radical cure) operates at high temperatures and usually employs organic peroxides like benzoyl peroxide or di-*t*-butyl peroxide.[15] The temperature needed is related to the amount of heat needed for homolytic cleavage of the peroxide bond to generate peroxide radicals. These radicals are used for the abstraction of an H$^{\bullet}$ from a methyl group or to generate a vinyl radical (Figure 1-8a,b). Vinyl groups typically require less heat as addition reactions with radicals occur quite readily. The generated vinyl radical either occurs through the addition of the peroxide radical.

Instead of dimerization of vinyl radicals, crosslinking involves the coupling of a vinyl radical and methyl radical to generate a new C-C bond or propagation of a radical to a vinyl group to create crosslinks. These two processes compete with one another and are controlled by the rates of radical addition and H• abstraction respectively (Figure 1-8c,d).

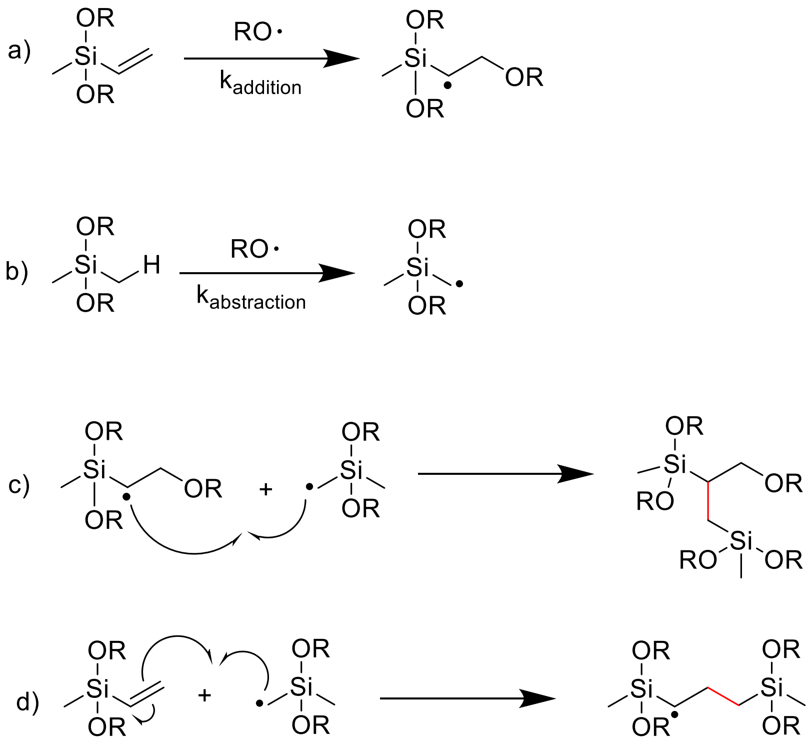


Figure 1-8 – Generation of radicals through a) addition of RO• to a vinyl silicone or b) hydrogen abstraction using RO• to form a methyl radical.. Then HTV chemistry forms C-C bonds crosslinks through c) coupling of methyl and vinyl radicals and d) propagation of radicals onto a vinyl group.

If the vinyl groups are not well distributed across the silicone backbone, there is a competition between crosslinking (linking different chains) with homopolymerization (Figure 1-9). The crosslinking density and physical properties of materials made from this type of cure are varied and difficult to control. An even distribution of vinyl groups on the silicone results in more effective linkages, but it is not always easy to obtain such materials. This too is a method for which alternatives need to be developed.

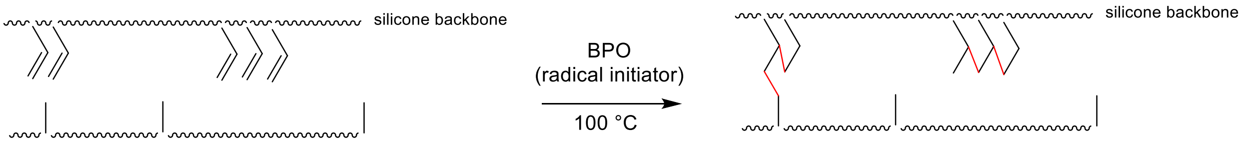


Figure 1-9 - Homopolymerization of irregularly distributed vinyl silicones through HTV.

1.3 Modern crosslinking motifs

While traditional silicone curing methods are effective and convenient, there has been motivation to explore other crosslinking motifs that evade the use of expensive and endangered metal catalysts like platinum or toxic catalysts like tin. Some of the research has explored non-covalent crosslinking processes.

1.3.1 Ionic crosslinking

Previous work has shown that the ionic linkage created between negatively charged silicone carboxylates and positively charged aminosilicones yields thermoplastic elastomers with self-healing abilities.[19] The Gemini aminosilicones (containing two amines per functionality) used are commercially available, and the carboxylate was prepared by a thia-Michael reaction between the α,β-unsaturated carbonyl of maleic acid and a thiol-containing silicone to form a Gemini acid silicone (Figure 1-10). These elastomers do not dissolve in common organic solvents but can dissolve in chaotropic or basic solutions that break the ionic interactions apart. The degree of crosslinking and hardness of the materials are dictated by the number of ionic linkages made which is controlled by the degree of carboxylate functionalization on the silicone backbone. The number of carboxylate functionalities is easily controlled by choosing a commercially available thiol silicone with the desired degree of functionalization. The research also found that the presence of two amine ions and two carboxylate ions increased to robustness of the materials in comparison to the same number of ionic bonds provided by monofunctional ions. This speaks to the strength of the ionic linkages created through this Gemini interaction. These materials also displayed thermoplasticity, which is an advantage in comparison to traditional thermoset silicone elastomers, as it allows for material recycling or potential biodegradation.

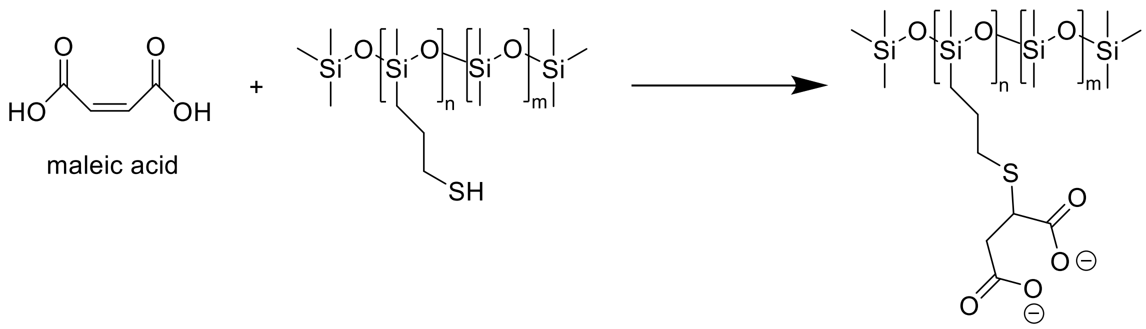


Figure 1-10- Thia-Michael addition of maleic acid to a pendent thiol silicone to form Gemini acid silicones.

Another route to silicone materials through ionic linkages was explored involving the use of phenolic antioxidants such as catechol and pyrogallol and their interaction with amines on telechelic aminosilicones.[20] These phenols contain several hydroxy groups which allowed them to act as crosslinkers when forming transient ionic bonds. Curing required small amounts of 2-propanol to solubilize the reagents, but no catalyst, which created elastomers that formed at room temperature over extended periods of time. The curing was much more efficient at higher temperatures (60-150 °C) and occurred over 4-15 days. A combination of ionic and hydrogen bonding was observed to occur between the hydroxyl moieties and the amine groups (Figure 1-11). These linkages were strong enough to prevent solubilization in regular organic solvents, but in a chaotropic solution, the interaction could be interrupted. Again, due to the nature of the bonding interactions, thermal reprocessing was possible with little to no observable change in elastomer properties after reprocessing. The physical properties of the elastomers could be controlled by adjusting the ratio of phenol to amine functionalities – the optimal hardness arose at a 1:1 functionality to maximize bonding interactions. Interestingly, the elastomers that were created in this process possess antioxidant activity due to the presence of phenols in the material. This outcome proved that exploring alternate ways to create silicone materials can simultaneously introduce new, advantageous properties to the resulting materials.

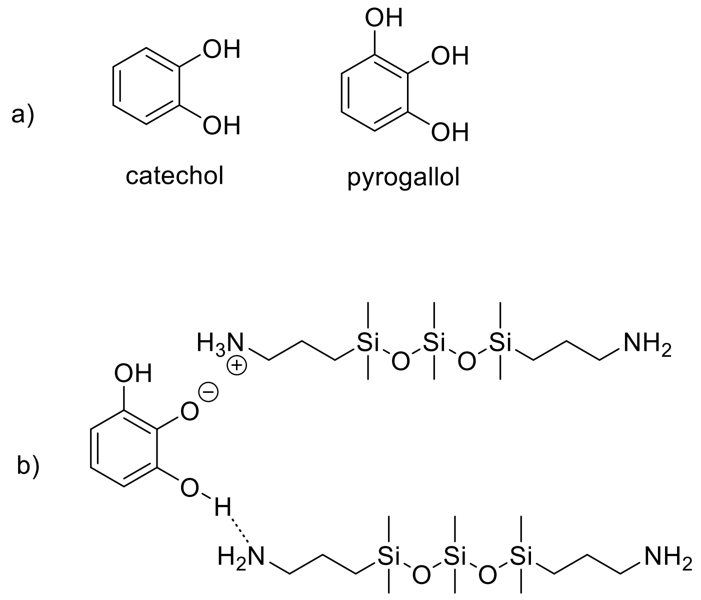


Figure 1-11 - A) Structures of catechol and pyrogallol. B) Ionic and hydrogen bonding between telechelic amino silicones to pyrogallol.

1.3.2 Hydrogen bonding

Ionic bonds are a great example of a non-covalent interaction that can facilitate silicone crosslinking, but it is not the only transient linkage available. Another interaction that can facilitate crosslinking is hydrogen bonding – although it is weaker than ionic bonding. In previous work, glucose residues were successfully attached to aminosilicones by ring-opening gluconolactone to form gluconamidosilicones (Figure 1-12).[21] This led to materials that ranged from viscous liquids to glass-like solids depending on the ratio of glucose residues to silicone content.

The sugar residues (hydroxyl functionalities) introduced interesting viscoelastic properties to the materials. The fluids created would shear thicken due to the transient crosslinks created by the H-bonding between glucose residues that transiently formed under compression. Over time, these crosslinks would break, and reform which allows the material to flow under the force of gravity. This behaviour produced a stimuli-responsive material that would respond to the different forces applied to it. For instance, a metal ball was dropped onto a 30-weight% solution of the gluconamidosilicone dispersed in D_5 and initially, the ball bounced several times off the surface. However, if the ball was allowed to rest on the surface, it slowly sank to the bottom of the vial. This behaviour speaks to the nature of the transient linkages created through hydrogen bonding. The degree of transient crosslinking could also be controlled by adjusting the amount of sugar present, which subsequently adjusts the number of hydrogen bonds that could be formed. The sugar silicones are not crosslinked elastomers in the traditional sense – even those that are glass-like solids at room temperature have melting points below 100 °C. So, although they possess unique behaviour, these materials may not be suitable for applications requiring higher temperature resistance.

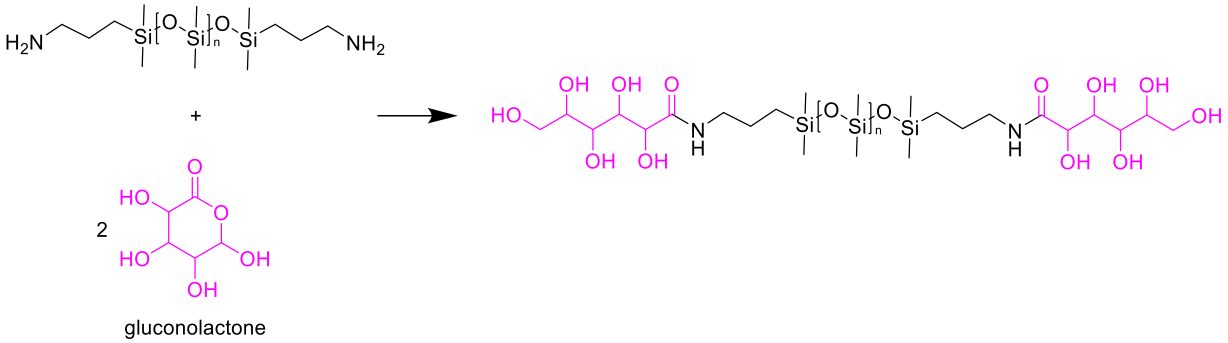


Figure 1-12 - Functionalization of a telechelic aminosilicone with gluconolactone.

1.4 Other bonding motifs

In addition to atypical bonding motifs in silicone, including ionic and hydrogen bonds, that can produce thermoplastic and/or transiently linked materials, there remain alternative ways to create more permanent bonded materials, both through permanent and dynamic covalent bonds.

1.4.1 Oxidative phenolic coupling

Several groups have pursued biomimetic strategies as part of a strategy to create bonding processes that better fit the principles of Green Chemistry. One of these is oxidative phenolic coupling, which occurs widely in nature.[22] Phenols are excellent at scavenging radicals by transferring a hydrogen radical to yield a neutral molecule and a hydroxy radical ($R^\bullet$ + PhOH → RH + $PhO^\bullet$).[23] Two phenoxy radicals can recombine under appropriate conditions to generate a large diversity of phenolic structures in nature.[24] The formation of lignin in trees is one biopolymer that is, in part, synthesized by such processes. Oxidative phenolic coupling creates a new covalent C-C bond that should be robust. The idea behind mimicking a biosynthetic process is to create materials using a relatively facile reaction that can have the potential to be recognized as a bioagent in nature and degraded. That is, a silicone crosslinked with this link should offer robustness in use but could be biodegradable.

1.4.2 Boronic ester bonding

Ionic bonds are formed in an equilibrium process. Bonds like imines,[25] esters and boronate esters form under mild equilibrating conditions. Boronate esters have found an important place in analytical chemistry because of the reversible interaction between them and sugars, [26] usually via 1,2 or 1,3-diols (Figure 1-13). Including these types of boronate bonds opens the potential to create materials that have reversible crosslinks; the reversibility could contribute – in a tuneable way – to viscoelastic properties. The equilibrium is controlled by many factors including the structure of the diol and the presence of water[27] which provides a path to reverse the crosslinks when the materials reach their end of life. We saw this as an opportunity to create silicone elastomers that are more robust than materials crosslinked through ionic or hydrogen bonds alone, but that may also possess reprocessability.

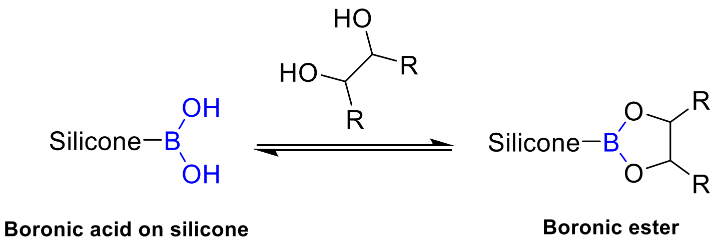


Figure 1-13 - Reversible boronic ester formation with a boronic acid-modified silicone and a 1,2-diol.

1.5 Research goals

There is a general desire to improve the sustainability of silicone materials by reducing: intensive energy consumption demand during initial synthesis; the use of expensive and unretrievable metal catalysts during cure; and the lifetime of silicone elastomers once they have entered the environment at the end of life. One way to mitigate these issues is by incorporating more sustainable resources into these materials, thus, diluting the overall silicone content required for a given application. Another solution involves creating silicone elastomers that will revert to their linear chain precursors in response to a trigger, for example, chemical treatment; it is anticipated that, like normal silicone fluids, they will spontaneously degrade in the environment. Lastly, it is interesting to research crosslinking motifs that are as effective as traditional crosslinking methods but bypass the need for expensive, unretrievable metal catalysts; the use of biological links might facilitate eventual biodegradation.

Chapter 2 of this thesis focuses on diluting the silicone content in elastomers with a natural product and explores an alternate crosslinking method that avoids the capturing of metal catalysts. The idea is based on a biomimetic process that employs the oxidative phenolic coupling of eugenol – a compound that is abundant in clove oil and known for its antioxidant properties.[28] It is based on a phenyl ring that bears a hydroxy group, methyl ether, and an allyl moiety, respectively. The allyl group makes this molecule a perfect candidate for silicone functionalization and its phenolic character is promising for oxidative coupling reactions (Figure 1-14).[22,29] In fact, eugenol is one of the many breakdown products of lignin which is a large structure synthesized by trees via numerous enzyme-catalyzed oxidative coupling reactions.[30] An investigation of eugenol-functionalized silicone oils was performed to determine their efficacy in forming crosslinks through oxidative phenolic coupling reactions as well as the retention of their antioxidant activity.

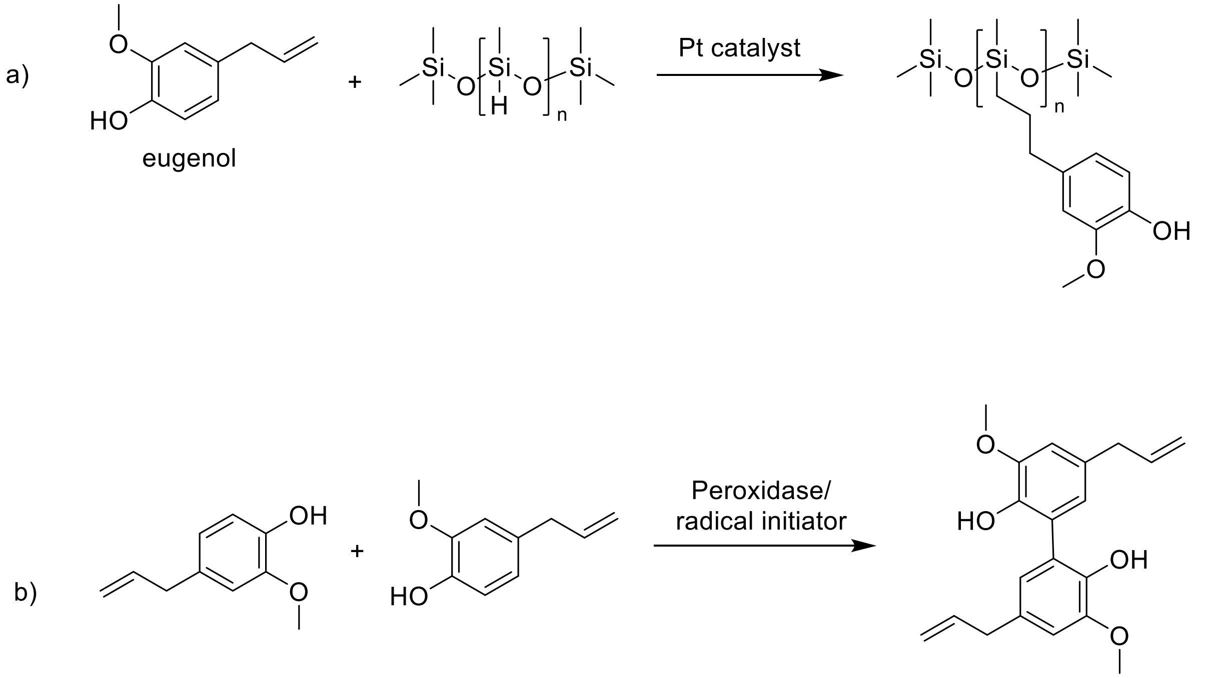


Figure 1-14 – A) The functionalization of a silicone polymer with eugenol through Pt-catalyzed hydrosilylation. B) Example of the phenolic coupling of eugenol molecules.

While eugenol-functionalized silicone elastomers introduce a novel way to cure silicones, these are thermoset materials that still require a source of heat to cure. In Chapter 3, another crosslinking method is explored which exploits boronic ester bonding with glucose.[26,27] Unlike boric acid, which is found in nature, boronic acids are synthetically produced but their ability to form dynamic covalent bonds, similar to boric acid, might allow the formation of robust silicone materials with room for a pathway to controlled degradation. The degree of crosslinking would be controlled by the amount of boronic esters formed. Work done by previous students has allowed a way to functionalize silicone polymers with 4-vinylphenylboronic acid (4VPBA) (Figure 1-15). It was also found that gluconolactone could be used to functionalize aminosilicones through ring-opening reactions.[21,31] 4-VPBA is a phenylboronic acid (PBA) which are known to effectively bind glucose amongst other sugars.[32]

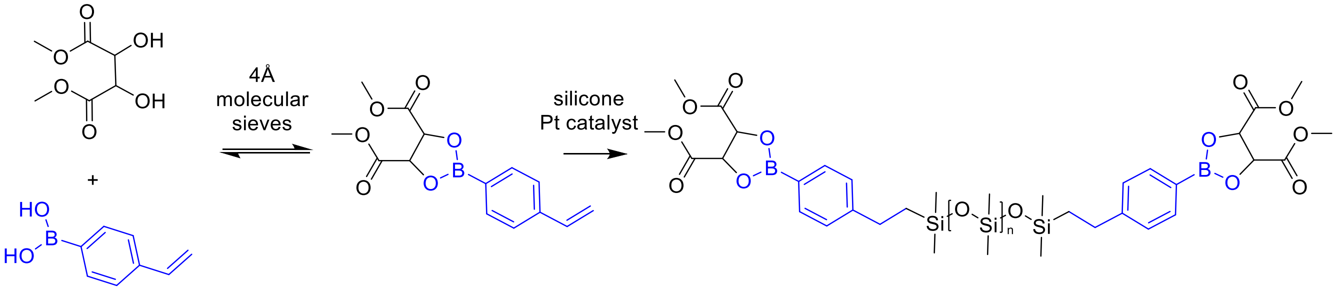


Figure 1-15 - Tartrate-protected 4-vinylphenylboronic acid to boronic acid-modified silicone.

The binding affinity of PBA to various sugars is dependent on the *pKa* of the boronic acid as well as the three-dimensional structure of the sugars.[26,33] For instance, fructose often binds PBA with a much higher affinity compared to glucose because it often exists in a conformation with a pair of *syn*-periplanar hydroxyl groups.[34] This chapter explores the range of viscoelastic materials that can be fabricated by changing the loading of glucose to boronic acid residues. The rheological properties along with the hardness of the materials were evaluated. Methods to further stabilize the boronic ester bond and increase the robustness of the materials are also discussed.

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2 Learning from the Trees: Biomimetic Crosslinking of Silicones by Phenolic Coupling

2.1 Abstract

Phenolic compounds undergo radical coupling under oxidizing conditions. Silicone oils were modified with eugenol using hydrosilylation to create oils and elastomers that exhibited antioxidant activity due to the presence of phenols, as shown by DPPH and other oxidative assays. At room temperature, phenolic coupling was not observed, as judged by the lack of changes in viscosity or formation of gels. By contrast, peroxide oxidants at temperatures above 90 °C led to crosslinked materials whose physical properties (related to crosslink density) correlated with eugenol content, equivalents of peroxide added and reaction time. The product elastomers were also efficient antioxidants, although there was some attenuation of activity in higher crosslinked materials, consistent with diverse radical recombination processes.

2.2 Introduction

2.2.1 Oxidative phenolic coupling

Oxidative processes are common in nature and are often highly beneficial. Oxidative stress, by contrast, is caused by the generation of excessive free radicals that result from an abundance of reactive oxidative species (ROS, e.g., hydroxy radical, superoxide, singlet oxygen). In humans, oxidation can cause damage to human cells including DNA, which is known to play a role in the development of many diseases and has been linked to some cancers.[1]

Nature manages radicals caused by oxidation through the use of antioxidants (AO), among which phenols are particularly common, including tocopherol (vitamin E), curcumin, catechols, etc.[2-5] Highly stabilized radicals readily form from the reaction of phenols with ROS. Once formed, quenching of the phenolic radical can arise through atom abstraction or recombination. One important outcome of the latter process is phenolic coupling that involves new C-C bond formation between the aromatic groups to generate biphenyls (Figure 16A→D).[6] Such motifs are particularly prevalent in lignin, the highly complex polymer structures produced by trees and other plants to assist in providing structural integrity. Lignin consists of both aromatic and aliphatic components that are produced from phenols including *p*-coumaryl, sinapyl and coniferyl alcohol monomers (Figure 16A-C).[7, 8]

Elegant chemical syntheses that utilize phenolic coupling have been reported.[9, 10] Although many reagents, including peroxides and other ROS generators, can be used to initiate the reaction, nature typically exploits enzymes such as laccases and peroxidases to mediate radical generation and propagate radical coupling,[11] processes that have also been exploited by synthetic chemists.[12]

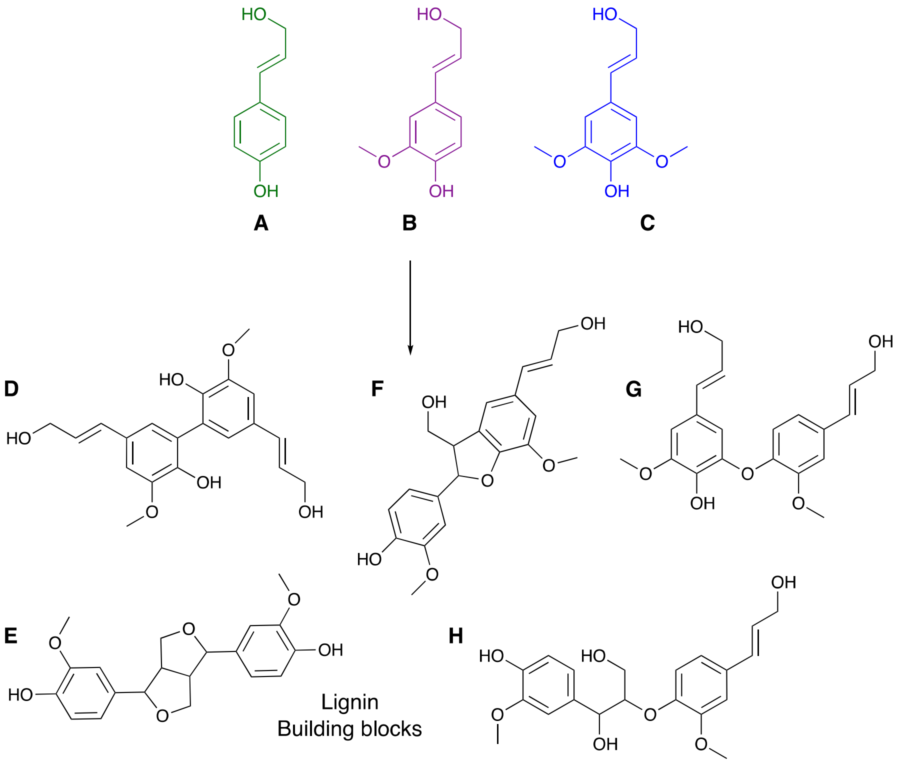

Figure 16. Conversion of A-C *p*-coumaryl alcohol, coniferyl alcohol and sinapyl alcohol into lignin building blocks in which D, and E phenols are preserved or F-H partly consumed (adapted from ref. 8).

2.2.2 Silicones

Silicones are synthetic polymers that possess very different properties than their organic analogues and are exploited for their thermostability, oxygen permeability, biocompatibility and, in the case of personal care products, they are excellent emollients. Silicone elastomers are very resistant to oxidative decomposition.[13] Silicone oils undergo facile decomposition in the environment to yield sand, water and CO_2; the rate of elastomer decomposition is less well understood. The synthesis of all silicones has a high energy toll (via the conversion of sand to silicon). One strategy to exploit the benefits of the silicone materials, but mitigate the energy costs, is to dilute silicones with natural materials.

2.2.3 Eugenol

Eugenol is a natural phenolic compound that can be extracted from various plants but is the main component in clove oil. It is well known for its antioxidant properties along with antimicrobial properties and for its fragrance.[14, 15] For these characteristics, eugenol is popularly used in the food industry, cosmetics, dentistry, and in the medical field.[16-19]

Having previously developed strategies to encode antioxidant activity in silicones using eugenol,[19] we wondered if the first-formed phenoxy radicals could also be exploited in a biomimetic process to generate crosslink sites on silicone oils. We report the oxidative crosslinking of eugenol-modified silicone oils using various peroxides and examine the residual antioxidant activity in the resulting elastomers.

2.3 Results

Model compound

The phenolic coupling process was first optimized using a small model compound **1** formed by hydrosilylation of the double bond of eugenol with a disiloxane copolymer in the presence of very small quantities of a platinum catalyst.[20] The process was clean and high yielding – 82% (Figure 17A, Table 1). ^{1}H NMR showed that the terminal adduct was the only product (Figure S1).

It was straightforward to create a library of silicone-eugenol polymeric oils, both telechelic **M^{H}M^H**, **T12-Eu** and pendent **P15-Eu**, **P30-Eu**, **P50-Eu**, by hydrosilylation of telechelic or pendent H-bearing silicones with eugenol (nomenclature: **Tn** telechelic, n=number of backbone Me_2SiO (D) units; **Px** x = percent of functional monomers containing eugenol groups compared to D units in the backbone Figure 17D,E, Table 1, Figure S2). Both telechelic and pendent HSi starting materials were, respectively, reacted with a slight excess of eugenol to ensure complete conversion of HSi groups. Excess eugenol partitioned into a methanol/water mixture. The oils were produced in good to excellent yields and were transparent, slightly yellow oils.

Phenolic antioxidants (AO) work by converting reactive radicals into more stable phenolic radicals (Figure 17B,F). Measuring AO activity is straightforward using DPPH, including with silicone-eugenol oils, which indicates colorimetrically that the reaction had occurred (Figure 17H, Figure S6A);[19] a very distinct purple to yellow transition occurs upon reaction with phenol reducing agents.[21, 22] Based on these assays, the AO activity directly correlated with the quantity of eugenol present on the silicone polymer for the product **Tn-Eu** and **Px-Eu** oils, (Figure S6). Although phenolic radicals were produced using DPPH at room temperature, none of the reaction mixtures with telechelic **T12-Eu**, pendent **P15-Eu**, **P30-Eu**, **P50-Eu** were converted to a viscous fluid, gel or elastomer over 60 days; no phenolic coupling was observed.

Biologically controlled phenolic couplings can occur with enzymes at ambient temperatures[7, 23] but, as noted, coupling was not observed in eugenol silicones that reacted with DPPH at room

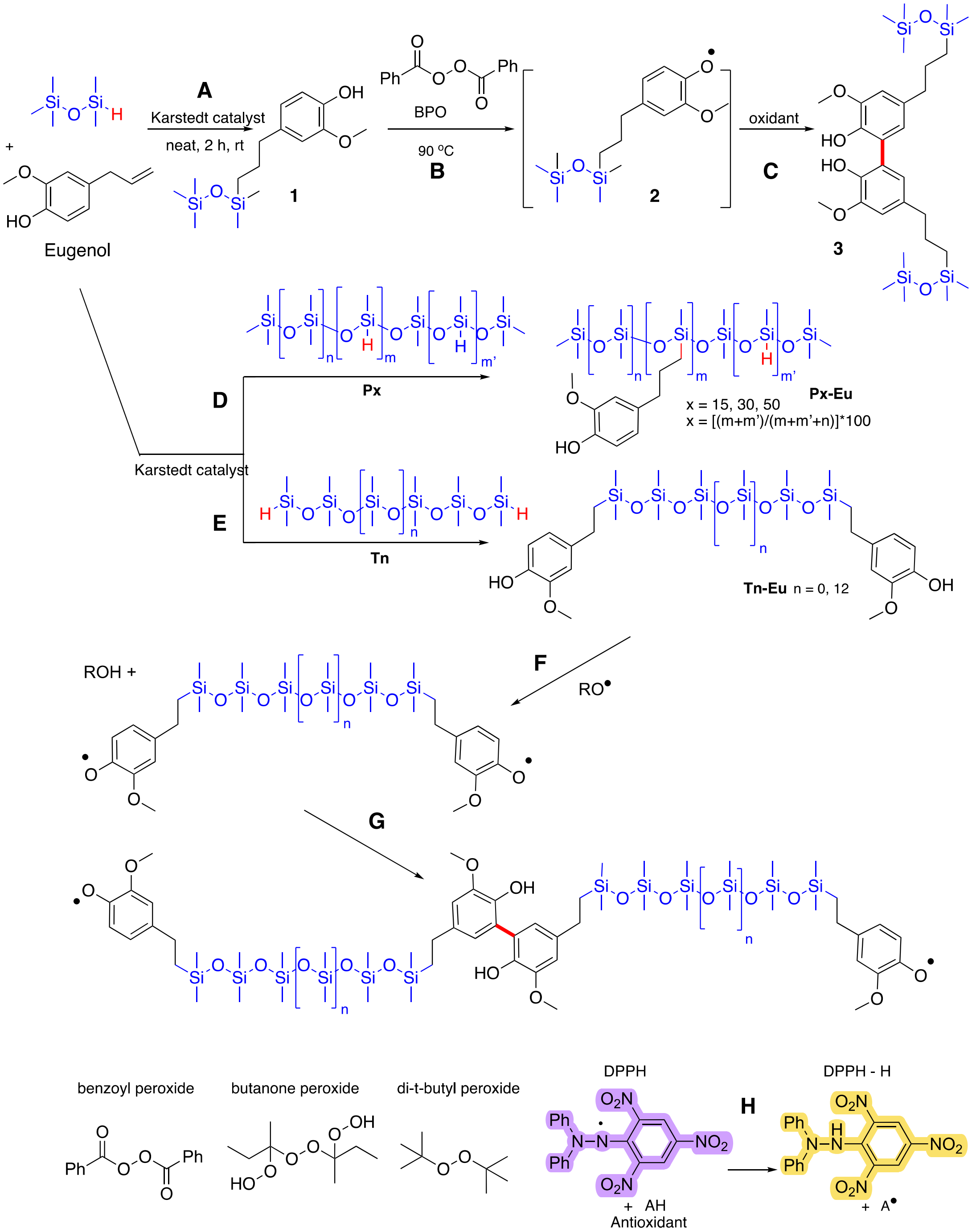

Figure 17. A) Preparation of **1** and B,C) its oxidative dimerization. D,E) Preparation of telechelic and pendent eugenol-modified silicone oils. F) Phenolic coupling leading to chain extension of a telechelic eugenol-modified silicone. G) DPPH reaction.

temperature. This observation suggests that in the absence of (biological) catalysts, the aromatic C-C coupling reaction to produce biphenyl compounds has a much higher reaction barrier when compared to the formation of the phenoxy radical from the phenol reaction.[24, 25]

2.3.1 Oxidative phenolic coupling

2.3.1.1 BPO

A variety of chemical processes have previously been used to oxidatively dimerize phenols. For example, vanillin is readily oxidized by aqueous ferricyanide.[26] Silicones, of course, are very low surface energy materials that are typically water insoluble[27] and therefore not conducive to (oxidation) reactions in aqueous media. Initial oxidation experiments were therefore performed with organosoluble benzoyl peroxide (BPO) because it is easy to handle and has a very well defined offset temperature, with a one hour ½ life ($t_{½}$) at 100 °C.[28] BPO in toluene was used at 100 °C for 2 hours to oxidize **1**, via the phenoxy radical **2**, to give **3**. It was rather difficult to distinguish the starting material from the dimer product by ^{1}H NMR or ^{13}C NMR. However, GC-MS showed conversion to the dimer **3** in about 20% yield when using 1 equiv. BPO, with the remainder being unreacted starting material (Figure 17B,C, Figures S3, S4).

The formation of silicone elastomers from oils through oxidative radical coupling was initially performed at elevated temperatures using benzoyl peroxide. **P50-Eu** was exposed to different equivalents of benzoyl peroxide (BPO) dissolved in a small amount of toluene and heated to 100 °C for 2 hours to give **P50-Eu-E**. It was immediately apparent that, for a given silicone-eugenol oil, the hardness of the resulting solvent swollen elastomers (gels) produced correlated with the quantity of radical initiator added to the reaction until a maximum was reached near double the stoichiometric ratio of 0.5 BPO/eugenol (Figure 17F,G, Figure 18, Tables S2, S3). As the solvent evaporated from the gel, however, the benzoic acid by-product (as later confirmed by NMR) crystallized into the elastomer. Benzoic acid is essentially insoluble in silicone oils, and it proved very difficult to find solvents that would both readily swell in silicone and dissolve the benzoic acid to allow its removal by extraction *without damaging the elastomer*, which had voids after benzoic acid removal. These studies, therefore, provided proof of principle for oxidative phenolic crosslinking within silicones but were synthetically impractical with BPO as initiator.

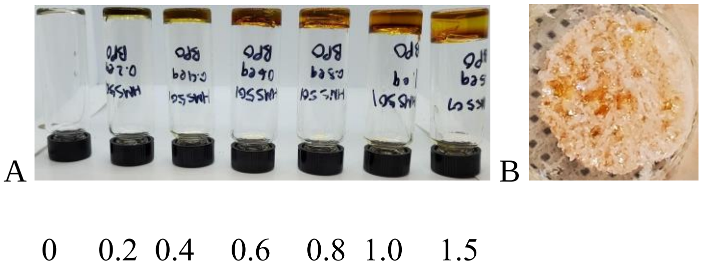

Figure 18. A) Photographs of toluene-containing gels **P50-Eu-E** formed from **P50-Eu** with different equivalents of BPO (0 ➞ 1.5, larger volumes are due to use of a stock BPO solution) before solvent evaporation and B) **P50-Eu-E** after solvent evaporation showing the presence of crystalline benzoic acid.

2.3.1.2 MEKP/DTBP

Alternative organic peroxides were examined that would generate volatile products that should be readily able to escape the evolving elastomer: butanone peroxide (methyl ethyl ketone peroxide, MEKP); or di-*t*-butyl peroxide (DTBP). Butanone peroxide **4** (Figure 17) is used as a low temperature radical initiator, typically for acrylate polymerization; the compound is a mixture of peroxides[29] and is soluble in silicone oil. Iodometric titration of the butanone peroxide showed that ~ 5 radicals per molecule were generated at 21 °C. Optimization of the curing process was initially undertaken with a molar ratio of **4**:eugenol moiety of 1:10, a slight deficit of oxy radicals. The reaction of **4** with eugenol-silicone **P50** at room temperature led to no significant changes in viscosity over 72 hours. Selected experiments were made at increasingly elevated temperatures to permit a better understanding of the rate at which phenolic coupling would occur, as shown by an increase in viscosity or conversion to an elastomer. Only at about 130 °C did crosslinking begin to take place and was complete at ~12-24 hours, after which no further changes in hardness of the elastomer were observed. However, if one adds an additional bolus of peroxide, some additional hardening is observed. An additional 0.5 equiv. of DTBP to elastomers made with 1 equiv. of DTBP resulted in an increase of Shore OO by 10 (e.g., **P30-eu-E** cured with 1 equiv. of DTBP experienced an increase of Shore OO from 70 to 80 after 24h). Thus, the aspiration to operate at lower temperatures was not met with this initiator, but at least there were no attendant problems with by-products.

A full study of phenolic coupling was undertaken with the library of silicone-eugenol compounds and DTBP **5** as initiator at 130 °C. This peroxide is not a mixture of compounds and was therefore easier to quantitate. It generates 2 radicals upon heating and has $t_{½}$ of ~1 hour at 146 °C.[28] Cure of a 1:1 ratio of DTBP: **P30-Eu** eugenol-silicone starting material (Figure 17) was tracked by changes in Shore OO hardness, which showed that about 2 hours was required before any changes in viscoelastic properties were observed and complete cure to give **P30-Eu-E** took 8-12 hours; crosslink density, determined by swelling measurements, followed the same trend (Figure 19A, Table S4).

2.3.2 Elastomers

A library of opaque, brown elastomers was created from **P15-Eu**, **P30-Eu** and **P50-Eu** using different molar ratios of DTBP at 130 °C for 48 hours (sometimes longer, (Figure 19B, Table S3). Note that if the reaction mixtures were left for extended periods of time at elevated temperatures, they would turn an increasingly darker brown colour over time but remain elastomers with little or no change in the Shore hardness. By contrast, no change (including in viscosity) was noted in the starting oils if the reactions were performed at room temperature was observed over 7 days. The as-produced elastomers, **P15-Eu-E**, **P30-Eu-E** and **P50-Eu-E**, are actually gels. Extraction showed low sol fractions up to about 1 equiv. of peroxide, at which point the elastomer contained about 15wt% sol (Figure 19C, Table S6). Post extraction, the elastomers were slightly harder.

Analogous phenolic coupling could be utilized to chain-extend telechelic eugenol-terminated silicone oils. Both BPO and DTBP were examined for this process; the issues with elastomeric silicones and benzoic acid do not present in this case as oils are produced. It can be seen that significant chain extension results, particularly at higher peroxide levels (Figure 19D, Tables S1, S2).

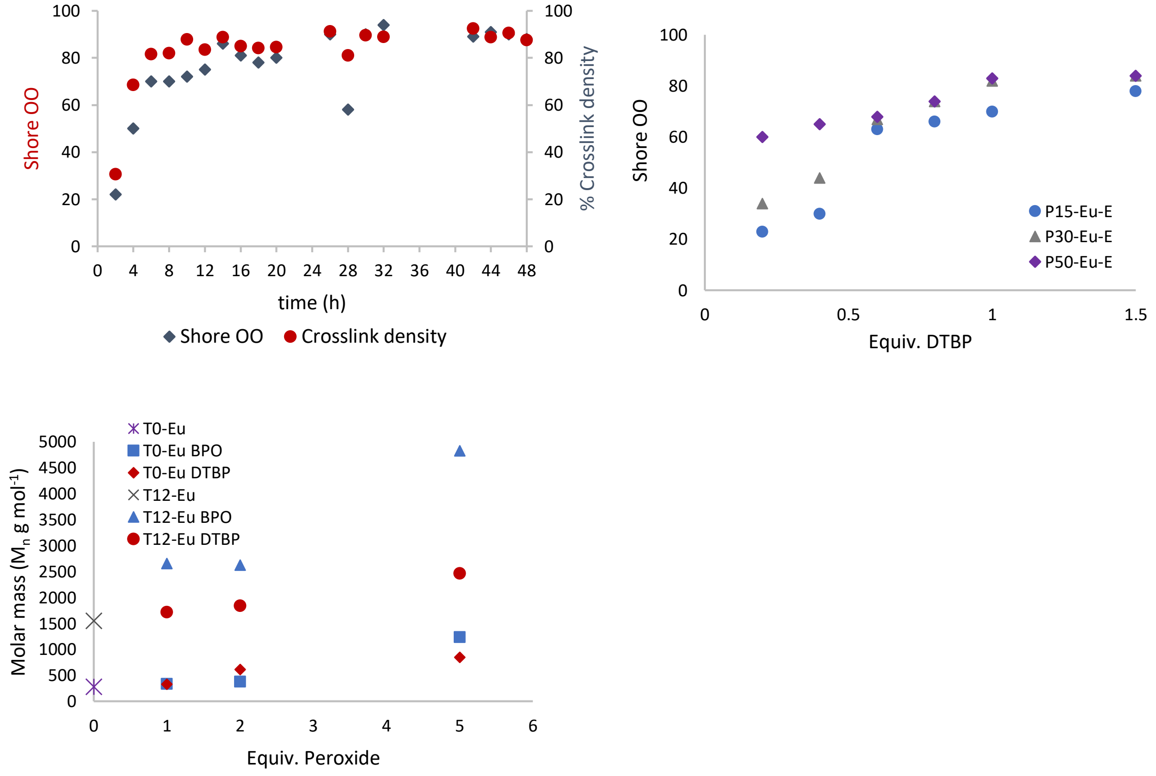

Figure 19. A) Changes in Shore Hardness and crosslink density with reaction time in elastomers made by reaction of 1 equiv. DTBP with **P30-Eu** (we feel the data at 28 h is an outlier). B) Shore

OO hardness of elastomers **P15-Eu-E**, **P30-Eu-E** and **P50-Eu-E** (for analogous crosslink density data, see Figure S5,) as a function of the molar ratio of DTBP. C) Increases in molecular weight data due to chain extension via phenolic coupling of telechelic silicones **T0-Eu** and **T12-Eu** with BPO or DTBP (Table S2,).

2.3.3 Antioxidant activity

The starting oils **Tn-Eu** and **Px-Eu** are very efficient antioxidants, as shown by DPPH assays (Figure 17H). The elastomeric products **P15-Eu-E**, **P30-Eu-E** and **P50-Eu-E** were also efficient antioxidants. As crosslinking increases, there was a relatively small decrease in AO performance of the products (Figure 20, Figure S6).

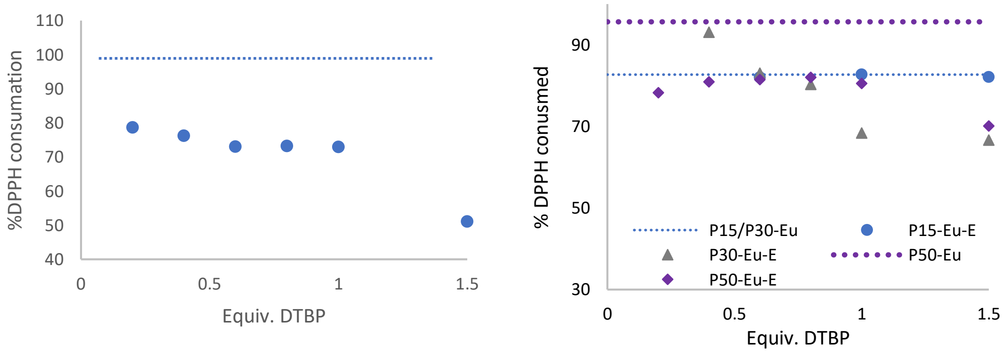

Figure 20. Antioxidant activity of A) chain extended **T12-Eu** with different equivalents of DTBT and B) **P15-Eu-E**; **P30-Eu-E**; **P50-Eu-E** prepared using different quantities of DTBT. 100% consumption indicates that each phenol in the starting silicone had reacted once.

2.4 Discussion

Silicone elastomers are widely used as adhesives, sealants and in film forming processes. Users typically select the pre-elastomers by desired cure type, temperature, and rate of cure for processing. More important, however, are the physical properties of the cured produce, which normally include water repellency and hardness; for certain applications extension at break is also important. Silicones are typically filled with reinforcing agents that usually decrease extension at break, increase hardness, and really improve tear resistance; fumed silica is a common filler. Unreinforced silicone elastomers typically have high Shore OO (up to 80-90) to low Shore A (typically below 30) values (to compare Shore values and Young's modulus see the discussion in the).[30] The materials prepared using phenolic coupling thus fall into the typical range of hardnesses for unfilled silicone elastomers (Figure 4A,B). Adding even low wt% filler significantly increases the hardness (for a comparison of commercial filled vs homemade unfilled elastomers prepared using tin, platinum and the peroxide cure, see Table S6,).

Silicone elastomers are usually water repellent with water contact angles over 100°. They range from transparent/translucent to opaque materials depending on filler loading and may be pigmented. The silicones produced by phenolic coupling have the feel and water repellency of commercial silicones. However, these materials are always yellow/brown and opaque because the biphenyl domains have a different refractive index than the silicone components.

Most industrial cure processes for silicone elastomers involve moisture cure with tin catalysts (RTV – room temperature vulcanization), or platinum-catalyzed hydrosilylation, which is highly efficient but expensive. While green chemistry calls for the use of catalysis, neither of these catalysts are ideal, tin because of issues of toxicity, and platinum for cost. Worse, platinum is a highly valuable 'endangered' element and single use in an elastomer followed by disposal in the environment may be considered reckless. Silicones may also be cured using radical chemistry at elevated temperatures that are similar to those used for phenolic coupling.[31]

Any consideration of the work described above must begin with contextualization around silicones. The vast majority of silicone polymers exhibit little to no solubility in water;[32] much of their utility is based on this fact. As a consequence, the chemistry used for silicone synthesis and crosslinking typically requires processes that avoid, or at least are not inhibited by water. Nature, of course, mostly does reactions under ambient conditions and is not normally constrained by having to work in low moisture environments.

2.4.1 Phenoxy radical generation

Phenolic dimerization requires that two challenges are overcome: creation of a phenoxy radical and controlling the coupling of 2 radicals to create a biphenyl structure. DPPH studies showed that it is straightforward to create the radical – the basis of AO activity – at room temperature simply by mixing.[19] However, neither chain extension nor crosslinking was observed at room temperature with any oxidant including DPPH, nor with elevated temperatures up to about 70 °C. It was hoped that MEKP, with its low degradation temperature and relatively benign by-products would drive the coupling reaction at moderate temperatures. Instead, 100 °C was needed; this peroxide offered no benefits.

The observed data make clear that there is a significant energy barrier to overcome in bringing the two phenoxy radicals in close enough proximity to react (Figure 17→C, →G), a much larger barrier than for creation of the radicals in the first place (Figure 17B,F). The difficulty in forcing phenoxy radical coupling, observed here in a silicone environment, exemplifies nature's efficiency with reactions of this type in water. Copper rich enzymes like laccase efficiently mediate linking processes in lignin formation.[12] There is a very low barrier to forming phenoxy radicals, and without the structurally precise active sites provided by an enzyme, the barrier to radical coupling is higher than we anticipated; elevated temperatures were required. This is, perhaps, unsurprising. For phenolic coupling and, therefore, crosslinking to occur two relatively large, sterically encumbered moieties need to orient themselves within limited degrees of freedom to permit biphenyl formation.

In most silicone elastomers, the final crosslink density is selected by controlling the number of functional groups that crossreact in the presence of a catalyst. With phenolic homocoupling, the degree of cure is controlled by the amount of peroxide added. In all cases, as cure occurs, chains are increasingly captured in the growing network and the sol fraction decreases. At the end of cure for all silicone elastomers there remain untethered starting materials, typically ranging from 1-10% for commercial silicones, although both lower and higher levels are sometimes observed/achieved. There was a direct correlation between extractables in the phenol coupled elastomers and the quantity of peroxide added to induce cure, with final sol fractions in the range of 10-15%, which would be considered on the high end of the spectrum (Table S4). This is attributed to the greater difficulty in forming phenolic coupling crosslinks just discussed.

2.4.2 Phenolic coupling

BPO was a convenient oxidant when used for chain extension (Figure 19C) but, in our hands, was problematic with elastomer synthesis due to challenges in removing by-products. Even if the crystals of benzoic acid that formed in the elastomers could be removed, the resulting material had a foam-like structure, with voids left in the elastomer (Figure 18). High quality elastomers were obtained using DTPB as an oxidant, as the by-product *t*-BuOH is volatile. DTBP led to higher molar mass polymers when used for chain extension of telechelic polymers (Figure 19D).

Most crosslinking reactions were complete at about 1 equivalent of peroxide/eugenol within 12 hours (Figure 19A,B); the addition of peroxide after 24 hours did lead to small increases in crosslinking. This, of course, actually represents an excess, a 2:1 ratio, of $RO^\bullet$ / phenol. Not all radicals are produced simultaneously; DTBP has a half-life ($t_{1/2}$) of ~1 hour at 146 °C, and the reaction was run at a lower temperature of 130 °C. This lack of efficiency – half the radicals are lost – compromises the process but was judged to be better overall than further increasing the temperature. At ‘full cure’ about 15% of the materials were extractable from the elastomer, which is relatively common in silicone elastomers.[33] The peroxide coupling reactions were even less efficient with telechelic materials **Tn-Eu** (Figure 19D). There are better ways to make linear antioxidant silicone oils than this radically mediated approach.

2.4.3 Antioxidant activity and physical properties

Elastomers **Px-Eu-E** possessed high AO properties that were only about 20% lower in activity than the starting oil, up to the addition of up to 1 equivalent of DTBP (Figure 20). The slight loss of AO activity is ascribed to coupling processes that consume phenols. The desired coupling leads to a biphenyl structure (Figure 17C,G). However as has been shown with lignin, there are related coupling motifs in which one of the phenols is consumed during linking and is thus lost from the products (in analogy to those shown in Figure 16F-H). It is noteworthy that one can choose the desired crosslink density, when converting a eugenol-silicone oil to an elastomer, without significantly affecting the AO activity. The ability of silicone oils to efficiently coat surfaces makes them attractive as film formers. **Px-Eu oils** can simply be spread, with an oxidant, on a surface and the modulus of the resulting film after heating is simply controlled by peroxide oxidant concentration and/or heating time to give antioxidant films.

2.4.4 Alternative to silicones

We note that during the synthesis of silicone-eugenol oils **Tn-Eu** and **Px-Eu**, we also turned to the efficient Pt-catalyzed reaction. However, unlike elastomers, the platinum used to prepare these oils is readily recovered from the oils by adsorption on supports like activated carbon or Celite so that it can be reused or, once spent, returned to the manufacturer for conversion back to active catalysts. The oxidants – **MEKP, BPO, DTBP** – required for oxidative chain extension of **Tn-Eu** or crosslinking of **Px-Eu** into elastomers **Px-Eu-E** were used in stoichiometric quantities, which breaks Green Chemistry rule 9. It is nevertheless noteworthy that the oxidants used are relatively benign. Benzoyl peroxide is prepared from, and after reaction returns to, benzoic acid, a material commonly found as a preservative in foods; BPO is used to bleach flour. DTBP is converted, during reaction, into *t*-BuOH a compound that is readily metabolized.[34]

Nature, of course, performs better in this regard by using even more innocuous stoichiometric oxidants like O_2, H_2O_2, etc. Having set the precedent for phenolic coupling as a viable cure motif for silicones, we can turn to the use of more benign oxidation strategies. Previous work has shown, in silicones, it is possible to use these oxidants, for example, with hemin as a peroxidase mimic in silicone aqueous H_2O_2,[35] or tethered porphyrins that lead to the photogeneration of singlet oxygen.[36] Work exploring these oxidants for phenolic coupling is ongoing.

Biomimicry is part of the justification of this work. A biomimetic oxidative process utilizing natural constituents to give natural crosslinks permits control of silicone elastomer properties; we have learned from the trees. The natural products also convey new antioxidant properties to the silicones that, at the same time, benefit from their redox insensitivity. However, more tangible now is the ability to maintain function while diluting the silicone by natural constituents (rule 7). Silicone polymers have a high energy content as a consequence of the need to first make silicon from sand. The polymers and processes described here mitigate, in part, that energy cost by diluting the silicones with the natural product eugenol (by 16% in the case of **P15-Eu-E** to 41% for **P50-Eu-E**).

2.5 Experimental

2.5.1 Materials

Eugenol, di-tert-butyl peroxide (BPO), benzoyl peroxide, 2-butanone peroxide, 2,2'-azobis(2-methyl-2-propionitrile), benzoic acid and platinum(0), 1,3-divinyl-1,1,3,3-tetramethyldisiloxane (Karstedt's catalyst, 2% Pt in xylenes), Celite® S, sodium thiosulfate, and 2,2-diphenyl-1-picrylhydrazyl (DPPH) were purchased from Sigma Aldrich. MM^H (pentamethyldisiloxane $Me_3SiOSiMe_2H$), pendent, trimethylsiloxy-terminated $MeHSiO-Me_2SiO$ copolymers (HMS-501 900-1200 g mol^{-1}, 45-55% SiH monomer **P50**; HMS-301 1900-2000 g mol^{-1}, 25-35% **P30**; HMS-151 1900-2000 g mol^{-1}, 15-18% **P15**); telechelic HSi-silicones 1,1,3,3-tetramethyldisiloxane (M^HM^H, **T0**, and DMS-H11 **T12**, n =12, Figure 17) were purchased from Gelest. Sodium bicarbonate and potassium iodide were purchased from Fischer Chemical. Potato starch was purchased from Buckman Laboratories. Sulfphuric acid was purchased from Caledon. Solvents toluene, methanol, ethyl acetate, hexanes, isopropyl alcohol, deuterated chloroform, and dichloromethane were purchased from Sigma Aldrich.

2.5.2 Methods

NMR analysis: ^1H and ^{13}C NMR were recorded on a Bruker Advance 600 MHz nuclear magnetic resonance spectrometer.

Electrospray ionization mass spectrometry (ESI-MS) was performed using an Agilent 6340 Ion Trap mass spectrometer.

GC-MS analyses were performed using an Agilent 6890 N gas chromatograph (Santa Clara, CA, USA) equipped with a DB-17ht column (30 m × 0.25 mm i.d. × 0.15 µm film, J & W Scientific), and coupled to an Agilent 5973 MSD single quadruple mass spectrometer (Santa Clara, CA, USA). One microliter of sample was injected using Agilent 7683 autosampler (Santa Clara, CA, USA) using an injector temperature was 250 °C and a carrier gas (helium) flow of 0.8 mL/min. The transfer line was set to 280 °C and the MS source temperature was 230 °C. The column temperature started at 40 °C, raised to 70 °C at 5 °C/min, raised to 95 °C at 10 °C/min, raised to 300 °C at 40 °C/min, and was then held at 300 °C for 8 min for a total run time of 21.73 min. Full scan mass spectra between m/z 50 and 800 were acquired, with the MS detector turned off between 2.0–2.8 min for solvent.

Centrifugation was performed using a Thermo Fisher Durafuge 100 precision centrifuge. UV−vis spectra were obtained on a BioTek Syngery LX multimode reader. Shore hardnesses were measured using a Shore OO or A durometer (Rex Gauge Company, Inc. U.S.) and the values reported are the mean of at least 3 measurements.

Gel Permeation Chromatography was performed on a Waters 1500-series HPLC pump coupled to a Waters 2414 refractive index detector. Calibration was done using polystyrene calibration kit S-M-10 (Lot 85) from Polymer Laboratories; HPLC grade toluene was used as eluent.

Crosslink density was measured using traditional swelling experiments. Since the c parameters for these silicones are not available, we utilized simple swelling measurements that correlate with crosslink density.[37] A sample of each elastomer (150 mg) was weighed into a 20 mL glass vial. Each elastomer was swelled over 72h in 5 mL of toluene which was then removed using filter paper. The mass of the swollen elastomers was measured (swelling wt% of "raw" elastomers). The elastomers were oven dried at 130˚C for 18h and weighed (weight of "extracted" elastomers). A sample of each extracted elastomer (50 mg) was placed into a 20 mL vial with fresh toluene (3 mL) for a second 72 hour extraction. The toluene was removed again using filter paper and the mass of the swollen elastomers was measured (swelling wt% of "extracted" elastomers). The resulting elastomers were then oven dried at 130 °C for 18h and weighed again. The difference in weight after extraction was recorded as the sol fraction (Table S4, Figure S5).

2.5.3 MEKP

Potassium iodide (0.1 g) was weighed into a 125 mL Erlenmeyer flask. A solution of distilled water (68 mL) and sulfuric acid (2 mL) was added to the same flask along with a starch indicator (2 mL, 1 g/100 mL). MEKP (4.5 mL) was pipetted into the solution and swirled. The solution was titrated with a stock solution of sodium thiosulfate (0.01506 M) in distilled water to determine the concentration of I_2 formed.[38] The endpoint showed ~10 mmol radicals generated / mmol of MEKP.

2.5.4 Synthesis of eugenol silicones

A model compound **1** was first synthesized for the purpose of studying the coupling reaction prior to experimentation with silicone polymers (adapted from ref. 19). A hydrosilylation reaction between MM^H (5 g, 33.7mmol) and eugenol (6.09 g, 37.1 mmol, 1.1 equiv.) was performed in a dry 250 mL round-bottomed flask containing a stir bar. Toluene (10-20 mL) along with Karstedt's catalyst (10 μL, 0.02 mmol) was added to the flask, which was then capped with a rubber septum. The reaction proceeded while stirring continuously for 12 h at room temperature. An ^{1}H-NMR of the reaction mixture was taken to confirm complete reaction after which time the platinum catalyst was quenched by adding activated charcoal (300 mg) to the flask and stirring for 12 h. The resulting crude product was filtered through a Celite pad, rinsed with toluene, followed by rotary evaporation to remove solvents. The reaction mixture was purified by centrifugation (5 x 5 min each, 4000 rpm); unreacted eugenol partitioned into a 6:1 mixture of methanol and water to leave the purified eugenol-silicone The methanol/water layer was extracted, and the product was placed under a flow of air to ensure removal of all solvents to give **1** (8.58 g, 82%). The same process was used to modify various silicone copolymers with eugenol using the parameters in Table 1.

Characterization of these starting materials was accomplished through ^{1}H-NMR (Figure S1). Both pendent and telechelic silicones bearing HSi groups were prepared using the same process from starting materials bearing HSi compounds. The conversion of all HSi groups into eugenol derivatives was targeted in these reactions (Table 1). The ^{1}H NMR and ^{13}C NMR spectra of representative pendent **P15-EU** and telechelic **T12-Eu** polymers are shown in Figure S2; these compounds are different from their molar mass analogues simply by the intensity of the Me_2Si peaks.

^{1}H NMR (600 MHz, $CDCl_3$): δ = 6.84 (d, *J* = 8.2 Hz, 1H), 6.68 (s, 1H), 6.67 (s, 1H), 5.53 (s, 1H), 3.88 (s, 3H), 2.56 (t, *J* = 7.7 Hz, 2H), 1.62 (m, 2H), 0.56 (m, 2H), 0.07 (s, 9H), 0.05 (s, 6H)(see Figure 1S).

Table 1. Hydrosilylation of eugenol with HSi-silicones

Silicone starting material	**Silicone g (mmol)**	**Eu eq, g (mmol)** [b]	**T °C**	**Pt µL** [c]	**T mL** [d]	**% Yield (mg)**
MM^H	5 (33.7)	1.1, 6 (37.1)	25	10	0	82 (8.58)
P50	10 (61.6)	1.15, 11.6 (70.9)	60	10	20	84 (17.0)
P30	15 (59.7)	1.1, 10.8(65.6)	25	10	20	80 (19.6)
P15	15 (32.2)	1.3, 6.9 (41.9)	60	10	20	91 (19.1)
T12	5 (4.3)	2.1, 1.43 (8.7)	25	5	10	65 (4.2)
T0	5 (6.9)	2.1, 2.31 (14.1)	25	5	10	67 (4.9)

[a] Eu = Eugenol. [b] ml of Karstedt's catalyst. [c] mL of toluene.

2.5.5 Dimerization of eugenol silicone **1** with BPO

Compound **1** (0.5 g, 1.6 mmol) was weighed into a glass vial (10 mL) along with BPO (1 eq, 0.388 g, 1.6 mmol) dissolved in a minimal amount of toluene. The mixture was stirred with a glass pipette, then capped and placed in a 100 °C oven for 2 h. The vial was uncapped and left in the same oven to allow for evaporation of the solvent. The resulting crystallized benzoic acid by-product was extracted with a 1M solution of sodium bicarbonate and DCM. This process was repeated for 6 other vials with varying equivalents of BPO. A sample of the purified product was characterized by ^{1}H-NMR and GC-MS (Figures S3, S4, Table). The distinctions between product and starting material in ^{1}H NMR were subtle. Mass spectrometry showed that >20% of the dimeric product was produced when 1 equiv. of BPO were used (ESI†).

2.5.6 Synthesis of silicone elastomers through eugenol radical coupling with different initiators

2.5.6.1 BPO

In a glass vial (10 mL), the eugenol-modified silicone copolymer **P50** (0.2 g, 0.612 mmol) was placed along with BPO (0.2 eq, 29.67 mg, 0.124 mmol) in a minimal amount of toluene (225 µL). The mixture was stirred with a glass pipette, then capped and placed in a 100 °C oven for 2 h. The vial was uncapped and left in the oven to allow for the evaporation of the remaining toluene for 1 h. This process was repeated for other vials with different equivalents of BPO (Table S1). Crystals of benzoic acid (as shown by ^{1}H NMR) were found in all the product elastomers. They were allowed to swell in toluene (0.2 g in 5 mL) over 24 h, then washed several times with the same solvent to remove benzoic acid. The elastomers were then completely dried in a 100 °C oven. The crystals remained. An alternative attempt to remove these crystals was performed by increasing the post-cure temperature to 200 °C to evaporate the remaining solvent and to decompose benzoic acid to benzene and CO_2. This too failed as did other protocols, including aqueous solutions.

2.5.6.2 Phenolic coupling

Survey experiments were done to ascertain the temperature at which MEKP would initiate crosslinking. No change was observed after 24 h at 60 °C. Gradually increasing the temperature led to cure only starting at 100 °C. In a 10 mL glass vial, **P50-Eu** (0.8 g, 2.43 mmol) was added with MEKP (40.4 µL, 0.20 mmol, ~0.8 equiv.). The mixture was stirred and then cured by capping the vial (and duplicates) and heating at 130 °C for 72 h. The vials were uncapped and left in the oven to allow evaporation of by-products. The resulting elastomers were removed from their glass vials. This process was repeated with a larger quantity of MEKP (1.7 eq, 80.9 µL, 0.41 mmol). The cure was less effective than with DTBP (see next section) and the hoped for benefit of lower temperature cure was not realized.

Table 2. Shore hardness of ***P50-Eu-E*** *elastomers made with MEKP.*

Equiv. MEKP	Shore OO
0.8	45
1.7	53

2.5.6.3 DTBP: establishing complete conversion times

P30-Eu (0.4g, 0.98 mmol) was weighed into a 2 mL glass vial along with DTBP (180 µL, 0.98 mmol, 1 equiv and stirred with a glass pipette. Multiple vials were prepared in this manner. The vials were allowed to cure at 130 ˚C and a vial was removed from heat to room temperature every two hours for 48 h. Elastomers were removed from their vials to obtain Shore hardness and crosslink density data of **P30-Eu-E** (Figure 19A, Table S4, Figure S5).

2.5.6.4 DTBP: preparation of elastomers

Having determined crosslinking times at 130 °C using **P30-Eu**, the elastomers were also prepared from **P15-Eu** (0.8 g, 1.333 mmol) and DTBP (48.97 µL, 0.267 mmol, 0.2 equiv.) into the vial.

This step was repeated for varying equivalents of DTBP as well as with **P30-Eu** and **P50-Eu** (Figure 19B). The mixture was stirred with a glass pipette and the vial was capped before placing at 130 ˚C for 48 h. The vials were then uncapped and left at 130 ˚C for another 2 h to ensure evaporation of the tert-butanol byproduct. The resulting elastomers were removed from the glass vial then mechanical properties such as hardness (Shore OO), crosslink density, and antioxidant activity were gathered (Table S7, Figure S6). Note: if the prepared samples were not heated, no changes were observed over a week at room temperature.

2.5.7 Chain extension of telechelic through radical coupling of eugenol

The chain extension of **T0-Eu** was induced by adding varying equivalents of either BPO or DTBP as radical initiators. Eugenol-modified **T0-Eu** (0.4 g, 0.86 mmol) was weighed into a 10mL glass vial equipped with a stir bar. DTBP (159 µL, 0.86 mmol, 1 equiv.) was added to the same vial and capped before placing it in an oil bath at 130 ˚C for 12 h. The vial was then uncapped and left to stir for another 2 h before removing from heat to obtain GPC and antioxidant data. The same process was to perform a systematic study with increasing peroxide levels and BPO as initiator; **T12-Eu** was subjected to the same experiments (Figure 19D, Tables S2).

2.5.8 DPPH assays

Both eugenol-silicone oils were characterized for antioxidant activity. A stock solution of DPPH (0.2 mM in IPA) was prepared and stored at 3 ˚C before use (Figure S6). Then, eugenol-modified polymer solutions were prepared as 80 mM stock solutions (with the exception of **5T**, which was prepared as a 40 mM stock solution) and then serially diluted to give solutions of 60, 40, 20, 4, 0.4 mM, 40, 4, 0.4 µM concentrations, respectively (with the exception of **5T**, was diluted into 30, 20, 10, 2, 0.2 mM, 20, 2, 0.2 µM) in a total volume of 1 mL with IPA in 2 mL centrifuge tubes. Each solution (0.5 mL) was transferred to another 2 mL centrifuge tube to which was added DPPH (0.5

mL, 0.2 mM, to give a total volume of 1 mL). The solutions were vortexed and placed in the dark for 15 min to react. The resulting solution (200 μL) was added into a well in a 96 well plate in triplicate. DPPH solution was used as a control (0.1 mM), also in triplicate. Scans were taken for each well at 520 nm from the plate reader and the results were recorded (Figure S6).

2.5.9 Collecting antioxidant data using DPPH tests

A stock solution of DPPH (2 mM) in IPA was prepared for all assays beforehand and. The stock solution was diluted to 0.2 mM just before use. Each eugenol-modified silicone copolymer oil was diluted based on the relative concentration of eugenol on each polymer chain (Figure S6) and each serial dilution was pipetted (100 µL) into a separate well in a 96 well-plate. Chain extended materials are prepared from **T0-Eu** as well as **T12-Eu** and diluted as shown in (Figure S6). For cured silicone elastomers **P15-Eu-E**, **P30-Eu-E** and **P50-Eu-E**, each elastomer was weighed (50 mg) and placed into a 12-well plate. The diluted stock solution (0.2 mM) was pipetted (1000 µL) into each of these wells and left to react for 30 min in the dark. UV-vis data (at 520 nm) was then collected and concentration was established by comparison with the calibration curve.

2.6 Conclusions

Biomimetic chemistry can be effectively applied to create eugenol-modified, chain extended silicone oils or silicone elastomer materials with tuneable mechanical properties and antioxidant activity. The curing of the elastomers was possible through the radical phenolic coupling of eugenol functionalities using organic peroxides, similar to phenolic coupling processes commonly employed by nature. In addition to the biomimicry of the curing process, the materials possess new functionality compared to traditional silicones and, by virtue of dilution by eugenol, better fit with the principles of Green Chemistry.

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3 Sugar boronic ester silicones

3.1 Abstract

Boronic acids can undergo boronic ester formation with 1,2- and 1,3- diols. They have a particular affinity for various sugars including glucose. Telechelic silicones were modified with boronic acid through hydrosilylation while gluconamidosilicones were prepared through a simple click reaction between gluconolactone and telechelic/pendent aminosilicones. These two silicones were combined to form translucent, colour elastomers that possessed a range of viscoelastic properties. Their robustness could be manipulated by adjusting the degree of glucose modification on the silicone, switching between telechelic and pendent silicones, and introducing a dative B-N bond to stabilize the boronic ester bond.

3.2 Introduction

3.2.1 Boronic acid

Boronic acids are one of several existing classes of organoboron compounds. They are characterized by a boron center bound to an alkyl or aryl chain and two hydroxyl groups (Figure 3-1); they alkylated versions of boric acid, $B(OH)_3$. Boronic acids are synthetic compounds, but they are known to degrade through oxidation and subsequent hydrolysis processes to form boric acid, a compound found readily in nature.[1,2] On top of their relatively low impact on the environment, boronic acids are also known for their binding abilities, such as the hydrogen bonding between the B-OH groups which can result in the formation of dimerization or the formation of boroxine species through dehydration processes (Figure 3-1a,b).[3] Boronic acids also possess an empty *p* orbital and are, therefore, Lewis acids; they can form dative bonds with Lewis bases like amines. However, one of the most interesting interactions that boronic acids participate in is the dynamic covalent bonds they form with 1,2 or 1,3- diol species to produce boronic esters (Figure 3-1c).

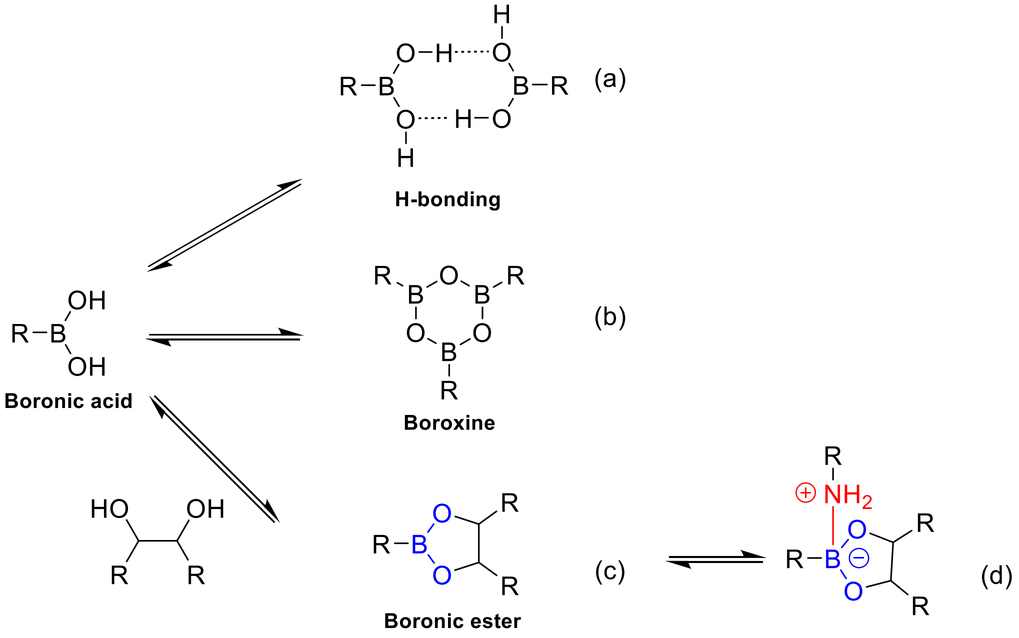

Figure 3-1 - Boronic acid interactions forming a) hydrogen bonded dimers, b) boroxine structures, and c) dynamic boronic esters with 1,2-diols. C) The equilibrium between boronic acid, boronic ester, and tetracoordinate dative bonded boronic ester.

3.2.2 Boronic esters

Boronic ester linkages between boronic acids and 1,2 or 1,3- diol groups arise from a condensation reaction that exists in dynamic equilibrium between free and bound boronic acids (Figure 3-1c). This strong but reversible interaction is affected by numerous factors including, but not limited to, the *pKa* of the boronic acid, the structure of the diol reagent, and the presence of water which all influence the equilibrium constant between bound and unbound boronic acids.[3,4]

The pH of the reaction solution will affect the behaviour of the boronic acid depending on its unique *pKa*. The *pKa* is the pH at which bound and unbound boronic acid exist at a 1:1 ratio. Tetracoordinate boronates tend to form more stable ester bonds – this means that boronic acids will preferably form boronic ester bonds above the pH of their p*Ka*. The structure of the diol is important to consider as well – boronic acids preferably bind to cis-diols when compared to their trans-diol analogues.[2] This is a result of the orientation of the hydroxyl groups, they must be on the same plane to effectively bind and form a boronic ester. For example, boronic acids typically have higher binding affinities to fructose in comparison to glucose due to the orientation of their hydroxyl groups.[5,6] Sugars exist in many conformations (β-D-fructofuranose) in solution and fructose exists in a conformation that contains a pair of syn-periplanar hydroxyl groups at a higher percentage than glucose (α-D-glucofuranose).[5] Another factor that influences the equilibrium is the formation of water in boronic ester synthesis. Water must be removed to successfully form boronic esters, to push the equilibrium to product. An anhydrous environment is ideal for this and may be achieved using molecular sieves or a continuous distillation of water as it forms. Introducing dative bonds like a B-N bond to the boronic ester pushes the equilibrium further right through the formation of a tetracoordinate boron atom which, as mentioned previously, is thought to increase stability (Figure 3-2d).

The ability to exploit this interaction – to influence the equilibrium between a free boronic acid and its ester – has allowed researchers to create interesting materials with the ability to self-heal and sense changes in their surroundings.[7,8] One of the most famously researched applications for boronic acids is their different binding affinities to sugars. A particularly useful application for this interaction has been extensively explored in the medical field for developing glucose sensors that help monitor conditions like type I and II diabetes.[9]

3.2.3 Silicone rubber

Silicone materials are incredibly versatile and are a part of everyday life. They are chemically and thermally stable, permeable to oxygen, flexible, and they are hydrophobic.[10] Although useful, silicone elastomers are not known to be the most sustainable material due to their high energy synthesis, the consumption of endangered metal catalysts, and their lack of an easy end-of-life pathway to benign materials in the environment. However, it is difficult to find replacements for silicone because of the unique properties that siloxane (Si-O) bonds provide to the material. Instead of replacing these materials entirely, their sustainability can be improved by incorporating crosslinks that would allow for reprocessing or degradation at their end of life. Creating silicone materials that are crosslinked using dynamic bonds, for example, would allow for easier reprocessing and multiple uses before the end of life, which would increase their sustainability.

It has been shown that materials containing boronic esters may be formed and broken under external stimuli, such as the introduction of different sugars or simple physical force which may facilitate ways to reprocess/reshape silicone materials.[11] Boronic ester linkages also allow for the potential to reverse the crosslinks by manipulating the equilibrium and to obtain back the linear starting materials that have a better chance of degrading in nature, as we know silicone oils can degrade back into sand and carbon dioxide. Additionally, both the boronic acid and glucose residues are relatively non-toxic to the environment as glucose is a requirement of many metabolic processes and boronic acid is often degraded back to boric acid, which already exists in nature.[12]

3.2.4 Viscoelasticity

Materials are often described as ‘solids’ or ‘liquids’, but a material possessing the properties of either one or the other is rare. Most materials fall under the umbrella term ‘viscoelastic’ which means that it exhibits both viscous (liquid) and elastic (solid) behaviour.[13] Examples include objects like memory foam, gel shoe insoles, or Silly Putty™. These types of materials can be useful for comfort – they can contort to the shape of your body, they can offer protection in the form of energy dissipation, or they can simply be fun to play with. Viscoelastic materials are also known to be more durable for their ability to both flow and resist deformation, allowing for materials to have a longer life span typically.[14]

3.2.5 Objective

The motivation behind this work is to explore facile and sustainable ways to create silicone materials that avoid the limitations of traditional curing methods which require precious metal catalysts. Given the versatility of materials that can be made with boronic esters, they were a top research candidate; we drew inspiration from the extensively researched interactions between boronic acids and sugar. It is hypothesized that gluconamidosilicone (glucose-modified aminosilicones) could be combined with boronic acid-modified silicone to make new materials linked through boronate esters. Such materials should be dynamically crosslinked silicone material with tuneable viscoelastic properties through boronic ester linkages. The boronic ester linkages could, in principle, be further modified by adding in dative B-N bonds to stabilize the linkage and push the equilibrium towards to product. The following research reports the mechanical and rheological properties of elastomers prepared using these constituents.

Results

3.2.6 Library of dynamically bonded silicone materials

A library of silicone materials glucose-modified aminosilicones both telechelic **GATx** and pendent **GAPy** (gluconamidosilicones) of various molecular weights were fabricated using polymers with different percentages of amines and reacted with gluconolactone to achieve 100% functionality of the active groups (Figure 3-2). These were combined, in different ratios with telechelic boronic acid silicone (**BA77** chain length 77 units) to give translucent, colourless silicones, named by their constituents, (Figure S15). that possessed a range of viscoelastic properties. Different amounts of each glucose silicone were ‘dialed in’ to **BA77** to observe both the effects of switching between telechelic and pendent polymers as well as the effect of net glucose concentration in the material.

There were obvious differences between sets of materials made from telechelic gluconamidosilicones **GATx** compared to their pendent counterparts **GAPy**. For instance, the telechelic sets appeared initially to be elastomer-like materials but would be observed to flow at room temperature over the period of several days and these materials were also soluble in isopropanol, analogous in behaviour to Silly Putty. On the other hand, materials made from pendent glucose silicones resisted flow at room temperature and were insoluble in isopropanol. When applying heat (heat gun), the telechelic materials began flowing at a more accelerated speed and while the pendent materials softened, they remained resistant to flow (Figure 3-3). In fact, the glucose residues oxidized and browned from the extensively high temperatures without exhibiting flow. These results speak to the observable nature of the boronic ester materials.

Control experiments were also conducted to confirm the change in physical properties with the introduction of boronic esters. Telechelic aminosilicones **GATx** (x = 8, 64, 334) were added to **BA77** by itself and no formation of elastomers was observed, the materials simply became more viscous fluids. Similarly, the aminosilicones **GATx** (x = 8, 64, 334) were also added to gluconamidosilicones without any boronic acid and similarly, no elastomers were formed – the formulations became less viscous.

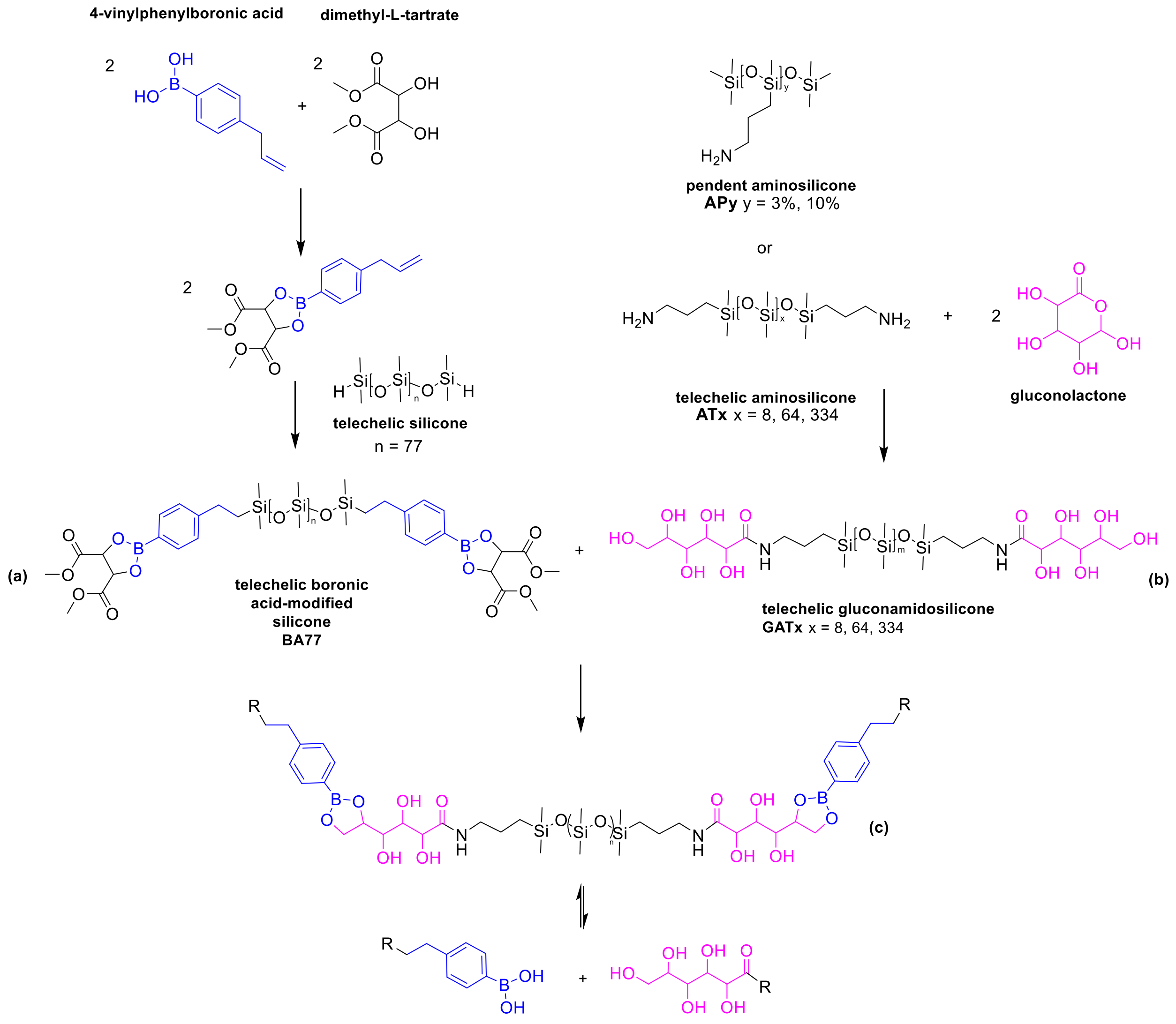

Figure 3-2 – The synthesis of a) a tartrate-protected boronic acid-modified silicone and b) telechelic glucose-modified aminosilicones (gluconamidosilicone). C) The combination of gluconamidosilicone and boronic acid-modified silicone to create silicones linked through dynamic boronic ester bonds.

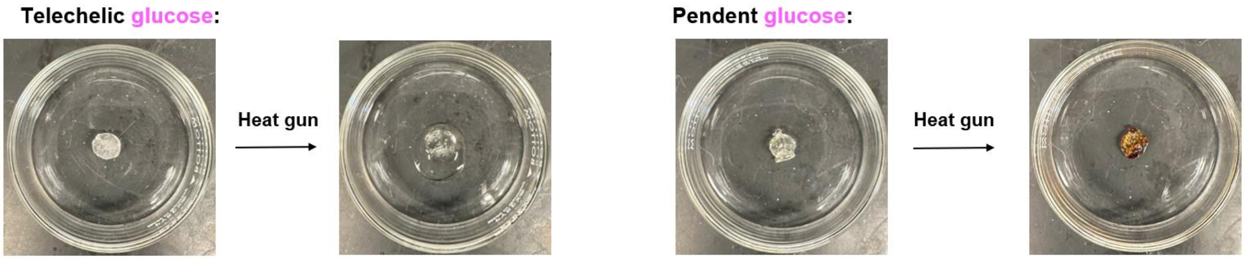

*Figure 3-3 - Flow of telechelic **GAT64-BA77** versus pendent **GAP3-BA77** materials under applied heat using a heat gun.*

3.2.7 Young's Modulus

Young's Modulus (YM, mPa), a measure of a material's elasticity, was obtained as a function of the glucose-to-boronic acid ratio for materials formulated with different glucose-modified silicones. Various loadings of each gluconamidosilicone **GATx** (0.25-1.5 eq.) were mixed in with **BA77 (**1 eq) based on the molar amounts of their active groups. A table was created from the collected YM data as a function of the various loadings of **GATx/GAPy** (Table 3-1). For the pendent gluconamidosilicones **GAPy**, the viscosity of the starting materials even with heat was significantly higher than the telechelic materials so lower loadings were used (0.125-0.75 eq). A general trend observed through the graphs of all sets of materials is that there is a peak (maximum) in YM as the loadings increase, but a decrease from there as glucose loadings continue to increase. This maximum occurs at different loadings for materials made with different aminosilicone starting materials. For instance, materials made with **GAT8**displayed a peak in YM at a 0.75 eq loading whereas the peak appears at a loading of 0.5 eq for the longer silicone **GAT64** materials. For both pendent materials made, the peak shows up around a loading of 1 eq (Figure S16 A→D).

As aminosilicones **A8** and **A64** were added to the boronic ester material **GAT64-BA77** and **GAT8-BA77**, there was an initial decrease of the YM in all samples compared to the samples without the aminosilicones. However, as more gluconamidosilicone was dialed in, the YM would trend upwards (Table 3-1). No maximum of the YM was observed with these sets of materials (Figure S16 E→F). Although interesting, many of the materials could flow under the Mach-1 which may impact the data collection. Additionally, YM is a great way to represent the elasticity or stiffness but due to the viscous nature of these materials – possessing viscoelastic properties, an alternate method was sought to encompass the loss moduli as well.

Table 3-1 - Young's Modulus data from telechelic and pendent boronic ester materials.

YM (MPa)								
Eq glucose to BA	**GAT334-BA77**	**GAT64-BA77**	**GAT8-BA77**	**GAT64-BA77 (0.5) AT8**	**GAT8-BA77 (0.5) AT8**	**Eq glucose to BA**	**GAP3-BA77**	**GAP10-BA77**
0.25	-	0.13	0.18	0.005	0.04	**0.125**	0.067	-
0.5	-	0.33	0.22	0.024	0.08	**0.25**	0.016	0.01
0.75	-	0.24	0.31	0.021	0.11	**0.375**	0.13	0.03
1	-	0.15	0.23	0.041	0.10	**0.5**	0.18	0.13
1.5	-	0.07	0.26	0.045	0.24	**0.75**	0.17	0.01

3.2.8 Rheology

Rheological tests were undertaken to allow for observation of both the elastic and viscous behaviour of the materials. Frequency sweeps of all boronic ester materials, telechelic **GATx-BA77** and pendent **GAPy-BA77**, were taken to compare the viscoelastic properties of materials containing various gluconamidosilicone loadings. The crossover points of the graphs were analyzed to determine the solid or liquid character that the materials present – this is the angular frequency (ω, rad/s) where the storage and loss modulus meet. The relaxation time ($\tau = 1/\omega$) was calculated using the crossover point. Materials that behaved more like solids would have a higher relaxation time and the opposite is true for a material that possessed more liquid character (Figure S17). In analogy to the YM results, the sample set made with **GAT8** displayed a peak in maximum solidity (when the relaxation time reached a maximum) before a dip as more gluconamidosilicone was added (Table 3-2). However, this was untrue for samples made with the higher molar mass **GAT64**, in which a minimum in solidity was observed (relaxation time reached a minimum) before increasing. Crossover points of the materials made with pendent gluconamidosilicones **GAP3** were absent, as the storage modulus was observed to be greater than the loss modulus at all ω, thus it was not possible to calculate the relaxation time. However, this also indicates that materials made with pendent polymers will display more robustness and solidity.

*Table 3-2 - Crossover point and relaxation time of telechelic boronic ester materials. N/A = no observable crossover point – material either consistently higher loss modulus (**GAT334-BA77 0.1**) or consistently higher storage modulus (**GAT8-BA77**).*

	GAT334-BA77		**GAT64-BA77**		**GAT8-BA77**	
eq GATx	ω (rad/s) at crossover	relaxation time (s)	ω (rad/s) at crossover	relaxation time (s)	ω (rad/s) at crossover	relaxation time (s)
0.1	N/A	N/A	-	-	-	-
0.25	-	-	0.23	4.5	0.31	3.2
0.5	19.0	0.05	0.33	3.0	N/A	N/A
0.75	-	-	0.90	1.1	0.28	3.6
1	0.1	11.0	3.3	0.3	0.23	4.4
1.5	1.0	1.0	0.13	7.7	8.85	0.1

Comparing rheological tests within sample sets (made with the same gluconamidosilicone) yielded various trends that became clearer by comparing between sets of materials made with different gluconamidosilicones. For instance, a telechelic gluconamidosilicone (**GAT64** not accompanied by boronic esters) had a moduli crossover point at around 5.25 rad/s (Figure 3-4a). By adding in the boronic acid silicone (**BA77**) at a 2:1 ratio between the boronic acid to glucose residues, an immediate shift of the crossover point to 0.33 rad/s was observed, which is indicative of a material with more solid-like behaviour (Figure 3-4b). An analogous pendent gluconamidosilicone to a pendent silicone (**GAP3**) at the same BA: glucose ratio resulted in a disappearance of the crossover point (Figure 3-4c), so it is important to look at the trends of the storage and loss modulus, as well as the phase angle. The phase angle dictates how much the storage and loss moduli contribute to a material's behaviour and it fluctuates from 0° to 90° for viscoelastic materials. A phase angle closer to 90° indicates more viscous contributions to the viscoelastic behaviour while an angle closer to 0° indicates more elastic contributions. For the pendent boronic ester material made with **GAP3** measured from low to high ω, the storage modulus was consistently higher than the loss modulus signifying that the material possesses a higher solid-like character. Both moduli also increase as the ω increases, but looking at the phase angle clarifies its behaviour. At low frequencies, the phase angle is 28° but at high frequencies, the phase angle decreases to 9°. This indicates that the material already behaves with more solid-like properties but displays even lower viscous contributions as the angular frequency increases. By subsequently changing the gluconamidosilicone for another pendent silicone polymer (**GAP10**) that possesses a higher degree of glucose functionalization still at a 2:1 boronate to sugar ratio, a similar trend was observed where storage modulus is consistently higher than the lost modulus except in this case, the phase angle at low frequencies is 18° and it decreases to 3° at high frequencies (Figure 3-4D). This is all indication that the materials are exhibiting more solid/gel-like behaviour in comparison to the **GAP3-BA77** materials.

3.2.8.1 Adding in a dative B-N bond

To observe the effects of dative bonds on boronic esters and how they influence their viscoelastic properties, a small diamino siloxane molecule 1,3-bis-(3-aminopropyl)trimethoxysilane (**APTMS**) was added to telechelic boronic ester material **BA77** and analyzed using the rheometer. This resulted in the shift from a crossover point at 0.33 rad/s to no crossover point (Figure 3-4b vs e). The addition of the amine to the boronic ester produced a similar effect on the rheological results as switching from a telechelic to gluconamidosilicone (**GAT64-BA77** to **GAP3-BA77**) to a pendent which introduces crosslinks into the system (

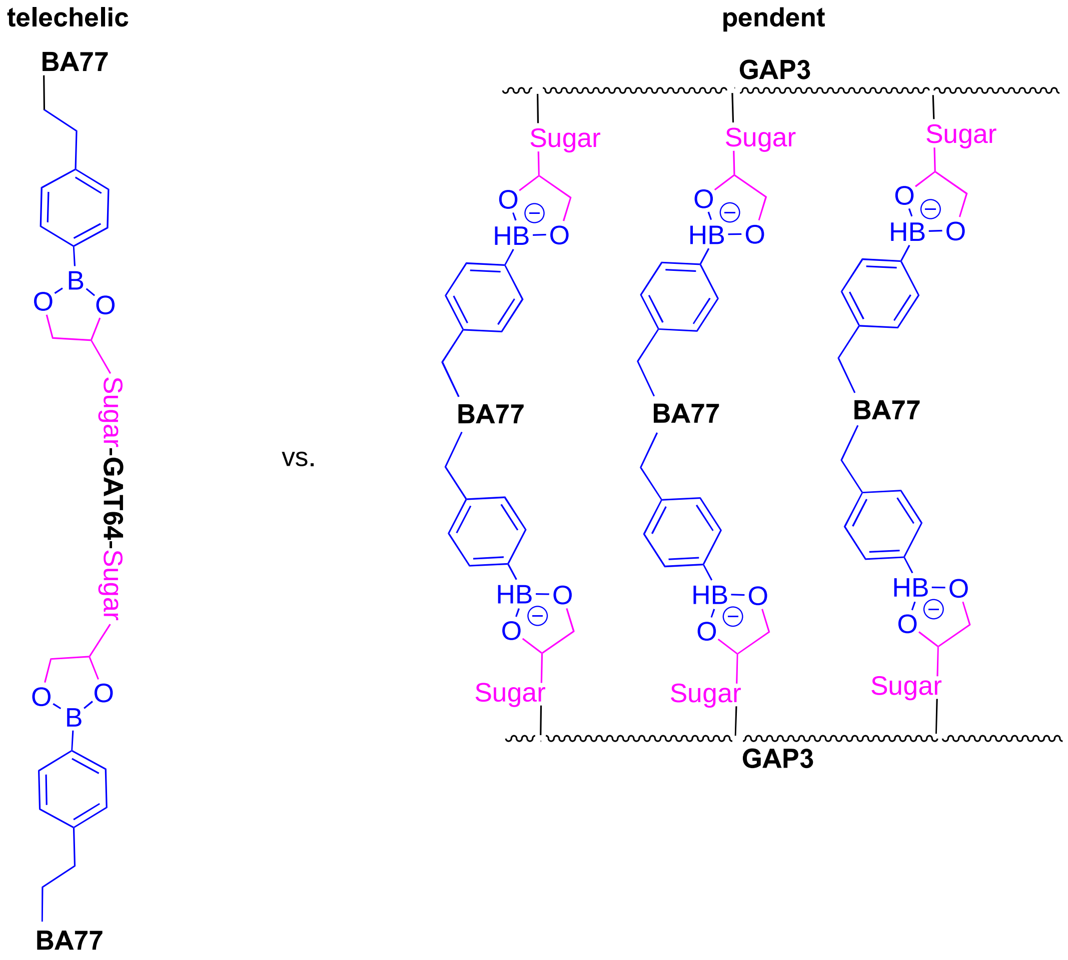
telechelic
BA77
O B O
Sugar-GAT64-Sugar
BA77
vs.
pendent
GAP3
Sugar
HB−O
BA77
Sugar
GAP3

Figure 3-5).

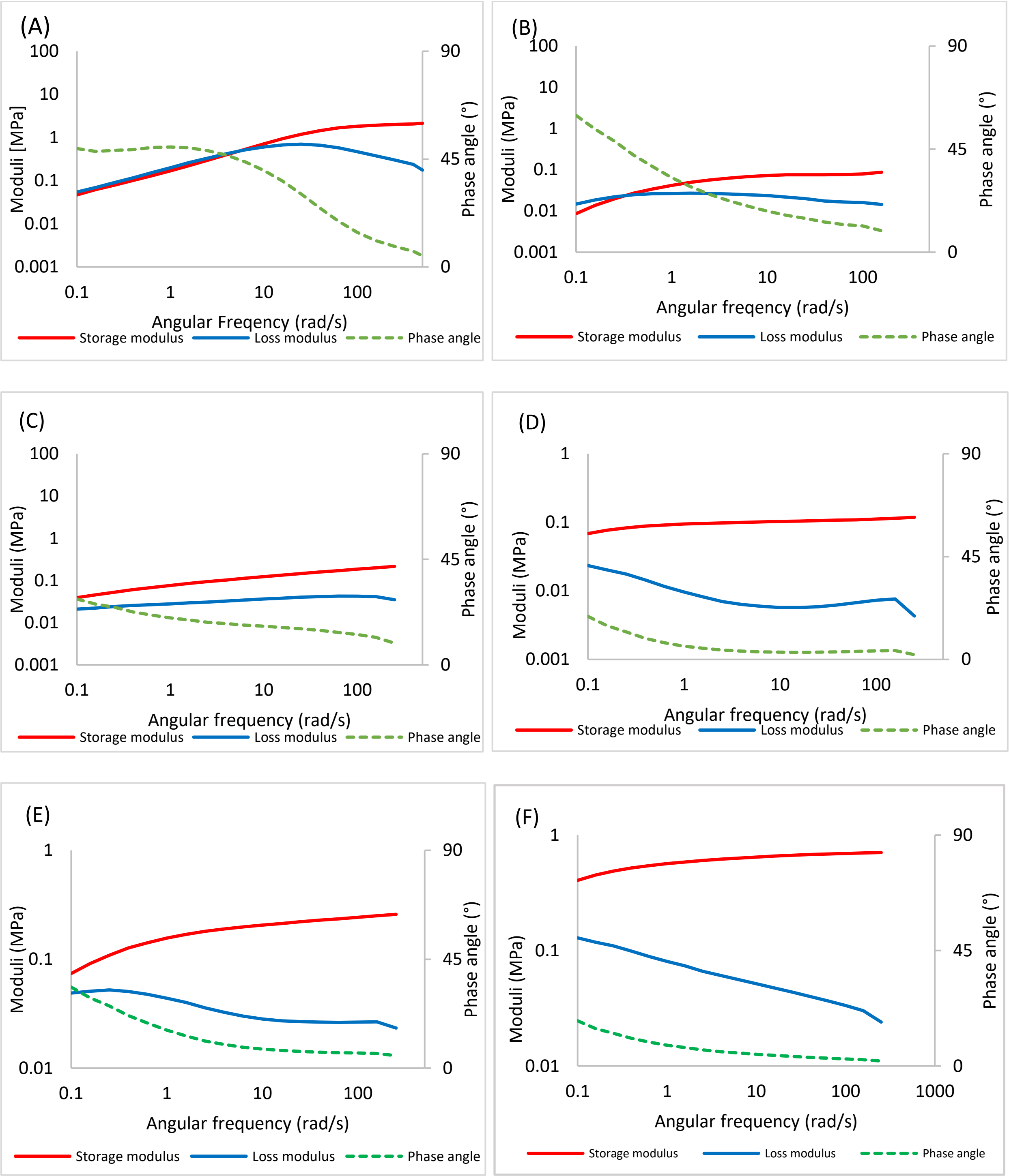

*Figure 3-4 - Rheological moduli and phase angle of a) telechelic **GAT64** with no boronic ester, b) telechelic **GAT64-BA77**, c) **GA3-BA77**, and d) pendent **GAP10-BA77**. E) Rheological moduli and phase angle of **GAT64-BA77** combined with the small amino siloxane crosslinker **APTMS** (*

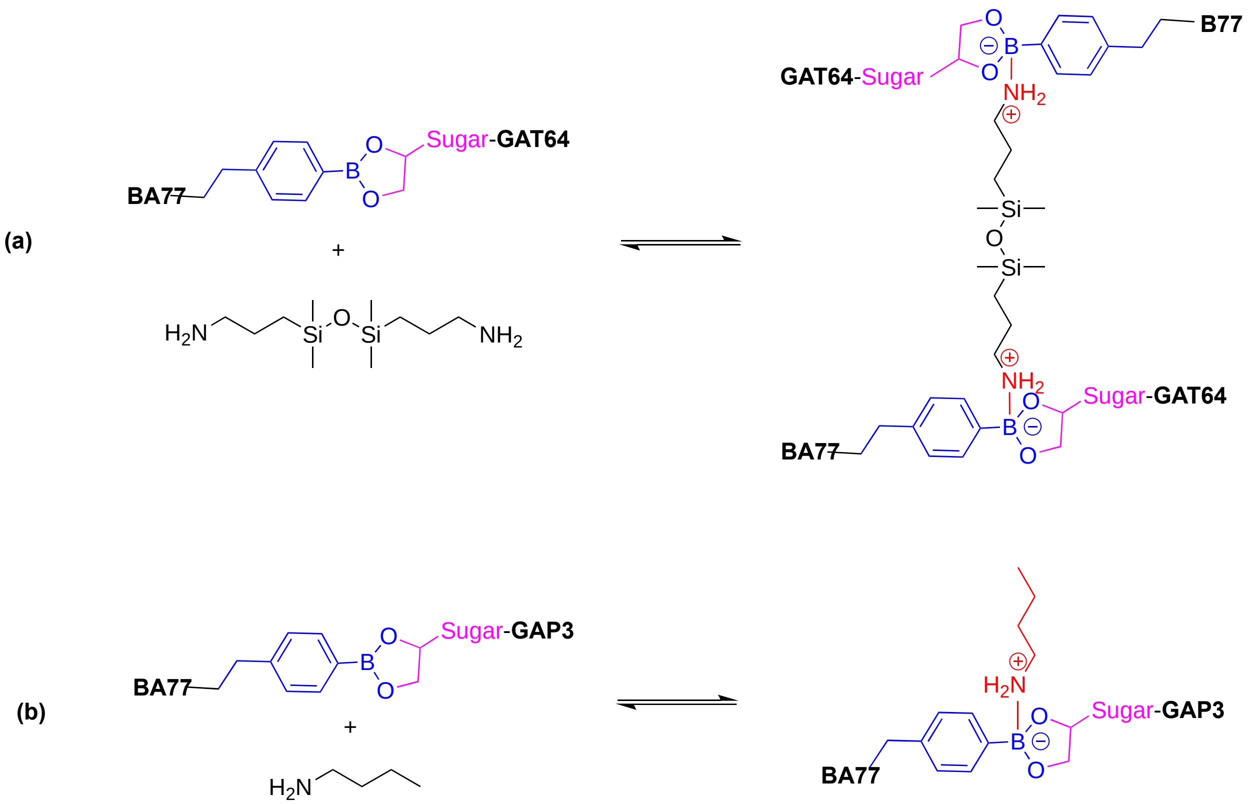

Figure 3-6). F) Rheological moduli and phase angle of ***GAP3-BA77*** *with butylamine dative bond.*

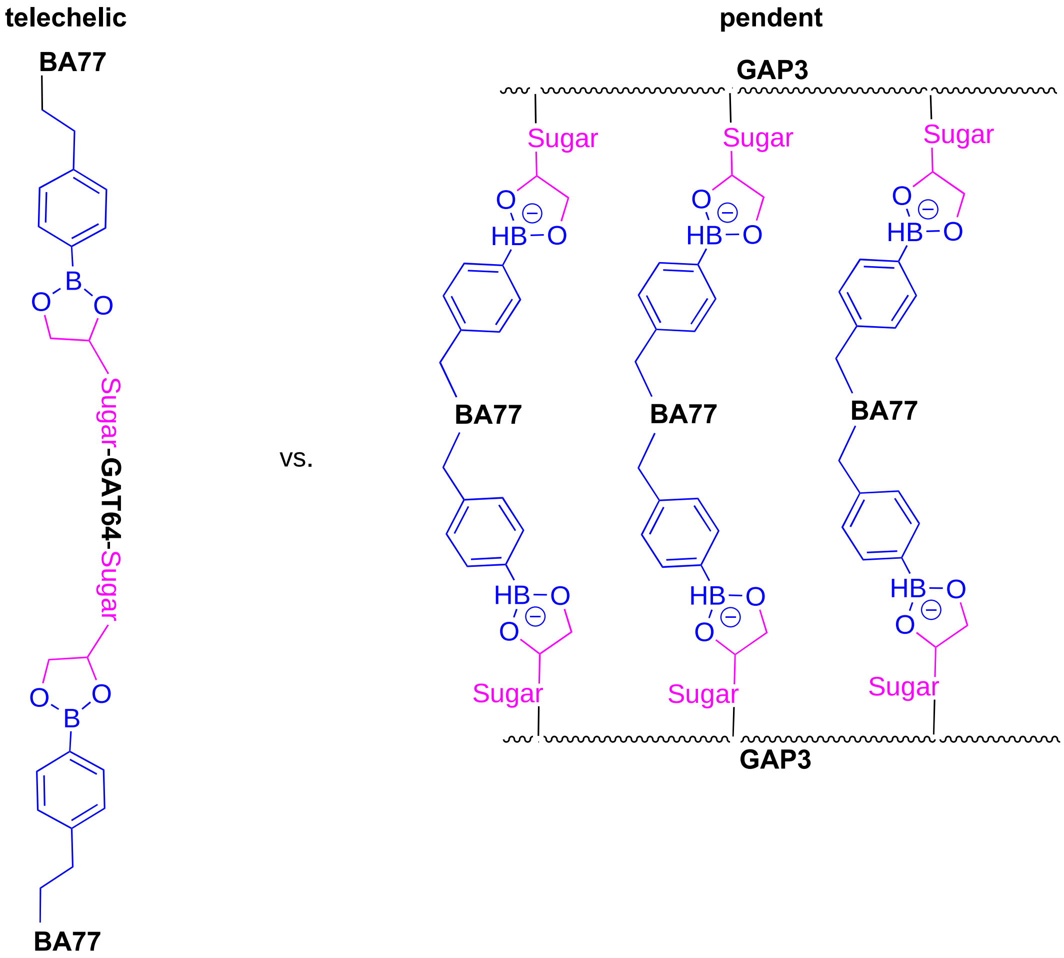

Figure 3-5 - Telechelic vs. pendent boronic ester materials.

In the case of **APTMS**, it can act like a crosslinker so it was unclear whether this behaviour was due to the dative bond per se, or the introduction of crosslinks to the telechelic material (

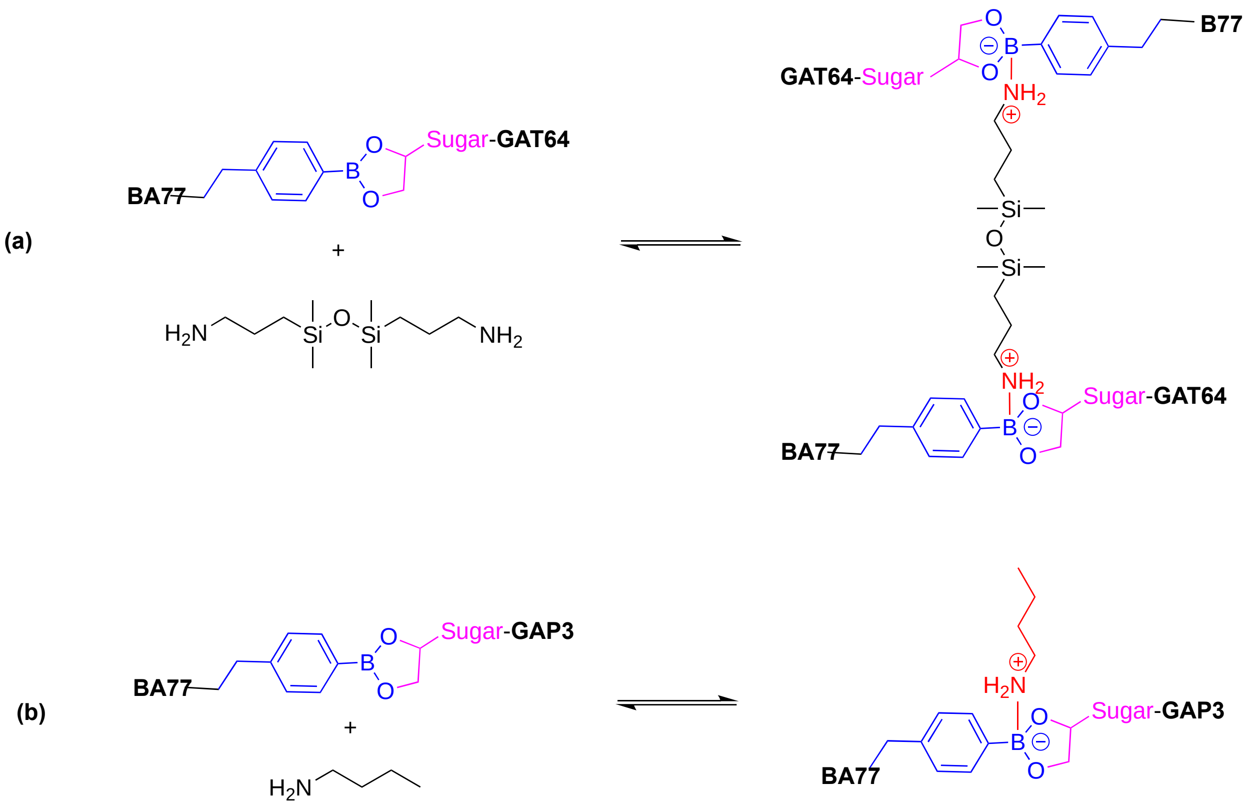

Figure 3-6a), so a secondary experiment was done using monofunctional butylamine that cannot act as a crosslinker.

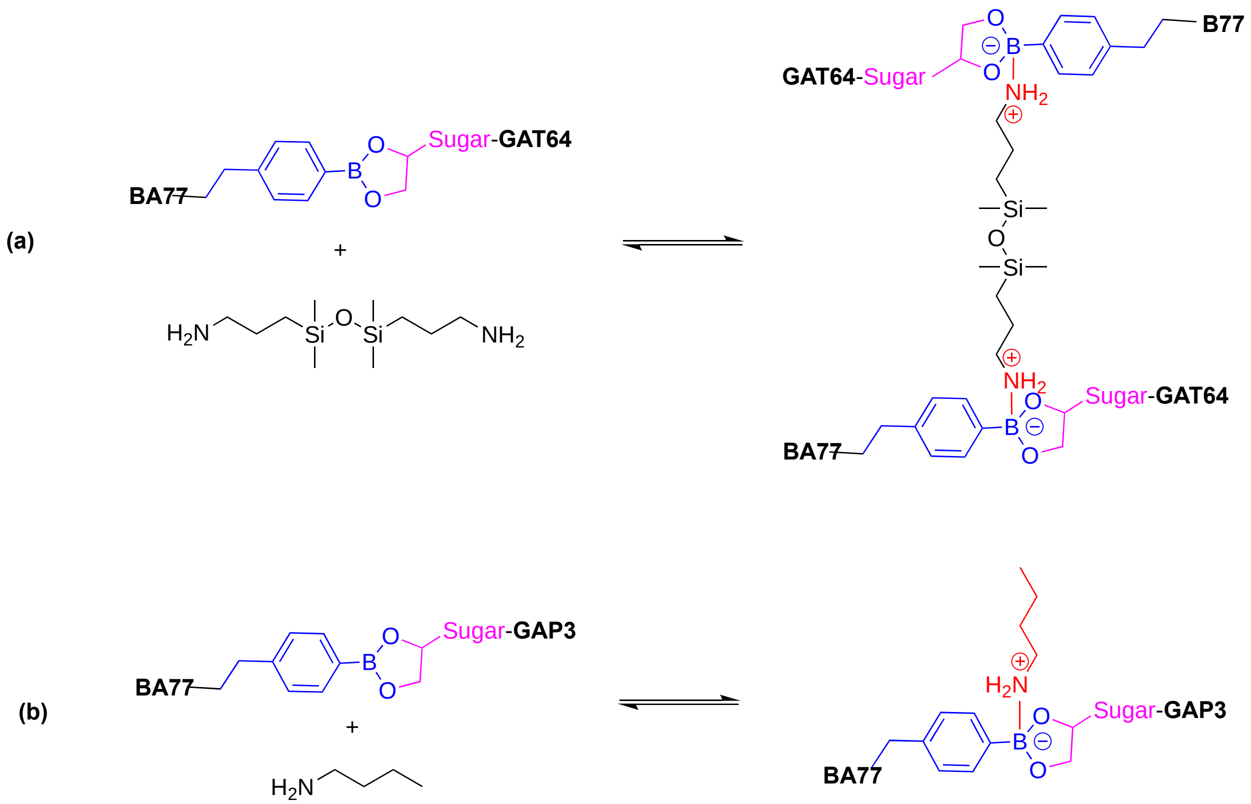

Figure 3-6 - Using a) 1,3-bis(3-aminopropyl)tetramethyldisiloxane to introduce dative bonds and crosslinks to boronic ester materials versus b) using butyl amine to introduce only dative bonds to the boronic ester materials.

When excess butylamine was added to the already combined boronic ester material, e.g., **GAT64-BA77** and **GAP3-BA77** (2:1 boronic acid: glucose), the telechelic and pendent samples were solubilized after several hours (~1-4 h). After evaporation of the amine, the elastomers reformed, and then rheological tests were taken of the pendent sample **GAP3-BA77**. The storage modulus increased significantly (0.4 MPa) when compared to the pendent materials that did not possess a dative bond (0.04 MPa) even at low angular frequencies and they remained relatively consistent up to 500 rad/s (Figure 3-4F). The loss modulus also increased compared to the sample without butylamine but was shown to decrease (from 0.13 to 0.03 MPa) as the angular frequency increased, whereas the storage modulus was observed to increase. The phase angle also started lower compared to the sample 18°, instead of 28° without the butylamine, and decreased to 2° at high angular frequencies. The graph generated by this dative bond-stabilized boronic ester displayed a more solid-like character which clarified the role of the B-N bond (Figure 3-4c vs f).

3.3 Discussion

3.3.1 Dynamically bonded viscoelastic silicone materials

The materials made from gluconamidosilicones and silicone boronic acids ranged from highly viscous liquids to rubbery materials that were robust and could hold their shape. Materials fabricated with telechelic silicones flow slowly at room temperature – the higher the molecular weight of the gluconamidosilicone used, the less viscous was the material. For instance, boronic ester materials made with **BA77** and all telechelic gluconamidosilicones, respectively, exhibited flow to some degree, which was increased with increasing temperature; in general, materials made with **GAT334** (25358 g mol^{-1}) are viscous liquids that resemble molasses, while those made with **GAT64** (5358 g mol^{-1}) resemble soft elastomers and those made with **GAT8** (1258 mol^{-1}) are similar to harder, rubbery material. Increases in the molar mass of the telechelic gluconamidosilicone dilute out the boronic acid/sugar ester bonds with silicone leading to softer and more liquid-like materials.

The effect of dilution on the boronic ester bonds was also reflected in the pendent materials, but due to the nature of the bonds (i.e., forming crosslinks rather than chain extension), the materials were rather robust with much higher YM (they were harder, see next section) than the telechelic analogues. The differences between materials made with two different pendent gluconamidosilicones with different degrees of glucose functionalization (i.e. **GAP3**– 1363 g mol^{-1}, 2-4% glucose to siloxane units, **GAP10**– 4385 g mol^{-1}, 9-11% glucose to siloxane units) were much less obvious than their telechelic counterparts and will need to be more thoroughly analyzed using rheology. Their resistance to flow under ambient and elevated temperatures can be attributed to their crosslinks. However, these are still dynamic bonds that can break and reform and, while the materials are not perfect thermosets, they soften with heating.

3.3.2 Young’s Modulus

Collecting YM data only represents the materials’ elastic behaviour and some of the materials were not ideal for the instrument (i.e. the surface was textured) so this is not the most optimal way to represent and encompass the entirety of their behaviour. However, the data collected can show general elasticity trends within sample sets. There is a consistent trend in all boronic ester materials (**GAT334-BA77, GAT64-BA77, GAP3-BA77, GAP10-BA77**) which the YM peaks at around a loading of 0.5 eq. of glucose residues in relation to the boronic acids with the exception of materials made with **GAT8** that displayed a peak at a 0.75 eq. loading. This result suggests that the optimal ratio for boronic ester binding occurs when there are half as many glucose residues present as boronic acids (i.e., 2 boronic acids/sugar units). The reason for this is that YM is also proportional to the hardness of the materials which in turn directly correlates to the crosslink density and chain extension – the more crosslinks there are, the harder the material is typically, and the more chain extended, the more viscous a material is. Below optimal loading, it is intuitive why lower YM values are observed; the crosslinking density is not sufficiently high because there are not enough residues to form boronic ester bonds, resulting in softer materials. However, once the 0.5 eq loading is surpassed, the maximum number of boronic ester bonds has been achieved and additional gluconamidosilicone acts as a plasticizer, effectively diluting the crosslinks and softening the material.

It was initially puzzling that the hardness peaked at this loading – theoretically, assuming all the functional groups reacted, there should still be 50% unbound boronic acid residues in the optimally crosslinked material. However, along with boronic ester linkages, there are hydroxyl groups that can participate in hydrogen bonding and that can form transient networks with themselves.[15] It is possible that above the 0.5 eq loading, the amount of hydroxyl groups introduced through the gluconamidosilicone allows for the formation of enough transient linkages that make it harder for the boronic ester to form, for example, for steric reasons. It is also possible that the introduction of the gluconamidosilicone is effectively diluting the boronic ester bonds (there is more silicone content than boronic ester linkages). Hydrogen bonds are weaker than covalent bonds and the introduction of more non-covalent bonds may be contributing to the crosslink density of the materials. Again, the YM does not give a full picture of the materials' behaviour so it cannot be used to make conclusive statements about the materials.

3.3.3 Rheology

The crossover point data and relaxation times illuminated the differences between sets of materials. In general, boronic ester materials displayed more solid-like properties than the hydrogen bonded gluconamidosilicone on its own. The chain extended telechelic boronic ester materials (**GAT334-BA77, GAT64-BA77**) behave more like a highly viscous liquid at low angular frequencies but solidify at higher frequencies. This is a characteristic of shear thickening materials that act as solids under quick, sudden forces but can flow over time under gravity.[15] This may be attributed to the dynamic nature of the boronic ester bond and/or a contribution from hydrogen bonding. The idea is that the boronic ester bond breaks and reforms over time as it exists as an equilibrium, but if a sudden force is applied to the material, the linkages stay intact as they do not have time to break apart and reform. The same idea applies to hydrogen bonds between hydroxyl residues – they form transient crosslinks under quick forces and can also break and reform over time.

Shear thickening behaviour was not observed in the pendent materials (**GAP3-BA77**) because they already behave more like solids at low angular frequencies. This is likely due to the nature of the distribution of glucose residues which allows for crosslinking through boronic ester formation. By switching from a telechelic to a pendent gluconamidosilicone, solid, robust materials can be created. Interestingly, by using a pendent gluconamidosilicone (**GA10-BA77**), which had a higher degree of glucose functionalization (i.e. more active groups on the backbone), even more robust, gel-like materials can be created (even using the same glucose: boronic acid ratio). This could potentially be due to the formation of tighter crosslinks/more between two gluconamidosilicones which in turn further restricts the chain flow and increases the elastic modulus.

3.3.3.1 Adding a dative B-N bond

The idea of introducing a dative bond via an amine to the boronic esters was to attempt to shift the equilibrium to favour the formation of boronic esters, thus improving the resilience of these elastomers. Initial experiments using **APTMS** *did* yield materials that displayed more gel-like behaviours; the materials made with telechelic gluconamidosilicones (**GAT64-BA77**) lost their shear thickening effect and displayed more characteristics of a solid. It is important to mention that this was an effect similar to that observed when either too little or too much gluconamidosilicone was present in formulations; the solid-like properties of the materials peak when the amine is dialed in at a 1:1 ratio to the boronic acid.

An alternative explanation for the increased elastomeric properties would be crosslinks introduced by diaminosilicone bridges an existing viscoelastic material (

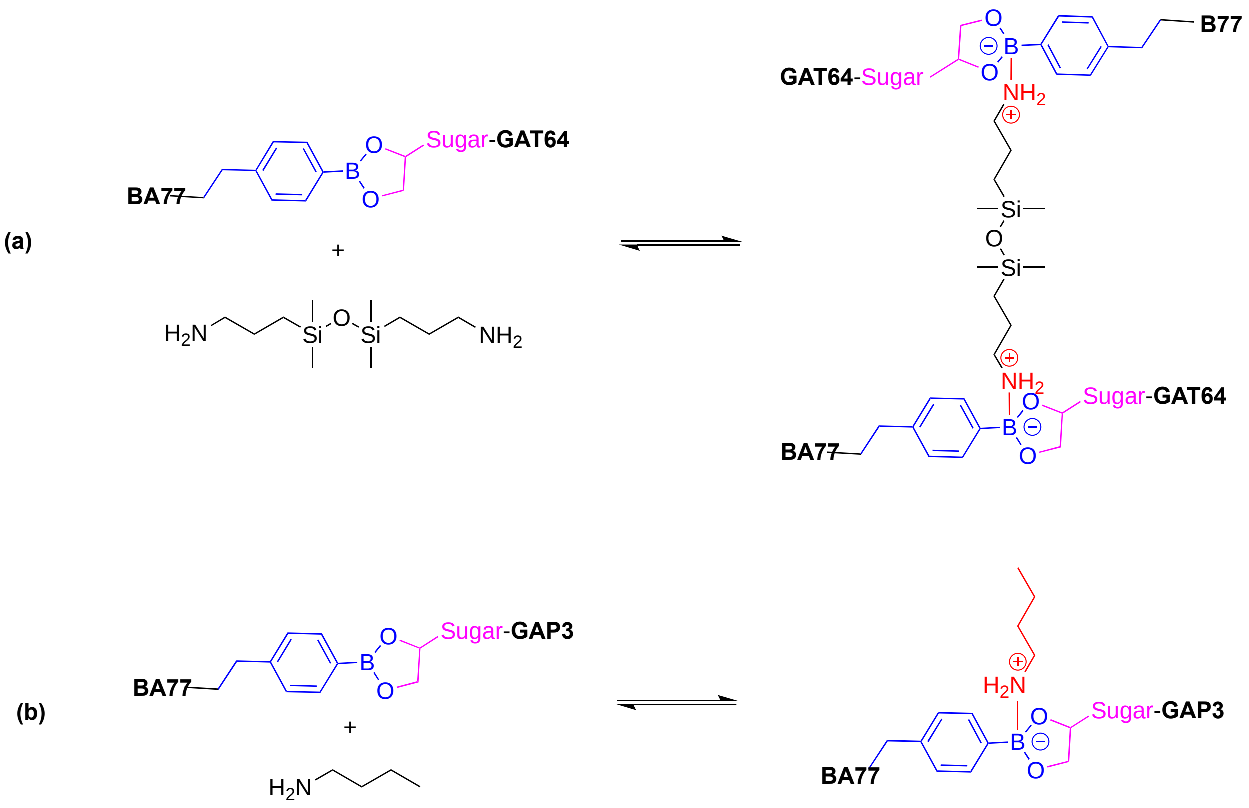

Figure 3-6a) into the telechelic system, which is effectively the same as switching from a telechelic to pendent material. Experiments with butylamine clarified that this was not correct; a similar change in viscoelastic properties was noted, and the monofunctional amine cannot bridge two chains. Upon addition of butylamine to the pendent material (**GAP3-BA77**), the graph immediately shifted from a material that possessed both solid and liquid properties to a material that predominantly exhibits solid behaviour. This is made clear by the phase angle that was low to begin with and was close to 0° at high angular frequencies. This means that the elastic modulus is contributing significantly more than the viscous modulus. These findings indicate that the B-N bond is changing the viscoelastic behaviour of the materials and that is potentially doing this by shifting the equilibrium toward the formation of the boronic ester (

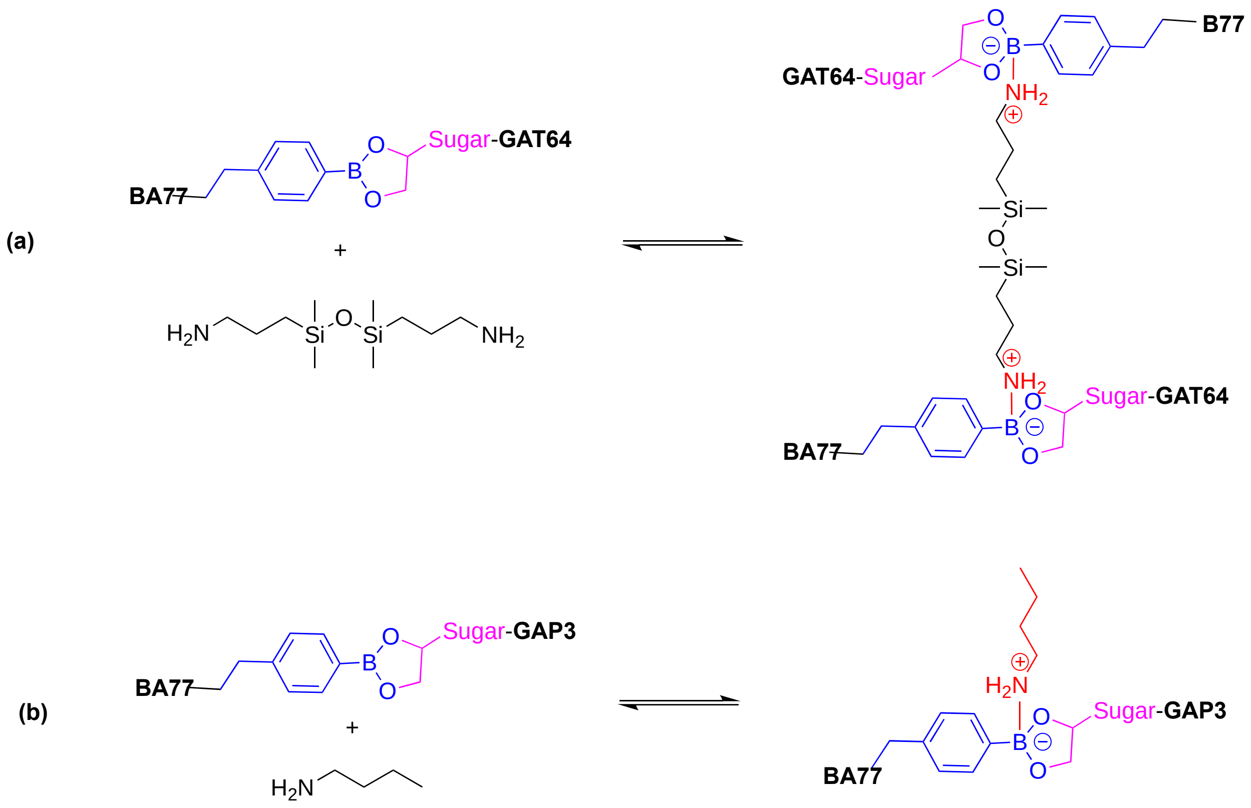

Figure 3-6b).

3.4 Experimental

3.4.1 Materials

The nomenclature of samples prepared is provided here to facilitate the discussion below. Samples are named by base aminopropylsilicones: telechelic **ATx** (x = number of D monomer units on the chain, D = (Me_2SiO)) or pendent **APy** (y = percentage of the functional monomer (propylmethylsiloxane) compared to D units). Gluconamidosilicones made from **AT** or **AP** are preceded with **G**, e.g., **ATx** ➞ **GATx** after reacting with gluconolactone. Boronic acid silicones are telechelic **Bz** (z – number of D monomer units on the silicone backbone).

3.4.2 Methods

NMR - NMR analysis: ^{1}H NMR and ^{13}C NMR were recorded on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer a Bruker Avance 600 MHz; spectra were processed using Bruker TopSpin version 4.2.0.

Rheometer – All rheological measurements were collected using the DHR-# rheometer (TA Instruments). The samples were prepared in a 24-well plate (Table 3-3) and punched into 8.0mm discs using a stainless-steel puncher. The sample was loaded onto the rheometer equipped with an 8.0mm stainless steel parallel Peltier plate. The spindle was brought to its trim gap (1050µM) and excess material was removed using a metal spatula. The gap was then brought to 1000 µM and a strain sweep (0.1-100%) was performed at 25 °C prior to further rheological tests to ensure that all measurements were taken in the linear viscoelastic regime.

All frequency (oscillatory) sweeps (0.1-500 rad/s) followed the same sample preparation procedure. The samples were brought to a trim gap of 1050µM, and excess material was removed. The samples were run with a gap of 1000 µM at 25 °C and at a constant strain of 1%.

All flow (rotational) sweeps (0.01-100 1/s) also followed the same sample preparation procedure. Note that, for some lower viscosity samples, an 8.0mm sandblasted Peltier parallel plate spindle was utilized, and the samples were brought to a trim gap of 412.35µM to remove excess material. The samples were then run with a gap of 387.35µM at 25°C and at a constant strain of 1%.

Young's moduli were measured on a MACH-1 micromechanical testing instrument (Biomomentum Instruments) equipped with a 17 N multi-axis load cell and 0.5 mm hemispherical indenter using a Poisson ratio of 0.5 and a constant indentation depth of 1.0 mm with a 1 s dwell time; all measurements were conducted at 22 °C and in triplicate.

DSC – Differential scanning calorimetry was performed on a DSC Q20 (TA-instruments) in a heat/cool/heat cycle. The sample pan was heated from 25 °C to 200 °C with a heating ramp of

10 °C/min. The sample was then cooled to -20 °C at a cooling rate of 20 °C/min and heated back up to 200°C at 10 °C/min.

3.4.2.1 Making sugar-aminosilicones

Gluconolactone (0.71 g, 4 mmol, 2 eq.) was weighed into an oven-dried 250 mL round-bottomed flask equipped with a stir bar and followed by **A64** (aminosilicone) (10 g, 2 mmol, 1 eq.). IPA (30 mL) was added to the same flask and the reaction proceeded under constant stirring over 24 h. Additional IPA was added to the flask to solubilize the product and to remove excess gluconolactone through gravity filtration. The resulting reaction product was placed under rotary evaporation to remove the remaining solvent resulting in a yield of 94.6%. The same process was repeated with amino silicones of various molecular weights following the values in Table 3-3. An ^{1}H NMR was taken to confirm the modification of the silicone with glucose (Figure S14).

Table 3-3 Quantities used to prepare various gluconamidosilicones.

starting material	aminosilicone eq g (mmol)	gluconolactone eq, g (mmol)	IPA (mL)	% yield
GA31	1 eq, 10 (0.4)	2 eq, 0.14 (0.8)	30	90
GA21	1 eq, 10 (2.0)	2 eq, 0.71 (4.0)	30	95
GA11	1 eq, 10 (11)	2 eq, 3.96 (22)	30	85
GA233	1 eq, 10 (2.6)	1 eq, 0.47 (2.6)	30	76
GA191	1 eq, 7.3 (8.0)	1 eq, 1.41 (8.0)	30	81

3.4.2.2 Making boronic acid-modified silicones

4-Vinylphenylboronic acid (0.8 g, 5.4 mmol, 1 eq.) was weighed into an oven-dried 250 mL round-bottomed flask along with dimethyl L-tartrate (1.1 g, 5.4 mmol, 1 eq.) as a protecting group.[4,16] Dry toluene (20-30 mL) was then added to the same flask and purged with nitrogen. 4Å molecular sieves (1 g) were added to the flask and the reaction was stirred for 18 h at room temperature under nitrogen flow. The reaction mixture was transferred to a 25 mL Falcon tube and the majority of the molecular sieves were removed following the centrifuge (5 min, 4000 rpm). The remaining solvent was transferred into a clean oven-dried 250 mL round-bottomed flask and an ^{1}H NMR spectrum was taken to confirm the protection of the boronic acid group had occurred. In the same flask, telechelic silicone **T77** DMS-H21 (5000g/mol, 16.2 g, 0.5 eq.) was added along with additional dry toluene (10 mL). Karstedt's catalyst (10 μL, 0.02 mmol) was pipetted into the flask and the reaction was allowed to stir over 12 h after which activated charcoal (500 mg) was added to quench the catalyst overnight (18 h). The product was vacuum filtered using a Celite pad to remove any remnants of molecular sieves and the activated charcoal. The remaining solvent was removed using rotary evaporation resulting in a 90.7% yield of compound **BA77** (telechelic boronic acid silicone, 77 D units). Another ^{1}H-NMR was taken to confirm the modification of the silicone with the tartrate-protected boronic acid group (Figure S33).

3.4.2.3 Dynamically bonded boronic acid silicone materials, general procedure

Shown for **GAT64**: **GAT64** (0.32 g, 0.04 mmol, 0.5 eq.) was weighed into a glass vial. The vial was placed under a heat gun (Master Appliance Corp. HG-501 A) just until melting/softening was seen, and then **BA77** (0.5 g, 0.08 mmol, 1 eq.) was added to the same vial (the equivalents are calculated for active groups i.e. boronic acid and glucose residues). The vial was heated again briefly to maintain the temperature and the materials were stirred vigorously for 1 min with a small metal spatula. This process was repeated with various equivalents of **GAT64** to create a library (Table 3-4). The resulting dynamically bonded materials were allowed to cool to room temperature overnight (18 h) and then removed from the glass vials to collect viscoelastic property data.

*Table 3-4 - Values used to formulate boronic ester materials using **BA77** and various gluconamidosilicones.*

Eq glucose	**BA77** g (mmol)	**GAT334** g (mmol)	**GAT64** g (mmol)	**GAT8** g (mmol)	Eq glucose	**GAP3** g (mmol)	**GAP10** g (mmol)
0.1	-	0.2 (0.008)	-	-	-	-	-
0.25	0.5 (0.08)	-	0.1 (0.02)	0.03 (0.02)	0.125	0.09 (0.01)	0.03 (0.01)
0.5	0.5 (0.08)	1 (0.04)	0.2 (0.04)	0.06 (0.04)	0.25	0.2 (0.02)	0.05 (0.02)
0.75	0.5 (0.08)	-	0.3 (0.06)	0.08 (0.06)	0.375	0.3 (0.03)	0.08 (0.03)
1	0.5 (0.08)	2 (0.08)	0.4 (0.08)	0.1 (0.08)	0.5	0.4 (0.04)	0.1 (0.04)
1.5	0.5 (0.08)	3 (1.2)	0.6 (1)	0.2 (1)	0.75	0.5 (0.06)	0.2 (0.06)

3.4.2.4 Dynamically bonded boronic acid silicone materials without heat

Shown for **GAT64**: **GAT64** (0.32 g, 0.04 mmol, 0.5 eq.) was weighed into a well of a 24-well plate along with just enough IPA to solubilize the starting material. **BA77** (0.5 g, 0.08 mmol, 1 eq.) was added to the same well and stirred vigorously for 1 min with a small metal spatula. This process was repeated with various equivalents of **GA** following (Table 3-4). The resulting material was placed in a desiccator under vacuum for 3 weeks to ensure the complete removal of IPA before moving on to data collection.

3.4.2.5 Control studies

Control studies were conducted by combining **BA77** with various aminosilicones **ATx** (x = 8, 64, 264) to confirm no formation of elastomers. To create these mixtures, **BA77** (0.3 g, 0.05

mmol, 1 eq.) was weighed into a 10 mL glass vial using a syringe. An aminosilicone **AT64** (0.12 g, 0.025 mmol, 0.5 eq.) was weighed into the same vial and stirred with a small metal spatula. The same procedure was performed for various aminosilicones and the same for the gluconamidosilicone controls (Table 3-5).

Table 3-5 - Table of values for control experiments.

	AT8 eq, mg (mmol)	AT64 eq, mg (mmol)	AT334 eq, mg (mmol)
BA77 (0.3 g)	0.50 eq, 20 (0.02)	0.50 eq, 10 (0.02)	0.5 eq, 600 (0.02)
AT334 (0.5 g)	0.50 eq, 9 (0.01)	0.50 eq, 50 (0.01)	0.5 eq, 250 (0.01)

3.4.2.6 Adding amines

Aminosilicones **ATx** (x = 8, 64) were added to telechelic boronic ester materials (**GAT8-BA77** and **GAT64-BA77**) by first mixing the gluconamidosilicone **GAT8** (0.05 g, 0.04 mmol, 0.5 eq.) or **GAT64** (0.2 g, 0.04 mmol, 0.5 eq.) with **AT8** (0.04 g, 0.04 mmol, 0.5 eq.) in a glass vial. Another set of samples would use the same gluconamidosilicones but instead mixed with **AT64** (0.2 g, 0.04 mmol, 0.5 eq.). The gluconamidosilicone and aminosilicones were heated with a heat gun (Master Appliance Corp. HG-501 A) just until melting/homogenization of the silicones was observed. The boronic acid silicone **BA77** (0.5 g, 0.08 mmol, 1 eq.) was added to all vials containing the aminosilicone and gluconamidosilicone and mixed with a metal spatula. The resulting materials were allowed to cool, removed from their vials using a metal spatula, and placed into 24-well plates. Their YM data was then collected afterwards. For samples made with **APTMS** [1,3-bis(3-aminopropyl)tetramethyldisiloxane] (0.01 g, 0.04 mmol, 0.5 eq.), it was placed in a vial along with **GAT64** (0.2 g, 0.04 mmol, 0.5 eq.), heated using a heat gun (Material Applicance Corp. HG-501 A), and mixed well with a metal spatula. **BA77** (0.5, 0.08 mmol, 1 eq.) was added to the same vial and mixed again with the spatula.

For the small compound dative bond, butylamine (1.2 mL, 12 mmol, 150 eq.) (equivalents corresponding to 1 eq. **BA77**) was pipetted into a vial with the boronic ester material **GAP3-BA77** (~0.67 g) at a 2:1 boronic acid: glucose ratio and a separate vial containing **GAT64** (~0.71 g) at a 2:1 ratio. The solution was stirred, and the vial was capped. When the materials were dissolved (~1-4 h), the caps of the vials were opened, and the butyl amine was allowed to evaporate over 65 h. The reformed elastomeric materials were removed from their vials to obtain rheological data.

3.5 Conclusions

Through this project, materials with a range of viscoelastic properties are achieved through the boronic ester linkage of boronic acid-modified silicones (**BA77**) and both telechelic and pendent gluconamidosilicones (**GATx** and **GAPy**). The viscoelastic properties can be manipulated by adjusting the degree of boronic ester formation as well as switching between telechelic and pendent polymers. The telechelic materials displayed shear thickening whereas pendent materials displayed gel-like behaviours. The introduction of dative bonds through the B-N bond to the boronic esters helps stabilize the linkage and increase the robustness of these materials. Overall, this Chapter explores the formulation of a silicone material linked through dynamic covalent linkages that has the potential to be reversed and opens a route to more sustainable materials.

3.6 References

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4 General conclusions

Silicone materials, prized for their thermal stability, chemical resistance, oxygen permeability, and biocompatibility, owe their properties to their stable siloxane (Si-O) backbone. Although advantageous, these materials have high-temperature synthetic processes, their degradation in the environment is not well understood, and popular cure methods rely on expensive or toxic metal catalysts. Despite the convenience of current methods, research into alternative crosslinking methods offers hope for enhancing silicone material sustainability while preserving their advantageous properties.

In Chapter 2, silicone copolymers were modified with eugenol and crosslinked through oxidative phenolic coupling, a biomimetic process. Radicals were generated using di-t-butyl peroxide in a solventless process at elevated temperatures to yield robust, thermoset elastomers that had tuneable physical properties and retained antioxidant activity. The hardness and crosslink density of these materials increases with increasing loadings of the radical initiator. The antioxidant activity, although retained after coupling of the eugenol, decreases as crosslink density increases.

In Chapter 3, boronic acid-modified silicones and glucose-modified aminosilicones were combined to create a dynamically crosslinked boronic ester material. These materials had a range of viscoelastic properties that can be adjusted through formulation. Telechelic materials tend to resemble elastomers but display shear thickening properties through rheological tests. Pendent materials were more robust and possessed more gel-like properties rather than that of a highly viscous liquid. By introducing dative B-N bonds, the robustness of both telechelic and pendent materials was further improved by stabilizing the boronic ester bond, shifting the equilibrium to favour their formation. This work allows for the potential to explore the reversal of this crosslink to create materials that can be degraded or reprocessed at their end of life.

These research projects highlight alternate paths to crosslinking silicone materials that do not utilize expensive or toxic metal catalysts that traditional methods call for. Future research may involve exploring their degradation whether it be observing the interaction of the oxidatively coupled crosslinks with nature (i.e., biodegradation in soil) or exploring the decrosslinking of boronic ester materials through their dynamic process. Overall, these are silicone materials that are made with sustainability in mind, and they have the potential for an easier end-of-life.

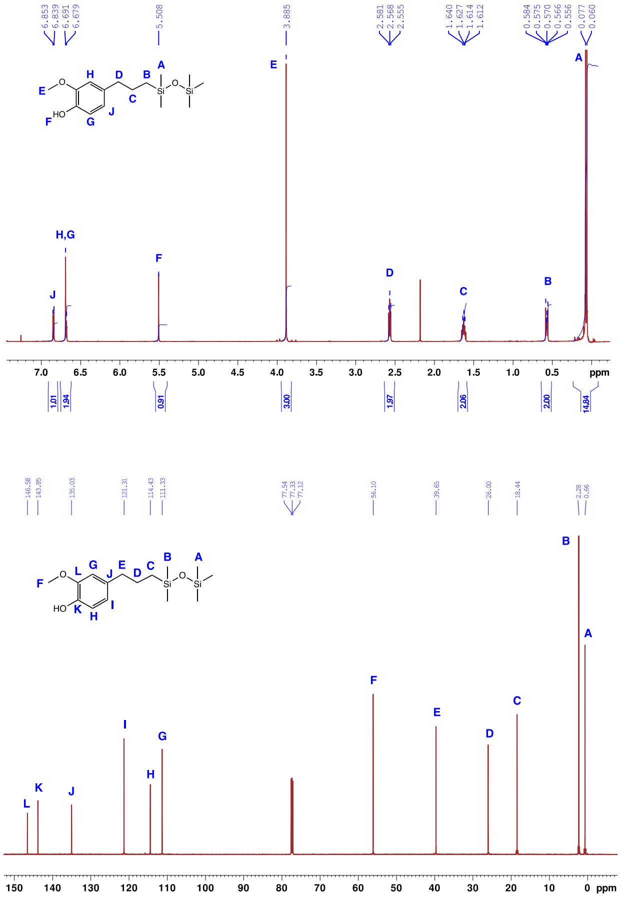
5 Supporting information

5.1 Supporting information for Chapter 2 - Learning from the Trees: Biomimetic Crosslinking of Silicones by Phenolic Coupling

Learning from the Trees: Biomimetic Crosslinking of Silicones by Phenolic Coupling

Angela Li,[a] Miguel Melendez-Zamudio,[a] Akop Yepremyen,[a] Michael A. Brook*

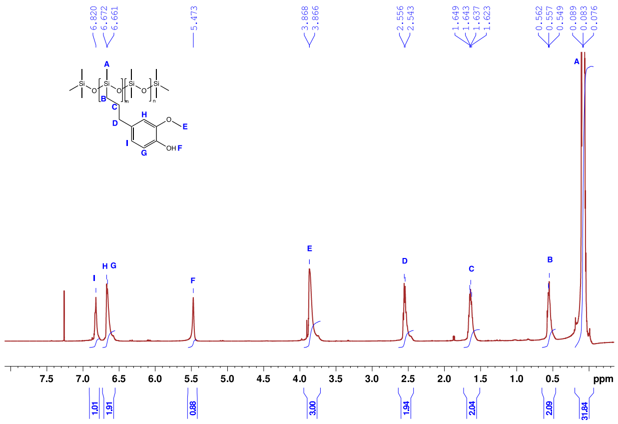
Supporting Information



A

B

Figure S27 A) ^{1}H NMR and B) ^{13}C NMR of 1.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6.672
6.661
5.473
3.868
3.866
2.556
2.543
1.649
1.643
1.637
1.623
0.562
0.557
0.549
0.089
0.083
0.076
A
B
C
D
E
F
G
H
I
OH
7.5
7.0
6.5
6.0
5.5
5.0
4.5
4.0
3.5
3.0
2.5
2.0
1.5
1.0
0.5
ppm
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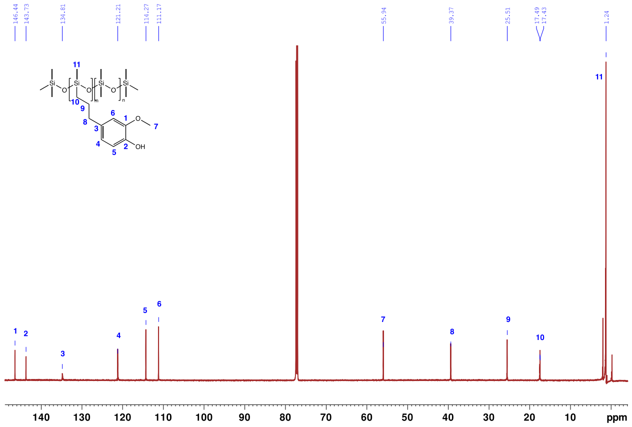
0.88
3.00
1.94
2.04
2.09
31.84

A

B


146.44
143.73
134.81
121.21
114.27
111.17
55.94
39.37
25.51
17.49
17.43
1.24
1
2
3
4
5
6
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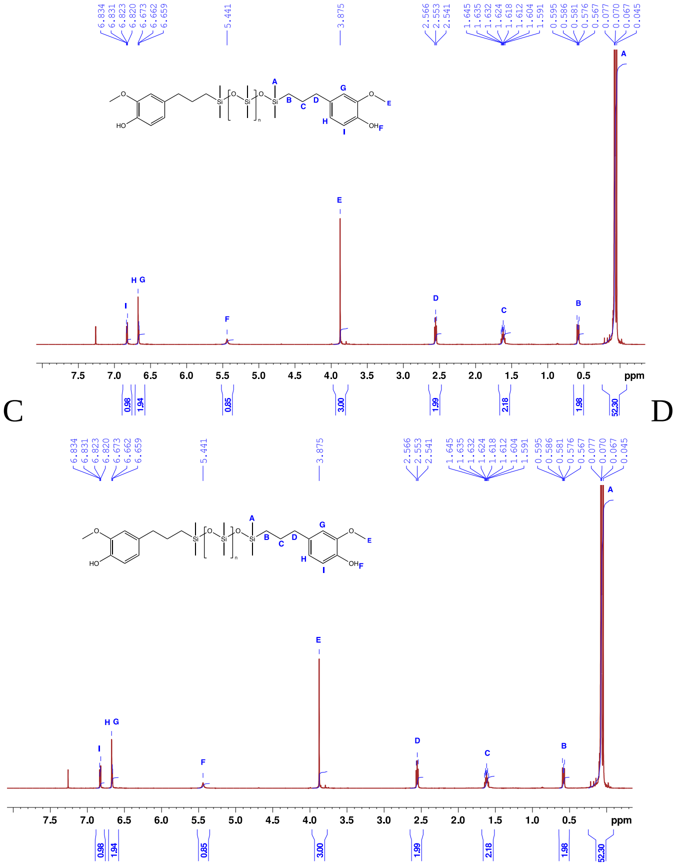
50
40
30
20
10
ppm



S28. A,C) ^{1}H NMR and B,D) ^{13}C NMR of **P15-Eu** and **T12-Eu**, respectively.

GC/MS

The GC/MS trace of the oxidation of **1** with BPO shows 6 principal compounds, labelled 1-6. Compounds 1/2; 3/4; and 5/6 are each related, with the latter being 2 amu less (missing the constituents of H2) that the earlier peak: 312 vs 310 (starting material **1**); 432 vs 430 and 622 vs 620 (dimeric product **3**). The compounds responsible for 432/430 are proposed to be compound **6** formed through equilibration from dimer **3**. Note that this compound was not seen in the starting materials. An alternative is the presence of small amounts of $M^{H}M^{H}$ in the original formation of compound **1**. With these assumptions, the product mixture is 55% product. A more conservative value shows the peak at 312 **1** and its dimer **3** in a 5:1 ratio, or 20%. Sensitivity factors have been assumed to be identical for all compounds.

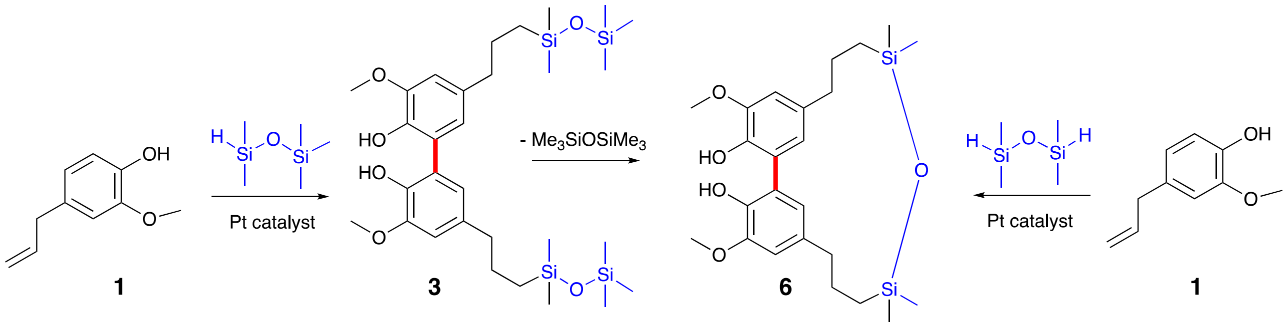
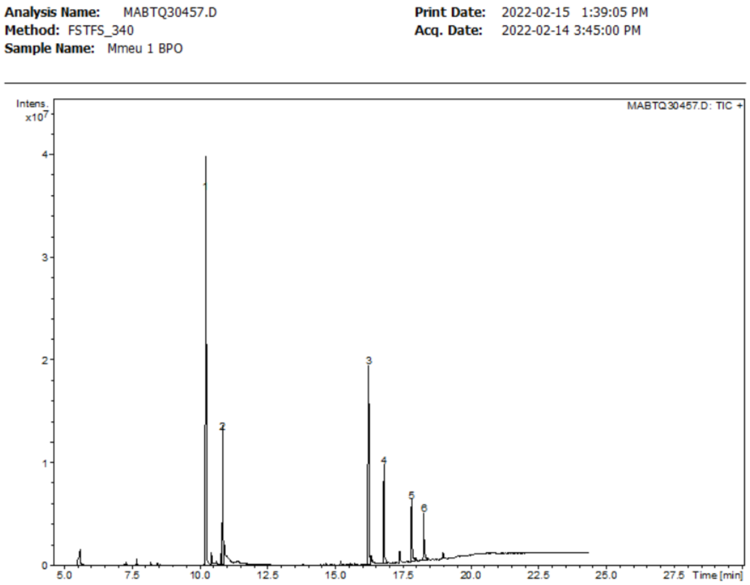


Figure S29 Proposed structures of products with m/z 2 less than expected.



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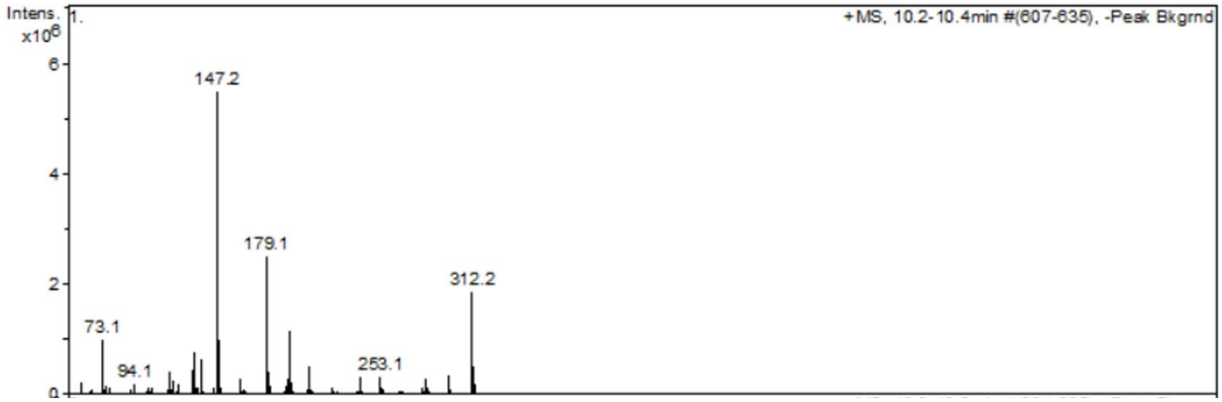
Method: FSTFS_340
Sample Name: Mmeu 1 BPO

Print Date: 2022-02-15 1:39:05 PM
Acq. Date: 2022-02-14 3:45:00 PM

Peak	Compound	Retention time	Area	Area%
1	**1**	15.5	61698478	26.9
2	**1**	11.0	18331738	8.0
3	**6**	16.5	68418186	29.8
4	**6**	17.0	34854476	15.2
5	**3**	18.1	11761055	5.1
6	**3**	18.5	13802773	6.0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4
2
0
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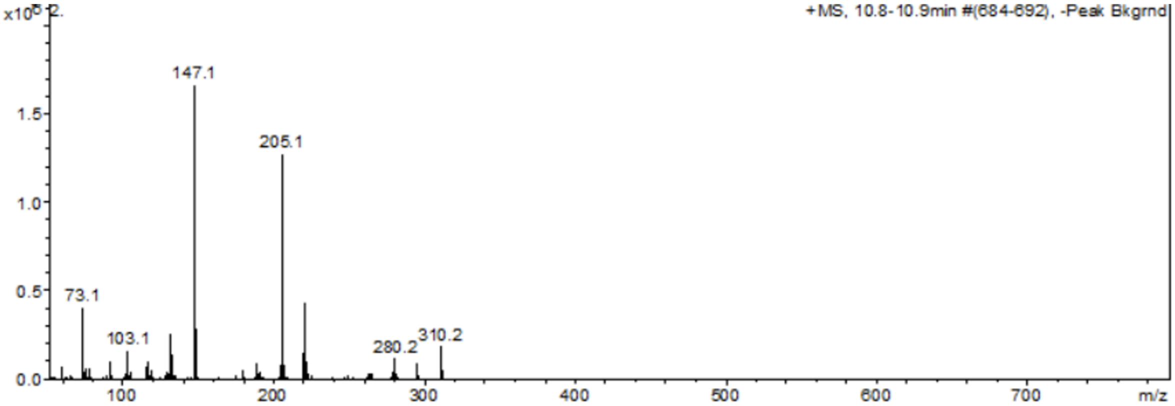
179.1
312.2
73.1
94.1
253.1

2)


x10^6
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0.5
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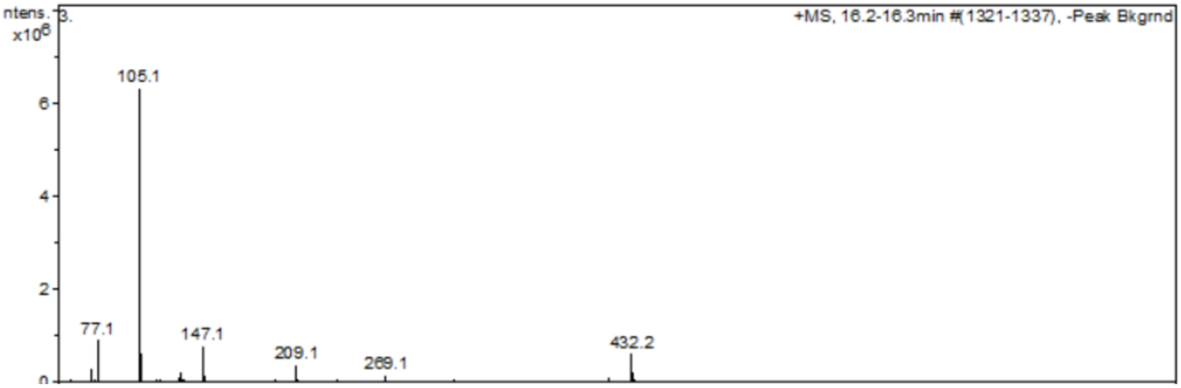
103.1
280.2
310.2
100
200
300
400
500
600
700
m/z

3)


ntens.
x10^6
3.
+MS, 16.2-16.3min #(1321-1337), -Peak Bkgrnd
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4
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0
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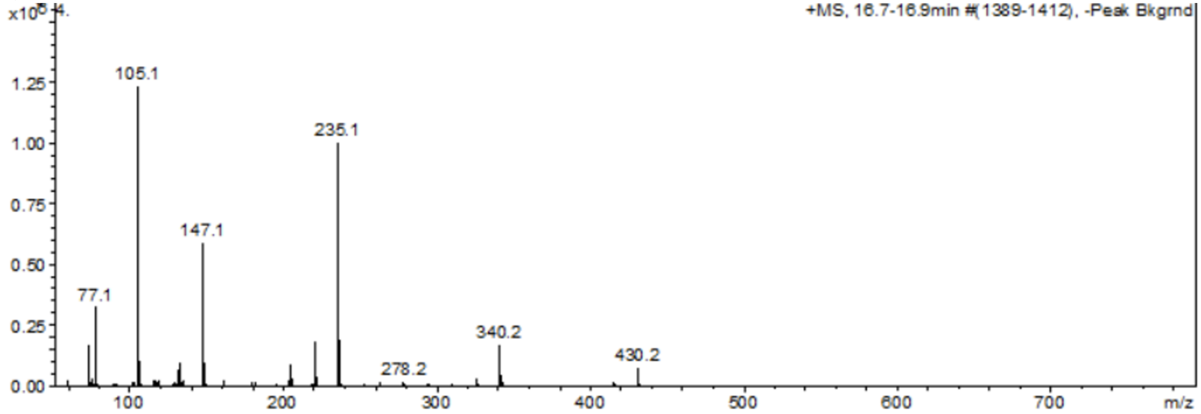
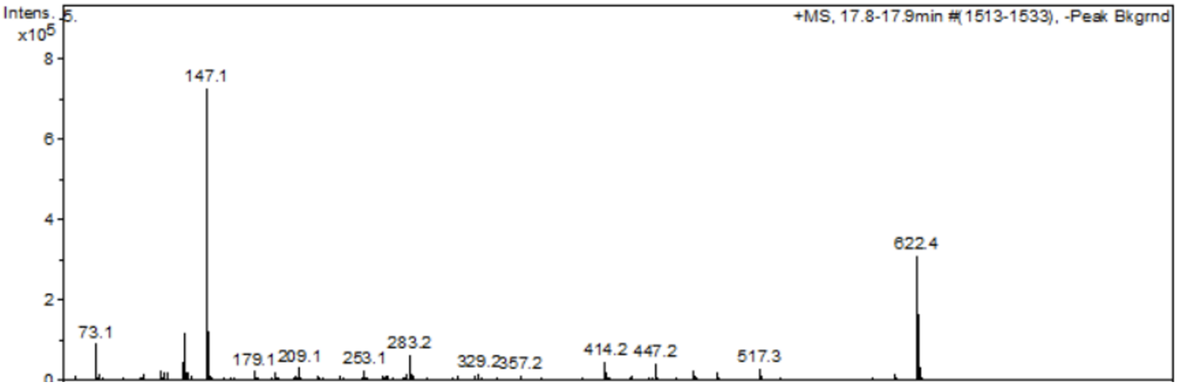
147.1
209.1
269.1
432.2

4)



5)



6)

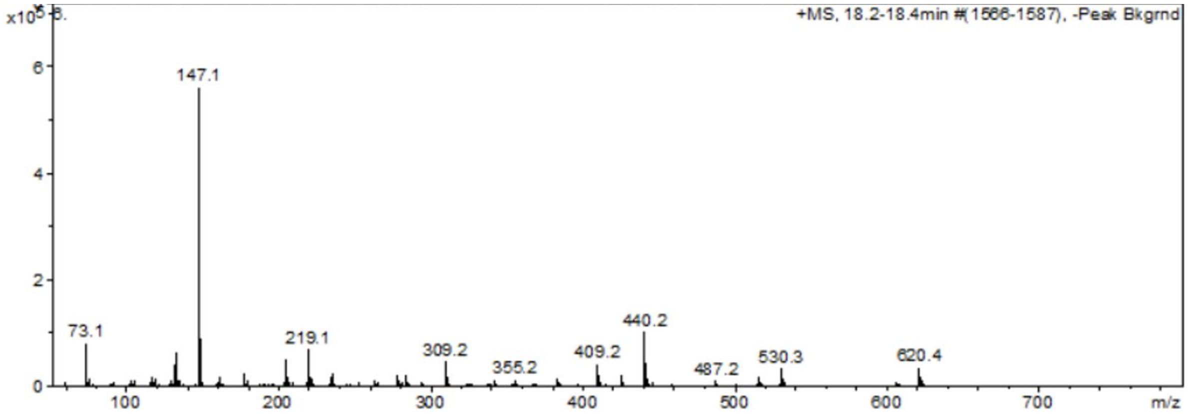


Figure S30 GC trace, intensity table of the 6 GC peaks seen, and their mass spectra Figure 1 A→*C showing conversion of about 20% of 3 from 1.*

Table S6. Chain extension parameters of **T0-Eu** and **T12-Eu**

T0-Eu			
T0-Eu (g)	**Molar equivalents of DTBP**	**mmol DTBP**	**Volume (µL)**
0.4	1	0.86	159
0.4	2	1.73	318
0.4	5	4.32	794
T0-Eu (g)	**Molar equivalents of BPO**	**mmol BPO**	**weight (mg)**
0.4	1	0.86	209.4
0.4	2	1.73	418.8
0.4	5	4.32	1047
T12-Eu			
T12-Eu (g)	**Molar equivalents of DTBP**	**mmol DTBP**	**Volume (µL)**
0.4	1	0.27	49
0.4	2	0.53	98
0.4	5	1.33	245
T12-Eu (g)	**Molar equivalents of BPO**	**mmol BPO**	**weight (mg)**
0.4	1	0.27	64.6
0.4	2	0.53	129.1
0.4	5	1.33	322.8

Table S7. GPC data from chain extension studies using varying equivalents of BPO and DTBP

Eugenol-modified M^HM^H				
Peroxide	**Equiv. peroxide**	**M_n**	**M_w**	**$Đ_M$**
No peroxide	0	283	297	1.0478
DTBP	1	329	394	1.1953
	2	616	686	1.1135
	5	847	1256	1.4826
BPO	1	339	400	1.1812
	2	381	499	1.3102
	5	1238	2098	1.695
Eugenol-modified T12				
No peroxide	0	1555	2147	1.38
DTBP	1	1718	2290	1.3329
	2	1842	2649	1.4381
	5	2464	5446	2.2104
BPO	1	2656	5046	1.8994
	2	2627	6201	2.3608
	5	4828	12120	2.5102

Table S8. Oxidative coupling to create elastomers with DTBP

Oxidative coupling of eugenol-modified P50-Eu (0.5 g, 1.51 mmol EUG)		
Molar equiv. DTBP	mmol DTBP	vol (µL)
0	0	0
0.2	0.30	56
0.4	0.60	111
0.6	0.90	167
0.8	1.21	222
1	1.51	278
1.5	2.27	417
Oxidative coupling of eugenol-modified P30-Eu (0.8 g 1.95 mmol EUG)		
0	0	0
0.2	0.39	72
0.4	0.78	143
0.6	1.17	215
0.8	1.56	287
1	1.95	359
1.5	2.93	538
Oxidative coupling of eugenol-modified P15-Eu (0.8 g 2.46 mmol EUG)		
0	0	0
0.2	0.49	49
0.4	0.98	98
0.6	1.48	147
0.8	1.97	196
1	2.46	245
1.5	3.69	367

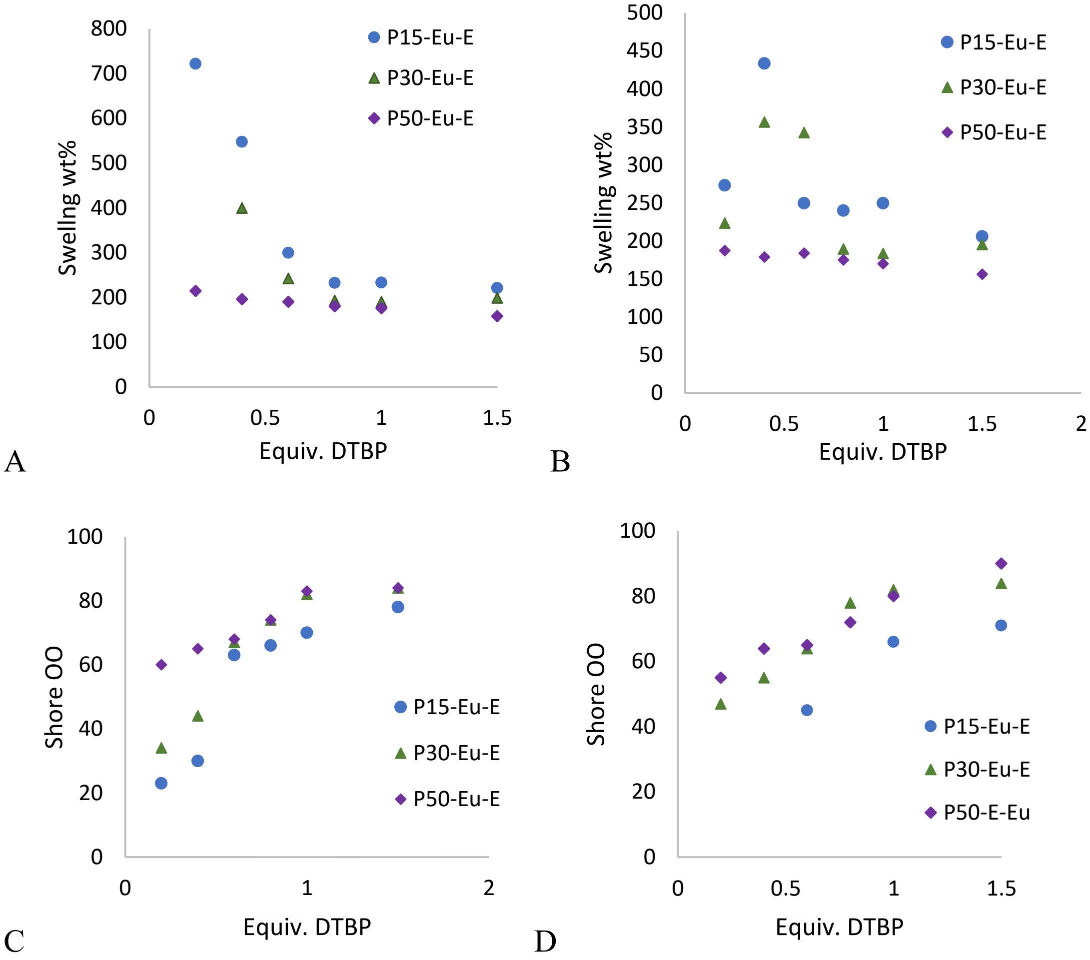


Figure S31**.** Swelling (wt% increase) of A) first prepared elastomers and B) after extraction with toluene. Shore OO hardness of C) first prepared elastomers and D) after extraction with toluene.

Table S9. Mass loss after first swelling in solvent and Shore OO data before and after extraction in toluene.

raw elastomers						
P50						
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	%sol[a]
0.2	60	0.1622	0.3472	0.1104	214.1	31.9
0.4	65	0.1604	0.3141	0.1275	195.8	20.5
0.6	68	0.163	0.3095	0.1291	189.9	20.8
0.8	74	0.1611	0.2903	0.1331	180.2	17.4
1	83	0.1608	0.2826	0.1341	175.7	16.6
1.5	84	0.1622	0.2564	0.1436	158.1	11.5
P30						
equivalents DTPB	Shore OO	starting	swollen	final	% swelling	%sol
0.2	34	0.1661	0.7204	0.1047	433.7	37.0
0.4	44	0.1579	0.6307	0.0999	399.4	36.7
0.6	67	0.1658	0.4014	0.1405	242.1	15.3
0.8	74	0.1615	0.3119	0.1471	193.1	8.9
1	82	0.1665	0.3159	0.154	189.7	7.5
1.5	84	0.1583	0.3148	0.1424	198.9	10.0
P15						
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	%sol
0.2	23	0.1649	1.1899	0.0563	721.6	65.9
0.4	30	0.1637	0.8965	0.0803	547.6	50.9
0.6	63	0.1659	0.4963	0.1234	299.2	25.6
0.8	66	0.1658	0.3845	0.1345	231.9	18.9
1	70	0.1645	0.3832	0.141	232.9	14.3
1.5	78	0.1619	0.3576	0.1364	220.9	15.6

[a] Mass loss after 1 extraction with toluene.

extracted elastomers						
P50						
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	% sol[a]
0.2	60	49	91.7	45.5	187.142857	7.14285714
0.4	65	49.4	88.3	46.6	178.744939	5.66801619
0.6	68	46.3	85.1	44.1	183.801296	4.75161987
0.8	74	51.1	89.3	49.5	174.755382	3.13111546
1	83	50.4	85.5	47.9	169.642857	4.96031746
1.5	84	50	78	47.6	156	4.8
P30						
equivalents DTPB	Shore OO	starting	swollen	final	% swelling	% sol
0.2	34	52.8	117.8	47.7	223.106061	9.65909091
0.4	44	52.9	188.4	43.2	356.143667	18.3364839
0.6	67	50.1	171.6	47.1	342.51497	5.98802395
0.8	74	48.3	91.4	45.8	189.233954	5.17598344
1	82	54.3	99.5	51.4	183.241252	5.34069982
1.5	84	46.5	90.7	44.4	195.053763	4.51612903
P15						
equivalents DTBP	Shore OO	starting	swollen	final	% swelling	% sol
0.2	23	40.9	111.6	31.3	272.860636	23.4718826
0.4	30	52.6	227.9	44.6	433.269962	15.2091255
0.6	63	53.1	132.5	48	249.52919	9.60451977
0.8	66	53.8	129	49.4	239.776952	8.17843866
1	70	48.8	121.7	45.8	249.385246	6.14754098
1.5	78	54.8	112.6	52.5	205.474453	4.19708029

[a] Mass loss after 3 extractions with toluene.

Table S10. Serial dilutions for DPPH assays

serial dilutions	[eugenol] (mM)	[DPPH] (mM)	total vol (mL)
100%	50	0.1	1
50%	25	0.1	1
10%	5	0.1	1
1%	0.5	0.1	1

0.10%	0.05	0.1	1
0.01%	0.005	0.1	1
0.001%	0.0005	0.1	1

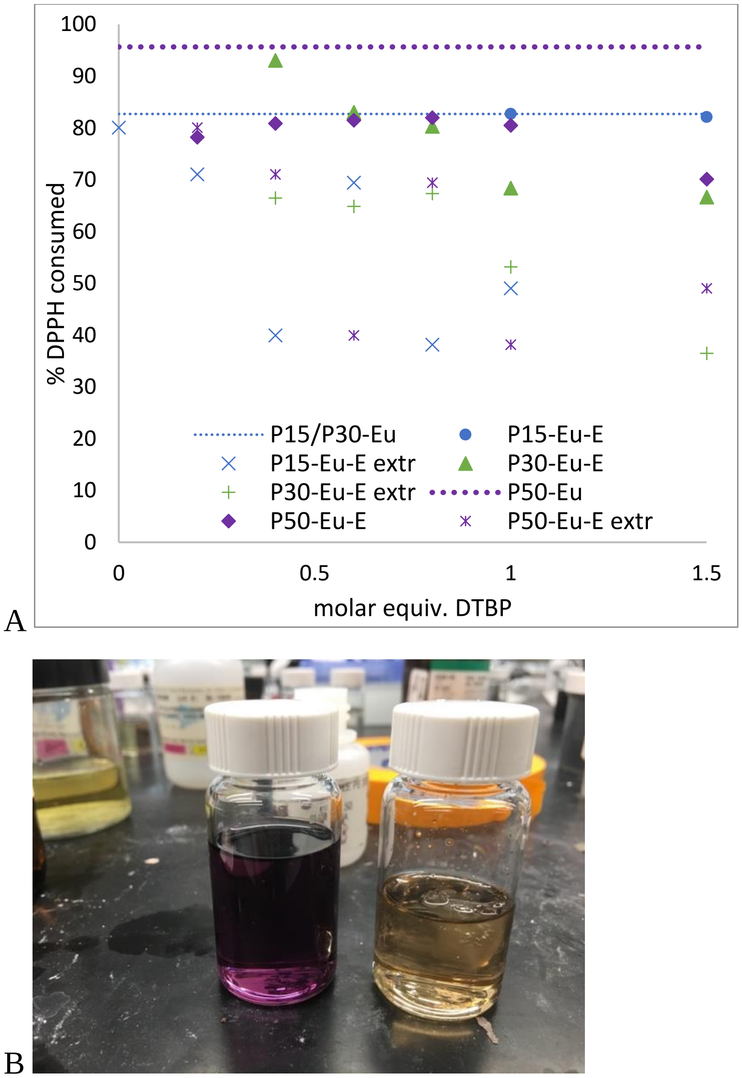


Figure S32 Antioxidant activity, by DPPH assay, of A) **P15-Eu-E**; **P30-Eu-E**; **P50-Eu-E** as prepared, and after extraction. B) Typical color change upon reaction of DPPH with phenols (left - before, right - after reaction).

The differences between Shore hardness (or Young's modulus[1]) for filled and unfilled silicones is rather significant. Note that Sylgard is typically filled with MQ resins, a related but distinct type of reinforcing agent.[2] Selected examples of elastomers cured using hydrosilylation, moisture cure (RTV) and phenolic coupling have comparable Shore hardness values (Table S11).

Table S11. A comparison of curing techniques for silicone elastomers (to prepare 0.8 g elastomer).

Commercial Platinum-cure silicone rubber (Sylgard 184)[a]					
Crosslinker	Chain extender	Pt[b]	Filler	Cure temp.	Shore OO
H-PDMS	vinyl-terminated PDMS	5-20 ppm	MQ resins	21 °C, 24 h	~ 83 (43 Shore A)[1]
Homemade Platinum cure silicone					
H-PDMS	vinyl-terminated PDMS	~ 5 ppm	NA	RT, 5 h	~ 40
Commercial RTV (Dowsil 786)					
Crosslinker	Chain extender	mol% of Snd	Filler	Cure temp.	Shore OO
$Si(OAc)_4$	HO-terminated PDMS	<1%	silica	RT, 24 h	~ 75 (25 Shore A)[d]
Homemade RTV (moisture cure)					
$Si(OEt)_4$	HO-terminated PDMS	1%	Filler	RT, 12 h	~ 80
P30-Eu-E					
Crosslinker	Chain extender	DTBP	Filler	Cure temp.	Shore OO
Pendent eugenol silicone	NA	195%	none	130 °C, 6 h	~ 80

[a] If higher temperatures are used, Sylgard will completely cure in about one hour at 100 °C, or 15 minutes at 150 °C (www.dow.com/content/dam/dcc/documents/en-us/productdatasheet/11/11-31/11-3184-sylgard-184-elastomer.pdf accessed May 30, 2023.). [b] Karstedt's Pt catalyst. [c] Dibutyltin dilaurate. [d] www.dow.com/content/dam/dcc/documents/en-us/productdatasheet/95/95-10/95-1047-01-dowsil-786-silicone-sealant.pdf?iframe=true, accessed May 30, 2023.

1. A. W. Mix and A. J. Giacomin, *Journal of Testing and Evaluation*, **39**, 696-705.
2. D. H. Flagg and T. J. McCarthy, *Macromolecules*, 2016, **49**, 8581-8592.

5.2 Supporting information for Chapter 3 - Sugar boronic acid silicones

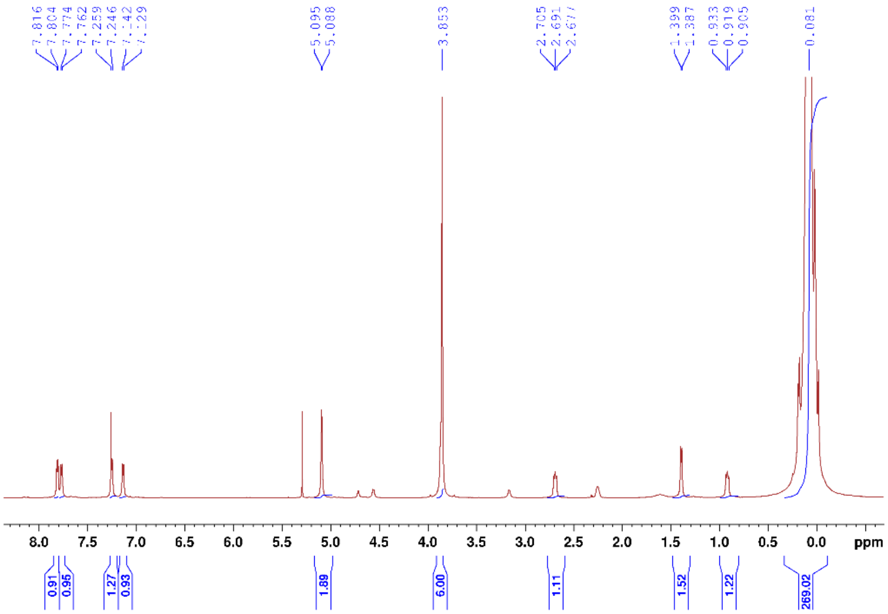


Figure S33 - ^{1}H NMR of **BA77** (600 MHz, CDCl3): δ = 7.78 (d, J = 8.0 Hz, 2H), 7.23 (d, J = 8.1 Hz, 2H), 5.07 (s, 2H), 3.83 (s, 6H), 2.67 (m, 2H), 0.89 (m, 2H), 0.3 to -0.1 (m, 269H). Contains both the terminal isomer (49%) and the internal isomer (51%).

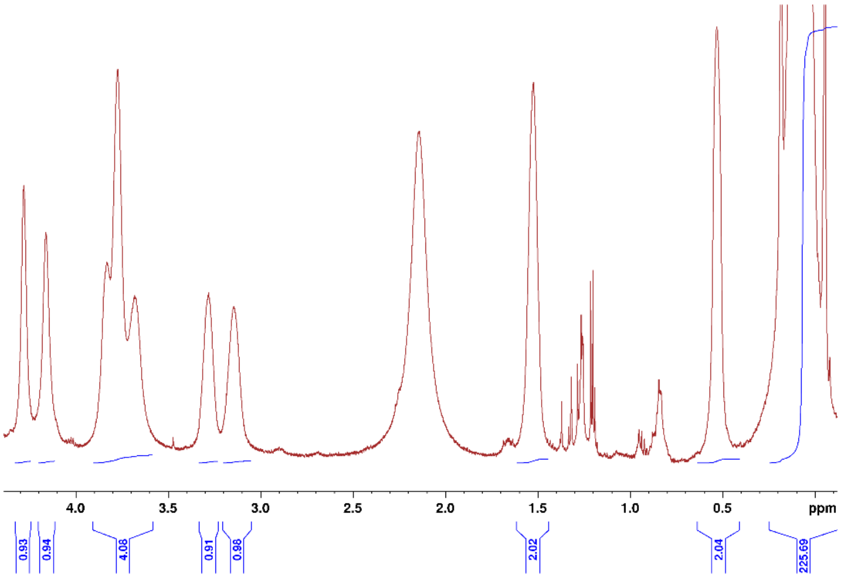


Figure S14 - ^{1}H NMR of **GAT64** (600 MHz, CDCl3): δ = 4.29 (s, 1H), 4.11 (s, 1H), 3.78 (m, 2H), 3.69 (m, 2H), 3.26 (s, 1H), 3.14 (s, 1H), 1.53 (m, 2H), 0.51 (m, 2H), 0.05 (m). Signals between 3.14-4.29 ppm (except 3.69 ppm) are correlated with the glucose residues.

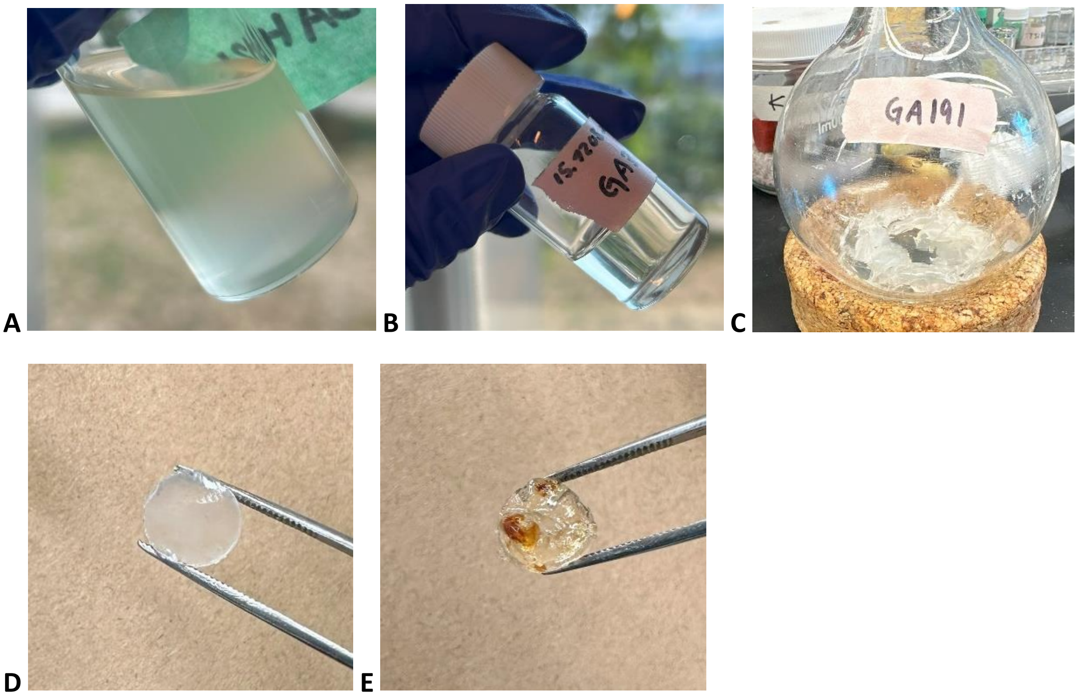
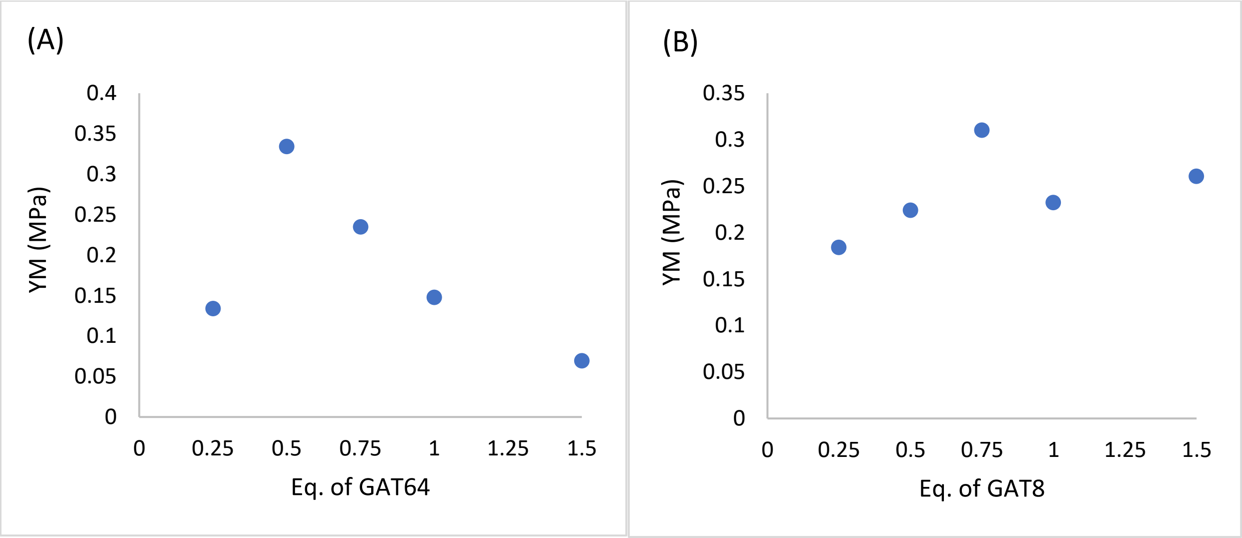


Figure S15 – Pictures of a) **BA77**, b) **GAT64**, c) **GAP3**, d) translucent elastomeric-like material **GAT64-BA77** (0.5 eq. loading of gluconamidosilicone), and e) translucent elastomeric material made from **GAP3-BA77** (0.5 eq. loading of gluconamidosilicone).



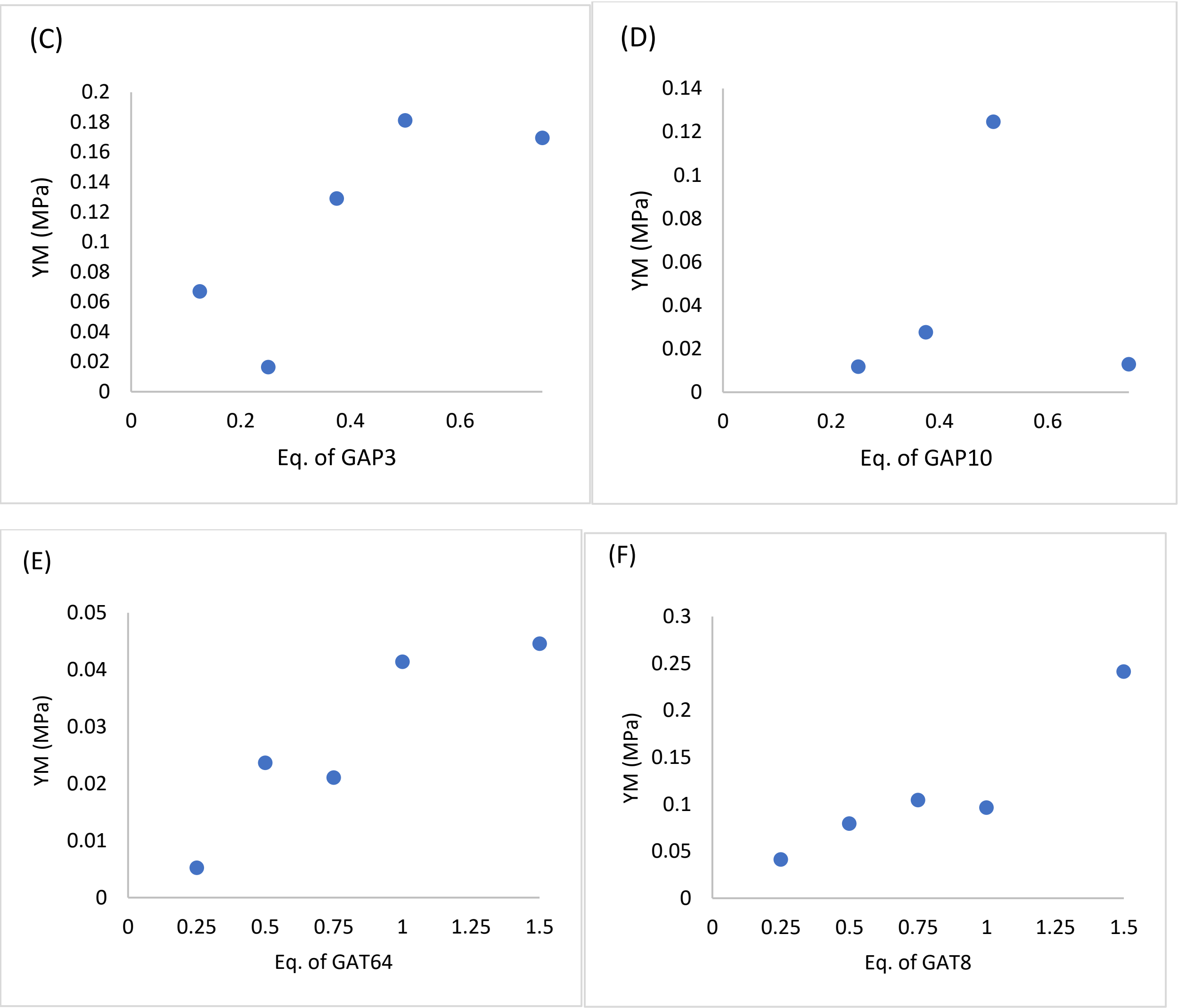


Figure S16 – Graphs of YM (MPa) to the function of the equivalents of gluconamidosilicone for a) **GAT64-BA77** materials, b) **GAT8-BA77** materials, c) **GAP3-BA77** materials, and d) **GAP10-BA77** materials. The addition of 0.5 eq. **AT8** to e) **GAT64-BA77** and f) **GAT8-BA77**.

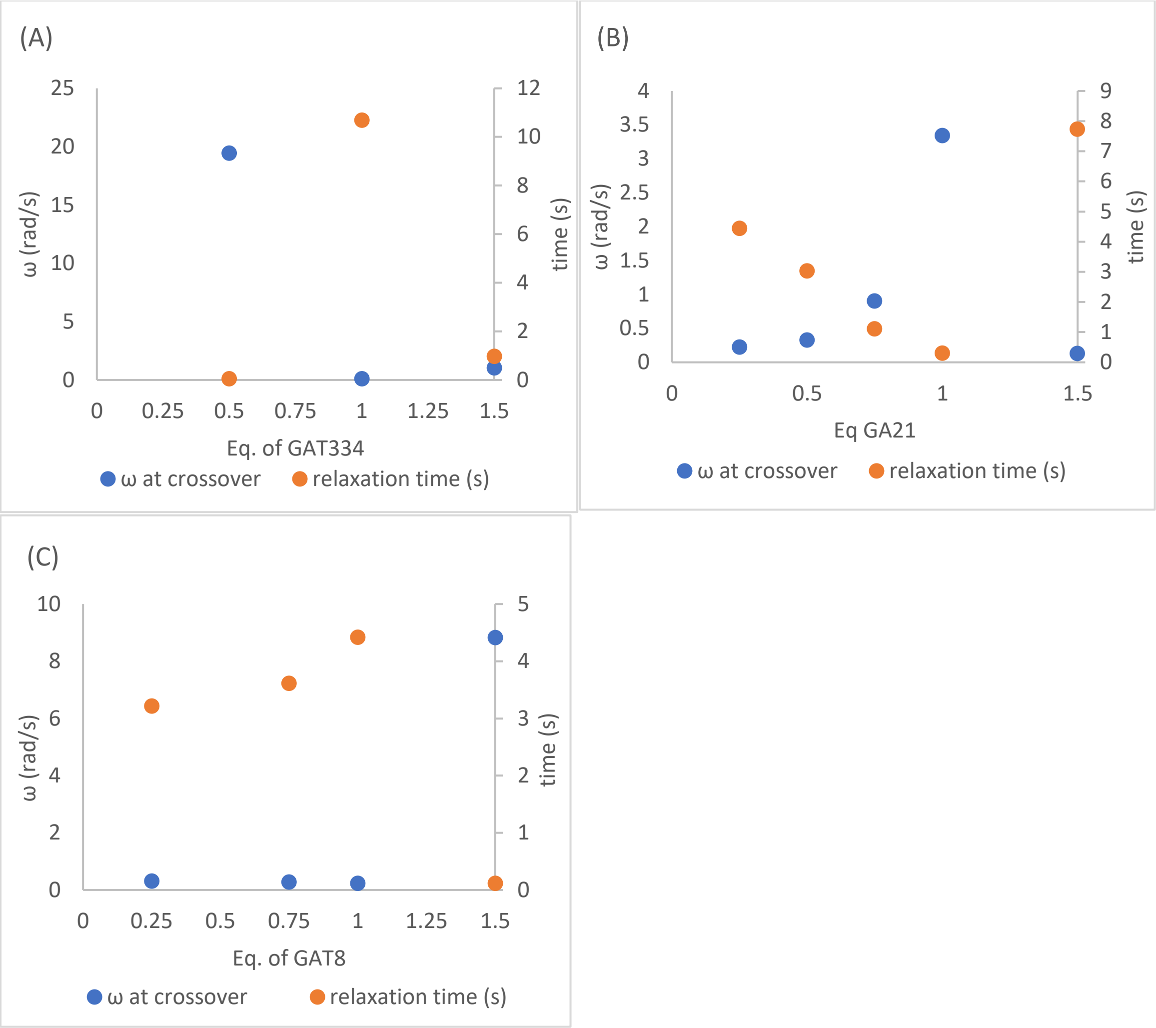


Figure S17 – Crossover points and relaxation times plotted against equivalents of gluconamidosilicones for a) **GAT334-BA77** materials, b) **GAT21-BA77** materials, and c) **GAT8-BA77** materials.

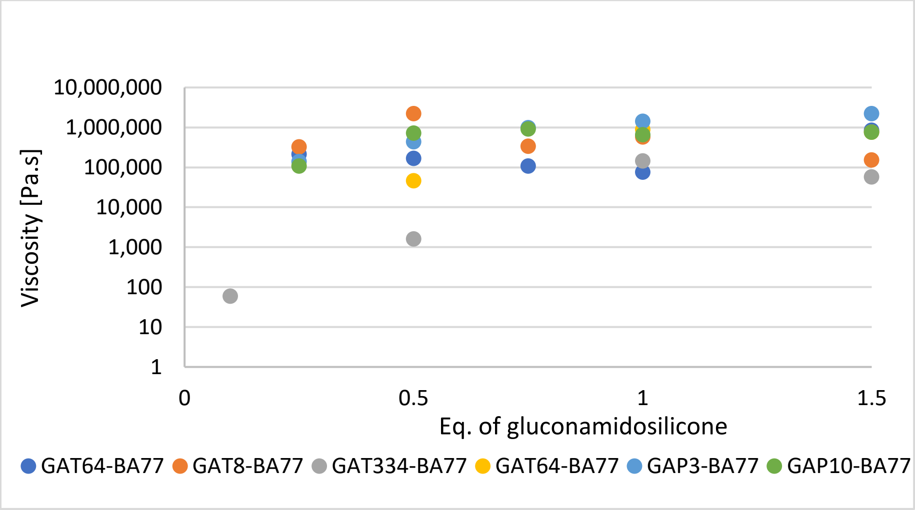


Figure S38 – Zero shear viscosities of all materials. Materials show around the same range of viscosities except for samples made with longer-chain telechelic aminosilicone **(GAT334)**.

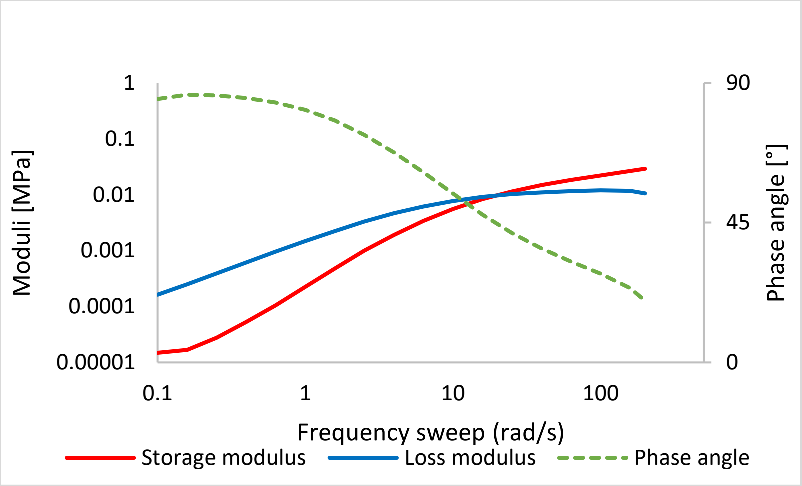
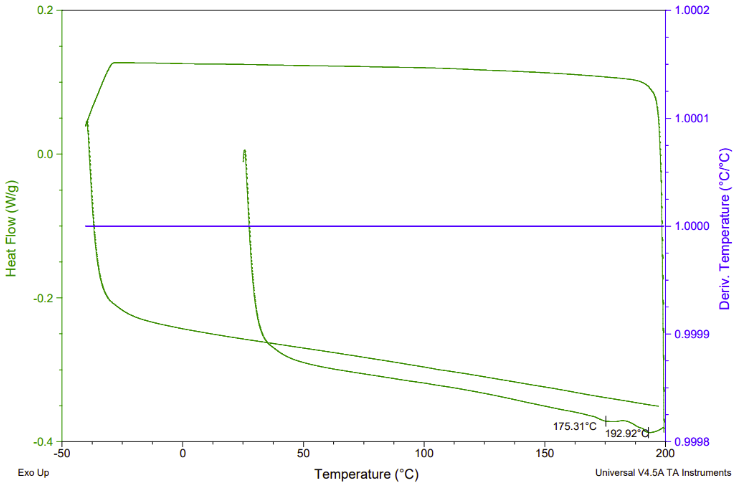
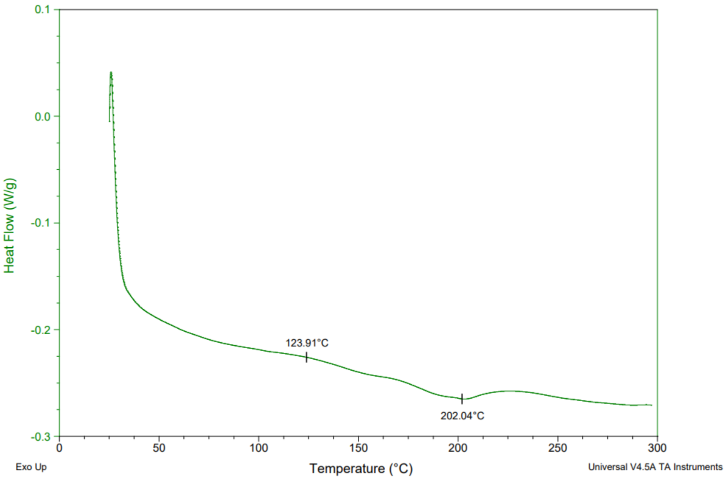


Figure S39 – Frequency sweep data of **GAT334-BA77** (0.5 eq. loading of **GAT334**).



A



B

Figure S40 – The DSC of a) **GAP3** and b) **GAP3-BA77** (1 eq.). A slight shift of the melting point is observed from 192 °C to 202 °C upon the introduction of boronic esters.