SILICONE-BORONIC ACIDS

SYNTHESIS AND CHARACTERIZATION OF NOVEL STIMULI-RESPONSIVE SILICONE-BORONIC ACID MATERIALS

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Abstract

Silicone polymers and network-materials have proven extremely useful in a variety of applications owing to their superb properties when compared to carbon-based polymers. Polysiloxanes containing functional groups other than simple alkyl moieties have allowed for further manipulations of pendant groups along the polymer backbone leading to a greater range of possible chemical transformations, as well as changes in physical/interfacial properties. One aspect of functional polymers that has yet to be explored with respect to primarily silicone-based systems is that of stimuli-responsive materials. In order for this unique application to work, silicones must be functionalized with a group or groups that can influence the polymer's properties based on that group's response to specific external stimuli. Boronic acids represent one such group, wherein the most common stimuli used to affect changes in ionization state and solubility are pH and diol-binding. Boronic acids are also capable of forming weak hydrogen-bonded dimers with other boronic acids, and dynamic covalent bonds with Lewis bases. It is proposed that the covalent attachment of boronic acids and their derivatives onto silicones could lead to stimuli-responsive silicone materials.

Herein, the synthesis of silicone-boronic acids and their protected boronic esters is described. The simple two-step method involving boronic acid protection followed by hydrosilylation has led to a variety of molecules differing in molecular weight and three-dimensional geometry through the use of commercially available hydride-functional silicones. Initial results regarding saccharide binding selectivity and the impacts on silicone solubility are provided.

The unique interfacial behaviour of silicone-boronic esters and their propensity to form self-assembled, crosslinked films at an air/water interface are also reported. Using several different diol protecting groups and a variety of aqueous sub-phases, the mechanism for changes in physical properties as well as crosslinking were revealed.

Finally, the production of new thermoplastic silicone elastomers from silicone-boronic esters and amine-containing molecules is discussed. The Lewis acid/Lewis base complexation that occurs between nitrogen and boron can provide enough strength to produce robust, yet recyclable, silicone elastomers without the use of catalyst or solvent. Elastomers can be easily dissolved and reformed through the introduction and removal of a mono-functional Lewis base. The impact of crosslink density, controlled by the quantities and molecular weights of each polymer component used, on physical characteristics is reported.

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ARES	Advanced Rheometrics Expansion System
AEAPS	2-4% Aminoethylaminopropylmethylsiloxane-dimethylsiloxane copolymer
APS	6-7% Aminopropylmethylsiloxane-dimethylsiloxane copolymer
BA	Boronic Acid
CSiBA	Catechol-protected Silicone Boronic Acid
DMSO-d_6	Deuterated Dimethylsulfoxide
DSC	Differential Scanning Calorimetry
FG	Functional Group
MM	Hexamethyldisiloxane
I/I	Internal isomer
G’’	Loss Modulus (Viscous Modulus)
MW	Molecular Weight
NMR	Nuclear Magnetic Resonance
M_n	Number-average Molecular Weight
D_4	1,1,3,3,5,5,7,7-Octamethylcyclotetrasiloxane
Pa	Pascals
PMDS	Pentamethyldisiloxane
PBS	Phosphate-buffered Saline
PSiBA	Pinacol-protected Silicone Boronic Acid
PDMS	Poly(dimethylsiloxane)
RAFT	Reversible Addition-fragmentation Chain-transfer
RTV	Room-temperature Vulcanization
SiBA/SBA	Silicone Boronic Acid
G’	Storage Modulus (Elastic Modulus)
TPVPBA	Tartrate-protected Vinyl Phenyl Boronic Acid
TSiBA	Tartrate-protected Silicone Boronic Acid
T/t	Terminal isomer
TGA	Thermogravimetric Analysis
TPE	Thermoplastic Elastomer
TAEA	Tris(2-aminomethane)
Tris	Tris(hydroxymethyl)aminomethane
UV	Ultraviole

CHAPTER 1: Introduction

1.1 Synthesis of functional silicone polymers

Polymers based on alkylated silicon atoms alternating with oxygen atoms, called silicones, were first discovered in the early 20th century[1] and were made industrially relevant through a simplified production method in the 1940s.[2] Silicone polymers most often possess methyl groups attached to silicon, producing poly(dimethylsiloxane) (PDMS, Figure 1.1), however, a variety of other alkyl and aryl moieties are also accessible. Although highly utilized commercially, fully methylated siloxane polymers on their own lack many of the properties that are sought after in certain emerging fields in the materials industry, namely the possibility for further chemical manipulations and the ability to elicit a response from the polymer based on some external stimuli such as light, heat, and changes in their chemical environment. Moving dimethylsilicone polymers forward is going to require introduction of reactive and/or responsive functional groups that can elicit novel physical and interfacial properties. It is for this reason that the study and synthesis of more complex functional silicones have become increasingly popular over the past several decades.[3] I will first outline traditional routes to silicones, and then describe the potential for boronic acids to provide the synthetic handle that could lead to responsive silicone materials.

In order to obtain high molecular weight linear PDMS, cyclic silicones (typically D_4, $(Me_2SiO)_4$) are inserted into low molecular weight oligomers (MM, $Me_3SiOSiMe_3$), also called end-cappers, in the presence of an acid or base catalyst (Figure 1.1A).[4] The equilibrium process leads to a mixture of cyclic oligomers and linear polymers, the molecular weights of which depend upon the initial concentration of the end-capper. Using this method, it is also possible to produce terminal- and pendant-functional silicones (Figure 1.1B) simply by replacing one methyl group on each end of MM with the desired terminal functional group (e.g., $Me_2FGSiOSiFGMe_2$, where FG = functional group), or replacement of one or several of the methyl groups on D_4 with the desired pendant functional group.[4]

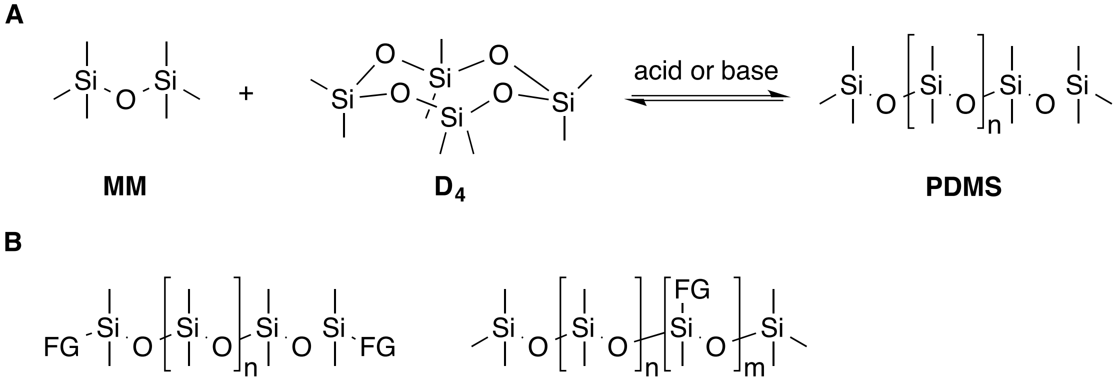


Figure 1.1. (A) Synthesis of linear PDMS and (B) examples of functional silicones

Insertion of functional groups into PDMS not only leads to changes in the physical properties of the polymers, but also provides a means for further chemical manipulations, including crosslinking to produce robust elastomeric networks (further discussed in Section 1.6) and introduction of other reactive or responsive functional groups that may not be compatible with the equilibration process.

An example of non-reactive functional groups that can be introduced by equilibration are long-chain (C_8-C_{40}) alkyl groups. Though not generally considered reactive, long alkanes can make PDMS much more compatible with other hydrocarbons, imparting greater solubility and lubricity to silicones.[5] Incorporation of chloropropyl groups to PDMS, on the other hand, can provide a synthetic handle for further transformations by nucleophilic substitution reactions. For example, Diao et al. recently reported a new heat-curable silicone rubber system that involves a reaction between chloropropyl-functional PDMS and two different amine-containing silicones; the resulting elastomers are comparable in strength to traditional peroxide- or hydrosilylation-cured materials.[6] The Brook group has also reported the indirect use of chloropropylsiloxanes in crosslinking through an initial azide-substitution reaction followed by Huisgen 1,3-dipolar cycloaddition to give functional silicone elastomers.[7] Using similar chemistry, thermoplastic silicone elastomers that can be covalently crosslinked by exposure to UV-irradiation have been produced from coumarin-functionalized PDMS. Thus, in addition to the use of somewhat limiting siloxane chemistry, silicones can also be synthetically manipulated using organic chemistry embedded in alkyl or aryl ligands.

The latter example represents a unique illustration of silicones as responsive polymers, a field that has been extensively studied in other polymeric systems[9] but has not yet been well established in the silicone world. Understanding the effects of other stimuli, such as changes in pH or the presence of biological molecules, on the interfacial and physical properties of functionalized silicones, would allow the design of new materials for applications in which stimuli-responsive polymers are currently used and, because of the unusual properties of silicones, could lead to creation of new applications.

1.2 Surface characteristics of silicone polymers

Silicone polymer backbones possess very high flexibility when compared to typical linear hydrocarbon polymers due to the 145° bond angle and low bending force constant of the Si-O-Si linkage.[10] This flexibility allows for methyl groups along the backbone of PDMS to present more readily at an air-water interface, providing lower surface energy (~20 dynes/cm) compared to typical hydrocarbon surfactants (30 dynes/cm) for which methylene groups dominate the interface.[11] The presentation of methyl groups at the air interface also means that silicones are hydrophobic and therefore resistant to water penetration.[4] Backbone flexibility is also responsible for providing low glass transition temperatures (~150 K) for even very high molecular weight silicones, meaning that they have high mobility and are liquids across a broad range of temperatures including room temperature.[12]

Much is known about the surface properties of non-functional PDMS, however, very little has been reported for silicone polymers containing small functional groups other than methyl owing to the fact that these modified silicones are often designed with the intent to maintain PDMS surface properties (with the exception of silicone surfactants, for which the surface properties are drastically different).[12] It is of interest to uncover whether or not there is the possibility for subtle changes in surface properties as a consequence of external stimuli. A versatile starting point, offering potential responsiveness to multiple different stimuli, could be provided by the introduction of boronic acids to silicones. The geometry, acidity, hydrophilicity, ionization state, and solubility of boronic acids can be altered in response to various stimuli, as discussed in Sections 1.3 and 1.4, and it was our proposal that their presence may afford similar changes in the interfacial characteristics of the silicone polymers to which they are tethered.

1.3 Synthesis and properties of boronic acids and their derivatives

Boronic acids (BA) are polar, Lewis acidic functional groups that consist of a carbon-boron bond with the remaining valence on boron occupied by hydroxyl groups (**1**, Figure 1.2). Typically water-insoluble in the non-ionic state, boronic acids have traditionally been applied to carbon-carbon bond formation reactions in chemical synthesis, the most notable example (due to its application in the synthesis of biologically relevant biaryl compounds) being the Suzuki-Miyaura cross-coupling reaction in which arylboronic acids are coupled with halogen-containing molecules in the presence of a palladium catalyst.[13] The broad range of substrates obtained from such reactions has been made possible by the variety of conditions available for the introduction of boronic acids to organic molecules, in particular, aryl functional groups. The direct synthesis of boronic acids can be achieved through treatment of aryl-metal intermediates with borates,[14] transmetallation of aryl silanes and stannanes,[15] coupling of aryl halides with diboronyl reagents[16] and direct boronylation by transition metal-catalysed C-H functionalization,[17] among others.[18] For the indirect synthesis of boronic acid-containing substrates, there are numerous commercial boronic acids containing synthetic handles, such as alkenes, amines, and halogens, such that alternative coupling reactions can be used to embed the boronic acid in the desired target.

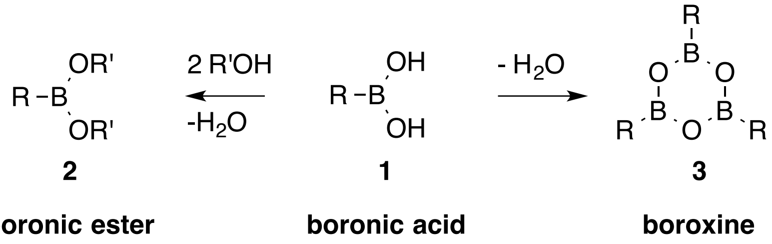
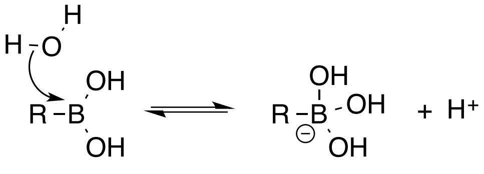


Figure 1.2. Boronic acid derivatives

The electronic configuration at boron in a boronic acid is such that the neutral boron atom bears six electrons and an empty p-orbital, and is therefore sp^2-hybridized, making it a Lewis acid. Boronic acids can readily be converted from sp^2- to sp^3-hybridized through electron pair donation by a Lewis base, leading to their use as water-tolerant and thermally stable Lewis acid catalysts.[19] The Lewis acidity of boronic acids is closely linked to their Brønsted acidity, in that they do not behave like traditional Brønsted acids by losing a proton from one of their –OH groups, but ionize a molecule of water upon coordination to yield a tetrahedral boronate anion **4** and a proton or hydronium ion, as demonstrated in Figure 1.3, thus defining the pK$_a$ of the boronic acid.[20] The Brønsted and Lewis acidities of boronic acids are therefore highly dependent upon the electron density at boron, with greater electron deficiency leading to higher acidity.[21] It is possible to adjust the electron density at boron by manipulating the electronic properties of the alkyl moiety of the boronic acid. For example, phenylboronic acid (pK$_a$ = 8.9) can be made more Lewis/Brønsted acidic by introducing a nitro group in the 4-position of the aromatic ring (4-nitrophenylboronic acid, pK_a = 7.1) or less acidic by introducing a methoxy group in the same position (4-methoxyphenylboronic acid, pK_a = 9.3).[21] As discussed later in Section 1.3.1, control over the acidity and therefore ionization state and geometry of boronic acids is essential for their successful use in biological applications.



1 **4**

Figure 1.3. Boronic acid ionization equilibrium

Despite their synthetic utility, the polarity and reactivity of free boronic acids can sometimes prove problematic and must be mitigated by temporary protection as the ester[21] or conversion to a boronic acid anhydride (boroxine, **3** Figure 1.2). Conversion of boronic acids into their corresponding boronic esters (**2**, Figure 1.2) is achieved through a condensation reaction between alcohols and boronic acid hydroxyl groups. Conditions required for these transformations can be quite straight-forward, by virtue of the fact that boronic esters tend to be less polar than their acid counterparts they often precipitate from solution upon formation. If precipitation is not practical or possible, azeotropic distillation of water, or dehydrating agents such as molecular sieves or magnesium sulphate may also be employed to drive the reaction forward.[21]

1.3.1 Boronic acid binding mechanisms

Complexation between alcohols and boronic acids is not only used for protecting or altering the reactivity of boronic acids, it also represents the basis for their major non-synthetic applications. The unique characteristics of the boronic acid functional group make it amenable to multiple modes of binding with various entities such as other boronic acids, diols, enzymes, cell surface saccharide biomarkers, and various Lewis basic molecules.[22] This has led to their use in areas of research such as saccharide sensing[23] and purification,[24] enzyme inhibition,[25] artificial lectin (carbohydrate-binding macromolecules) synthesis,[26] and drug delivery.[27] For the purposes of this thesis, focus will be placed on the diol binding, hydrogen bonding, and Lewis acid properties of boronic acids.

The equilibrium reaction of boronic acids with 1,2- and 1,3-diols produces particularly stable 5- or 6-membered cyclic boronic esters (Figure 1.4).

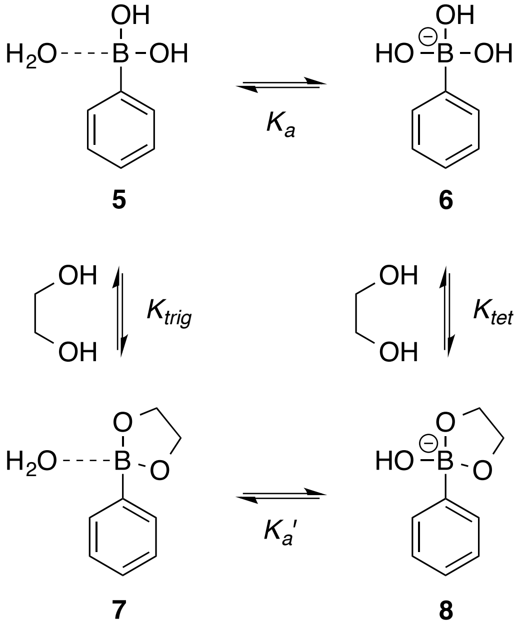


Figure 1.4. Boronate-diol binding equilibria[28]

The subscript notation for each binding constant describes the state in which binding occurs. Complexation between diols and tetracoordinate boronates occurs much more rapidly than with tricoordinate boronic acids,[29] and the boronic acid diol ester is known to be more acidic than the acid itself.[30] In other words, K_{tet} is greater than K_{trig} and K_a' is greater than K_a. The anionic boronate ester (**8**, Figure 1.4) is a relatively stable complex compared to the neutral ester **7** due to the release of strain in the ring upon conversion from trigonal planar to tetrahedral geometry at boron through coordination of an hydroxide ion.[28] Other Lewis bases can also provide this stabilizing effect on BA-diol complexes.[31] Rigid *cis* diols such as those found in sugars tend to form much more stable complexes with boronic acids than acyclic diols,[28] making boronic acids ideal for the detection of saccharides in solution. The coupled equilibria are important to consider when observing sugar/boronic acid binding, however, there are several other factors that complicate these experiments. For instance, pyranose to furanose isomerization of reducing saccharides can introduce an additional binding entity, and the multiple options for 1,2 and 1,3-binding on most natural sugars increases the number of potential complexes even further.[28] It is still possible to determine the structures of many complexes in solution[32] and the selectivity order (ᴅ-fructose > ᴅ -galactose > ᴅ-glucose) for monoboronic acids was determined over half a century ago.[20] In order for an appreciable (detectable) concentration of BA-sugar complexes to form in solution, it would be ideal to form the strongest complex (the tetrahedral boronate ester). The simplest way to achieve high concentrations of tetrahedral boronate ester is to increase the pH of the solution above pK_a', although other Lewis bases may facilitate this change at lower pHs (see below). The changes in physical properties induced by saccharide binding to boronic acid-containing molecules and polymers are discussed in further detail in Chapter 2.

Although not as strong in solution as the reversible covalent interactions discussed above, intermolecular interactions between boronic acids may also be of use to materials applications. Hydrogen bonding between BA hydroxyl groups leads to a common observation of dimers in the crystal structures of boronic acids (Figure 1.5). In general, hydrogen-bonded BA pairs have been studied in the solid state, with uses in supramolecular construction.[33] The relevance of boronic acid pairing in polymer chemistry will be discussed in Section 1.4.

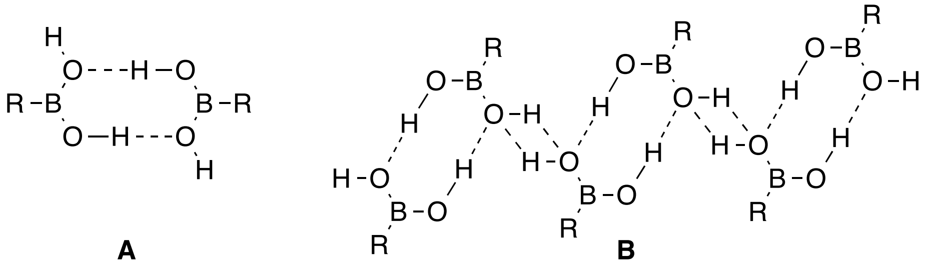


Figure 1.5. Hydrogen bonding of boronic acid (A) dimer and (B) extended system

Interactions between or replacement of the hydroxyl groups on boron are not the only ways in which boronic acids can associate themselves with other molecules. The coordination of electron-donating Lewis bases such as amines to the empty orbital on boron also leads to strong, yet reversible, covalent complexes. Analogous to the improved stability of BA-saccharide complexes in the presence of hydroxide ions (at high pH) discussed previously in this section, the intramolecular coordination of amines also leads to stabilization of such complexes.[34] Boron-nitrogen interactions are notably stronger for boron-containing molecules of higher electrophilicity, such as BF_3 and $B(C_6F_5)_3$,[35,36] however, binding between boronic acids and Lewis bases may be improved by removal of inhibitors such as competing Lewis bases or solvents.

A common approach that has been taken to improve the sensitivity or response of systems dependent upon intermolecular interactions and/or binding is to increase the concentration of binding sites in the system, which leads to the consideration of polymers and their role in boronic acid applications.

1.4 Boronic acids in polymers

A number of the previously mentioned applications of boronic acids involve their incorporation into polymers, producing stimuli-responsive materials. Polymers provide easy-to-handle scaffolds for response detection by means of swelling,[37] real-time fluorescence,[38] aggregation causing turbidity in solution,[39] macroscopic associations[40] and others that are otherwise unattainable for solution-based molecular systems. The interfacial characteristics and physical properties of BA-containing polymers can be tailored for specific applications based on the location and type of response required. For example, hydrophilic monomers have been co-polymerized with boronic acid monomers to afford block copolymers that are able to self-assemble into water-soluble aggregates that dissociate based on the boronic acid block's response to changes in pH and glucose concentration.[39] On the other hand, insoluble scaffolds such as BA-polymer monoliths have been produced for high yielding solid-phase extraction of diols.[41] An added benefit of polymeric, rather than unimolecular, systems containing boronic acids is the potential for multivalent binding for improved detection sensitivity to otherwise low-affinity compounds such as glucose.[23] Responsive boronic acid materials are not only useful for the detection of BA-binding molecules, but also for the stimulated release of actives such as insulin. Kataoka et al. reported a boronic acid containing gel system that selectively swelled and released insulin at a higher rate in the presence of glucose, and release was slowed when glucose was removed from the system.[37]

More subtle changes in polymeric surfactant behaviour have been observed for those containing boronic acids in comparison with their non-functional counterparts. Inclusion of boronic acids in surfactant structures can lead to strong intermolecular interactions that cause higher than usual surface tensions. One example of this phenomenon is the extraordinary monolayer cohesiveness observed by Hendel et al. for calixarene surfactants containing six boronic acid units as the "hydrophilic" portion.[42] The intention was to synthesize the BA-calixarenes and promote cohesiveness through dehydration to the corresponding crosslinked boroxine network, however, they determined that intermolecular BA-BA interactions were strong enough to produce a measureable increase in surface tension without dehydration. Cohesiveness was not observed for analogous mono-boronic acid calixarenes, once again outlining the importance of multiple binding sites if one hopes to generate enhanced properties.

The coordination of Lewis bases to boronic acids has also been employed in the production of poly(boronic acid) networks. Christinat et al. produced reversible polymer networks through the B-N association of bipyridines to di(boronic esters).[43] Although they were able to isolate and analyze the novel polymer networks, the B-N interactions were weak enough to be disrupted by placement of the polymer in hot chloroform.

The impact of PDMS interfacial characteristics on boronic acid containing systems is yet to be examined. There is great potential for the use of boronic acids in not only solution-based responsive systems (i.e., silicone surfactants) but also in gels and solid-phase systems produced from crosslinked silicone elastomers. The presence of boronic acids in silicones may lead to a variety of new behaviours: polar, responsive functional groups on silicones could lead to changes in solubility and other interfacial characteristics in response to boronic acid-specific stimuli such as pH and diols; self-association of boronic acids within silicone networks could provide cohesiveness that is not observed for other common functional groups on PDMS; and, Lewis bases could provide reversible formation of silicone-boronic acid networks. Preliminary research into each of these areas is presented within this thesis.

1.5 Thesis Focus I: Synthesis and properties of silicone-boronic acids

Functional PDMS can be obtained readily from methods discussed in Section 1.1, providing synthetic handles that can be used toward more reactive silicone polymers. Hydride-functional silicones of the pendant and terminal type are of particular value due to their applicability in hydrosilylation reactions of alkenes (Figure 1.6).[5] The platinum-catalyzed addition reaction creates a new silicon-carbon bond from hydrosilanes and alkenes, and results in the production of two isomers: β-silylation leads to the terminal (more prevalent) isomer, and α-silylation leads to the internal isomer. Although the most widely utilized application for hydride-functional PDMS has historically been in the production of elastomers (see Section 1.6), they have also been useful in the introduction of various functional groups to PDMS[44] and the synthesis of complex siloxane architectures.[45] Many hydrosilane oligomers and polymers are commercially available for these uses, leading to a convenient method for developing various substrates for the study of structure-property relationships in functional silicones.

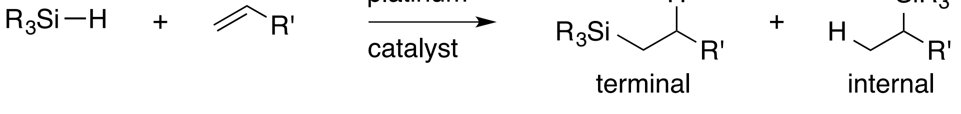


Figure 1.6. Metal-catalyzed hydrosilylation reaction

Polymers containing functional groups that can respond to stimuli such as pH, light, or heat appeal to the biomedical and analytical communities due to their selective and controllable behaviour. Stimuli-responsive silicone-based materials have not been the topic of much research, despite the favourable features of silicones in general. Recent work in the Brook research group has successfully demonstrated the heat-[8b] and light-responsive[8a] behaviour of certain functional silicones. Therefore, it was hypothesized that PDMS may also be amenable to additional functionalization to afford responses to small-molecule stimuli as well as changes in pH. Boronic acids and their derivatives may impart saccharide-sensing and pH-responsive properties if incorporated into silicone structures, provided their sugar-binding capabilities are not impeded by internal boronate complexation to the siloxane backbone or the high hydrophobicity of the material. In Chapter 2, the synthesis of small molecule and polymeric α,ω- and pendant-functional silicone-boronic esters and acids is disclosed and the impact of Lewis bases and varied pH on selective saccharide binding affinity is examined. It was observed that the presence of covalently attached silicone structures did not affect the ability of boronic acids to selectively bind to fructose. Binding was influenced by the presence of Lewis basic tris(hydroxymethyl)aminomethane, as shown using NMR spectroscopy.

1.6 Methods for crosslinking silicone polymers

1.6.1 Thermoset elastomers

Silicone-based materials offer a highly versatile platform for numerous applications owing to their desirable physical/mechanical properties. Most often, thermoset silicone elastomers are prepared by crosslinking high molecular weight poly(dimethylsiloxane) linear chains. A couple of books have been published that discuss the various existing crosslinking methods for silicones,[4,46] some of which are described in this section. An important aspect of siloxane crosslinking that must be considered when aiming for certain material properties is the specificity of crosslinking chemistry employed. It has been demonstrated that random crosslinking methods, like radiation-induced crosslinking, lead to a greater number of dangling ends in the network and ultimately have a detrimental effect on the physical properties of resulting elastomers.[47] More selective crosslinking of end-groups or pendant functional groups tends to provide greater order in the network and therefore better physical properties. Depending on the functional groups on silicon, crosslinking method and density, and the amount and type of filler used, materials can be made to be highly temperature/solvent resistant, flexible, and strong.[48] Improvements in processing and curing of silicones over the past several decades have expanded their applications; they are currently used for biomedical implants, sealants and various other aspects within automotive industry, bake ware and cookware, electrical and electronics (cable insulators, terminators, connectors), molding, encapsulation for semi-conductors and in the manufacture of toys.[49] Room-temperature vulcanization (RTV) and addition cure are two widely used methods for crosslinking silicone polymers.[50] The major difference between the end products for each method is that RTV, also known as condensation cure, can produce “pure” silicone networks where each silicon is linked through SiO bonds, while addition cure leads to hydrocarbon spacers within the network. RTV of silicones is achieved through a nucleophilic substitution at silicon between OH groups on hydroxyl-terminated PDMS and tri- or tetra-functional silanes ($RSiX_3$ or SiX_4 where X is a leaving group) to create new Si-O-Si bonds. The rate of condensation curing is dependent on the silane leaving group, while various acid, base, and metal catalysts, in addition to water as co-catalyst, may be employed to improve leaving group ability.[4] Addition cure leads to crosslinking via platinum-catalyzed hydrosilylation (Figure 1.6) between hydride-functional PDMS and vinyl-functional PDMS. Both types of crosslinking can occur rapidly under mild conditions.

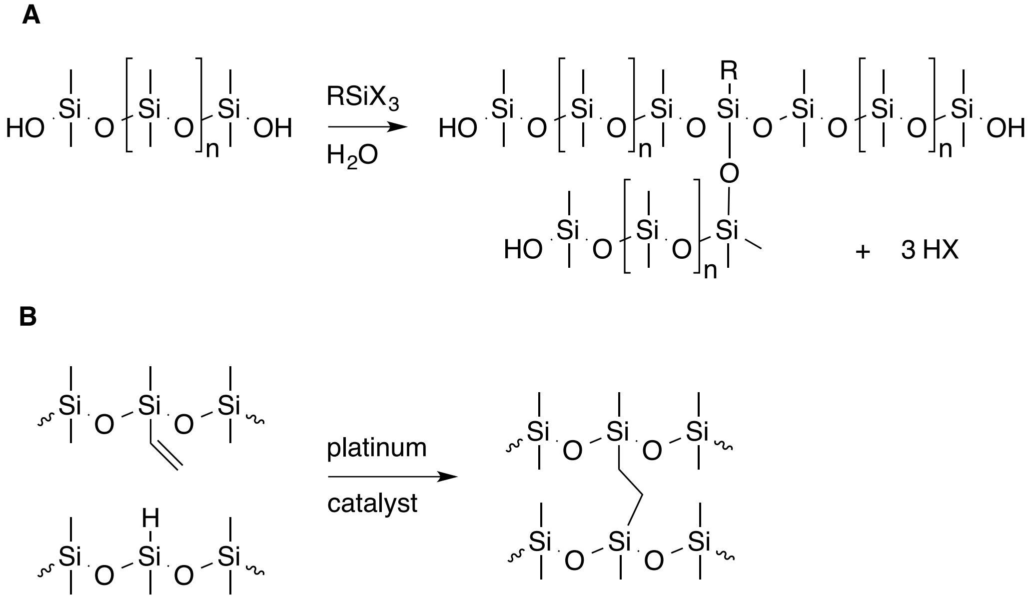


Figure 1.7. (A) Condensation and (B) addition cure of silicones

One common attribute of the frequently employed methods for silicone crosslinking is their irreversibility: covalent bonds formed between silicone polymer chains are not readily broken back down into their primary components. In other words, silicone elastomers, in general, are non-recyclable materials. From a materials perspective, this can be considered beneficial since silicones do not readily degrade and are therefore quite robust, however, this characteristic stability does not lend itself readily to the repurposing or remolding of silicones, or their application in tunable systems.

1.6.2 Thermoplastic elastomers

Thermoplastics are physically crosslinked materials that combine the processability of plastics (either by melting or dissolving in solvent) and the physical properties of rubbers.[51] This combination of properties is most often achieved through the synthesis of block copolymers that contain a "hard" plastic segment that co-crystallizes to produce physical crosslinks within a "soft" elastic segment.[52] Silicone polymers are ideally suited to play the role of the soft segment in thermoplastic elastomers (TPE) since even very high molecular weight PDMS remains liquid at room temperature. Examples of traditional TPE systems containing silicone soft segments include silicone polyurethanes,[53] poly(butylene terephthalate) or polystyrene block copolymers.[54] Three examples are known to exist that contain only linear, functionalized silicones: coumarin-functionalized PDMS synthesized through thermal azide/alkyne cycloaddition reactions,[8b] boronic ester-modified silicones that crosslink upon hydrolysis[55] (the topic of Chapter 2) and a system based on the formation of coordinate covalent bonds between aminosilicones (and other amine-containing polymers) and silicones containing at least three boronic ester groups,[56] as discussed in Chapter 4. In addition to possessing the desirable properties of silicones and thermoplastics, the last two examples also represent a class of stimuli-responsive polymer networks. Owing to the presence of boronic acids and their derivatives, silicone polymers modified with boronic acids possess the qualities of pH- and diol-responsiveness outlined in Section 1.3, providing tunable or triggerable surface activity and physical properties.

1.7 Thesis Focus II: Silicone-boronic acids at the air/water interface

As discussed in Section 1.2, PDMS on its own has unique properties at interfaces owing to its flexible inorganic backbone and methylated silicon atoms. These properties, particularly the low intermolecular forces between chains (high chain mobility), have led to the widespread use of silicones in applications in which wetting is required such as anti-foaming agents, water-repellent coatings, and cosmetics.[57] All of these applications make use of silicones as passive ingredients that impart predictable, static characteristics to the formulation. For those applications that require crosslinking for stabilization, curing is often achieved in a one-component system upon exposure to moisture in air,[57] leaving an irreversible silicone coating; coatings that are crosslinked through reversible molecular interactions have not been widely studied. In keeping with the state of the art, a moisture-curing silicone coating that could respond to changes in its environment could provide a new avenue for the exploration of responsive materials. The unusual behaviour of boronic acid-modified silicones with respect to protecting group hydrolysis and self-association into stable, load-supporting layers at the air/water interface is examined in Chapter 3. Silicone boronate esters were found to spread across water in a similar manner to non-functional PDMS with the exception that exposure to water led to physical crosslinking of the silicone phase on certain aqueous sub-phases. Competitive boronic acid binding molecules, and pH conditions that lead to the increased solubility of boronates led to disintegration of silicone-boronic acid layers.

1.8 Thesis Focus III: Thermoplastic silicone elastomers through Lewis acid/base interactions

Although some examples of thermoplastic silicone elastomers do exist, the majority of network materials made from PDMS are permanently crosslinked thermosets. The focus of Chapter 4 is given to the synthesis of novel silicone elastomers through reversible crosslinking between Lewis acidic silicone-boronic ester polymers and Lewis basic amine-containing molecules, including silicone polymers, organic polymers and multi-dentate small molecules. We hypothesize that silicone networks produced from Lewis acid/base interactions should be reversible through the introduction of small molecules that competitively bind to either component of the mixture. Networks produced from reversible covalent linkages should be more robust than those produced from physical interactions such as hydrogen bonding, and should therefore be amenable to characterization using typical elastomer analyses such as swelling and compression.

1.9 References

1. Klosowski, J. M.; Wolf, A. T., The History of Sealants. In *CRC Handbook of Sealant Technology*, Mittal, K. L.; Pizzi, A., Ed. CRC Press: 2009; pp 13-17.

2. Rochow, E. G., *J. Am. Chem. Soc.* **1945**, *67*, 963-965.

3. White, J. W., Recent Achievements in Industrial Silicon Polymer Science. In *Progress in Organosilicon Chemistry (Proceedings of the 10th International Symposium on Organosilicon Chemistry, Poznan, Poland, 1993)*, Marciniec, B.; Chojnowski, J., Ed. Gordon & Breach: Basel, 1995; p 363.

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

5. Marciniec, B., *Hydrosilylation*. Springer: Netherlands, 2009.

6. Diao, S.; Dong, F.; Meng, J.; Ma, P.; Zhao, Y.; Feng, S., *Mater. Chem. Phys.* **2015**, *153*, 161-167.

7. Rambarran, T.; Gonzaga, F.; Brook, M. A., *Macromolecules* **2012**, *45*, 2276-2285.

8. (a) Fawcett, A. S.; Hughes, T. C.; Zepeda-Velazquez, L.; Brook, M. A., *Macromolecules* **2015**, *Manuscript in preparation*; (b) Fawcett, A. S.; Brook, M. A., *Macromolecules* **2014**, *47*, 1656-1663.

9. Serpe, M. J., *J. Polym. Sci. A-1* **2013**, *51*, 2979-2979.

10. Grigoras, S.; Lane, T. H., Conformational Analysis of Substituted Polysiloxane Polymers. In *Silicon-Based Polymer Science: A Comprehensive Resource*, Ziegler, J. M., Fearon, F. W. G. , Ed. American Chemical Society Washington, DC, 1990; p 125.

11. Hill, R. M., Silicone Surfactants. Marcel Dekker: New York, 1999; p 3.

12. Owen, M. J.; Dvornic, P. R., General Introduction to Silicone Surfactants. In *Silicone Surface Science*, Owen, M. J.; Dvornic, P. R., Ed. Springer: 2012; Vol. 4.

13. Miyaura, N.; Suzuki, A., *Chem. Rev.* **1995**, *95*, 2457-2483.

14. (a) Seaman, W.; Johnson, J. R., *J. Am. Chem. Soc.* **1931**, *53*, 711-723; (b) Bean, F. R.; Johnson, J. R., *J. Am. Chem. Soc.* **1932**, *54*, 4415-4425.

15. (a) Sharp, M. J.; Cheng, W.; Snieckus, V., *Tetrahedron Lett.* **1987**, *28*, 5093-5096; (b) Haubold, W.; Herdtle, J.; Gollinger, W.; Einholz, W., *J. Organomet. Chem.* **1986**, *315*, 1-8.

16. (a) Marder, T. B.; Norman, N. C., *Top. Catal.* **1998**, *5*, 63-73; (b) Ishiyama, T.; Miyaura, N., *J. Organomet. Chem.* **2000**, *611*, 392-402.

17. Ishiyama, T.; Miyaura, N., *J. Organomet. Chem.* **2003**, *680*, 3-11.

18. Davies, M. W.; Johnson, C. N.; Harrity, J. P. A., *J. Org. Chem.* **2001**, *66*, 3525-3532.

19. Ishihara, K., Organoboronic Acids and Organoborinic Acids as Bronsted-Lewis Acid Catalysts in Organic Synthesis. In *Boronic Acids - Preparation, Applications in Organic Synthesis and Medicine*, 1 ed.; Hall, D. G., Ed. Wiley-VCH: Verlag GmbH & Co. KGaA, Weinheim, 2005.

20. Lorand, J. P.; Edwards, J. O., *J. Org. Chem.* **1959**, *24*, 769-774.

21. Hall, D. G., Structure, Properties, and Preparation of Boronic Acid Derivatives. In *Boronic Acids - Preparation, Applications in Organic Synthesis and Medicine*, 1 ed.; Hall, D. G., Ed. Wiley-VCH: Verlag GmbH & Co. KGaA, Weinheim, 2005.

22. Hall, D. G., *Boronic Acids - Preparation, Applications in Organic Synthesis and Medicine*. 1 ed.; Wiley-VCH: Verlag GmbH & Co. KGaA, Weinheim, 2005.

23. Wu, X.; Li, Z.; Chen, X.-X.; Fossey, J. S.; James, T. D.; Jiang, Y.-B., *Chem. Soc. Rev.* **2013**, *42*, 8032-8048.

24. Xu, Z.; Deng, P.; Tang, S.; Li, J., *Mat. Sci. Eng. C* **2014**, *40*, 228-234.

25. Baker, S. J.; Tomsho, J. W.; Benkovic, S. J., *Chem. Soc. Rev.* **2011**, *40* (8), 4279-4285.

26. Dai, C.; Sagwal, A.; Cheng, Y.; Peng, H.; Chen,W.; Wang, B., *Pure Appl. Chem.* **2012**, *84*, 2479-2498.

27. Guan, Y.; Zhang, Y., *Chem. Soc. Rev.* **2013**, *42*, 8106-8121.

28. James, T. D., Boronic Acid-Based Receptors and Sensors for Saccharides. In *Boronic Acids - Preparation, Applications in Organic Synthesis and Medicine*, 1 ed.; Hall, D. G., Ed. Verlag GmbH & Co. KGaA: Weinheim, 2005.

29. Pizer, R.; Tihal, C., Equilibria and reaction mechanism of the complexation of methylboronic acid with polyols. *Inorg. Chem.* **1992**, *31*, 3243-3247.

30. James, T.; Shinkai, S., Artificial Receptors as Chemosensors for Carbohydrates. In *Host-Guest Chemistry*, Penadés, S., Ed. Springer Berlin Heidelberg: 2002; Vol. 218, pp 159-200.

31. Bosch, L. I.; Fyles, T. M.; James, T. D., *Tetrahedron* **2004**, *60*, 11175-11190.

32. Norrild, J. C.; Eggert, H., *J. Chem. Soc., Perk. T. 2* **1996**, *1996*, (12), 2583-2588.

33. Fournier, J.-H.; Maris, T.; Wuest, J. D.; Guo, W.; Galoppini, E., *J. Am. Chem. Soc.* **2002**, *125*, 1002-1006.

34. James, T. D.; Sandanayake, K.; Iguchi, R.; Shinkai, S., *J. Am. Chem. Soc.* **1995**, *117*, 8982-8987.

35. Deakyne, C. A.; Liebman, J. F., *J. Mol. Struc.-Theochem* **1991**, *234*, 343-355.

36. Qin, Y.; Jäkle, F., *J. Inorg. Organomet. P.* **2007**, *17*, 149-157.

37. Kataoka, K.; Miyazaki, H.; Bunya, M.; Okano, T.; Sakurai, Y., *J. Am. Chem. Soc.* **1998**, *120*, 12694-12695.

38. Suri, J. T.; Cordes, D. B.; Cappuccio, F. E.; Wessling, R. A.; Singaram, B., *Angew. Chem. Int. Edit.* **2003**, *42*, 5857-5859.

39. Roy, D.; Sumerlin, B. S., *ACS Macro Lett.* **2012**, *1*, 529-532.

40. Nakahata, M.; Mori, S.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H.; Harada, A., *ACS Macro Lett.* **2014**, *3*, 337-340.

41. Cakal, C.; Ferrance, J. P.; Landers, J. P.; Caglar, P., *Anal. Chim. Acta* **2011**, *690*, 94-100.

42. Hendel, R. A.; Janout, V.; Lee, W.; Regen, S. L., *Langmuir* **1996**, *12*, 5745-5746.

43. Christinat, N.; Croisier, E.; Scopelliti, R.; Cascella, M.; Roethlisberger, U.; Severin, K., *Eur. J. Inorg. Chem.* **2007**, *2007*, (33), 5177-5181.

44. Marciniec, B., Functionalisation and Cross-Linking of Organosilicon Polymers. In *Hydrosilylation*, Marciniec, B., Ed. Springer: Netherlands, 2009; pp 160-175.

45. Brook, M.; Grande, J.; Ganachaud, F., New Synthetic Strategies for Structured Silicones Using $B(C_6F_5)_3$. In *Silicon Polymers*, Muzafarov, A. M., Ed. Springer Berlin Heidelberg: 2011; Vol. 235, pp 161-183.

46. Stepto, R. F. T., Theoretical Aspects of Conformation-Dependent Properties. In *Siloxane Polymers*, Clarson, S. J.; Semlyen, J. A., Eds. Prentice Hall: Englewood Cliffs, NJ, 1993; p 373.

47. Mark, J. E., *Accounts Chem. Res.* **1985**, *18*, 202-206.

48. Burkus, F. S., Amarasekera, J., *Rubber World* **2002**, *June Edition*, 26-35.

49. Silicone Uses. http://sehsc.americanchemistry.com/Silicone-Uses - Rubber (accessed February 7th, 2015).

50. Thomas, D. R., Crosslinking of Silicones. In *Siloxane Polymers*, Clarson, S. J.; Semlyen, J. A., Eds. Prentice Hall: Englewood Cliffs, NJ, 1993.

51. Amin, S. A. a. M., *Rev. Adv. Mater. Sci.* **2011**, *29*, 15-30.

52. Gardner, H., *Thermoplastic Elastomers*. 2nd ed.; Munich, Germany, 1996.

53. (a) *NIIR Board of Consultants & Engineers. Silicone-modified Polyurethanes*. Asia Pacific Business Press: Delhi, India, 2006; (b) Thermoplastic Silicone-Urethane Copolymers: A New Class of Biomedical Elastomers. In *Medical Device & Diagnostic Industry Magazine*, 2000.

54. (a) Lei, C.-H.; Li, S.-L.; Xu, R.-J.; Xu, Y.-Q., *J. Elastom. Plast.* **2012**, *44*, 563-574; (b) Lautenschlager, H. D., J.; Keller, W.; Mayer, T.; Stark, K. Thermoplastic Silicone Block Copolymers, the Production Thereof and the use of the Same. US Patent No. 2004/0054115, Assigned by Wacker-Chemie GmbH, 2004; (c) Gerald A. Gornowicz, K. E. L., David J. Romenesko, Kim Struble, Hongxi Zhang Thermoplastic Silicone Elastomers. US Patent No. 6,013,715, Assigned by Dow Corning Corporation, 2000.

55. Zepeda-Velazquez, L.; Brook, M. A., *Chem. Mater.* **2015**, Manuscript in Preparation.

56. Dodge, L.; Chen, Y.; Brook, M. A., *Chem. – Eur. J.* **2014**, *20* (30), 9349-9356.

57. Owen, M. J.; Dvornik, P. R., Surface Applications of Silicones. In *Silicone Surface Science*, Owen, M. J.; Dvornik, P. R., Ed. Springer: 2012; Vol. 4.

CHAPTER 2: Sugar Complexation to Silicone Boronic Acids[†]

2.1 Abstract

A new class of surface-active compounds based on the combination of silicones and boronic acids is described. The properties of the compounds can be tuned by manipulation of both the hydrophobic (silicone size and 3D structure) and hydrophilic components (by binding different saccharides to the boronic acid). Stabilization of the four-coordinate boron structure is provided by Tris buffer that also maintains neutral pH to suppress silicone hydrolysis.

2.2 Introduction

Silicones are both highly mobile (Tg <123 °C)[1] and hydrophobic entities (surface energy 23 mN m^{-1})[2] and, as a consequence, are widely used – depending on formulation – as both foaming and defoaming agents.[3,4] When combined with hydrophilic entities,[5] particularly poly(ethylene glycol) and other polyether oligomers, they exhibit surface activities that cannot be matched by either fluorocarbon- or hydrocarbon-based surfactants. Silicone

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[†] This chapter is taken from M. A. Brook, L. Dodge, Y. Chen, F. Gonzaga and H. Amarne, *Chemical Communications*, **2013**, *49*, 1392-1394, and is reproduced by permission of Royal Society of Chemistry, 2013. Dodge developed the majority of experimentation with guidance from Chen, and Dodge performed all characterization and analyses. Dodge wrote the manuscript with additions, edits and guidance from Brook.

surfactants are used in applications ranging from polyurethane foam stabilization[3] to delivery of agricultural bioactives.[6]

It would be of interest to develop responsive surfactants, whose properties could be manipulated by external stimuli including pH, temperature, *etc.* Silicones are exceptionally stable near neutrality, but are subject to hydrolytic cleavage and depolymerization away from pH 7.[7] Amino- or carboxylic acid-modified silicones are readily available, but are not normally used as surfactants due to the associated pH sensitivity. As part of an examination of other potentially responsive organic functional groups, we chose to establish if boronic acids could be incorporated on a silicone backbone and used to mediate surface activity of the silicone.

Boronic acids ($RB(OH)_2$, BA) provide a highly flexible functionality that can be manipulated using a number of well-studied procedures. Not only can they be used in carbon-carbon bond forming reactions such as the Suzuki−Miyaura cross-coupling,[8] but the boronic acid hydroxyl groups provide pH-sensitive binding sites for appropriate diol-containing substrates.

The stability of boronate complexes is affected by the pH of the solution and the presence of any Lewis base. For example, the equilibrium between tri- **1** and tetracoordinate **2** boron compound favors the latter when Lewis bases are present, including hydroxide at higher pH.[9] The equilibrium is also affected by the R group on the boronic acid: arylboronic acids are more acidic than alkylboronic acids; and bulky substituents surrounding boron can cause a decrease in acidity due to the restricted access of water to the p-orbital on boron.[10]

Many applications of boronic acids rely on binding selectivity for specific 1,2- or 1,3-diol sites **3**, which are particularly prevalent on saccharides (Figure 2.1). This specificity has led to the use of boronic acids as tunable sensors for saccharides: the structure of a given BA will determine to which sugar it will preferentially bind. Based on selective binding several *in vivo* applications for BAs, such as drug delivery devices[11] and artificial lectin (sugar binding protein) mimics,[12] have been proposed. Key to the utility of boronic acids in such applications is the very large range of binding constants – over three orders of magnitude – for sugars with different diol stereostructures.[13,14] Stability of the cyclic products is enhanced when good Lewis bases are present **4**.

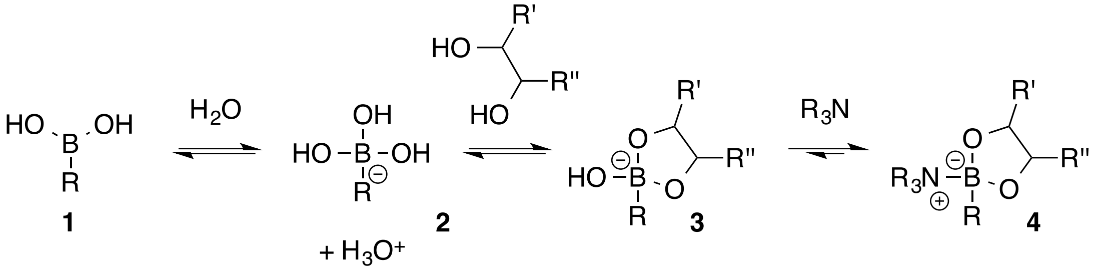


Figure 2.1. Boronate-diol binding equilibria[15]

Silicone-modified boronic acids should be interesting, tunable surfactants. If the presence of the hydrophobic silicone does not significantly affect the sugar binding properties of the boronic acid, it should be possible to modify the surface activity by controlling the size (length of linear polydimethylsiloxane chains) and 3D structure (the presence of branching in the silicone moiety) of the silicone hydrophobe, and also the hydrophilicity of the boron head group by manipulating the type and size of hydrophilic sugar to which the boron is temporarily grafted. We report the first synthesis of silicone boronic acids

(SiBAs) and provide preliminary data demonstrating their capacity to differentially bind saccharides.

2.3 Results and Discussion

4-Vinylphenylboronic acid (styrylboronic acid) **5** is a convenient starting material to which silicones can be grafted using the efficient hydrosilylation process.[16] Initial attempts to directly perform hydrosilylation on vinyl-substituted boronic acids, including **5**, were unfortunately only sporadically successful. Active hydrogen compounds including carboxylic acids and alcohols are known to react with Si−H groups to form H_2 and siloxanes in a process that can compete with the desired addition to alkenes, which is likely the origin of the inconsistent results.[17] It was necessary, therefore, to protect the B−OH groups. Although several protecting groups were examined many, including catecholates,[18] proved to be too stable to subsequent reactions: the conditions necessary for catecholate hydrolysis, for example, led to silicone redistribution/depolymerization.[7]

Therefore, a high yielding two-step synthesis was developed that required little purification and for which by-products were not observed (Figure 2.2). Dimethyl-L-tartrate boronic ester **6** was formed from the reaction of **5** with dimethyl tartrate. Simple dehydration using molecular sieves afforded **6** in near-quantitative yield, and required no purification prior to use in the subsequent reaction. The second step utilized platinum-catalyzed hydrosilylation of the protected acid **6** using Karstedt's catalyst at room temperature (Table 2.1). Compounds **7**, **8**, and **10**-**12** demonstrate the ability to vary the size of polydimethylsiloxane hydrophobes, while compound **9** has a different connectivity (branched 3D structure) between the hydrophobe and boronic acid moieties. The silicone-boronate compounds were isolated in good to excellent yield as a mixture of regioisomers that were inseparable by silica chromatography: their relative concentrations could be determined by ^{1}H NMR. Such regioisomeric mixtures during hydrosilylation are particularly problematic with aryl-substituted olefins.[16]

Prior to examining the ability of the silicone boronic acids to complex with sugars, the protecting tartrate had to be removed. Actually, it was necessary to maintain an anhydrous environment during the hydrosilylation to form compounds **7-12** because the tartrate boronic ester was very susceptible to hydrolysis (Figure 2.2). Silicone-boronic acids were liberated from their tartrate protecting groups to give **13t,i-18t,i** simply by treatment with PBS buffer within the pH range of 4.5 to 9.0. This was readily determined by observing changes in the chemical shift of diagnostic signals within the ^{1}H NMR spectra (for compound **7**, see Appendix Section 6.1).

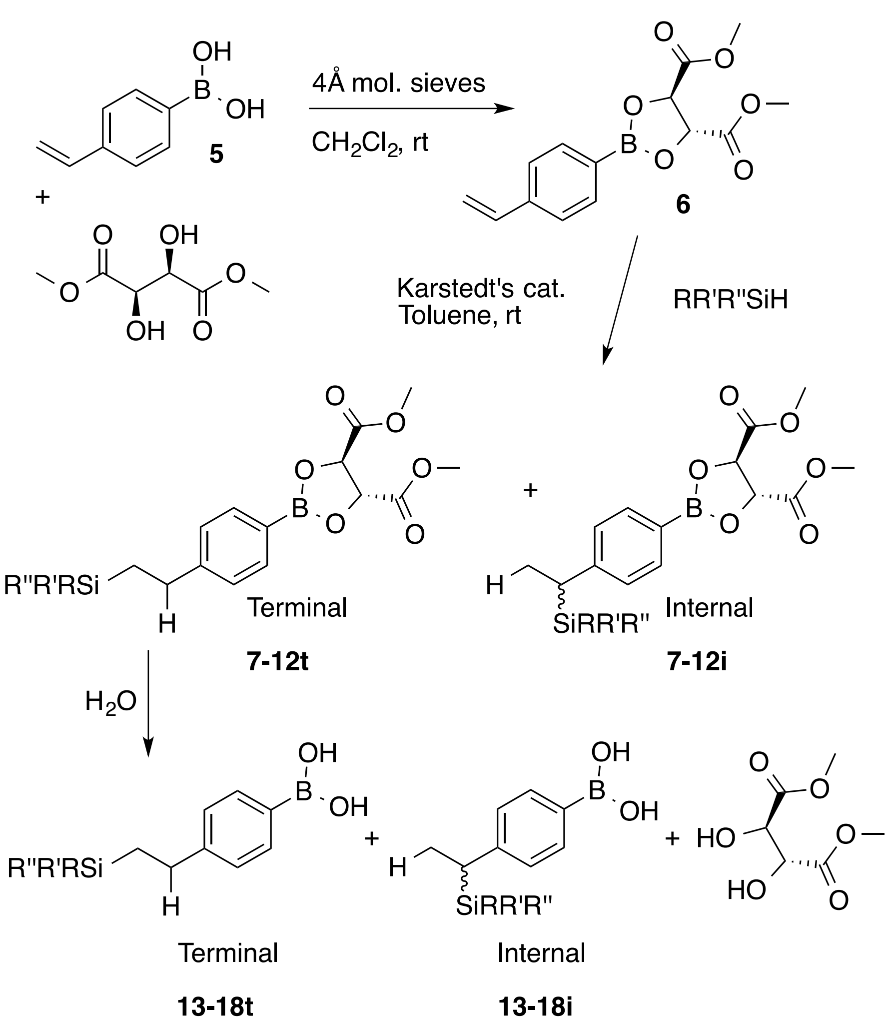
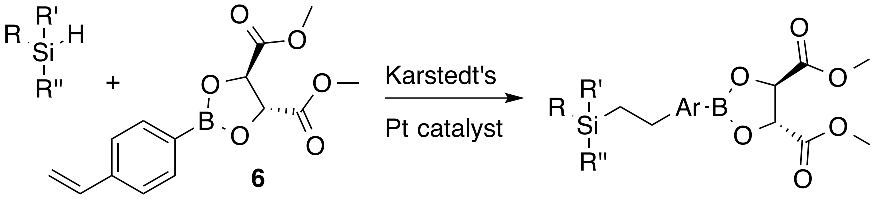
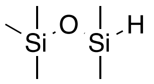
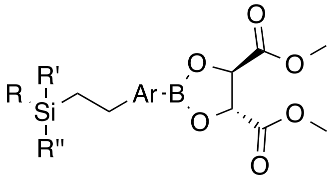
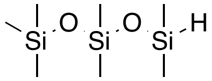
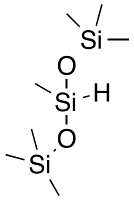
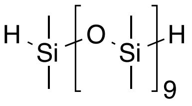
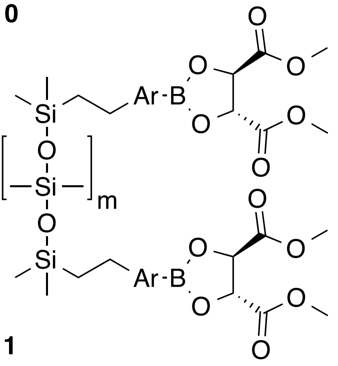
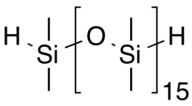
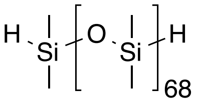


Figure 2.2. Tartrate protection of 4-vinylphenylboronic acid and synthesis of silicone-boronic esters **7-12** (for R,R,'R'', see Table 2.1)

Table 2.1. Preparation of silicone boronate esters



H-functional siloxane RR'R''SiH	Yield (%)	Ratio t : i (term : int)	Product[a]
Monofunctional linear			**7**
	87	10 : 7	
	59	10 : 7	**8**
Branched			
	61	5 : 2	**9**
Difunctional (α,ω)			**10**
	54	2 : 1	
	81	5 : 4	**11**
	76	5 : 4	**12**

[a] Shown for terminal regioisomer. The boronic acid products after hydrolysis (Fig. 2.2) are compounds **13**, **14, 15**, **16, 17** and **18.**

The resulting free boronic acids were relatively insoluble in water, which is not surprising given the hydrophobicity associated with silicones: even with the small disiloxane, the hydrophobic group trumped the hydrophilic boronic acid. However, this behavior could be altered by altering the character of the boronic acid.

The preference for boronic acid binding to fructose over glucose was first observed by Lorand and Edwards[19] and has since become accepted as a common property of many boronic acids.[13] The ability of free boronic acid **13i,t** to bind fructose or glucose, respectively, in D_2O was examined using ^1H NMR spectroscopy. The chemical shifts of relatively isolated aromatic proton peaks were monitored for changes due to binding at boronic acid. In particular, the signals near 7.6 and 7.1 ppm (Figure 2.3) were diagnostic for changes in the environment near boron. There was no change in the spectrum for silicone-boronic acid exposed to glucose in solution, however, upon exposure to fructose a new set of peaks was observed. Integration of these peaks with respect to the unbound compound signals demonstrated that approximately one-third of the silicone-boronic acid in solution was bound to fructose: as would be expected for boronic acids, no binding to glucose was observed. The fructose complex of **13i,t** exhibited enhanced water solubility: the solubility nearly doubled compared to the free boronic acid (Appendix Section 6.1); however, it was not possible to measure a critical micelle concentration for any of the compounds. Larger silicones such as **11** could be compatibilized with water by complexation with fructose. Thus, as with other boronic acids, the binding of SBAs to saccharides was dependent on diol structural characteristics.[13,20]

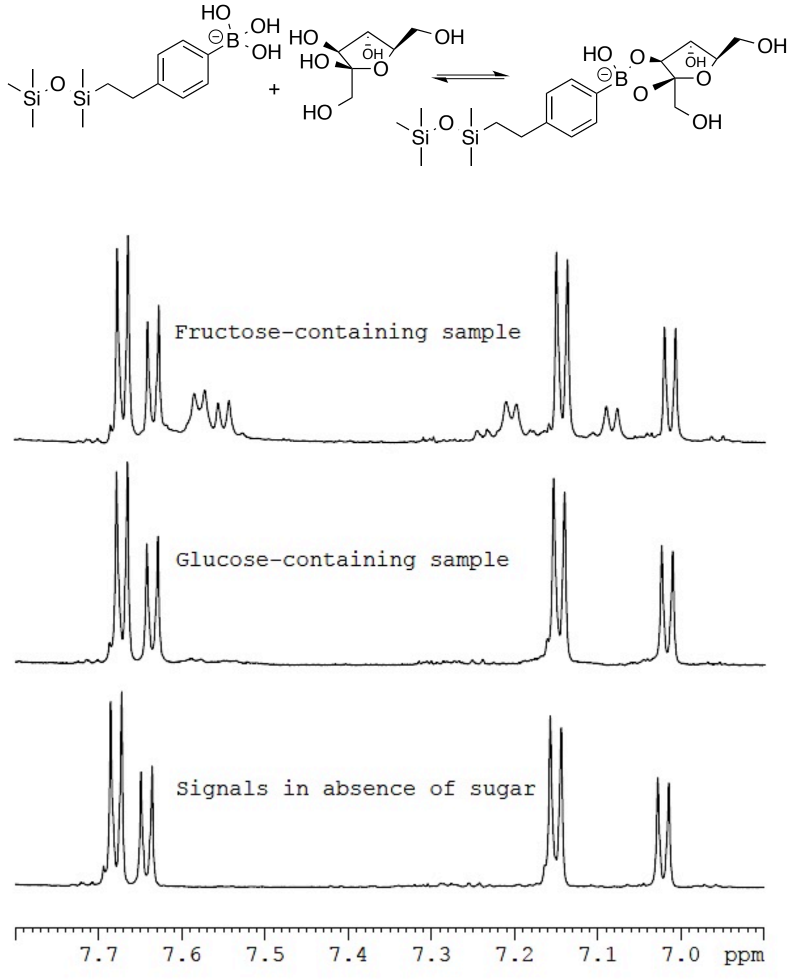


Figure 2.3. Selective sugar binding of **7** with fructose in PBS pH 7.4/DMSO-d_6

The equilibrium for free **2** and bound **3** boronic acids is highly dependent on the pH of solution and the presence of Lewis bases. Neutral conditions were used as much as possible to avoid silicone hydrolysis, particularly of the branched trisiloxane compound **15**.[2] Fortunately, Lewis bases that favour formation and also stabilize against hydrolysis the tetracoordinate complex **4** (Figure 2.1) are readily available. An examination of a series of buffers showed that tris(hydroxymethyl)aminomethane (Tris) was particularly efficacious in this regard. As the concentration of Tris was increased from 0–28 mM, the fraction of tetracoordinate boronate complexed to fructose (but not to glucose) increased, as demonstrated by enhanced solubility under these conditions (Appendix Section 6.1). That is, the hydrophilicity of the boronic acid head group could be increased both by complexing with saccharides and an appropriate Lewis base such as Tris, which also stabilized the product against hydrolysis. SBAs were less soluble in water alone.

Additional evidence for unusual physical properties of SBAs comes from rheological studies. The kinematic viscosities of starting silicone oils, of 2.8 and 97 mPa s (~liquid honey), respective, and their boronic acid products **11** and **12**, were low. Upon hydrolysis, dramatic changes occurred leading to increases in viscosity of several orders of magnitude (for complex viscosities of **17** and **18** see Appendix Section 6.1). Normally, the viscosities of homologous polymers track with chain length. In this case, however, the density of boronic acid groups is more important, as shown by the higher viscosity exhibited by the silicone with shorter chain lengths. We propose that segregation of boronic acids from silicones act as physical crosslinks leading to the significant change in viscosity.

2.4 Conclusion

Boronic acids offer a series of interesting properties based on their ability to reversibly and selectively bind diols, particularly those affiliated with saccharides. New silicone surfactants based on boronic acids have been prepared using a straightforward synthetic strategy. The hydrophilic boronic acid termini allow for these surface-active materials to bind selectively to *cis*-diols of biologically interesting molecules, changing their surface activity. The self-affinity of boronic acids in a silicone environment suggests their broader use to structure silicone networks.

2.5 Acknowledgements

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2.6 References

1. R. F. T. Stepto, Theoretical Aspects of Conformation-Dependent Properties, in *Siloxane Polymers*, ed. S. J. Clarson and J. A. Semlyen, Prentice Hall, Englewood Cliffs, NJ, 1993, p. 373.
2. *Silicone Surfactants*, ed. R. M. Hill, Marcel Dekker, New York, 1999.
3. B. Kanner, B. Prokai and W. R. Rosemund, *US Patent No.* 3,796,696 (to Union Carbide), 1974.
4. M. J. Owen, Antifoaming Agents, in *Encyclopedia of Polymer Science and Engineering*, ed. H. F. Mark, N. M. Bikales, C. G. Overberger and G. Menges, Wiley, New York, 2nd edn, 1985, vol. 2, p. 59.
5. H. Sebag and G. Vanlerberghe, *US Patent No*. 4,609,750 (to Th. Goldschmidt), 1986; H. –J. Kollmeier, R. –D. Langenhagen and K. Hoffman, *US Patent No.* 4,654,161 (to Th. Goldschmidt), 1987; B. Y. Zhu and M. J. Rosen, *J. Colloid Interface Sci.*, 1985, **108**, 423; K. W. Hermann, *J. Colloid Interface Sci.*, 1966, **22**, 352.
6. S. Fabrice, *US Patent Appl.* 2006/0,140,842 (University of Liege, Belg.), 2005.
7. M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, 2000, pp. 256-308.
8. N. Miyaura and A. Suzuki, *Chem. Rev.*, 1995, **95**, 2457.
9. D. G. Hall, Structure, Properties, and Preparation of Boronic Acid Derivatives, in *Boronic Acids*, ed. D. G. Hall, Wiley-VCH: Verlag GmbH & Co. KGaA, Weinheim, 2005, ch. 1.

10. K. Torssell, in *Progress in Boron Chemistry*, ed. H. Steinberg and A. L. McCloskey, Pergamon, New York, 1964, vol. 1, pp. 369-415.
11. D. Shiino, Y. Murata, A. Kubo, Y. J. Kim, K. Kataoka, Y. Koyama, A. Kikuchi, M. Yokoyama, Y. Sakurai and T. Okano, *J. Controlled Release*, 1995, **37**, 269.
12. W. Yang, S. Gao, X. Gao, V. R. Karnati, W. Ni, B. Wang, W. B. Hooks, J. Carson and B. Weston, *Bioorg. Med. Chem. Lett.*, 2002, **12**, 2175.
13. G. Springsteen and B. Wang, *Tetrahedron*, 2002, **58**, 5291.
14. G. Springsteen and B. Wang, *Chem. Commun.*, 2001, 1608.
15. T. D. James, Boronic Acid-Based Receptors and Sensors for Saccharides, in *Boronic Acids,* ed. D. G. Hall, Wiley-VCH: Verlag GmbH & Co. KGaA, Weinheim, 2005, pp. 442-443.
16. L. N. Lewis, *J. Am. Chem. Soc.*, 1990, **112**, 5998.
17. E. Lukevics and M. Dzinatra, *J. Organomet. Chem.*, 1985, **295**, 265.
18. H. G. Kuivila, A. H. Keough and E. J. Soboczenski, *J. Org. Chem.*, 1954, **19**, 780.
19. J. P. Lorand and J. O. Edwards, *J. Org. Chem.*, 1959, **24**, 769.
20. M. Rietjens and P. A. Steenbergen, *Eur. J. Inorg. Chem.*, 2005, 1162.

CHAPTER 3: Spread and Set Silicone-Boronic Acid Elastomers[‡]

3.1 Abstract

The capacity of boronic acids to complex other boronic acids and a variety of ligands has been utilized to prepare stimuli-responsive self-assembled silicone elastomers. Silicone-boronic esters were synthesized using hydrosilylation. Exposure to moisture led to deprotection of tartrate- and to a lesser extent catechol-protected boronic acids, and the transformation of the polymer from a liquid to a viscoelastic film. Film stability was tested using water penetration studies, and was greatest below pH 6 where neutral boronic acids are produced through hydrolytic deprotection, and then dimerized leading to crosslinking in the silicone phase. Layer stability was diminished at high pH and in the presence of coordinating Lewis bases and diols due to the anchoring of boronates in water and prevention of crosslinking. Hydrolysis of boronic esters occurred at the silicone-water interface, leaving unhydrolyzed liquid silicone-boronic ester at the air-silicone interface. The result of this phenomenon was the subsequent self-spreading of silicone-boronic esters over newly introduced water droplets, leading to the formation of stable films without addition of polymer, and allowing for water droplet stacking. The strength and

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[‡] This chapter is taken from L. Zepeda-Velazquez and M. A. Brook, *Chemistry of Materials*, **2015**, Manuscript in preparation. Zepeda-Velazquez developed all experimentation, and performed all characterization and analyses. Zepeda-Velazquez wrote the manuscript with additions, edits and guidance from Brook.

behavior of self-assembled stimuli-responsive silicone materials can be tailored using the various analytes and conditions known to impact the coordination and ionization state of boronic acids.

3.2 Introduction

Stimuli-responsive materials have garnered a great deal of attention in the past several decades due to their potential applications in drug delivery,[1] analytical devices,[2,3] microfluidic devices,[4] and switchable surfaces[5,6] among others. Biomedical applications in particular often require responsive polymers that are able to operate at interfaces, where pH- and molecular recognition-responses are highly sought after. Boronic acids and their polymers are ideally suited for the production of stimuli-responsive materials due to their pH-sensitive ionization and solubility,[7] as well as their capacity to selectively and reversibly bind to 1,2- and 1,3-diols.[8] In order to affect the desired response in biological environments, boronic acids are often appended to or included in polymers that are partially[9] or fully water-soluble,[10] however, hydrophobic polymers containing boronic acids may also find utility at certain interfaces.

Poly(dimethylsiloxane) (PDMS) is a mixed organic/inorganic hydrophobic polymer that can provide a high degree of oxygen permeability[11] and is generally considered biocompatible.[12] Silicones are exceptionally surface active.[13] The introduction of boronic acids to silicone polymers could provide an interesting platform from which (reversible) interactions of boronic acids at interfaces, including silicone/air or silicone/water interfaces, could be manipulated by the contents of the sub-phase. Such changes could be used to tune the utility of a silicone for certain applications.

Silicone-boronic acids (**SiBA**s) represent a new class of silicone polymers and small molecules that contain covalently attached boronic acid or boronic ester functional groups through a hydrocarbon spacer. Obtained via a simple two-step synthesis involving boronic acid protection followed by hydrosilylation onto the desired silicone entity,[14] **SiBA**s with varied three-dimensional structures and molecular weights have demonstrated selective saccharide sensing capacities in solution,[14] as well as providing a mechanism for the production of novel thermoplastic silicone elastomers.[15] PDMS oil, similar to other hydrophobic liquids, will spread on water with a rate proportional to its viscosity.[16] Surprisingly, during initial studies of bolasilicone boronates on water, it was discovered that rapid spreading was accompanied by the formation of responsive, elastomeric films that self-assembled at the aqueous interface. The unusual gelling behavior of **SiBA** bolaamphiphiles at the air/water interface, as well as their response to chemical changes in the sub-phase including pH and the presence of competitive boronic acid-binding molecules is reported below.

3.3 Results

Two types of silicone-boronic acids were prepared for this study: a monofunctional silicone-boronic acid of molecular weight 296.32 g/mol and α,ω-telechelic polymers with molecular weights (M_n) up to ~7600 g/mol. In all cases, the compounds were prepared by the hydrosilylation of the appropriate Si-H functional silicone with styrylboronic acids: both terminal and internal isomers resulted, which were not separated (Figure 3.1).

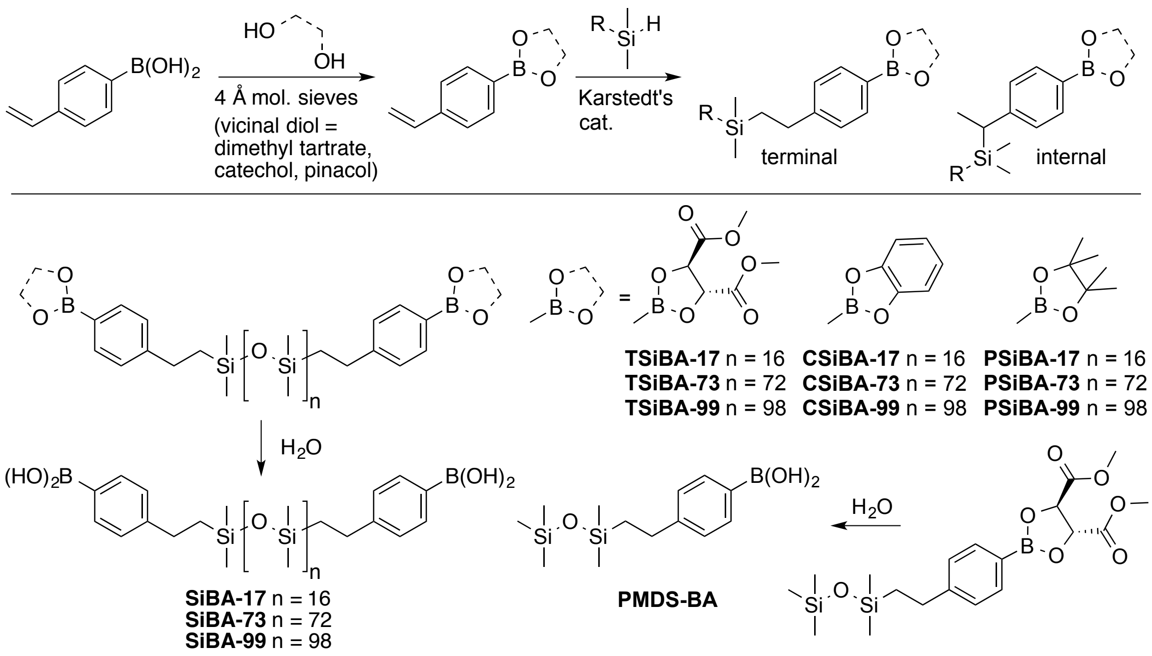

Figure 3.1. Synthesis and hydrolysis of protected silicone-boronic acids

Protected **SiBA**s were found to be liquids that, when placed as a neat drop on aqueous solutions, rapidly spread across the surface of water in a manner similar to other types of silicone polymers (Figure 3.2A). Spreading was rapid (less than two seconds): more rapid than silicone oils of the same viscosity, but less rapid than silicone superwetters.[17] Shortly after spreading, and unlike silicone oils or functional silicones such as α,ω-aminopropylsilicones, thin (submicron thick films of **TSiBA**, Figure 3.2, Table 3.1) viscoelastic films of sufficient strength to support water droplets were observed to form on the surface from **TSiBA** (note that water droplets placed sequentially on the viscoelastic film surface generally did not coalesce, Figure 3.2B).

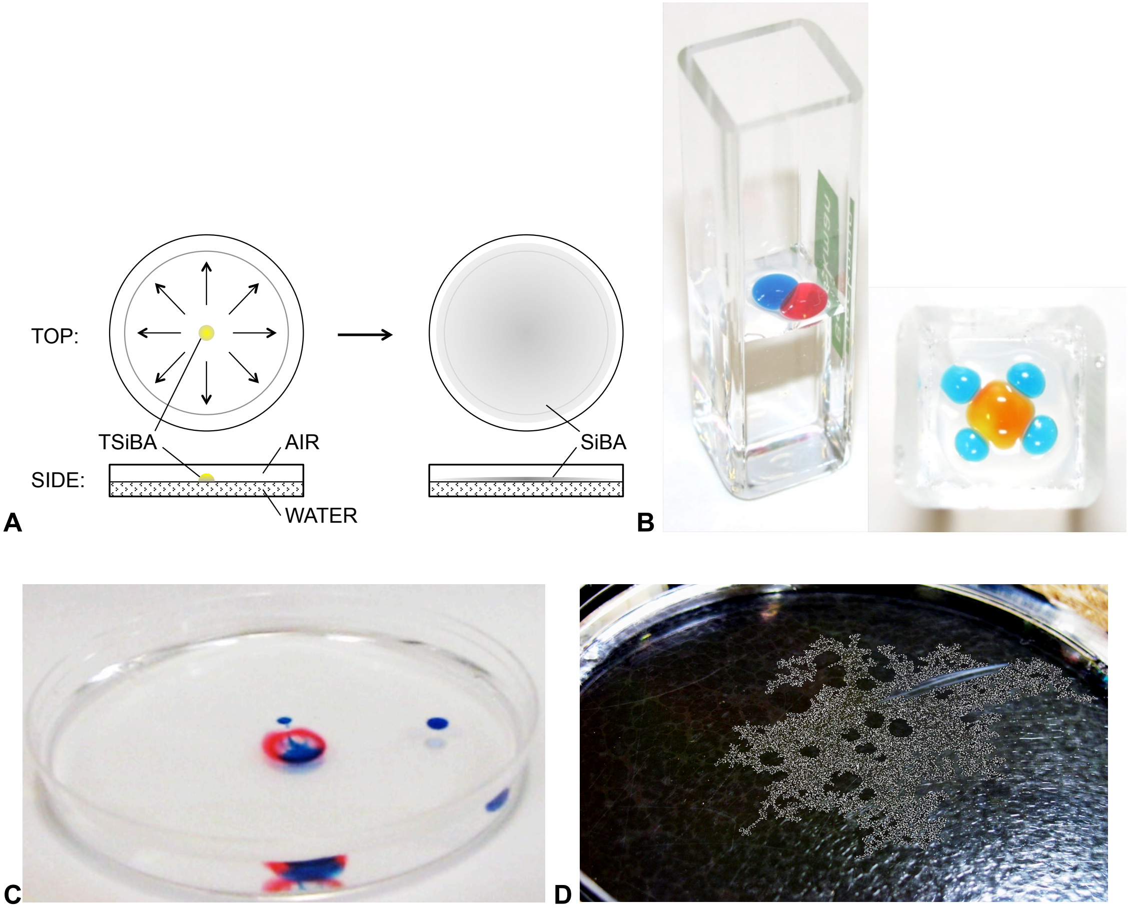

Figure 3.2. A) Schematic showing spreading of **TSiBA** on distilled water in a Petri dish. B) colored water droplets, added one-by-one, supported on the same film in a 1 x 1 cm cuvette: note, the drops do not merge. C) After resting on the surface for ~ 3 minutes, the red water droplet generated a defect and penetrated the silicone film. A blue water droplet then placed on the defect (left) immediately penetrated while the other blue droplet (right) added at the same time was supported. D) holes/cracks developed in a 24 hours aged **SiBA-73** layer (artificially colored for clarity)

Table 3.1. Water penetration times for various quantities of spread **TSiBA-73** and **TSiBA-17** with diluents

SiBA	Amount dispensed [μL][a]	Thickness [μm][b]	Penetration time[c] TSiBA-17 [s]	Diluent
TSiBA-73	**2.5**	**0.42**	**4 ± 1**	**-**
	3.5	**0.60**	**25 ± 7**	**-**
	5.0	**0.84**	**170 ± 45**	**-**
	10	**1.70**	**>480[d]**	**-**
TSiBA-17	**10**	**1.70**	**13 ± 4**	**D_4[e]**
	10	**1.70**	**26 ± 12**	**PDMS 50,000 cSt[f]**

[a] **TSiBA-73** was dispensed using an Eppendorf pipette; [b] Approximate thickness based on volume of SiBA dispensed and an internal Petri dish diameter of 8.7 cm; [c] Time measured from placement of 100 μL water droplet until complete transfer through the **SiBA** layer was observed; average over 4-6 trials; [d] Water took more than 480 s to penetrate for all trials; [e] D_4 = octamethylcyclotetrasiloxane; [f] DMS-S45 hydroxyl-terminated PDMS, 110,000 g/mol.

Increasing the quantity of **SiBA** initially dispensed onto the aqueous solution to give thicker layers increased the stability of the layers with respect to their ability to support water droplets (Figure 3.3, Table 3.1): thicker layers could bear more weight for longer periods of time. However, the stability of the layers changed over time irrespective of thickness. For example, after a few minutes, defects (holes) in the film beneath supported droplets could develop, and the droplet could breach the silicone layer. Once a defect formed, it did not heal: subsequent droplets placed at the same location appeared to penetrate the layer into the aqueous sublayer solution below without resistance (Figure 3.2C). After aging overnight, films derived from **TSiBA** could no longer support water droplets anywhere on the surface; they passed straight through because defects/cracks had developed in the film (Figure 3.2D).

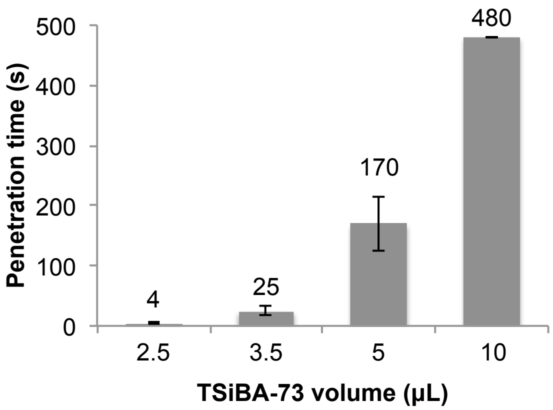

Figure 3.3. Penetration times for a 100 µL drop of water through **TSiBA-73** layers of various thicknesses; the layer produced from 10 µL **TSiBA-73** on a 60 cm^2 surface continued to support the water droplet beyond 480 seconds (Table 3.1).

Not all protected **SiBA** polymers led to elastomeric films. It was found that the robustness of the surface silicone layer to penetration by water was affected by the degree to which the boronate esters had hydrolyzed. Pinacol boronate esters **PSiBA**, which did not undergo hydrolysis within days of being placed on water, spread rapidly across the water surface, but never formed a cohesive layer: water droplets always penetrated rapidly through. This behavior mimicked the behavior of films of non-functional PDMS at the water interface. Catecholates **CSiBA** hydrolyzed slowly over about 1 day. Prior to hydrolysis, mobile oils rapidly coated the surface, but did not immediately form elastomeric films. As hydrolysis began to occur, viscoelastic films began to form that, after one day, were similar to those formed from **TSiBA**. The most labile esters derived from dimethyl-L-tartrate **TSiBA**, hydrolyzed essentially on contact with water, such that viscoelastic films formed at a rate concomitant with spreading (seconds). Complete hydrolysis took from minutes to hours depending on film thickness.

NMR spectroscopy was used to confirm the rates of boronate ester hydrolysis (Table 3.2): exposure of silicone boronate ester to deuterated water followed by integration of the peaks corresponding to the liberated protecting groups demonstrated rapid and complete hydrolysis of dimethyl-L-tartrate, slower and incomplete hydrolysis of catechol, and negligible hydrolysis for pinacol under the experimental conditions tested.

Table 3.2. ^{1}H NMR detection of hydrolyzed **SiBA** protecting groups

Sample	Relative integration[a)]	Time [h]
TSiBA-17	**0.0015**	**0.08**
	0.0448	**5.5**
	0.0761	**21.5**
	0.0812	**99.5**
CSiBA-99	**0.0026**	**2**
PSiBA-99	**N/A[b)]**	**2**

[a)] Relative integration of dimethyl-L-tartrate CH_3 (6 total) protons or catechol C-H protons (4 total) to solvent peak proton impurity; proton impurity was calibrated to 1.00; [b)] No visible signal for pinacol CH_3 present in spectrum.

The characteristics of ester-protected boronates were compared with the hydrolysis products – silicone boronic acids. Pure, unprotected **SiBA-73** was obtained by liquid extraction of a THF/water solution of **TSiBA-73** with hexanes; the resulting material was a cohesive viscoelastic material after removal of the hexanes solvent. Attempts to produce uniform, water-supporting layers of **SiBA** on water were unsuccessful with the unprotected silicone boronic acid. Non-uniform **SiBA** ‘islands’ were observed, after slow evaporation of hexanes, when a quantity (similar to spreading experiments with **TSiBA** described above) of **SiBA-73** in hexanes was spread evenly across water in a glass Petri dish. Only the small islands that formed could support water droplets (Figure 3.4A). Thus, the film formed directly upon spreading neat **TSiBA** on water was completely different from the film created by evaporating a hexanes solution of **SiBA**. Rapid spreading across the water surface was similar in both cases, but the resulting films were quite different.

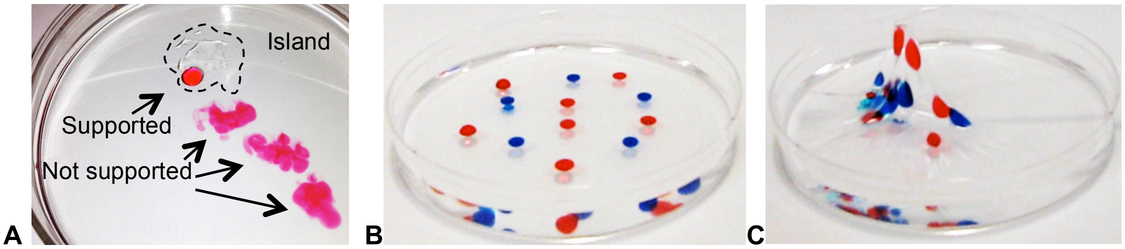

Figure 3.4. Island of (unprotected) **SiBA-73** produced on water sub-phase using solvent evaporation; red-colored water drops were only supported where islands were located. Photos demonstrating the stability of **SiBA** on water. (B) Colored water drops on top of a layer of **SiBA-73** (from **TSiBA-73**) on water. (C) Silicone layer and accompanying droplets being lifted from the sub-phase

The physical properties of **SiBA** layers, once lifted/removed from the water substrate, are similar to those of Silly Putty, a copolymer of dimethylsiloxane fluids and boric oxide:[18] the layer can be rolled into a ball, bounced, and stretched (Figure 3.4B,C). Under force of gravity, **SiBA** will slowly flow to conform to the shape of the container in which it is held, while the substance will fracture and break apart under sudden stress (e.g., hitting with a hammer). Dynamic crosslinking in Silly Putty arises from Lewis acid/Lewis base interactions between oxygen atoms and the vacant site on boron. Boronic acids, however, are known to form dimers,[19,20] which should be an even stronger interaction, and which could be the origin of the viscoelastic films.

The proposal that boronic acid dimers were providing crosslinks to give the elastomers was tested by titrating a monofunctional boronic acid into **SiBA-73**. If crosslinking occurs by aggregation of boronic acids, little effect of the monofunctional boronic acid is expected; the monofunctional material would just add to the cluster. However, disruption of a dimeric crosslink should occur with the formation of each polymeric boronic acid:simple boronic acid complex. It was determined that the elastic properties resulting from physical crosslinking between boronic acids could be disrupted completely when **PMDS-BA** was mixed with **SiBA-73** at a 1:1 ratio of boronic acids (two molecules of **PMDS-BA** for one bolaamphiphilic **SiBA-73**) confirming that the primary interaction responsible for viscoelasticity of **SiBA**s is the dimerization of boronic acids. Dimers, of course, would only lead to chain extension, not elastomers. Crosslinks require higher order interactions, which must be available in addition to the chain extension caused by dimerization of an α,ω-telechelic silicone boronate. These are ascribed to additional Lewis acid/Lewis base complexes similar to those found in Silly Putty.

The stability of **SiBA** gel layers could also be modified by the composition of the aqueous sub-phase upon which they were spread. The relative layer stability was measured by tracking the duration of time required for a 50 μL water droplet to fully penetrate a **SiBA** layer produced from the spreading of 10 μL of **TSiBA** on a 60 cm^2 surface of water. The results from various solutes or changes in pH of the aqueous sub-phase and their effect on **SiBA** layer stability are summarized in Table 3.3.

SiBA layers remained stable below pH 5 but rapidly lost stability as the pH was increased. At pHs above 7, the layers tended to be less uniform and resulted in concentrated regions (not quite discrete islands) centered around the initial location where the **SiBA** was deposited. Analytes that are known to bind boronic acids also caused a marked decrease in film stability (Figure 3.6C), while addition of non-coordinating ions, such as sodium chloride, to the sub-phase had little effect. **SiBA** layers produced on the sub-phases were visualized using microscopy to look for differences between stable vs. unstable layers (Table 3.3, see Supporting Information). Further characterization of the film was possible after transferring to a flat silicon wafer. Each **SiBA** was spread in a similar manner to the initial drop-penetration studies with the addition of a 1 x 1 cm silicon wafer fragment submerged vertically in the sub-phase before spreading. After spreading, the silicon was carefully removed leading to a small portion of **SiBA** film deposited on the substrate. The deposited film was then visualized under a microscope. Stable layers (e.g., low pH sub-phase) had a tendency to appear more uniform, with occasional folds produced during layer transfer onto silicon, while unstable layers appeared non-uniform and did not have folds or creases.

The molecular weight of the silicone core played a role in the stability of **SiBA** films on water. Films derived from the highest molecular weight **TSiBA-99** were outperformed by the two shorter **TSiBA** bolaamphiphiles at all pH values tested. This behavior is attributed to the low concentration of boronic acids, with respect to silicone, in layers produced by high molecular weight polymers, leading to a low crosslink density. Dilution of the layer derived from **TSiBA-17** by low (25% octamethylcyclotetrasiloxane (D_4)) or high molecular weight silicone (25% HO-PDMS-OH terminated PDMS, MW ~ 110000 g/mol) led to only marginal changes in the ability of water droplets to penetrate the silicone film

(Table 3.1) supporting this proposal: the crosslink density remained high with this shortest oligomer.

Film stability for **TSiBA-17** and **TSiBA-73** was associated with optimal crosslink density that reflected boronic acid concentration and losses of crosslinks as boronic acids were converted to non-linking anionic boronates. At low pH, **TSiBA-17** was not as effective at producing stable layers as **TSiBA-73** due to complete hydrolysis of boronic ester to boronic acids and over-crosslinking of the short silicone chains leading to brittle layers. By contrast, **TSiBA-17** performed better than **TSiBA-73** at mid-pH values because partial conversion of boronic acids to anionic boronates helped to decrease the crosslink density in the silicone phase and prevent overcrosslinking. However, as the pH was further increased the crosslink density further decreased reducing the robustness/cohesiveness of the elastic layers.

Other moieties that bind to boronic acids inhibited boronic acid/boronic acid crosslinking when introduced in the sub-phase. Compounds like glycerol and tris(hydroxymethyl)aminomethane caused a reduction in elastic layer stability to the point where none of the **TSiBA** polymers tested could produce a water droplet-supporting layer (Table 3.3). Tris(hydroxymethyl)aminomethane and tris(aminoethyl)amine, in addition to increasing the solution pH, also behave as Lewis basic molecules that bind to boronic acids. These too will inhibit crosslinking. Phosphate and citrate anions are known to form complexes with boronic acids and boronate esters[21] and account for the differences in **SiBA** layer stability when produced on pure water compared to pH 7.00 buffer, where the layers produced on pure water tended to be much more stable than those produced on pH

7.00 buffer. Since the concentration of competitive binder in solution was far greater than the expected concentration of released dimethyl-L-tartrate, the probability of observing large quantities of free boronic acids that could crosslink under these conditions is low.

Table 3.3. Water penetration times for various sub-phases and pH values

Sub-phase[a)]	Penetration time[b)] **TSiBA-17** [s]	Penetration time[b)] **TSiBA-73** [s]	Penetration time [b)] **TSiBA-99** [s]
Water	**12 ± 3**	**331 ± 63**	**20 ± 5**
pH 2.84	**97 ± 17**	**259 ± 33**	**3 ± 0**
pH 3.91	**281 ± 42**	**120 ± 19**	**3 ± 0**
pH 4.93	**296 ± 9**	**82 ± 26**	**5 ± 0**
pH 5.99	**34 ± 4**	**35 ± 7**	**3 ± 0**
pH 7.00	**10 ± 5**	**21 ± 4**	**2 ± 0**
pH 7.84	**19 ± 9**	**31 ± 9**	**-**
pH 9.07	**-**	**-**	**-**
pH 9.96	**-**	**-**	**-**
pH 11.09	**-**	**-**	**-**
10% NaCl	**99 ± 19**	**452 ± 121**	**46 ± 40**
1M HCl	**40 ± 23**	**122 ± 35**	**27 ± 16**
1M NaOH	**-**	**-**	**-**
10% glycerol	**-**	**-**	**-**
10% TRIS[c)]	**-**	**-**	**-**
10% tris(2-aminoethyl)amine	**-**	**-**	**-**

[a)]Full details of sub-phase composition can be found in the Experimental section; [b)]Time measured from placement of water droplet until complete transfer through the **SiBA** layer was observed; average over 3-6 trials; the symbol "-" indicates no resistance to drop penetration; [c)]tris(hydroxymethyl)aminomethane.

SiBAs spread rapidly across water interfaces and, in the case of **TSiBA**, hydrolysis of the water contacting layer was rapid, an effect that anchors the film to the water interface. However, unhydrolyzed **TSiBA** was still able to migrate on top of the anchored film, including along the interfaces of water droplets placed on the **SiBA** film, as shown in Figure 3.5 (30-40 μL **TSiBA** was spread onto 1 x 1 cm of uncolored water). As seen in Figure 3.5B, B', a light blue water droplet (50 μL) is supported on top of a partly hydrolyzed **SiBA** layer. The newly added water droplet can itself support placement of a dark blue water droplet (10 μL, Figure 3.5E, E’) because unhydrolyzed **TSiBA** migrates along the droplet interface (Figure 3.5B, C). No mixing of the two droplets was observed. Thus, multilayers of silicone/water/silicone/water/silicone/water are possible (Figure 3.5E’, F, see also Figure 3.2C). Achieving these multilayer structures required that enough time was permitted for partial hydrolysis of the **SiBA** to occur, and that sufficient **SiBA** remained to create a coherent film on any newly added water.

Each water droplet is pinned to the film on which it rests, and becomes enveloped by a viscoelastic film. When the surfaces are tilted, there is no movement of the droplets. The strength of the film is apparent from Figure 3.4B, C in which a gel layer with several blue and red colored droplets is being lifted from the surface of water upon which it was originally produced carrying the colored droplets without dripping or rolling off of the gel-air interface. Only during this manipulation do the colored droplets burst.

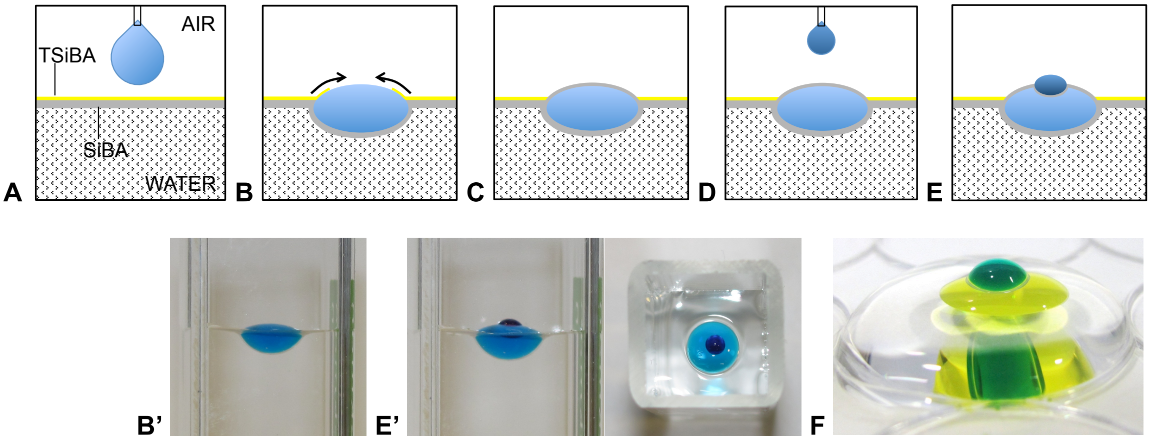

Figure 3.5. Stacking water droplets on **SiBA**; (A) **TSiBA** hydrolyzes partially on contact with water to form a viscoelastic film. (B, B’) A water droplet (light blue) is supported by the **TSiBA**: unhydrolyzed **TSiBA** spreads around the water droplet. (C) New **SiBA** film formed on light blue droplet from self-spreading/hydrolysis. (D) Addition of a second

droplet (dark blue) leads to a multilayer structure of alternating water/silicone (E,E’). No additional **TSiBA** was added during this sequence. (F) Three stacked water droplets (colorless in a 24-well plate lid, diameter ~ 10 mm, yellow, green) were analogously created with addition of **TSiBA** between each addition of water

3.4 Discussion

Spreading across water is a typical behavior for hydrophobic, non-functional silicones, but also end-functional silicones that bear hydrophilic groups including amines/ammonium ions or carboxylic acids/carboxylates.[22] Deprotected **SiBA** bolaamphiphiles perform similarly to other end-functional silicones in that they produce high molecular areas at low surface pressures during monolayer studies.[23] All protected **SiBA** polymers (**TSiBA**, **CSiBA**, and **PSiBA**) rapidly spread along the air/water interface to the boundaries of the container. Spreading behavior was not limited to two-dimensional spreading across a horizontal surface, but was also found to occur upon exposure of a small drop of water to the air/**SiBA** layer interface. With sufficiently thick layers of **TSiBA**, it was found that unhydrolyzed **SiBA** at the air interface retained its ability to spread across water (Figure 3.5A and B), and covered the newly introduced colored droplet (Figure 3.5C), as demonstrated by the observation of water droplets “clinging” to the **SiBA** layer in Figure 3.4C and production of stacked water droplets shown in Figure 3.5E’ and F. By contrast, without a protecting group, even in hexanes solution (normally an excellent spreading solvent), the free silicone-boronic acid was not able to spread across a water interface: a typical film layer produced from a given quantity of **TSiBA-73** extended to the edge of the vessels, but only a small crosslinked silicone island was produced from the same quantity of **SiBA-73** spread from a solution of hexanes (Figure 3.4A). Thus, there is nothing exceptional about the spreading behavior of the **SiBA**s on water as long as the boronic acid protecting group remains intact.

Silicone-based materials that do not undergo covalent crosslinking do not create viscoelastic films on water, at least not of the strength to also support water drops. All protected **SiBA** polymers (**TSiBA**, **CSiBA**, and **PSiBA**) were observed to spread on water, but only polymers with boronic acids protected with the readily hydrolyzable groups were observed to "set" into stable layers (**TSiBA** within a few seconds: **CSiBA** eventually formed a film, but after more than one day). We have previously demonstrated that the tartrate protecting group of silicone-boronic acids can be removed across a wide pH range,[14] and it is known that free boronate anions exist preferentially over their boronate ester counterparts at high pH.[24] This was confirmed by correlating film formation with the detection of liberated protecting groups by NMR spectroscopy, which indicated that a large quantity of dimethyl-L-tartrate was released in a short period of time compared to a very little amount of catechol over an extended period of time (a day) and no pinacol (2 days) within the sensitivity of the NMR instrument.

After hydrolysis, the **SiBA**s exhibited characteristics that were reminiscent of Silly Putty: they could be irreversibly stretched by a slow tensile force (or would flow under gravity), would bounce when rolled into a ball, and would shatter when subjected to a sharp compressive force. Thus, it seems reasonable that the nature of crosslinking is, at least, analogous in the two materials. In Silly Putty, a mixture created primarily from silanol-terminated PDMS and boric oxide,[18] a network structure arises from condensation B-OH and Si-OH groups to give B-O-Si linkages as well as transient interactions between the open valence on boron and the oxygen atoms in the backbone of PDMS.[25] Boric acid provides the necessary linkages to observe the dual properties of viscosity at low shear rates and elasticity at high shear rates. Free boronic acids, like partly condensed boric acid, appear to be able to crosslink through coordination bonding associations with siloxane backbones. However, these are relatively weak effects as shown by the inability of the mono-boronic acid **PDMS-BA** to form a cohesive layer on water (data not shown).

The ability to disrupt the elastomer by the addition of mono-boronic acid **PMDS-BA** to pure **SiBA-73** indicated that the stronger crosslinks in the viscoelastic films are provided by 1:1 boronic acid interactions (Figure 3.6).[23] Although the experiments performed in this study cannot prove whether hydrogen bonding or acid/base interactions are individually responsible for this particular boronic acid association, our previously reported results indicated that typical Lewis acid/base complexes of **SiBA**s (with amines) in solution similarly form in a 1:1 ratio.[15] Hendel et al. previously demonstrated that calixarenes containing multiple boronic acids produced strongly cohesive monolayers at the air/water interface as measured by a canal viscometer.[26] Their suggestion was that intermolecular interactions between calixarenes, such as hydrogen bonding, acid/base interactions, or boroxine formation were responsible for crosslinking that led to the observed results in multi-boronic acid containing compounds but not in their mono-boronic acid analogues. Since boroxines, the anhydride trimers of boronic acids, are unlikely to form in the presence of water[27] it is more likely that one or a combination of the other two possibilities give rise to the observed cohesiveness of **SiBA** layers on water.

Aging of the silicone films led to a loss of cohesivity through shrinking and cracking, but other factors could be used to disfavor film formation. The capacity to chemically affect crosslink stability supports the proposal that boronic acid/boronic acid interactions mostly drive elastomeric stability. Boronic acids can be converted from 3-coordinate at low pH to 4 coordinate at higher pH: 4-coordinate compounds undergo further substitution less efficiently than their 3-coordinate counterparts.[19] It is not surprising, therefore, that there was a strong correlation between the pH of the sub-phase and elastomeric film strength (Table 3.3). At acidic pH, below the pK_a of **SiBA**, hydrolysis of the boronate ester will produce a neutral, water-insoluble trigonal planar boronic acid that can readily participate in hydrogen bonding or acid/base interactions with other boronic acids within the silicone phase to produce highly stable layers. When the pH of the sub-phase is raised above the pK_a of **TSiBA**, tetracoordinate, anionic boron species will be formed and forced into the aqueous phase,[24] thereby restricting the ability for the ends of **SiBA** molecules to interact favorably with one another: crosslinking is suppressed. This process will convert both dimers at the water interface and distal from it into free silicone chains (Figure 3.6B vs C). Other ligands in the sub-phase that bind to boronic acids similarly interfered with the 1:1 boronic acid/boronic acid complex formation leading to a decrease in crosslink density and film cohesivity.

The pH-dependent association/dissociation of boronic acid-containing polymers has also been demonstrated in boronic acid block copolymers.[9] Using RAFT polymerization, Roy et al. were able to synthesize polymers containing permanently hydrophilic and hydrophobic segments, as well as pH- and glucose-responsive boronic acid segments capable of forming reversible aggregates in physiologically relevant conditions.[9] Similar to **SiBA** behavior, it was the switch between neutral boronic acid and anionic boronate that caused the dissociation of polymer aggregates at high pH. The primary difference between the RAFT copolymer system and **SiBA**s is the hydrophobic nature of the silicone polymer backbone that prevents the polymer from fully entering the aqueous solution, leading to the observation of layers at the air/water interface rather than water-soluble aggregates.

Nakahata et al. have also recently demonstrated an unique application for the pH-dependent binding of boronic acids to diols in poly(acrylamide) gels containing boronic acids and catechols.[28] In basic media, two separate gels (one containing boronic acids, the other catechols) self-associated at the macroscopic level due to the favorable formation of catechol boronate ester crosslinks between gels, which could then be disrupted through the introduction of sugars that competitively bind with boronic acids and displace catechol. This behavior closely resembles the response of **SiBA** layers to competitive binders and basic conditions in the sub-phase, where dissociation is occurring at the molecular level between silicone chains. **SiBA** polymers represent a new class of pH responsive materials that are capable of boronic acid binding internally as well as toward external analytes such as diols.

We can rationalize the behavior of silicone boronic acids by considering the rates of hydrolysis, and the ability of the resulting boronic acids to form 1:1 crosslinks, without which viscoelastic films could not form. After application of a protected **SiBA** to a water layer, they effectively spread across the surface: 1 drop (~0.01 ml) **TSiBA** was more than sufficient to spread across an 8.7 cm Petri dish (~60 cm^2) and then create a cohesive film (Figure 3.2A, Table 3.1). Until hydrolysis, the resulting silicone films were not resilient and could not support the weight of additional water droplets placed on them, similar to the case of non-functional and $\alpha,\omega-$functional silicone oils. As hydrolysis of the boronate ester occurred, the cohesive film was established through specific boronic acid/boronic acid complexes and weaker interactions between boronic acids and silicone chains (Figure 3.6A). Water droplets placed on the not-completely-hydrolyzed **SiBA** film also became coated at their air/water interface, to create an elastomer encapsulated droplet (Figure 3.5B → C). Over time and with full hydrolysis of the protecting groups, further crosslinking led to shrinking of the film and cracking (Figure 3.6B). The presence of appropriate binding agents in the sub-phase could also overcome boronic acid/boronic acid interactions converting the viscoelastic film back to an oil (Figure 3.6C).

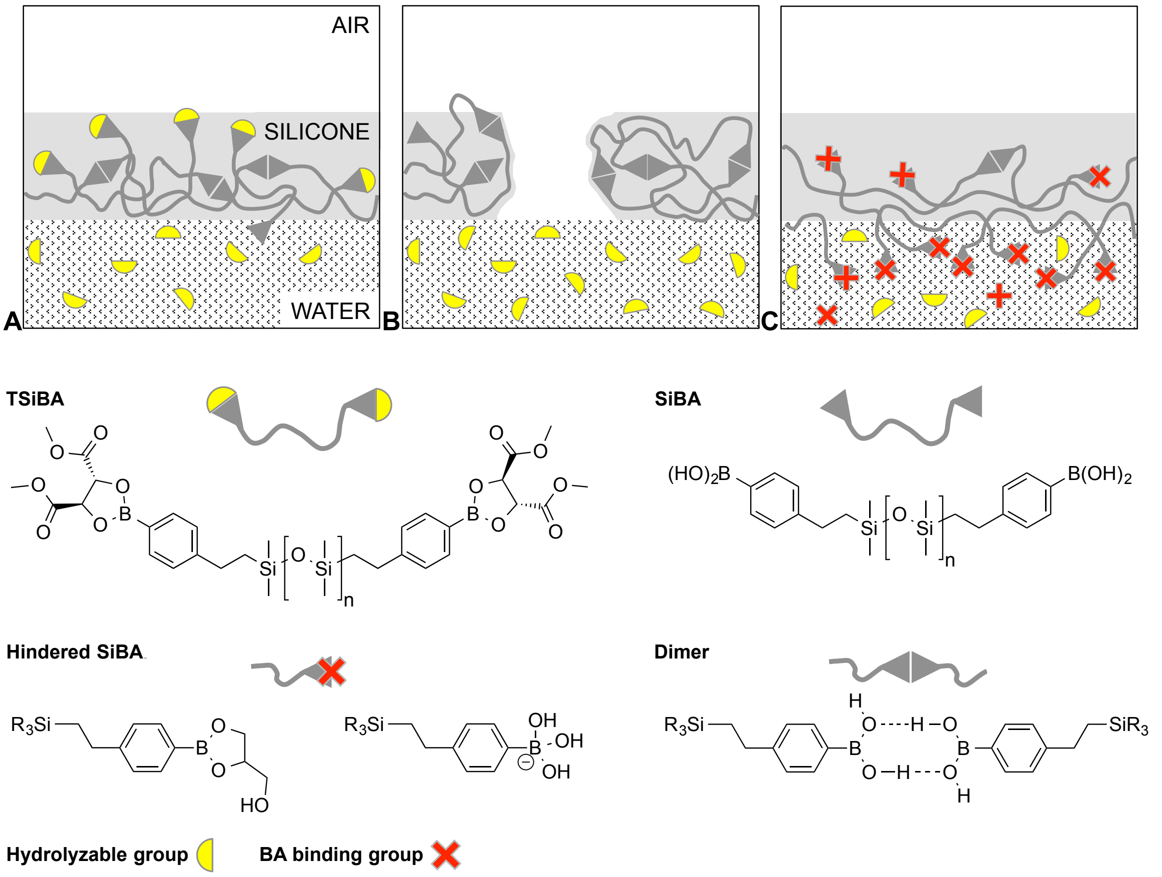

Figure 3.6. Spreading followed by hydrolysis and crosslinking of silicone-boronic acids on water: (A) Cartoon representing boronic acid interactions in silicone phase after partial hydrolytic deprotection of boronic acids, (B) defect formation caused by over-crosslinking of fully hydrolyzed **SiBA** layer, (C) disruption of crosslinking due to the presence of Lewis bases or competitive boronic acid binding molecules

Spread and set polymers are most effectively produced from boronic acids that possess a diol-based protecting group with a low association constant,[29, 30] like dimethyl-L-tartrate, rather than a strongly binding protecting group like catechol[30] or pinacol.[31] The precursors rapidly spread across water interfaces. Following hydrolysis, the resulting films can be quite robust, depending on boronic acid density and thickness. From an application perspective, one could envision utilizing the relative rates of hydrolysis of boronic acid esters to control and tailor the rate of setting for a **SiBA** system to the desired timeframe for a given application (gelation, sealants, coatings, etc.), the examination of which is underway.

3.5 Conclusion

Protected silicone-boronates readily spread across a variety of aqueous surfaces. Hydrolysis of the protecting groups on contact with water converts low to medium viscosity fluids into semipermeable elastomeric membranes. The pinacol protecting group was found not to hydrolyze over extended periods of time at room temperature, while catechol esters hydrolyzed slowly. By contrast, the tartrate hydrolyzed at a rate that was slower than, but competitive with, spreading (within seconds of contact with water) to rapidly form elastomeric films. The robustness of these films, as determined by the ability to support a droplet of water, was dependent upon the thickness of the **SiBA** layer on the aqueous surface and the presence of solutes in the sub-phase that changed the pH or provided competitive boronic acid binding. Moieties that bind to boronic acid, for example glycerol, disrupted crosslinks within the film. The suggested mechanism for **SiBA** crosslinking involves complexation of free boronic acids in the silicone phase to produce 1:1 physical boronic acid/boronic acid complexes in addition to boronic acid/silicone interactions. Tartrate-protected boronate esters that did not come into contact with the aqueous sub-phase remained very mobile, as was demonstrated by the ability of **TSiBA** to spread over a newly introduced water droplet to produce multilayer structures. These spread and set elastomers provide new opportunities for the physical structuring of silicones and water containing fluids.

3.6 Experimental

3.6.1 Materials

Silicone-boronate esters were synthesized according to previously published procedures.[14,15] All spreading experiments were performed on aqueous solutions prepared using 18.1 MΩ-cm water (EASYpure ® II ultrapure water system) or distilled water. Glycerol (reagent grade, Caledon), tris(2-aminoethyl)amine (96%, Aldrich), tris(hydroxymethyl)aminoethane (99.9%, Boehringer Mannheim), potassium hydrogen phthalate (99.97%, Fisher Scientific), potassium dihydrogen orthophosphate (99%, BDH), disodium hydrogen orthophosphate (99%, BDH), sodium hydrogen carbonate (99%, EMD), hydrochloric acid (36.5-38%, Caledon), sodium hydroxide (97%, EMD), sodium chloride (99.0%, Caledon), octamethylcyclotetrasiloxane (D_4, Gelest), hydroxy-terminated polydimethylsiloxane DMS-S45 ($HOMe_2Si(OSiMe_2)_nOSiMe_2OH$ MW = 110000, Gelest), deuterium oxide (99.9%, Cambridge Isotope Laboratories) were used as received. Silicon wafers (SiO_2 on silicon, thickness = 500 μm, University Wafers) were untreated.

3.6.2 Characterization

3.6.2.1 Crosslinking suppression

TSiBA-73 was hydrolyzed by dissolution in THF (2 g/ ~15 mL) then mixing with water (~15 mL). The mixture was then extracted with hexanes three times (3 x 15 mL); the organic extracts were combined and washed with water and saturated sodium chloride, then dried over sodium sulfate. The organic solvent was removed on a rotary evaporator to give the deprotected **SiBA-73** as a translucent, beige viscoelastic putty. Tartrate-protected **PMDS-BA** was hydrolyzed in the same way. **SiBA-73** was dissolved in CH_2Cl_2 and mixed with **PMDS-BA** at a 1:1 molar ratio of boron for each component (381 mg **SiBA-73** with 21 mg **PMDS-BA**) then the solvent was allowed to evaporate under nitrogen.

3.6.2.2 Water penetration studies

Solutions of various pH were prepared using 18.1 MΩ-cm water and the following components (diluted to a final volume of 500 mL): pH 3.0, potassium hydrogen phthalate (5.105 g), HCl (0.1 M, 111.5 mL), actual pH 2.84; pH 4.0, potassium hydrogen phthalate (5.105 g), HCl (0.1 M, 0.5 mL), actual pH 3.91; pH 5.0, potassium hydrogen phthalate (5.105 g), NaOH (0.1 M, 113mL), actual pH 4.93; pH 6.0, potassium dihydrogen orthophosphate (3.405 g), NaOH (0.1 M, 28 mL), actual pH 5.99; pH 7.0, potassium dihydrogen orthophosphate (3.405 g), NaOH (0.1 M, 145.5 mL), actual pH 7.00; pH 8.0, potassium dihydrogen orthophosphate (3.405 g), NaOH (0.1 M, 233.5 mL), actual pH 7.84; pH 9.0, disodium hydrogen orthophosphate (6.78 g), HCl (0.1 M, 22.5 mL), (actual pH 9.07); pH 10.0, disodium hydrogen orthophosphate (6.85 g), NaOH (0.1 M, 16.8 mL), actual pH 9.96; pH 11.0, sodium bicarbonate (1.05 g), NaOH (0.1 M, 113.5 mL), actual pH 11.09. pHs were determined using a CORNING pH meter 320 with a Corning 3 in 1 combo with RJ electrode. A stock solution of sodium chloride (10 %) was prepared by dissolving sodium chloride (25 g) in 18.1 MΩ-cm water (225 mL). A stock solution of hydrochloric acid (1 M) was produced by dilution of 2.7 M hydrochloric acid (58 mL) to a final volume of 156 mL using 18.1 MΩ-cm water. A stock solution of sodium hydroxide (1 M) was prepared by dissolving sodium hydroxide (10 g) in 18.1 MΩ-cm water (250 mL). A stock solution of glycerol (10%) was prepared by dissolving glycerol (20 g) in 18.1 MΩ-cm water (180 mL). A stock solution of tris(hydroxymethyl)-aminomethane (10 %) was prepared by dissolving tris(hydroxymethyl)-aminomethane (25 g) in 18.1 MΩ-cm water (225 mL). A stock solution of tris(2-aminoethyl)amine (10 %) was prepared by dissolving tris(2-aminoethyl)amine (2.5 g) in 18.1 MΩ-cm water (22.5 mL). 25 mL of each solution was placed in a polystyrene Petri dish (100 mm x 15 mm, Fisher Scientific), then 10 µL of **TSiBA-17**, **73** or **99**, respectively, was placed on the surface of the solution using an Eppendorf pipette. After 60 s of time had passed, 50 µL drops of colored water were placed on the **TSiBA** layer and a timer was set to measure the amount of time that elapsed until the colored drop was observed to pass completely through the layer. Sample droplets were measured for penetration time in triplicate.

3.6.2.3 Microscopic visualization

Layers of **TSiBA-73** were transferred from various pH solutions (those used for water penetration studies) onto 1 x 1 cm silicon wafer pieces then visualized under an upright Nikon Eclipse LV100N POL microscope equipped with a 10x/0.25NA objective and a Lumencor SOLA white light illumination source. Images were captured and processed using an Infinity 1 camera and software.

3.6.2.4 NMR monitoring of protecting group hydrolysis

Experiments were performed on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using deuterium oxide (D_2O) as solvent. The proton impurity of the deuterated solvent was used as a reference for ^{1}H NMR spectra (deuterium oxide = 4.80ppm). Catechol deprotection was monitored by collecting a ^{1}H-NMR spectrum of a sample composed of **CSiBA-73** (~10 mg) on D_2O (~0.6 mL) in a glass NMR tube after sample had aged for ~120 min. Pinacol deprotection was monitored by collecting a ^{1}H NMR spectrum of a sample composed of **PSiBA-73** (~10 mg) on D_2O (~0.6 mL) in a glass NMR tube after sample had aged (capped, in air) for ~120 min. Dimethyl-L-tartrate deprotection was monitored over the course of 100 hours by collecting ^{1}H NMR spectra of a sample composed of **TSiBA-17** (~30 mg) on D_2O (~0.6 mL) in a glass NMR tube. For all samples, the quantity of free protecting group was estimated by comparing the integration for the proton impurity of the solvent to the integration of the free protecting group signal(s).

3.7 Acknowledgements

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3.8 References

(1) Zheng, H.; Xing, L.; Cao, Y.; Che, S., *Coordin. Chem. Rev.* **2013**, *257*, 1933-1944.

(2) Ruan, C.; Ong, K. G.; Mungle, C.; Paulose, M.; Nickl, N. J.; Grimes, C. A., *Sensor. Actuat. B-Chem.* **2003**, *96*, 61-69.

(3) Islam, M. R.; Lu, Z.; Li, X.; Sarker, A. K.; Hu, L.; Choi, P.; Li, X.; Hakobyan, N.; Serpe, M. J., *Anal. Chim. Acta* **2013**, *789*, 17-32.

(4) Argentiere, S. G., G.; Mortato, M.; Gerges, I.; Blasi, L., Smart Microfluidics: The Role of Stimuli-Responsive Polymers in Microfluidic Devices. In *Advances in Microfluidics*, Kelly, R., Ed. InTech: Rijeka, Croatia, 2012; p 127.

(5) Kotsuchibashi, Y.; Wang, Y.; Kim, Y.-J.; Ebara, M.; Aoyagi, T.; Narain, R., *ACS Appl. Mater. Inter.* **2013**, *5*, 10004-10010.

(6) Stratakis, E.; Mateescu, A.; Barberoglou, M.; Vamvakaki, M.; Fotakis, C.; Anastasiadis, S. H., *Chem. Commun.* **2010**, *46*, 4136-4138.

(7) Hall, D. G., Structure, Properties, and Preparation of Boronic Acid Derivatives. In *Boronic Acids - Preparation,Applications in Organic Synthesis and Medicine*, 1 ed.; Hall, D. G., Ed. Wiley VCH: Weinheim, 2005; pp 9-10.

(8) James, T. D., Boronic Acid-Based Receptors and Sensors for Saccharides. In *Boronic Acids - Preparation, Applications in Organic Synthesis and Medicine*, 1 ed.; Hall, D. G., Ed. Wiley VCH: Weinheim, 2005.

(9) Roy, D.; Sumerlin, B. S., *ACS Macro Lett.* **2012**, *1*, 529-532.

(10) Kuzimenkova, M. V.; Ivanov, A. E.; Galaev, I. Y., *Macromol. Biosci.* **2006**, *6*, 170-178.

(11) Chekina, N. A.; Pavlyuchenko, V. N.; Danilichev, V. F.; Ushakov, N. A.; Novikov, S. A.; Ivanchev, S. S., *Polym. Advan. Technol.* **2006**, *17*, 872-877.

(12) Lee, J. N.; Jiang, X.; Ryan, D.; Whitesides, G. M., *Langmuir* **2004**, *20*, 11684-11691.

(13) Owen, M. J., Surface Chemistry and Application. In *Siloxane Polymers*, Clarson, S. J.; Semlyen, J. A., Eds. Prentice Hall: Englewood Cliffs, 1993; p 309.

(14) Brook, M. A.; Dodge, L.; Chen, Y.; Gonzaga, F.; Amarne, H., *Chem. Commun.* **2013**, *49*, 1392-1394.

(15) Dodge, L.; Chen, Y.; Brook, M. A., *Chem. Eur. J.* **2014**, *20*, 9349-9356.

(16) Camp, D. W.; Berg, J. C., *J. Fluid Mech.* **1987**, *184*, 445-462.

(17) Hill, R. M., Siloxane Surfactants. In *Silicone Surfactants*, Hill, R. M., Ed. Marcel Dekker, Inc.: New York, 1999; p 360.

(18) Armitage, D. A.; Hughes, M. N.; Sinden, A. W., *J. Chem. Educ.* **1973**, *50*, 434.

(19) Hall, D. G., *Boronic Acids*, 2 ed.; Wiley VCH: Weinheim, 2011.

(20) Niwa, M.; Shibahara, S.; Higashi, N., *J. Mater. Chem.* **2000**, *10*, 2647-2651.

(21) Bosch, L. I.; Fyles, T. M.; James, T. D., *Tetrahedron* **2004**, *60*, 11175-11190.

(22) Lenk, T. J.; Lee, D. H. T.; Koberstein, J. T., *Langmuir* **1994**, *10*, 1857-1864.

(23) Mansuri, E.; Zepeda-Velazquez, L.; Schmidt, R.; Brook, M. A.; DeWolf, C. E., *Langmuir* **2015**, submitted.

(24) Lorand, J. P.; Edwards, J. O., *J. Org. Chem.* **1959**, *24*, 769-774.

(25) McGregor, R. R.; Leathen, E. (Corning Glass Works, USA) Treating dimethyl silicone polymer with boric oxide. US Patent 2,431,878, December 2, 1947.

(26) Hendel, R. A.; Janout, V.; Lee, W.; Regen, S. L., *Langmuir* **1996**, *12*, 5745-5746.

(27) Marinaro, W. A.; Schieber, L. J.; Munson, E. J.; Day, V. W.; Stella, V. J., *J. Pharm. Sci.* **2012**, *101*, 3190-3198.

(28) Nakahata, M.; Mori, S.; Takashima, Y.; Hashidzume, A.; Yamaguchi, H.; Harada, A., *ACS Macro Lett.* **2014**, *3*, 337-340.

(29) Springsteen, G.; Wang, B. H., *Chem. Comm.* **2001**, 1608-1609.

(30) Springsteen, G.; Wang, B. H., *Tetrahedron* **2002**, *58*, 5291-5300.

(31) Bowie, R. A.; Musgrave, O. C., *J. Chem. Soc. (Resumed)* **1963**, 3945-3949.

CHAPTER 4: Silicone Boronates Reversibly Crosslink Using Lewis Acid−Lewis Base Amine Complexes[§]

4.1 Abstract

Silicone elastomers are normally thermosets, which are not readily recycled or repurposed. The few examples of thermoplastic silicone elastomers depend on reversible covalent and non-covalent molecular interactions. It is demonstrated that amine-boronate complex formation provides a simple and flexible route to reversible crosslinked silicones. A variety of network structures were prepared by use of terminal and pendantly functionalized silicone boronates and amines. The crosslink density was quantified using a combination of Shore-hardness measurements, swelling, and rheological analyses. Stress induced by compressive force could be relieved through dynamic B−N bond reformation at 60°C. Materials could be fully disassembled through introduction of *n*-butylamine and successfully reformed upon removal of the monofunctional amine by evaporation.

[§] This chapter is taken from L. Dodge, Y. Chen and M. A. Brook, *Chemistry A European Journal*, **2014**, *20*, 9349-9356, and is reproduced with permission from Wiley, 2014. Dodge developed all experimentation and performed the majority of formulations, characterization and analyses. Chen contributed to formulations and analyses. Dodge wrote the manuscript with additions, edits and guidance from Brook.

4.2 Introduction

The desire to exploit "change-on-demand" properties in polymers has led to innovations, particularly in the area of elastomers. Numerous examples of elastomers that are able to respond to stimuli have been reported.[1] One subset of such materials depends on covalent linkages that respond to temperature, such as Diels-Alder cycloadditions,[2] photochemical responses including 2+2 cycloadditions,[3] and ligand exchanges at metal centres.[4] A second class of responsive elastomers depends on non-covalent intermolecular interactions, which may include hydrogen bonding, exemplified by the seminal studies of Meier and co-workers,[5] pH sensitive ionic interactions[6] and π stacking that can be based on polymer blocks[7] or individual molecules.[8] Surprisingly, few examples of responsive elastomers, the behavior of which is based upon formation of Lewis acid−Lewis base complexes, have been reported.

Classical Lewis acids, including halide derivatives of Sn, Ti, Al, B and related elements are not suitable as constituents of Lewis acid−Lewis base responsive polymers because of their hydrolytic instability. There is increasing interest in Lewis acid catalysts that remain stable to hydrolysis, including examples from indium[9] and lanthanides.[10] Organically modified boron derivatives, including alkyl and arylboranes, particularly those derived from pentafluorophenyl groups and boronic acids, are very stable to hydrolysis and should serve as Lewis acidic constituents in such elastomers.

Linkages involving various aspects of boron chemistry have been employed to produce polymers and network structures, including the dehydration of boronic acids to form boroxines,[11] boron-diol complexation in amphiphilic sugar-based linkers[12] or polyols,[13] as well as nitriogen−boron dative bond formation.[11] The group of Severin has combined both Lewis acid−base complexation and boronate ester formation, demonstrating it is possible to join small molecules to form polymers.[14] An excellent review of boronic acid-related self-assembly is provided by Nishiyabu et al.[15] One aspect of the versatility of boronic acids in polymers is the inherent reversibility of many of the reactions, which can permit the formation of healable (reversible) polymers.[12,16]

Silicone elastomers are most commonly fabricated using irreversible covalent crosslinking methods, such as hydrosilylation or condensation curing.[17] While such thermosets are found in a broad range of applications, one major drawback of these elastomers is the general inability to recycle or reuse the materials once they have been cured. There are few examples of reprocessable silicone elastomers that exploit hydrogen-[18,19] or ionic[20] bonding, ligand−metal coordination,[21,22] or shape memory materials using phase-separation[23] as the basis of crosslinking.

Previously, we described the preparation of silicone boronic acids and their esters with α,ω-telechelic structures SiBA (Figure 4.1).[24] We report that these and related structures efficiently lead under mild conditions to responsive, reversible elastomers resulting from Lewis acid−Lewis base interactions with amine-bearing small molecules and polymers.

4.3 Results

Silicone boronate ester polymers **SiBA** were synthesized according to a published procedure[24] that was adapted to provide gram quantities of these materials. Synthesis involved the platinum-catalysed hydrosilylation of *p*-vinylphenylboronic acid dimethyl-L-tartrate ester with HMe_2Si-containing silicone polymers of various molecular weights. The silicone boronates synthesised were comprised of an approximately 10:9 mixture of two isomers favouring the terminal isomer (as shown, Figure 4.1). In addition to a monofunctional example **PMDS-BA**, and α,ω-silicone diboronates **SiBA-17**, **73** and **99**, a series of pendant boronates **P-SiBA-2**, **8** and **12** were prepared.

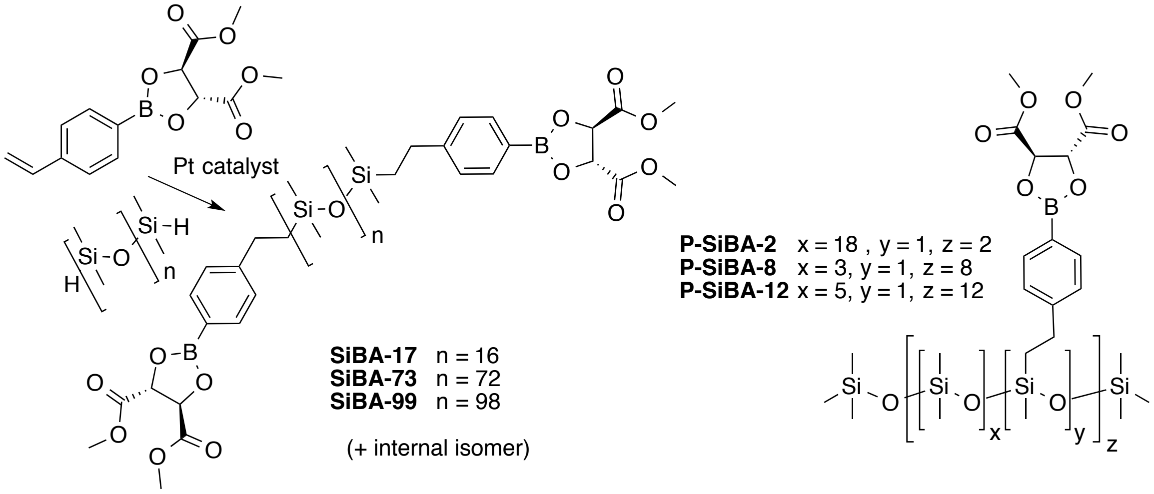

Figure 4.1. General structure of bolaamphiphilic **SiBA** molecules

In order to assess the ability of amines to form complexes with the **SiBAs**, the Lewis acidity of boron in silicones was first investigated through a series of model studies. Upon complexation, changes in the chemical environment surrounding boron could be directly observed with ^{11}B NMR spectroscopy, a method that has been previously employed to monitor the binding of sugars to boron in the presence of Lewis bases.[26]

Aryl boronic acid/ester molecules (trigonal planar geometry about boron) normally show ^{11}B chemical shifts near 30 ppm. However, coordination of nitrogen[25] or other Lewis bases, such as hydroxide,[26] to these molecules to give a tetrahedral geometry about boron leads to a significant shift to approximately 10 ppm. A model compound **PMDS-BA** (Figure 4.1), derived from pentamethyldisiloxane,[24] was treated with ethylenediamine in the absence of other Lewis bases. It is clear from the change in chemical shift of about -23 ppm that the boron atom of **PMDS-BA** is participating in Lewis acid−base complexation with ethylenediamine in solution (Table 4.1). An analogous experiment involving polymer **SiBA-17** and a polymeric aminosilicone (APS, Figure 4.3) similarly led to a considerable change in chemical shift at boron upon coordination. Thus, like other boronic acids, boronate ester-containing silicones in solution will efficiently complex with amines, including amine-containing silicones.

Table 4.1. ^{11}B NMR chemical-shift changes due to boron-nitrogen coordinate covalent bond formation.

SiBA	δ before amine addition (ppm)[a]	δ after amine addition (ppm)[a]
PMDS-BA	32.43	9.16
SiBA-17	32.47	11.46

[a] BF_3OEt_2 external reference was used to calibrate spectra.

In principle, both substitution by nitrogen and complexation at the boronate centre could occur. To test this possibility, ^{1}H NMR spectroscopy was used to establish the nature of the interaction. TPVPBA was exposed to various concentrations of tris(2-aminoethyl)amine (TAEA, Figure 4.2). The aromatic protons are very diagnostic for complexation, and show that complete complexation occurs at just over a 1:1 ratio of boron to amine **1**; no further changes, including substitutions giving **2** or **3**, were observed. The inability of the network to perfectly form at an exact 1:1 stoichiometric match of functional groups is attributed to the incomplete efficiency with which the Lewis acid−Lewis base reacting partners find each other in the elastomeric matrix.

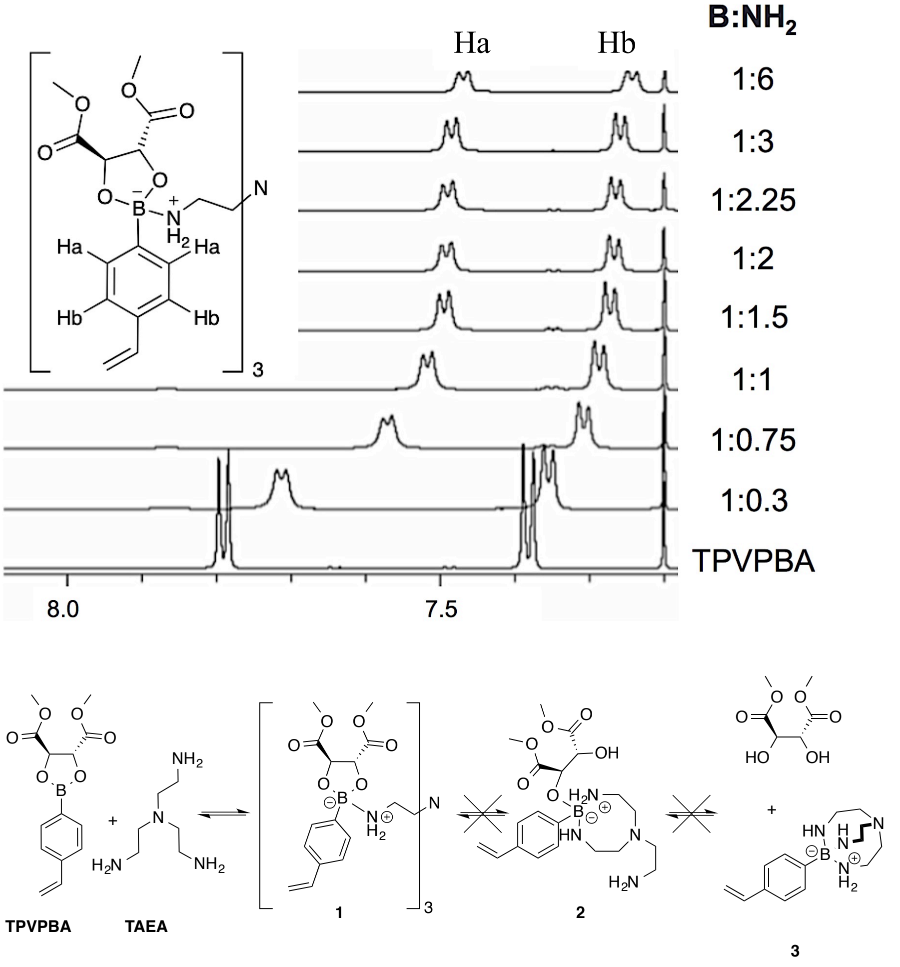

Figure 4.2. Titration of TAEA into the boronate shows only 1:1 complexation.

The liquid state of silicone-boronic acid polymers lends itself to convenient elastomer formulation; the method requires neither solvents nor intensive mixing. Transparent colourless, yellow or, in some cases, translucent rubbers of varying hardness were obtained simply by stirring amine-containing silicone polymers, with more than two -NH_2 groups per silicone chain, with an α,ω-telechelic boronic acid silicone polymer, and then allowing the mixture to cure under ambient conditions to give all samples listed, with the first digits being **17**, **73** or **99** (Table 4.2, Figure 4.3 structure **4**). The curing process started immediately, as shown by an immediate increase in viscosity, but took up to 12 h to complete. The efficiency of formation of a B−N Lewis acid−base complex was such that no heating or catalyst was required in this process. The range of amino compounds that were independently combined with **SiBA**s (Figure 4.1), as well as a network structure formed between the two compounds through Lewis acid−Lewis base interactions are shown in Figure 4.3. Note that the boronate esters, once complexed by amine, do not undergo facile hydrolysis.

Two other network morphologies were prepared. In the first, analogous to **SiBA**, pendant boronic acid-modified silicones **P-SiBA** were crosslinked with α,ω-telechelic aminoalkyl silicone polymers. In the other case, the organoamine TAEA (Figure 4.5) was used to crosslink α,ω-telechelic silicone boronate **SiBA**. The low solubility of TAEA made it more difficult to mix with the boronic acids than the other aminopolymers and, therefore, small quantities of dichloromethane were added to obtain homogenous elastomers.

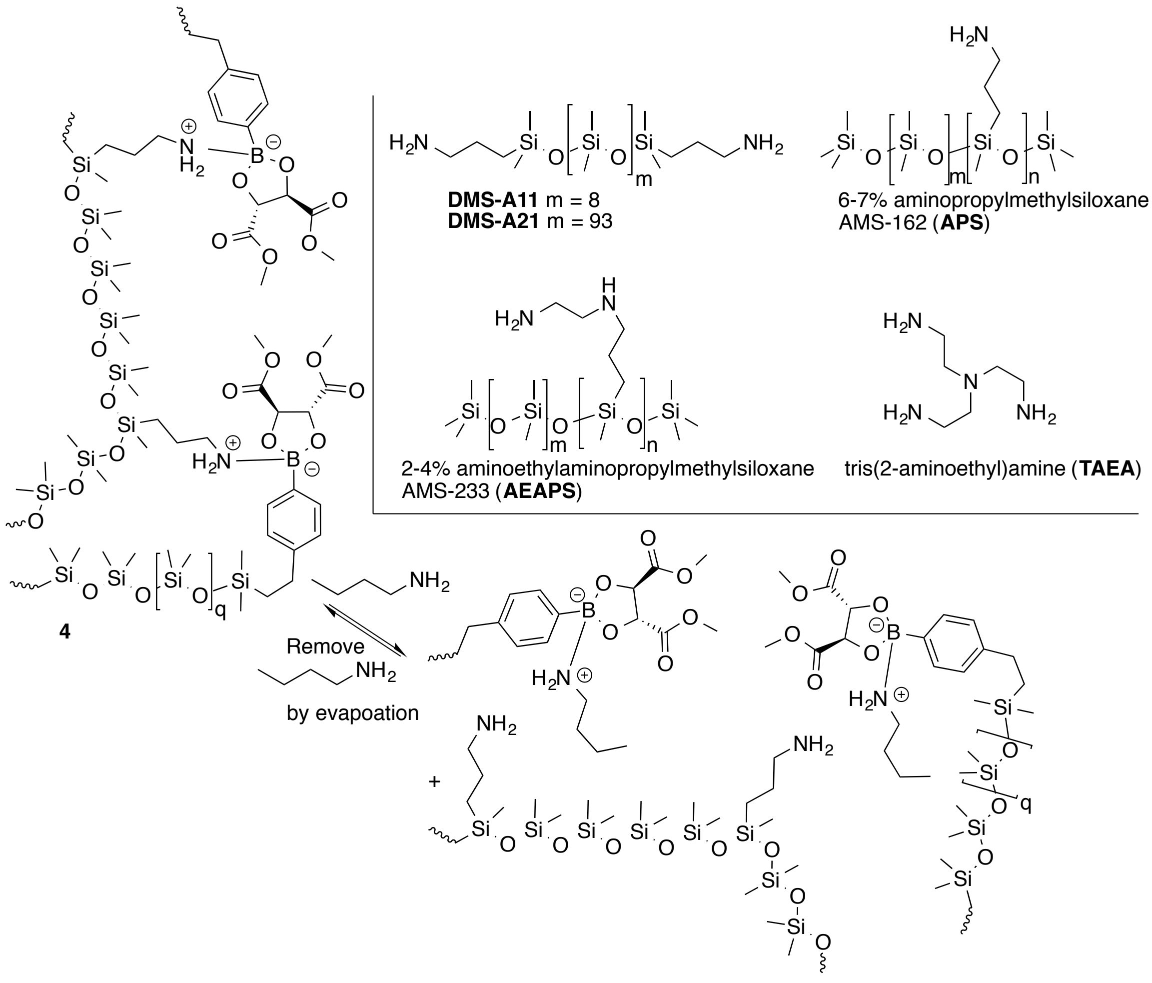

Figure 4.3. Lewis acid/base crosslinking between silicone-boronic acids and commercial aminosilicones and polyamines

Selected formulations for elastomers that are rich in amines, rich in boron, or matched, respectively, are shown in Table 4.2 (see Appendix Section 6.2 for a complete listing). As would be expected for an approximately 1:1 Lewis acid−Lewis base binding process, the optimum crosslinking occurred near 1:1 stoichiometry as shown by Shore-hardness experiments (e.g., **99-B-50**, **73-A-50**, **2-C-75**). Excess functional groups, whether present on the side chain or the termini, led to highly branched but less crosslinked structures.

The effects of mismatched stoichiometry were more pronounced when excess boron was available (many of these samples were viscous liquids or very soft rubbers), while samples containing excess amine tended to have more elastomeric physical properties, perhaps due to interchain affinity through hydrogen bonding. The crosslinked materials exhibited swelling to different degrees in various solvents (see Appendix Section 6.2). However, toluene, in which all samples swelled, was used to provide complementary crosslink density information to hardness measurements (Table 4.2).

The crosslink density was dependent on the molar ratio of boron to nitrogen in each formulation, and also on the chain lengths of the α,ω-functional base polymers. Holding the ratio of boron to nitrogen constant, it can be seen, for example, that sample **12-C-75**, containing a lower molecular weight diamine, was harder than sample **12-D-75**, which contained a higher molecular weight diamine. Samples crosslinked with TAEA, which have a tighter network structure with star crosslinks, tended to be more glassy and brittle than those derived from polymeric crosslinkers (Figure 4.5).

Table 4.2. Selected formulations of amino/boronic ester elastomers

Product Name[a]	Boronate	Amino Compound	Molar ratio B/NH_2	Shore OO[b]	Swelling [%]	Relaxation time (s)[c]
99-B-25	**SiBA-99**	AEAPS (2-5% NH_2)	1 to 4.8	28.0 ± 0.8	2926	>6.28
99-B-50	**SiBA-99**	AEAPS (2-5% NH_2)	1 to 1.6	56.0 ± 0.8	1339	>6.28
99-B-75	**SiBA-99**	AEAPS (2-5% NH_2)	1 to 0.5	47.0 ± 0.8	dissolved	1.25
73-A-25	**SiBA-73**	APS (6-7% NH_2)	1 to 7.2	24.0 ± 1.4	dissolved	0.50
73-A-50	**SiBA-73**	APS (6-7% NH_2)	1 to 2.4	51.7 ± 1.2	1284	>6.28
73-A-75	**SiBA-73**	APS (6-7% NH_2)	1 to 0.02	33.3 ± 1.2	dissolved	0.16
17-A-25	**SiBA-17**	APS (6-7% NH_2)	1 to 2.2	86.7 ± 0.5[d]	537	>6.28
17-A-50	**SiBA-17**	APS (6-7% NH_2)	1 to 0.7	40.7 ± 3.3	507	≈0
17-A-75	**SiBA-17**	APS (6-7% NH_2)	1 to 0.2	too soft	dissolved	liquid
99-E-0.5	**SiBA-99**	TAEA	1 to 0.5	64.7 ± 2.1	dissolved	15.78
99-E-1.0	**SiBA-99**	TAEA	1 to 1	67.3 ± 1.7	dissolved	>62.83
99-E-1.5	**SiBA-99**	TAEA	1 to 1.5	69.3 ± 1.2	dissolved	>62.83
2-C-25	**P-SiBA-2**	DMS-A11	1 to 11.8	too soft	dissolved	liquid
2-C-50	**P-SiBA-2**	DMS-A11	1 to 4.0	49.7 ± 2.5	dissolved	0.84
2-C-75	**P-SiBA-2**	DMS-A11	1 to 1.3	72.7 ± 1.2	dissolved	0.63
12-C-25	**P-SiBA-12**	DMS-A11	1 to 5.3	NH[e]	dissolved	NH
12-C-50	**P-SiBA-12**	DMS-A11	1 to 1.8	NH	dissolved	NH
12-C-75	**P-SiBA-12**	DMS-A11	1 to 0.6	76.3 ± 1.2	336	29.16
12-D-25	**P-SiBA-12**	DMS-A21	1 to 0.6	71.7 ± 0.5	dissolved	0.63
12-D-50	**P-SiBA-12**	DMS-A21	1 to 0.2	61.3 ± 0.5	dissolved	1.35
12-D-75	**P-SiBA-12**	DMS-A21	1 to 0.07	68.0 ± 0.8	dissolved	0.92

[a] Nomenclature is explained in more detail in the Experimental Section; see also Figure 4.1 and Figure 4.3. [b] Values for Shore hardness reflect averages of three readings on one sample for each formulation. Measurements were taken after samples were aged for 2-7 weeks. [c] Values for relaxation time are calculated from the average G'/G" crossover frequencies found for three experiments on three samples for each formulation. A relaxation time value of >6.28 or >62.83 indicates that the crossover frequency fell below the observed frequency range for the experiment (1-100 or 0.1-100 rad s^{-1}, respectively, too hard for the instrument to measure) and a value of ≈ 0 indicates that there was no observable crossover frequency (indicating viscous, non-elastomeric fluids). [d] Shore A = 22.3 ± 0.5. [e] NH = non-homogenous (solid/liquid mixture).

Crosslink densities from swelling or hardness data are complemented by rheological data that showed changes in elastic/storage (*G'*) and viscous/loss (*G''*) moduli with respect to frequency at constant strain could be observed for all samples. The majority of samples exhibited rheological behavior characteristic of networks composed of reversible bonds (i.e., frequency-dependent moduli) with observable crossover frequencies, ω_c (the angular frequency at which $G' = G''$), thereby allowing for the calculation of the characteristic relaxation time τ ($\tau = 2\pi/\omega_c$),[27] which reflects the time required for the elastic structures within a viscoelastic material to relax.

In a reversibly crosslinked network, such as the **SiBA**/aminosilicone elastomers described here, a high relaxation time indicates that the material is highly crosslinked, and is behaving more like a permanently crosslinked elastomer (boron−nitrogen bond is effectively fixed), while a low relaxation time suggests that fewer crosslinking sites are present, or that crosslinking is readily reversibly under the conditions of the experiment.[28] Within Table 4.2 are shown examples of materials that are highly crosslinked elastomers (**99-E-1.0**, **12-C-75**), very lightly crosslinked gels (**17-A-50**, **8-D-25**) and a range of soft to rigid elastomeric samples, **73-A-25**, **99-E-0.5**, etc.

Increased relaxation time and Shore-hardness values were observed after six months of storage at room temperature, which indicated that most samples anneal over time and undergo further crosslinking of initially free boronic esters and amines, or equilibration of existing B−N crosslinks, to afford a more stable network.

The ability of **SiBA-N** elastomers to anneal over time was indicative of a responsive, reversible network. The thermal dependence of the responsiveness of selected networks was examined by thermogravimetric analysis (TGA), differential scanning calorimetry (DSC), and melt-rheology (Table 4.3). Three samples containing different proportions of the same **SiBA-17** and aminopolymer APS showed that thermal stability increased with increasing crosslink density, and that only one decomposition-related event was observed for each sample. Thermal degradation occurred at temperatures at which the silicone polymer itself starts to undergo decomposition,[29] over 350 °C. Somewhat unexpectedly, the presence of more nitrogen was associated with greater thermal stability: residual amines were not facilitating base-catalysed decomposition of the silicone polymers.[30]

The samples were subjected to a heat/cool/heat cycle in the DSC to determine whether thermal de-crosslinking and re-crosslinking could be observed. A small and reversible endothermic event associated with de-crosslinking upon heating was observed at approximately 50 °C, provided the sample was not heated above 120 °C, because the samples underwent irreversible degradation after an exothermic transition near 130 °C.

Table 4.3. TGA and DSC analysis

Product name	Molar ratio B/NH_2	Decomposition T [°C][a]	DSC event T [°C][b]
17-A-25	1:2.2	492	132-260
17-A-50	1:0.7	432	143-208
17-A-75	1:0.2	382	N/A

[a] Taken as the temperature at 50 % mass loss. [b] The temperature range of an endothermic peak observed in the DSC spectrum for each sample.

Reversible temperature-induced dissociation of the Lewis acid−base pairs responsible for elastomeric properties was demonstrated using melt-rheology in which a sample of **17-B-50** was heated from 35 to 120 °C at a constant frequency and under constant strain. As discussed previously, the rheological results show that a highly crosslinked network will have an elastic modulus that is greater than the viscous modulus at room temperature. Upon increasing the temperature, the effect is reversed: the viscous modulus overcomes the elastic modulus and the sample effectively melts (Figure 4.4, and the Appendix Section 6.2). Cooling the sample to room temperature restores the moduli to their previous states.

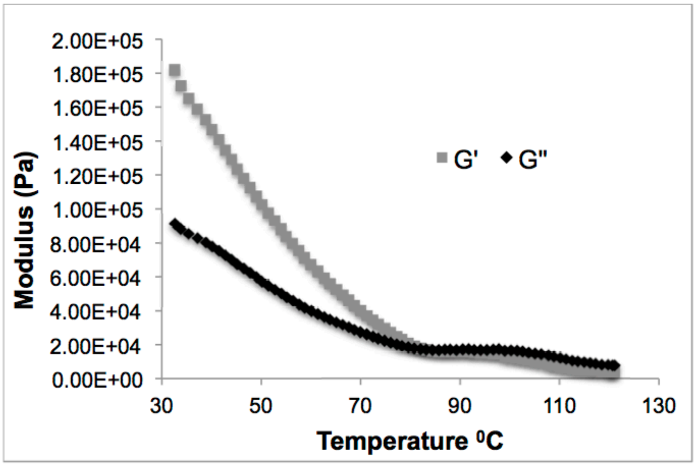

Figure 4.4. Loss of elastic behaviour upon heating of **17-A-50**

The thermal reversibility of B−N crosslinks could also be demonstrated through a simple shape-recovery experiment. Two pieces of the same elastomer sample (**73-B-25**, ~1.4 × 0.3 × 0.2 cm) were placed under equal loads (~2000 g) at either room temperature or at 60 °C. After heating for 24 h, the sample was allowed to cool to room temperature while still under pressure. Once the weight was removed from the sample held at room temperature, near-complete shape recovery (± 14%) was observed. By contrast, the sample compressed at 60 °C exhibited a linear extension of 136% and did not recover after the weight was removed after cooling. These results demonstrate that the system is able to anneal at 60 °C, significantly reducing the restoring force. That is, the silicone had taken a compression set due to reformation of crosslinks in the new, compressed, shape.

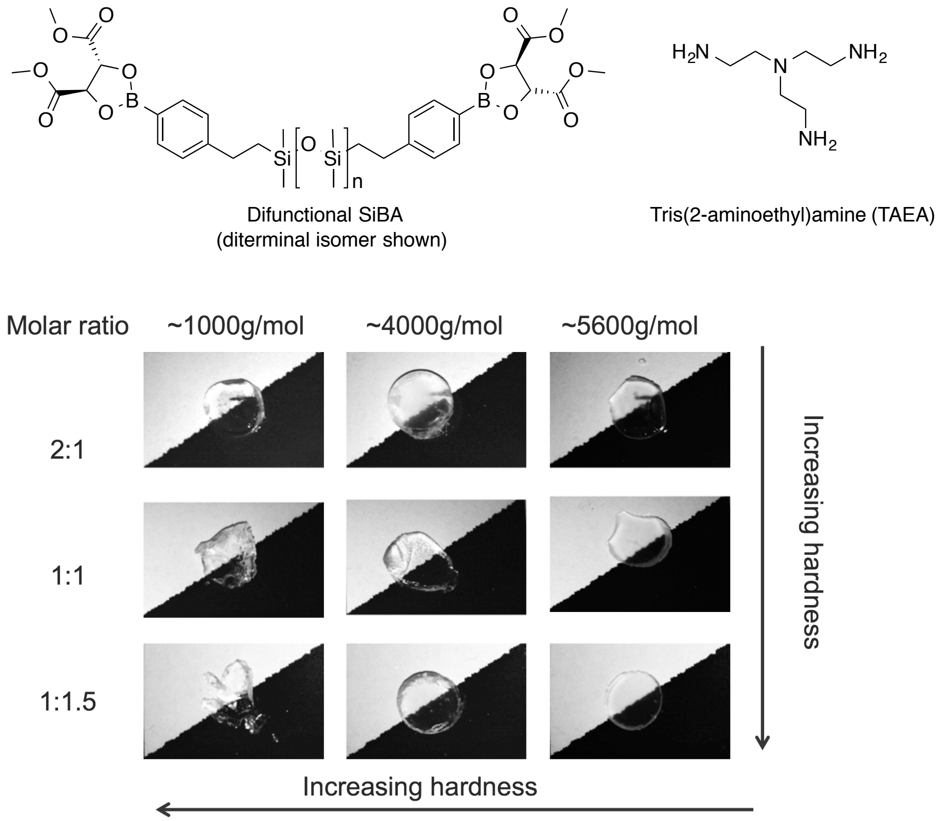

Figure 4.5. Representative photographs of **SiBA**/TAEA elastomers

An alternative method for disrupting the B−N bonds in these elastomeric systems involved the addition of a competing, monofunctional Lewis base. Severin et al. have previously demonstrated that B−N linked polymers can be disrupted in solution.[14] We chose to employ *n*-butylamine as a competitive Lewis base because it can be easily removed through evaporation. After exposure to excess *n*-butylamine, pieces of an initially elastomeric sample **73-B-50** were converted into a highly viscous liquid (Figure 4.3). The fact that discrete pieces of the original elastomer were no longer present indicated that the network had been disassembled. Upon removal of *n*-butylamine by evaporation, however, a uniform elastomer reformed. Rheological measurements indicated the crosslink density of the product was of the same order as the sample before de-crosslinking (see Appendix Section 6.2).

4.4 Discussion

The most famous silicone that relies on Lewis acid−Lewis base complex formation os arguably "bouncing putty" or "silly putty" wherein a linear silicone polymer is interrupted by boric acid units.[31] Oxygen atoms on adjacent chains can form Lewis acid−Lewis base complexes at boron. These are relatively weak such that under slow stress (stretching), the material behaves as a fluid; at intermediate stress, the elastomer bounces, but at high stress, a sharp shock, it shatters like glass. Otherwise we are unaware of any examples of silicone elastomers that utilise Lewis acid−Lewis base complexation to form (reversible) networks.

Strong boron-based Lewis acids like BF_3 form complexes with free amines with relatively high bond energies, ranging up to about 160 kJ mol^{-1}.[32] Qin and Jäkle showed that strong binding occurred between triarylborane polymers and pyridine derivatives: boronic acids did not have the same efficiency of binding to amines.[33] Weaker binding is expected, as they noted, because of π donation from the oxygen atoms, but relatively strong bonds can nevertheless form with amines. Shinkai et al. used the special case of intramolecular chelation of an amine to stabilise boronate sugar complexes.[34] The group of Severin et al. combined binding of catechol-like boronic esters with complexes containing bipyridine. While B−N complexes formed readily, they dissociated simply on dilution in polar solvents.[14]

The compounds described above have intermediate stability to those described in the literature. Complexation between the amines and boronic acids is favoured in the hydrophobic medium provided by the silicone chains themselves, and is strong enough to overcome swelling by toluene. However, heating to only 60 °C is sufficient to facilitate reversible dissociation. That process is further facilitated by the presence of competitive Lewis bases, as in the case of the addition of butylamine.

The Lewis acid−Lewis base crosslinks are dynamic, even at room temperature, as shown by the annealing observed over a few months: the off/on rate increases with heating such that stresses built up by a compressive force are released by reforming crosslinks. The material takes a compression set on release of the compressive force. Dynamic silicone elastomers have previously been described. Chang and Buese described living elastomers through which acid catalysts percolated. Multiple embedded rings continually underwent acid-catalysed equilibration that, when present, preferably relieved induced stresses.[35] McCarthy's group generalised this concept and showed that other catalytic processes also applied.[36] In the current case, the outcome is similar, but catalysts are unnecessary: the

B−N compounds have sufficient fragility at slightly elevated temperature that they equilibrate by dissociation/re-association.

It is this intermediate stability of the boronate amine complex that is the source of its utility as a crosslinker for silicones. The complexes rapidly form on mixing, in the absence of any additional solvent with the exception of the TAEA complexes. Viscosities rapidly build to give materials ranging from fluids through soft and hard elastomers up to glasses in a predictable way. The polymers can be repurposed upon heating or temporary treatment with a competing, volatile Lewis base.

4.5 Conclusion

Boronates bound to silicone polymers in a variety of different configurations undergo complexation with amines, both small molecules and organic and silicone-based polymers. Even when an excess of amines is present, a single Lewis acid−Lewis base interaction is observed: substitution of the boronate esters by amines is not observed. A variety of network morphologies was accessed by the use of α,ω-boronate plus polyamines or pendant oligoboronates plus α,ω-diamines. Materials ranging from soft gels to brittle glasses could be prepared simply by manipulating the crosslink density, as shown by solvent swelling, hardness and rheological experiments. Above 130 °C a permanent change to the elastomer structure occurs, such that network relaxation through Lewis acid−Lewis base decomplexation is no longer possible. At temperatures over approximately 60 °C stresses induced by compressive force are relieved by de/recomplexation. Reversible de-crosslinking is also possible when monofunctional amines are added, such that the network amine complexes are replaced. Evaporation leads to restoration of the network. These readily available silicone materials offer potential utility on their own, or in combination with other silicones because of the ability to redirect network stress under readily accessible conditions.

4.6 Experimental

4.6.1 Nomenclature

Abbreviated five-digit labels are used to represent each formulation, for example, **17-A-25**. The first two digits **99**, **73**, and **17** represent the approximate siloxanes length of the bolaamphiphilic silicone−boronic acid **SiBA**, or **2**, **8**, and **12** represent the approximate number of pendant boronate esters per siloxanes chain used in the formulation, the central letter (**A-E**) represents the amino compound used in the formulation where **A** is 6−7% aminopropylmethylsiloxane−dimethylsiloxane copolymer (APS), **B** is 2−4% aminoethylaminopropylmethylsiloxane−dimethylsiloxane copolymer (AEAPS), **C** is aminopropyl-terminated polydimethylsiloxane (low molecular weight ~840 g mol^{-1}), **D** is aminopropyl-terminated polydimethylsiloxane (high molecular weight 7150 g mol^{-1}), **E** is TAEA; and the last two digits represent the percent by weight of silicone−boronic acid present in the formulation, or the molar equivalents of boron in TAEA samples.

4.6.2 Synthesis of bolaamphiphilic silicone−boronic acid esters

4.6.2.1 Hydrosilylation of hydride-terminated polysiloxanes: general procedure using DMS-H25 $HMe_2SiO(Me_2SiO)_{\sim 97}SiMe_2H$ (SiBA-99)

The approximate molecular weight was determined by ^{1}H NMR spectroscopy end-group analysis (ratio of terminal to internal $SiMe_2$ groups) ≈ 7330 g mol^{-1}.

4-Vinylphenylboronic acid dimethyl-L-tartrate ester (TPVPBA) (1.66 g, 5.72 mmol) was added to a 100 mL round-bottomed flask containing a magnetic stir bar. After addition of dry toluene (30 mL) to the reaction flask, a solution of DMS-H25 (19.06 g, 2.60 mmol) in dry toluene (10 mL) was added using a Pasteur pipette. At that point, the reaction mixture was a clear, colourless solution. Karstedt's catalyst (25 µL, 2% solution in xylenes) was added to the reaction, causing the solution to immediately turn bright yellow. The reaction was stirred at room temperature for 20 h, during which time the yellow colour faded considerably. The reaction was then stirred with activated carbon (~2 g) for 24 h prior to filtration through a fritted funnel containing approximately 10 g Celite, eluting with hexanes. The volatile solvents were removed by distillation on a rotary evaporator, giving the product as a clear, colourless oil. Yield: 19.8 g (96%); ratio of products (terminal/internal) was 5:4. Note that it is not possible to quantify the fraction of polymers with α,ω-diterminal versus diinternal versus internal + terminal end groups. The NMR spectroscopy data for only the favoured (~55%) terminal isomer is presented. Terminal isomer: (55%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, J = 7.9 Hz, 4 H), 7.22

(d, *J* = 7.9 Hz, 4 H), 5.07 (s, 4 H), 3.83 (s, 12 H), 2.67 (m, 4 H), 0.89 (m, 4 H), 0.2 to −0.05 ppm (m, ~600 H).

4.6.3 NMR spectroscopy experiments to gauge B−N interactions

4.6.3.1 Test reaction

A standard glass NMR tube was charged with **PMDS-BA** (50 mg) and deuterated chloroform (approx. 0.6 mL). A ^{11}B spectrum was recorded and calibrated according to a boron-trifluoride diethyl etherate (BF_3•OEt_2) external standard. Ethylenediamine (7 mg) was then added to the sample. The sample was mixed thoroughly by inverting the capped NMR tube. A second ^{11}B spectrum was recorded and calibrated as before. In order to reduce interference from background signals, a linear back prediction was performed on all ^{11}B NMR data.

4.6.4 General synthesis of physically crosslinked PDMS elastomers

4.6.4.1 Elastomer from SiBA-73/APS 1:1 composition (73-A-50)

Liquid APS (2 g) and liquid **SiBA-73** (2 g) were placed in a plastic Petri dish (internal diameter = 3.5 cm) lined with Teflon and immediately mixed by being stirred with a plastic rod. A loose-fitting lid was placed over the Petri dish and the sample was left on a flat surface exposed to ambient conditions for at least 1 week before any testing was performed. The resulting material was a transparent and colourless rubber.

4.6.5 Rheology

Samples were analysed using an advanced rheometrics expansion system (ARES) rheometer (TA Instruments) using the program TA Orchestra for data acquisition. Samples were punched into discs (diameter 9.5 mm) and placed in between two parallel plates and compressed to a diameter of the plates (7 or 14 mm) to give good contact between the bottom plate, sample, and the top plate. The total distance between plates varied between 1.5−2 mm depending on sample thickness. The first measurements performed were the dynamic strain-sweep test between 0.1−100% strain at a constant frequency of 1 Hz. The dynamic strain-sweep test was performed to determine the linear viscoelastic region of the sample. The strain for linear region (unique for each formulation) was used in subsequent dynamic frequency-sweep tests. A dynamic frequency-sweep test was performed to determine how the modulus of the elastomer changed with respect to frequency, while being independent of strain. All frequency-sweep measurements were performed at a frequency range between 1−100 rad s^{-1}. All tests were performed at 23−24 °C.

4.6.6 Hardness measurements

Shore A hardness measurements were made using a Durometer Hardness type “A2” from The Shore Instrument & Mfg. Co., NY. Shore OO experiments were taken using a Rex Durometer, Type OO, Model 1600 from Rex Guage Co.

4.6.7 Thermal studies

Thermogravimetric analysis was performed on a TA Instruments TGA Q50 equipped with a platinum sample plate and argon operating gas. Samples ranged from 2−5 mg, and were measured from 40−800 °C at a heating rate of 20 °C min^{-1}. Differential scanning calorimetry was performed on a TA Instruments DSC Q20 under an atmosphere of argon. Samples (9−13 mg) were placed inside hermetically sealed sample holders and analysed under various conditions (see Appendix Section 6.2).

4.7 Acknowledgements

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4.8 References

1. a) Y. Wang, J. D. Byrne, M. E. napier, J. M. DeSimone, *Adv. Drug Delivery Rev.* **2012**, *64*, 1021-1030; b) J. P. Phillips, X. Deng, R. R. Stephen, E. L. Fortenberry, M. L. Todd, D. M. McClusky, S. Stevenson, R. Misra, S. Morgan, T. E. Long, *Polymer* **2007**, *48*, 6773-6781; C. C. Ferraz, G. H. C. Varca, J.-C. Ruiz, P. S. Lopes, M. B. Mathor, A. B. Lugao, E. Bucio, *Radiat. Phys. Chem.* **2014**, *97*, 298-303; P. K. Annamalai, K. L. Dagnon, S. Monemian, E. J. Foster, S. J. Rowan, C. Weder, *ACS Appl. Mater. Interfaces* **2014**, *6*, 967-976; J. A. Crow-Willoughby, D. R. Stevens, J. Genzer, L. I. Clarke, *Macromolecules* **2010**, *43*, 5043-5051; D. A. Stone, N. D. Wanasekara, D. H. Jones, N. R. Wheeler, E. Wilusz, W. Zukas, G. E. Wnek, L. T. J. Korley, *ACS Macro Lett.* **2012**, *1*, 80-83.
2. T. Defize, R. Riva, C. Jerome, M. Alexandre, *Macromol. Chem. Phys.* **2012**, *213*, 187-197.
3. A. Lendlein, H. Jiang, O. Junger, R. Langer, *Nature* **2005**, *434*, 879-882.

4. S. L. Jeon, D. M. Loveless, S. L. Craig, *Supramol. Chem.* **2010**, *22*, 697-703.
5. R. P. Sijbesma, F. H. Beijer, L. Brunsveld, B. J. B. Folmer, J. H. K. K. Hirschberg, R. F. M. Lange, J. K. L. Lowe, E. W. Meijer, *Science* **1997**, *278*, 1601-1604.
6. F. Herbst, D. Dohler, P. Michael, W. H. Binder, *Macromol. Rapid Commun.* **2013**, *34*, 203-220.
7. G. Holden, H. R. Kricheldorf, R. P. Quirk, in *Thermoplastic Elastomers*, Hanser Gardner, Munich, **2004**.
8. A. S. Fawcett, M. A. Brook, *Macromolecules* **2014**, *47*, 1656-1663.
9. K. K. Chauhan, C. G. Frost, *J. Chem. Soc. Perkin Trans. 1* **2000**, 3015-3019.
10. S. Kobayashi, K. Manabe, *Pure Appl. Chem.* **2000**, *72*, 1373-1380.
11. a) M. Grosche, E. Herdtweck, F. Peters, M. Wagner, *Organometallics* **1999**, *18*, 4669-4672; b) M. Fontani, F. Peters, W. Scheer, W. Wachter, M. Wagner, P. Zanello, *Eur. J. Inorg. Chem.* **1998**, 1453-1456; c) Y. Qin, C. Cui, F. Jäkle, *Macromolecules* **2007**, *40*, 1413-1420.
12. a) M. Mikami, S. Shinkai, *Chem. Commun.* **1995**, 153-154; b) I. Nakazawa, S. Suda, M. Masuda, M. Asai, T. Shimizu, *Chem. Commun.* **2000**, 881-882.
13. J. K. Day, C. Bresner, I. A. Fallis, L. L. Ooi, D. J. Watkin, S. J. Coles, L. Male, M. B. Hursthouse, S. Aldridge, *Dalton Trans.* **2007**, 3486-3488.
14. N. Christinat, E. Croisier, R. Scopelliti, M. Cascella, U. Rothlisberger, K. Severin, *Eur. J. Inorg. Chem.* **2007**, 5177-5181.
15. R. Nishiyabu, Y. Kubo, T. D. James, J. S. Fossey, *Chem. Commun.* **2011**, *47*, 1124-1150.
16. B. M. Rambo, J. J. Lavigne, *Chem. Mater.* **2007**, *19*, 3732-3739.
17. M. A. Brook, in *Silicon in Organic, Organometallic and Polymer Chemistry*, Wiley, New York, **2000**, Chapt. 9.
18. B. J. B. Folmer, R. P. Sijbesma, R. M. Versteegen, J. A. J. van der Rijt, E. W. Meijer, *Adv. Mater.* **2000**, *12*, 874-878.
19. N. E. Botterhuis, D. J. M. van Beek, G. M. L. van Gemert, A. W. Bosman, R. P. Sijbesma, *J. Polym. Sci. Part A* **2008**, *46*, 3877-3885.
20. P. Antony, S. Bandyopadhyay, S. K. De, *J. Mater. Sci.* **1999**, *34*, 2553-2560.
21. J. Han, H. Lu, J. Zhang, S. Feng, *Mater. Chem. Phys.* **2012**, *136*, 36-42.

22. X. Wang, R. McHale, *Macromol. Rapid Commun.* **2010**, *31*, 331-350.

23. J. Leng, X. Lan, T. Liu, S. Du, *Prog. Mater. Sci.* **2011**, *56*, 1077-1135.

24. M. A. Brook, L. Dodge, Y. Chen, F. Gonzaga, H. Amarne, *Chem. Commun.* **2013**, *49*, 1392-1394.

25. a) S. L. Wiskur, J. J. Lavigne, H. Ait-Haddou, V. Lynch, Y. H. Chiu, J. W. Canary, E. V. Anslyn, *Org. Lett.* **2001**, *3*, 1311-1314; b) N. Kano, J. Yoshino, T. Kawashima, *Org. Lett.* **2005**, *7*, 3909-3911; c) L. Zhu, S. H. Shabbir, M. Gray, V. M. Lynch, S. Sorey, E. V. Anslyn, *J. Am. Chem. Soc.* **2006**, *128*, 1222-1232.

26. J. Yan, H. Fang, B. Wang, *Med. Res. Rev.* **2005**, *25*, 490-520.

27. J. M. Dealy, R. G. Larson, in *Structure and Rheology of Molten Polymers*, Hanser Gardner, Munich, **2007**.

28. A. Kulmyrzaev, D. J. McClements, *J. Food Eng.* **2000**, *45*, 219-224.

29. T. H. Thomas, T. C. Kendrick, *J. Polym. Sci. A-2* **1969**, *7*, 537-549.

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

31. R. R. McGregor, E. Leathen, Treating dimethyl silicone polymer with boric oxide, US Patent 2431878 (to Corning Glass Works) Dec. 2, 1947.

32. C. A. Deakyne, J. F. Liebman, *J. Mol. Struct.* **1991**, *234*, 343-355.

33. Y. Qin, F. Jäkle, *J. Inorg. Organomet. Polym. Mater.* **2007**, *17*, 149-157.

34. T. D. James, K. Sandanayake, R. Iguchi, S. Shinkai, *J. Am. Chem. Soc.* **1995**, *117*, 8982-8987.

CHAPTER 5: General Conclusions

The exceptional surface characteristics and ease with which useful functional groups can be introduced onto siloxane backbones have led to the widespread use of silicones in multiple industries for multiple applications. Functional silicones provide the means to modify the physical and chemical properties of PDMS, as well as produce robust elastomers through covalent crosslinking. Modification of the interfacial behaviour of silicones in real time through the use of responsive functionality has not been thoroughly explored. Through the covalent attachment of boronic esters to various siloxane architectures, a new class of responsive small-molecule, polymeric, and elastomeric silicones has been produced.

In Chapter 2, the synthetic approach to silicone-boronic esters is reported. Platinum-catalyzed hydrosilylation of dimethyl-L-tartrate protected 4-vinylphenylboronic acid was performed using pendant- and terminal- Si-H containing silicones, leading to varied three-dimensional architectures as well as different molecular weight polymeric structures. Hydrolysis of the protecting group tartrate was observed across a broad pH range and was detected using NMR spectroscopy. Upon hydrolysis, the hydrophilic boronic acids present in the PDMS chain were able to preferentially bind to fructose over glucose, in keeping with the observed trends for boronic acid/saccharide binding found in the literature. The presence of Lewis basic tris(hydroxymethyl)aminomethane stabilized the sugar-boronate complex and led to increased solubility for small-molecule silicone-boronic acids. The unusual self-associative behaviour of boronic acids in silicone was observed after deprotection, leading to highly viscous materials. Thus, the surface activity and physical properties of silicones could be modified in response to boronic acid interactions with entities such as diols and Lewis bases.

Chapter 3 of this thesis further explores the phenomenon of self-associated boronic acids in silicone. Three protected bolaamphiphilic silicone-boronic esters, pinacol, catechol, and dimethyl-L-tartrate, were synthesized with varied PDMS backbone molecular weights. The compounds were liquids at room temperature with spreading characteristics typical of PDMS on water, however, those with hydrolyzable protecting groups (tartrate and to a lesser extent catechol) set into viscoelastic films after spreading. The change in viscosity and formation of crosslinks was attributed to the dimeric self-association of freed boronic acids within the silicone phase. The relative change in stability (physical crosslinking) of silicone-boronic acid layers was measured by timing the penetration of water droplets introduced at the silicone/air interface after spreading. Mid-molecular weight silicone-boronic acids produced the most stable layers owing to a balance between silicone chain length and boronic acid concentration. Low and high molecular weight bolaamphiphiles tended to produce less stable layers due to over- and under-crosslinking respectively. Conversion of neutral boronic acids to anionic boronates through an increase in sub-phase pH led to increased water-solubility of the boron-containing functional groups and destruction of physical associations. The presence of diols and Lewis bases in the sub-phase (known to bind with boronic acids) also caused destabilization of crosslinking. Manipulation of the well-known binding capabilities of boronic acids led to the first demonstration of stimuli-responsive behaviour for functional silicone polymers at the air/water interface.

In Chapter 4 of this thesis, coordinate covalent bonding between Lewis acidic silicone-boronic esters and Lewis basic polymers and small molecules was explored as an option for reversible PDMS crosslinking. Silicones with terminal boronic esters were crosslinked using pendant-functional aminosilicones, as well as the small molecule tris(2-aminoethyl)amine, while pendant-silicone boronic esters were crosslinked using aminopropyl-terminated PDMS. Since networks produced with this method were quite robust, it was possible to quantify the crosslink density using swelling, Shore hardness measurements, and rheology. As predicted, higher crosslink density led to lower percent swelling, higher Shore hardness, and elastomeric characteristics in frequency-sweep tests. Heating of these materials under compressive force led to a change in shape due to dynamic B-N bond reformation as a mechanism to relieve stress. The covalent network could be fully disassembled via the introduction of *n*-butylamine, a competing Lewis base, and reformed upon removal of the volatile amine. This process of Lewis acid/base pairing to afford reversibly crosslinked silicone networks is the first of its kind.

The introduction of reactive functional groups to silicone polymers is not in itself a novel idea: amino- and carboxy-terminated silicones are two examples of commercially available pH-responsive polymers similar in structure to the α,ω-silicone-boronic acids discussed within this thesis. The acidic and basic nature of carboxylic acids and amines causes them to ionize at high- and low-pH, respectively. The important difference between these functional silicones and SiBA polymers is the fact that the ionization of boronic acids can affect their ability to bind or interact with other species, including themselves, thereby leading to a tunable rather than simply switchable system. Although N-H and O-H containing silicones are also theoretically capable of hydrogen bonding, boronic acid-functionalized silicones are unique in their cohesive behaviour. It is apparent that the additional Lewis acidity of boronic acids plays an important role in their interactions with themselves and with the siloxane backbone, while avoiding the inherent degradation process that silicones undergo in the presence of Brønsted acids and bases. Finally, the selective binding between boronic acids and certain diol-containing biomolecules allows for their use in multiple-stimuli-responsive materials.

In conclusion, this thesis presents the characteristics and properties of a new class of stimuli-responsive functional silicone compounds and polymers. Using boronic acid as a diol-, Lewis base-, and pH-responsive handle, the interfacial and physical properties of silicones can be tuned through interactions between boronic acids and: (1) themselves, (2) aqueous solutes, and (3) Lewis basic polymers and small molecules. Manipulation of the medium in which these compounds were studied has led to the development of selective saccharide-binding surfactants, self-associating viscoelastic layers that form on aqueous solutions, and thermoplastic silicone elastomers that can be broken down in the presence of a competitive monodentate Lewis base.

CHAPTER 6: Appendix

6.1 Supporting Information for CHAPTER 2: Sugar Complexation to Silicone Boronic Acids

6.1.1 Materials and Methods

4-Vinylphenylboronic acid (95%), dimethyl-ʟ-tartrate (99%), platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst, solution in xylenes 2% Pt), tris(hydroxymethyl)aminomethane (99.9%), ᴅ-(+)-glucose (99.5%), and ᴅ-(-)-fructose (98%) were obtained from Sigma-Aldrich. 1,1,1,3,3,5,5-Heptamethyltrisiloxane was obtained from Fluorchem. Pentamethyldisiloxane, bis(trimethylsiloxy)methylsilane, and hydride-terminated polydimethylsiloxane ($HMe_2Si(OSiMe_2)_nOSiMe_2H$ where n = 8, 14, and 67, respectively) were obtained from Gelest. The solvents (Caledon Laboratories) dichloromethane and toluene were dried over activated alumina prior to use.

IR analysis was performed using a Thermo Scientific Nicolet 6700 FTIR infrared spectrometer. NMR spectra were recorded on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using deuterated solvents (chloroform-*d*, acetone-d_6 or DMSO-d_6). High-resolution mass spectrometry was performed using a Waters Quattro Ultima Global quadrupole time-of-flight mass spectrometer with electrospray ionization mode.

6.1.2 Synthesis

6.1.2.1 Synthesis of dimethyl-L-tartrate protected 4-vinylphenylboronic acid 6

Molecular sieves (4Å, approximately 1 g) and a magnetic stir-bar were placed in a 50 mL round-bottomed flask and dried in an oven at 100 °C for 20 h. The dry flask was purged with nitrogen, and then 25 mL dry dichloromethane were added followed by 4-vinylphenylboronic acid (500 mg, 3.38 mmol) and dimethyl-ʟ-tartrate (602 mg, 3.38 mmol). The reaction mixture consisted of a suspension of a white solid in colorless, clear solvent. The mixture was stirred at room temperature under nitrogen atmosphere for 3 h, after which it appeared as an opaque, colorless mixture. Following removal of molecular sieves via filtration and rinsing with dichloromethane, the volatiles were removed *in vacuo* to afford the product as a colorless, opaque waxy solid. Yield: 826 mg (84 %). ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.83 (d, *J* = 8.0 Hz, 2H), 7.42 (d, *J* = 8.0 Hz, 2H), 6.72 (dd, *J* = 11.0, 17.1, 1H), 5.82 (d, *J* = 17.6 Hz, 1H), 5.31 (d, *J* = 11.0 Hz, 1H), 5.08 (s, 2H), 3.84 (s, 6H). ^{13}C NMR (150.92 MHz, $CDCl_3$): δ = 170.05, 141.41, 136.88, 136.14, 135.76, 125.91, 115.76, 78.08, 53.25. MS (ES-positive mode): *m/z* [M + H$^+$] calculated = 291.1040; [M + H$^+$] found = 291.1023.

6.1.2.2 Hydrosilylation of 6: General Procedure Using Pentamethyldisiloxane (PMDS-derivative)

Freshly prepared (within 12 h) TPVPBA (102 mg, 0.35 mmol) was added to a 50 mL round-bottomed flask containing a magnetic stir bar. After addition of 4 mL dry toluene to the reaction flask, pentamethyldisiloxane (82 μL, 0.42 mmol) was added using an automatic pipette. At that point, the reaction mixture was a clear, colorless solution. Karstedt's catalyst (10 μL, 2% solution in xylenes) was added to the reaction, causing the solution to immediately turn bright yellow. The reaction was stirred at room temperature for 1 additional h, during which time the yellow color faded considerably. The reaction was then stirred with activated carbon (~1 g) for 20 h prior to filtration through a short (2 cm) column of Celite, eluting with hexanes. The volatile solvents as well as excess pentamethyldisiloxane were removed in vacuo and under a stream of nitrogen, giving the product as a clear, colorless oil. Yield: 133 mg (87 %); ratio of products (terminal: internal) was 10:7.

Terminal Isomer: **7t** (62%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.79 (d, *J* = 8.0 Hz, 2H), 7.24 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.83 (s, 6H), 2.65 (m, 2H), 0.87 (m, 2H), 0.07 to -0.03 (m, 15H).

Internal Isomer **7i** (38%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.75 (d, *J* = 8.0 Hz, 2H), 7.10 (d, *J* = 8.0 Hz, 2H), 5.06 (s, 2H), 3.83 (s, 6H), 2.19 (m, 1H), 1.35 (d, *J* = 6.7 Hz, 3H), 0.07 to -0.03 (m, 15H).

Mixture: ^{13}C NMR (150.92 MHz, $CDCl_3$): δ = 172.10, 170.19, 170.13, 150.54, 150.13, 135.63, 135.25, 127.72, 127.19, 78.05, 78.02, 72.16, 53.34, 53.19, 32.33, 29.96, 20.35, 14.28, 2.19, 2.05, 1.81, 1.21, 0.50, -0.20, -1.21. ^{29}Si NMR (119.22 MHz, $CDCl_3$): δ = 8.13, 7.66, 6.98, 5.22. ^{11}B NMR (192.55 MHz, $CDCl_3$): δ = 32.66. MS (ES-positive mode): *m/z* [M + Na$^+$] calculated = 461.1599; [M + Na$^+$] found = 461.1598.

1,1,1,3,3,5,5-Heptamethyltrisiloxane derivative: Following the same general procedure, TPVPBA (102 mg, 0.35 mmol) and 1,1,1,3,3,5,5-heptamethyltrisiloxane (115 μL, 0.42 mmol) were combined with 10 μL of Karstedt's catalyst solution (~ 9×10^{-4} mmol Pt) in dry toluene. The reaction was stirred for 1 h before activated carbon (~1 g) was added. Purification using the above described extraction afforded the product as a clear, slightly yellow oil. Yield: 106 mg (59 %). Ratio of products (terminal : internal) was 10:7.

Terminal Isomer: **8t** (58): ^{1}H NMR (600 MHz, $CDCl_3$): 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, 21H).

Internal Isomer: **8i** (42): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 2H), 7.11 (d, *J* = 7.9 Hz, 2H), 5.06 (s, 2H), 3.83 (s, 6H), 2.22 (m, 1H), 1.36 (m, 3H), 0.3 to -0.1 (m, 21H).

Mixture: ^{13}C NMR (150.92 MHz, $CDCl_3$): δ = 170.15, 170.09, 150.42, 150.06, 135.59, 135.25, 127.66, 127.17, 78.00, 72.10, 53.34, 53.17, 32.25, 29.85, 29.33, 20.19, 15.49, 14.27, 1.98, 1.96, 1.45, 1.32, 0.31, -0.29, -1.29. ^{29}Si NMR (119.22 MHz, $CDCl_3$): δ = 7.84, 7.25, 7.12, 6.89, -20.67. ^{11}B NMR (192.55 MHz, $CDCl_3$): δ = 32.69. MS (ES-positive mode): *m/z* [M + Na$^+$] calculated = 535.1787; [M + Na$^+$] found = 535.1780.

Bis(trimethylsiloxy)methylsilane derivative: Following the general procedure, TPVPBA (102 mg, 0.35 mmol) and bis(trimethylsiloxy)methylsilane (114 μL, 0.42 mmol) were combined with 10 μL of Karstedt's catalyst solution (~ 9×10^{-4} mmol Pt) in dry toluene. The reaction was stirred overnight (approximately 17 h) before activated carbon (~1 g) was added. Purification using the above-described extraction afforded the product as clear, slightly yellow oil. Yield: 86 mg (48 %). Ratio of products (terminal : internal) was 5:2.

Terminal Isomer: **9t** (72%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.9 Hz, 2H), 7.22 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.83 (s, 6H), 2.64 (m, 2H), 0.80 (m, 2H), 0.2 to -0.1 (m, 21H).

Internal Isomer: **9i** (28%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.1 Hz, 2H), 7.12 (d, *J* = 8.0 Hz, 2H), 5.07 (s, 2H), 3.83 (s, 6H), 2.12 (m, 1H), 1.32 (d, *J* = 7.4 Hz, 3H), 0.2 to -0.1 (m, 21H).

Mixture: ^{13}C NMR (150.92 MHz, $CDCl_3$): δ = 172.11, 170.20, 170.15, 150.21, 150.12, 149.12, 135.65, 135.22, 127.78, 127.72, 127.48, 78.07, 78.02, 73.28, 72.15, 53.38, 53.21, 31.80, 29.81, 29.39, 19.72, 15.55, 14.48, 14.44, 2.08, 1.96, 1.77, -0.10, -2.20. ^{29}Si NMR (119.22 MHz, $CDCl_3$): δ = 9.58, 9.35, 7.97, 7.81, -22.68. ^{11}B NMR (192.55 MHz, $CDCl_3$): *δ* = 32.44. MS (ES-positive mode): *m/z* [M + Na$^+$] calculated = 535.1787; [M + Na$^+$] found = 535.1786.

$HMe_2SiO(Me_2SiO)_9SiMe_2H$-Derivative: Approximate molecular weight determined by ^{1}H NMR end group analysis (ratio of terminal to internal $SiMe_2$ groups) ≈ 730 g/mol. Following the general procedure, TPVPBA (100 mg, 0.34 mmol) and DMS-H03 (140 µL, 0.17 mmol) were combined with 10 µL of Karstedt's catalyst solution (~9x10^{-4} mmol Pt) in dry toluene. The reaction was stirred for 3 h before activated carbon was added. After stirring with activated carbon (~1 g) for 20 h, the mixture was gravity filtered using 125 mm Ø Whatman filter paper and rinsed with hexanes. After removal of solvents, the product was isolated as a clear, colorless oil. Yield: 120 mg (54 %). Ratio of products (terminal : internal) was 2:1. Note that it is not possible to quantify polymers with α,ω-diterminal vs diinternal vs internal/terminal end groups.

Terminal Isomer: **10t** (66%): ^{1}H NMR (600 MHz, acetone-d_6): δ = 7.76 (d, *J* = 7.9 Hz, 4H), 7.32 (d, *J* = 7.8 Hz, 4H), 5.18 (s, 4H), 3.81 (s, 12H), 2.75 (m, 4H), 0.98 (m, 4H), 0.2-0.0 (m, 66H).

Internal Isomer: **10i** (33%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 7.9 Hz, 4H), 5.17 (s, 4H), 3.81 (s, 12H), 2.33 (q, *J* = 7.5 Hz, 2H), 1.42 (d, *J* = 7.5 Hz, 6H), 0.2-0.0 (m, 66H).

Mixture: ^{13}C NMR (150.92 MHz, acetone-d_6): δ = 170.73, 150.99, 150.70, 136.17, 135.85, 135.26, 128.51, 128.04, 127.93, 127.54, 78.73, 73.42, 53.16, 52.63, 32.74, 30.41, 20.97, 20.85, 14.65, 1.56, 1.47, 0.47, -1.53.

$HMe_2SiO(Me_2SiO)_{16}SiMe_2H$-Derivative: Approximate molecular weight determined by ^{1}H NMR by end group analysis ≈ 1170 g/mol. Following the general procedure, TPVPBA (100 mg, 0.34 mmol) and DMS-H11 (220 μL, 0.17 mmol) were combined with 10 μL of Karstedt's catalyst solution (~9×10^{-4} mmol Pt) in dry toluene. The reaction was stirred for 3 h before activated carbon (~1 g) was added. After stirring with activated carbon for 20 h, the mixture was gravity filtered using 125 mm Ø Whatman filter paper and rinsed with hexanes. After removal of solvents, the product was isolated as a clear, colorless oil. Yield: 217 mg (73 %). Ratio of products (terminal : internal) was 5:4.

Terminal Isomer: **11t** (56%): ^{1}H NMR (600 MHz, acetone-d_6): δ = 7.76 (d, *J* = 7.9 Hz, 4H), 7.32 (d, *J* = 7.9 Hz, 4H), 5.18 (s, 4H), 3.81 (s, 12H), 2.75 (m, 4H), 0.98 (m, 4H), 0.2 to 0.0 (m, 108H).

Internal Isomer: 11**i** (44%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 7.9 Hz, 4H), 5.17 (s, 4H), 3.81 (s, 12H), 2.33 (q, *J* = 7.4 Hz, 2H), 1.43 (d, *J* = 7.5 Hz, 6H), 0.2 to 0.0 (m, 108H).

Mixture: ^{13}C NMR (150.92 MHz, acetone-d_6): δ = 170.73, 150.70, 136.17, 135.85, 135.26, 128.50, 128.04, 127.93, 127.54, 78.73, 73.42, 53.15, 52.63, 32.74, 30.41, 20.85, 14.66, 1.72, 1.56, 1.47, 1.23, 0.47, -1.09, -1.53.

$HMe_2SiO(Me_2SiO)_{67}SiMe_2H$-Derivative: Approximate molecular weight determined by end group analysis using ^{1}H NMR ≈ 5100 g/mol. Following the general procedure, TPVPBA (68 mg, 0.23 mmol) and DMS-H21 (598 μL, 0.11 mmol) were combined with 10 μL of Karstedt's catalyst solution (~$9x10^{-4}$ mmol Pt) in dry toluene. The reaction was stirred for 3 h before activated carbon was added. After stirring with activated carbon (~1 g) for 20 h, the mixture was gravity filtered using 125 mm Ø Whatman filter paper and rinsed with hexanes. After removal of solvents, the product was isolated as a clear, colorless oil. Yield: 475 mg (76 %). Ratio of products (terminal : internal) was 5:4.

Terminal Isomer: **12t** (56%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 8.0 Hz, 4H), 5.07 (s, 4H), 3.83 (s, 12H), 2.66 (m, 4H), 1.36 (d, *J* = 7.4 Hz, 4H), 0.89 (m, 4H), 0.2 to -0.1 (m, 414H).

Internal Isomer: **12i** (46%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 5.06 (s, 4H), 3.83 (s, 4H), 2.22 (m, 2H), 1.36 (d, *J* = 7.4 Hz, 6H), 0.2 to -0.1 (m, 414H).

Mixture: ^{13}C NMR (150.92 MHz, $CDCl_3$): δ = 170.22, 170.17, 150.47, 150.13, 135.68, 135.34, 127.74, 127.24, 78.09, 72.16, 53.21, 32.33, 29.94, 20.26, 14.33, 1.50, 1.42, 1.26, 1.09, 1.01, 0.38, -1.19, -1.28, -1.85.

6.1.3 Sugar Binding: NMR Experiment

6.1.3.1 Boronic acid deprotection

Samples were prepared in standard-sized NMR tubes (Table 6.1). Phosphate-buffered saline (50 mM) was prepared in Milli-q water and the pH was adjusted using a 1.0M solution of sodium hydroxide. Samples were inverted several times to facilitate mixing prior to obtaining NMR spectra. Spectra were obtained after 5 min, 3.5 h, and 18 h from time of mixing. Sample 1 was used as a reference spectrum for the tartrate-bound silicone boronic ester, and was measured only once.

Table 6.1: Conditions used to optimize tartrate hydrolysis of **7**

Sample #	DMSO-d_6 (mL)	PMDS-deriv. (µL)	PBS buffer (µL)	H_2O (µL)	pH
1	0.6	20	-	-	-
2	0.6	20	-	20	-
3	0.6	30	20	-	4.5
4	0.6	30	20	-	7.4
5	0.6	30	20	-	8.0
6	0.6	30	20	-	9.0

6.1.3.2 Binding to fructose and glucose

Two NMR-scale samples were prepared with the same composition. To a standard-sized NMR tube was added DMSO-d_6 (0.6 mL), and Milli-q water (20 µL), phosphate-buffered saline (20 µL, 50 mM, pH 7.4). The mixture was inverted multiple times to facilitate mixing. To one sample was added pentamethyldisiloxane silicone-boronic ester derivative **7** (20 µL, approx. 0.035 mmol) and glucose in DMSO-d_6 (32 µL, 1.67 M, 0.053 mmol). To the other was added **7** (30 µL, 0.052 mmol) and fructose in DMSO-d_6 (52 µL 1.55 M, 0.080 mmol). Both samples were inverted several times prior to obtaining NMR spectra.

Table 6.2: Chemical shifts of aromatic peaks arising from sugar complexation to silicone-boronic acid **7** (^{1}H-NMR) (terminal isomer)

Contents	H^a (ppm)	H^b (ppm)	$H^{a'}$ (ppm)	$H^{b'}$ (ppm)
No Sugar	7.68	7.15	-	-
D-Glucose	7.67	7.15	-	-
D-Fructose	7.67	7.14	7.57	7.20

6.1.3.3 Binding to fructose in the presence of Tris

Tris buffer (100 mM, pH 7.4) was prepared by dissolving 303 mg (2.5 mmol) tris(hydroxymethyl)aminomethane in 10 mL D_2O. The pH of the solution was adjusted to 7.4 using 2.0 M HCl (in D_2O), then diluted to 25 mL with D_2O. A sample was prepared containing pentamethyldisiloxane silicone-boronic ester derivative **7** (20 mg, 0.046 mmol) and fructose (8 mg, 0.046 mmol) dissolved in DMSO-d_6 (1 mL). Aliquots of 100, 200, 300, and 460 μL were added to the same sample, and ^{1}H-NMR spectra were measured after each aliquot. Peak data and relative integration values within the aromatic region are summarized in Table 6.3.

Table 6.3: Binding of silicone-boronic acid **7** to fructose in the presence of Tris

		Relative Integration of all Aromatic Signals			
Tris added (μL)	Tris Molarity (mM)	H^a (int + term) ~7.59 ppm	H^b (int + term) ~7.06 ppm	$H^{a'}$ (int + term) ~7.52 ppm	$H^{b'}$ (int + term) ~6.82 ppm
0	0	2.00	2.07	-	-
100	8	2.00	2.05	-	-
200	14	2.00	1.90	1.63	1.88
300	20	2.00	1.80	4.13	5.14
460	28	2.00	2.12	8.42	9.50

6.1.3.4 Improved solubility of boronic acid-modified silicones in the presence of both fructose and Tris

Samples were prepared in standard-sized NMR tubes. Samples were prepared such that the molar ratio of **11** : sugar : Tris was 1:2:2. For example, a sample contained 20 mg **11**, 12 mg glucose, and 8 mg Tris. Each sample also contained one molar equivalent of tertiary-butanol as an internal standard, and samples were suspended/dissolved in 0.8 mL D_2O. ^1H NMR spectra were obtained and the relative integration of the entire aromatic region was compared to the signal arising from *t*-BuOH (calibrated to 9H) (Table 6.4).

Table 6.4: Solubility of **11** in water (*t*-BuOH internal reference)

Sugar	Tris	Relative integration*
None	No	0.34
None	Yes	0.12
Glucose	No	0.15
Glucose	Yes	0.28
Fructose	No	0.34
Fructose	Yes	0.43

* against *t*-BuOH (tBu peak integrates for 9H).

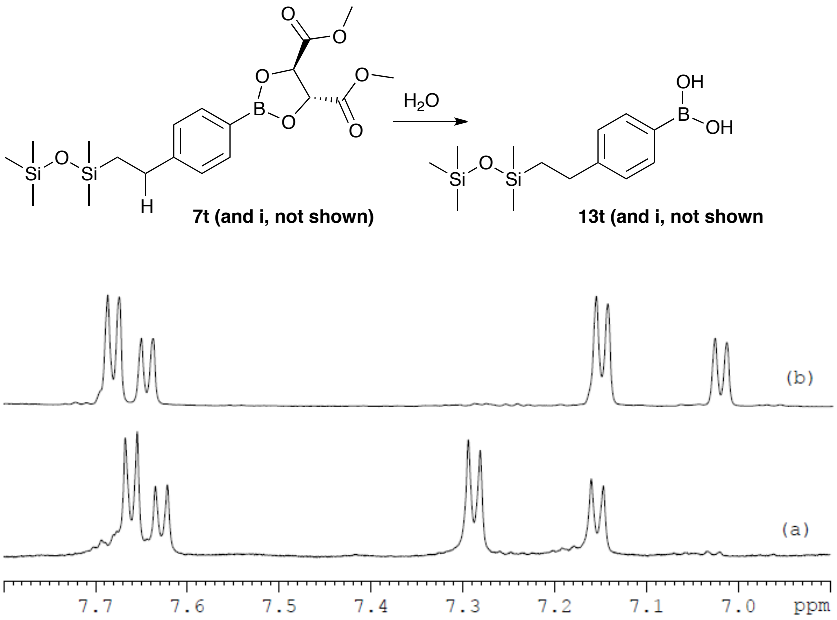


Figure 6.1: ^{1}H NMR spectra showing hydrolysis of tartrate from silicone-boronic acids **7t**,**i** to **13t**,**i** in the presence of PBS buffer pH 7.4

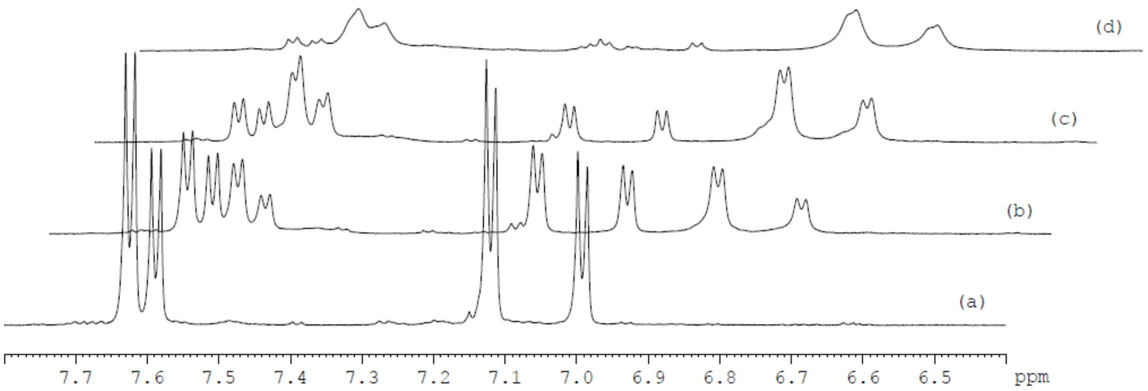


Figure 6.2: Addition of tris(hydroxymethyl)aminomethane solution (50 mM in D_2O) improved complexation of **7** to fructose. Amount of Tris added (a) 100 μL; (b) 200 μL; (c) 300 μL; (d) 460 μL

6.1.4 Rheology

Bolaamphiphilic silicone-boronic acids were hydrolyzed by pipetting the neat compound (as an oil) onto distilled water (approx. 75mL) in a 15cm-diameter glass Petri dish. The resulting rubbery film was lifted from the water and placed into a vial. The procedure was repeated until 175-200mg of each sample was collected.

Samples were analyzed using an Ares Rheometer (TA Instruments) using the program TA Orchestra for data acquisition. Samples were punched into discs (diameter 9.5 mm) and placed in between two parallel plates and compressed to the diameter of the plates (14 mm), giving good contact between the bottom plate, sample, and top plate. The total distance between plates varied between 1-2 mm depending on sample size. The first measurements performed were the dynamic strain-sweep test between 0.1-100% strain at a constant frequency of 1 Hz. The dynamic strain-sweep test was performed to determine the linear viscoelastic region of the sample. The strain for the linear region (unique for each formulation) was used in subsequent dynamic frequency-sweep tests. A dynamic frequency-sweep test was performed to determine how the modulus of the elastomer changed with respect to frequency, while being independent of strain. All frequency-sweep measurements were performed at a frequency range between 1-100 rad/s. All tests were performed at 23-24 °C (Figure 6.3).

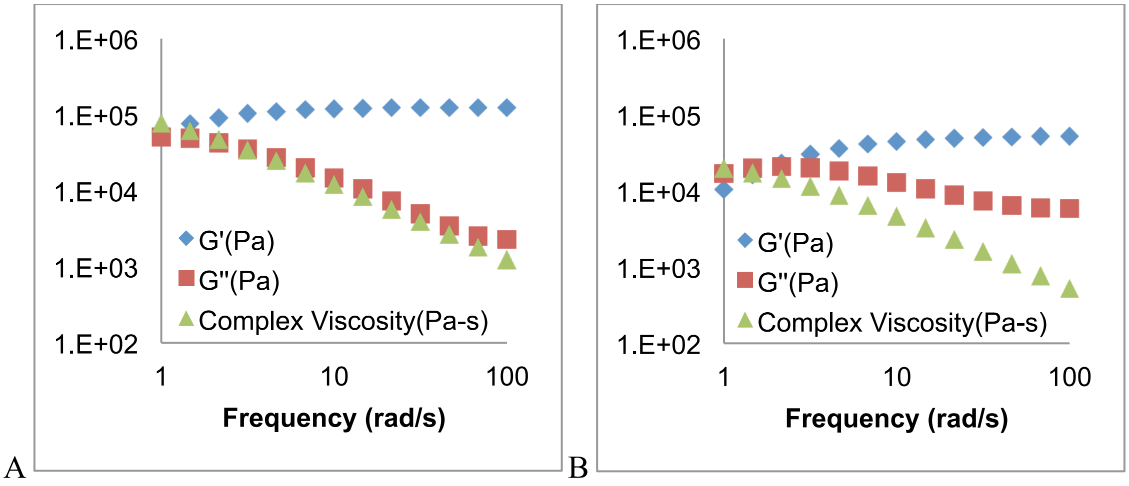


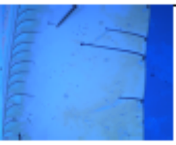
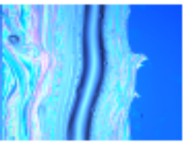
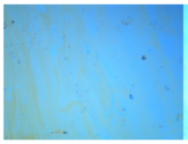
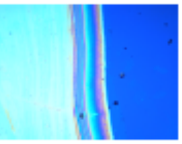
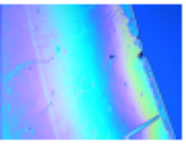
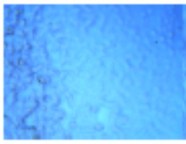
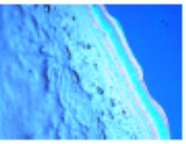
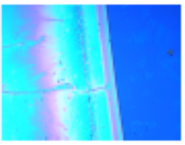
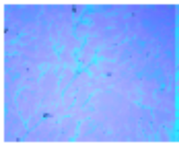
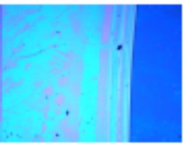
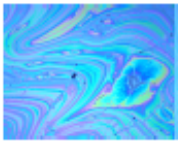
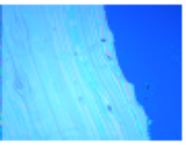
Figure 6.3. Complex viscosities of (A) **17** (i.e., **11** after hydrolysis of tartrate ester) and (B) **18** (i.e., **12** after hydrolysis of tartrate ester)

6.2 Supporting Information for CHAPTER 4: Spread and Set Silicone-Boronic Acid Elastomers

6.2.1 Video

An electronic video file can be accessed free of charge via the Internet at http://pubs.acs.org.

Table 6.5. Optical microscope images of **SiBA** transferred from various sub-phases onto silicon wafer

Sub-phase[a]	Image of center[b]	Image of edge[b]	Sub-phase	Image of center[b]	Image of edge[b]
Water			pH 9.07		
pH 2.84			pH 9.96		
pH 3.91			pH 11.09		
pH 4.93			10% NaCl		
pH 5.99			10% glycerol		
pH 7.00			10% tris (hydroxymethyl) aminomethane		
pH 7.84					

[a] Full details of sub-phase composition can be found in the Experimental section (Section 3.6); [b] 10x magnification

6.3 Supporting Information for CHAPTER 3: Silicone Boronates Reversibly Crosslink Using Lewis Acid−Lewis Base Amine Complexes

6.3.1 Materials

4-Vinylphenylboronic acid (98%) was obtained from Abblis Dimethyl-L-tartrate (99%), ethylenediamine (99%), methanol (99.8%) and platinum(0)-1,3-divinyl-1,1,3,3-tetramethyldisiloxane complex (Karstedt's catalyst, solution in xylenes 2% Pt) were obtained from Sigma-Aldrich. Reagent grade toluene, dichloromethane, and diethylether were obtained from Caledon Laboratory Chemicals. Triethylamine (99.5%) was obtained from EMD Chemicals. Deuterated chloroform (99.8%) was obtained from Cambridge Isotope Laboratories. Amino functional silicones AMS-233 (6-7% aminopropylmethylsiloxane – dimethylsiloxane copolymer) and AMS-162 (2-4% aminoethylaminopropylmethylsiloxane – dimethylsiloxane copolymer) and hydride-terminated polydimethylsiloxanes DMS-H11, DMS-H21, DMS-H25 ($HMe_2Si(OSiMe_2)_nOSiMe_2H$ where n = 15, 71, and 99, respectively) were obtained from Gelest. All chemicals were used as received unless otherwise specified in the experimental section.

6.3.2 Characterization

6.3.2.1 NMR

NMR spectra were recorded on a Bruker Avance 600 MHz nuclear magnetic resonance spectrometer using chloroform-*d*. The proton impurity of the deuterated solvent was used as a reference for 1H NMR spectra (chloroform = 7.24ppm). Boron trifluoride diethyl etherate was used as an external spectral reference for ^{11}B NMR spectra.

6.3.2.2 Rheology

Samples were analyzed using an Advanced Rheometrics Expansion System (ARES) Rheometer (TA Instruments) using the program TA Orchestra for data acquisition. Samples were punched into discs (diameter 9.5 mm) and placed in between two parallel plates and compressed to the diameter of the plates (7 or 14 mm), giving good contact between the bottom plate, sample, and top plate. The total distance between plates varied between 1.5-2 mm depending on sample thickness. The first measurements performed were the dynamic strain-sweep test between 0.1-100% strain at a constant frequency of 1 Hz. The dynamic strain-sweep test was performed to determine the linear viscoelastic region of the sample. The strain for the linear region (unique for each formulation) was used in subsequent dynamic frequency-sweep tests. A dynamic frequency-sweep test was performed to determine how the modulus of the elastomer changed with respect to frequency, while being independent of strain. All frequency-sweep measurements were performed at a frequency range between 1-100 rad/s. All tests were performed at 20-24 °C.

Data regarding crossover frequency as it relates to relaxation time are given in Table 6.9.

Melt-rheology was examined using the same instrument, however the temperature-ramp tests were performed at constant strain and constant frequency in order to observe the temperature dependence of the storage and loss moduli. The results below demonstrate two runs performed on a single sample of elastomer **17-A-25**. After heating and re-cooling, the elastomer exhibits a very similar second change in modulus with heating, demonstrating the reversibility of crosslinking.

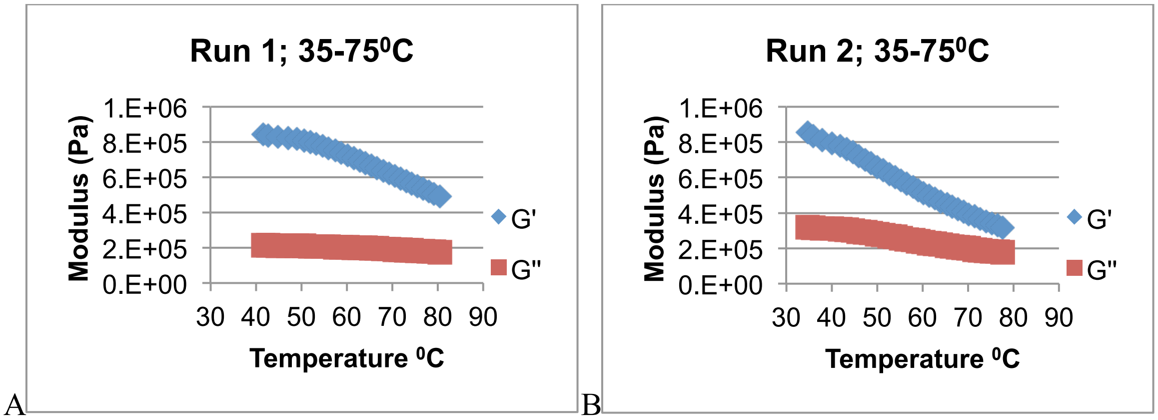


Figure 6.4. Temperature-ramp rheological measurements of **17-A-25**; (A) first run of sample (initially at room temperature) and (B) second run of sample after cooling to room temperature (performed on same day as Run 1)

6.3.2.3 Hardness

Shore A hardness measurements were made using a Durometer Hardness type ‘‘A2’’ from The Shore Instrument & Mfg. Co., NY. Shore OO experiments were taken using a Rex Durometer, Type OO, Model 1600 from Rex Gauge Co.

Data collected for elastomers are given in Table 1 below.

Table 6.6. Shore hardness values measured over time

Product Name	Shore OO 2-4 weeks	Shore OO 6 months
99-A-25	29.3 ± 1.7	49.0 ± 0.0
99-A-50	55.7 ± 3.9	54.7 ± 0.9
99-A-75	36.7 ± 1.2	71.7 ± 0.5
99-B-25	28.0 ± 0.8	48.7 ± 0.5
99-B-50	56.0 ± 0.8	71.0 ± 0.0
99-B-75	47.0 ± 0.8	75.0 ± 0.8
73-A-25	24.0 ± 1.4	14.7 ± 0.9
73-A-50	51.7 ± 1.2	71.3 ± 0.5
73-A-75	33.3 ± 1.2	49.7 ± 0.5
73-B-25	41.7 ± 0.9	69.0 ± 0.0
73-B-50	60.3 ± 0.5	80.7 ± 0.5
73-B-75	18.3 ± 0.5	70.7 ± 0.9
17-A-25	86.7 ± 0.5	89.0 ± 0.0
17-A-50	40.7 ± 3.3	80.3 ± 0.5
17-A-75	--	17.3 ± 2.1
17-B-25	73.7 ± 0.9	85.3 ± 0.9
17-B-50	56.3 ± 2.6	81.7 ± 0.5
17-B-75	--	52.3 ± 0.5

6.3.2.4 Gel Permeation Chromatography

Number average (M_n) and weight average (M_w) molecular weights and polydispersity indexes (PDI) were determined using Viscotek GPC system (GPCmax VE-2001) comprising of triple detectors of VE3580 RI detector, 270 dual detectors with viscometry and RALS/LALS (Right Angle Laser Light Scattering and Left Angle Laser Light Scattering), three columns of ViscoGEL I-guard-0478, ViscoGEL I-MBHMW-3078, and ViscoGEL I-MBLMW-3078 were equipped in series. Polystyrene narrow standard was used for multi detector GPC calibration. All measurement were carried out at 35°C and at a flow rate of 1.0 mL/min, using toluene as the eluent.

6.3.2.5 Thermal Studies

Thermogravimetric analysis was performed on a TA Instruments TGA Q50 equipped with a platinum sample plate and argon operating gas. Sample weights ranged from 2-5 mg, and were measured from 40-800 °C at a heating rate of 20 °C/min. Differential scanning calorimetry was performed on a TA Instruments DSC Q20 under an atmosphere of argon. Samples (9-13 mg) were placed inside hermetically sealed sample holders and analyzed under two sets of conditions. In one set, the sample was ramped at a rate of 5 °C/min from 0 °C to 300 °C then from 300 °C to -30 °C, and finally from -30 °C back up to 300 °C. In the other set, the heat/cool/heat cycle analogous to the first run was set between 0 °C and 120 °C.

6.3.2.6 Swelling

In order to examine elastomer-solvent interactions, elastomer samples were punched into 0.64 cm diameter discs, weighed and then placed into individual glass vials. To each vial was added 4 mL of solvent (see Table 6.7 for solvents used). Vials were capped and allowed to sit at room temperature for 5 h before observations regarding swelling were made.

Table 6.7. Solvent/sample interactions upon soaking SiBA elastomers for 5 hours. (/) not swollen, (+) swollen, (-) dissolved

Sample	H_2O	CH_3OH	NEt_3	CH_2Cl_2	$C_6H_5CH_3$	Et_2O
LD2-044A25	/	/	-	+	+	+
LD2-044A50	/	/	+	+	+	+
LD2-044A75	/	+/-	-	+	-	-
LD2-044B25	/	/	+	+	+	+
LD2-044B50	/	/	+	+	+	+
LD2-044B75	/	+/-	-	-	-	-

Percent swelling by volume (%S_v) was determined following a published procedure.[i] Samples (approx. 8 months old) were punched into 1/4" discs then placed into glass vials containing reagent grade toluene and allowed to reach equilibrium swelling at 22 °C for approximately 3 days. Solvent was removed from the vials then the swollen samples were weighed. Samples were then thoroughly dried in a vacuum oven at 60 °C for 24 h then reweighed. The following equation was used to calculate the percentage swelling by volume of each sample:

$$\%S_v = \frac{Swollen\ weight}{\rho_s} \times \frac{\rho_r}{Dry\ weight} \times 100$$

ρ_r = density of the rubber = 0.97g/mL for silicones

ρ_s = density of the solvent = 0.8669g/mL for toluene

All data obtained through swelling experiments are summarized in Table 6.9.

6.3.2.7 Elastic Recovery from Compression

Two pieces of **73-B-25** (each with approximate dimensions of 1.4 x 0.3 x 0.2 cm) were placed under a ~2 kg weight. One sample was stored in an oven at 60 °C while the other was left at room temperature, for 20 hours. The heated sample was cooled to room temperature (still under weight) before the weight was lifted from either sample. Upon removal of the weight, both samples appeared to be deformed (see Table 6.8). After 6.5 hours of rest at room temperature, the sample compressed at room temperature had nearly recovered its original shape while the sample compressed at 60 °C remained deformed.

Table 6.8. Elongation under compressive force

	Length before compression (cm)	**Length immediately after weight removal (cm)**	**Length 6.5 hours after weight removal (cm)**
Room Temp.	1.4	1.9	1.6
Heated to 60 °C	1.4	1.9	1.9

6.3.2.8 Disruption of Crosslinking with n-*Butylamine*

Into a glass vial were placed small pieces of **73-B-50** (633 mg total) and *n*-butylamine (5 mL). A tight-fitting cap was then placed on the vial. After approximately 22 hours, the sample appeared to be a highly viscous gel (individual portions of **73-B-50** were no longer discernible) and the cap was removed. The gel/solution was placed under a gentle flow of air to facilitate *n*-butylamine evaporation. After 17 hours, all *n*-butylamine was evaporated and an elastomeric film was observed on the sides and bottom of the vial. This film was gently removed from the vial and subjected to rheological analysis.

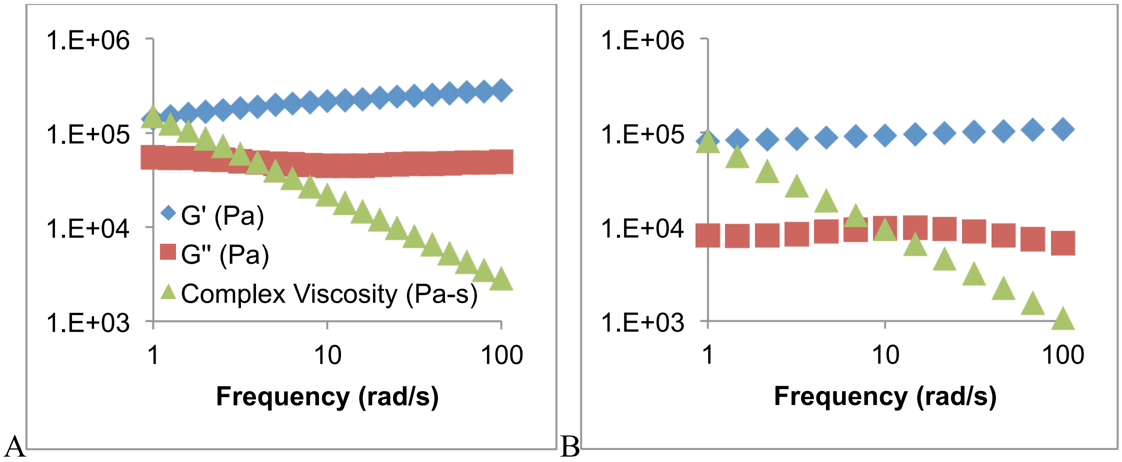


Figure 6.5. Rheological analysis of sample **73-B-50** (A) before de-crosslinking and (B) after sample was de-crosslinked with *n*-butylamine and re-crosslinking by evaporation of *n*-butylamine

6.3.3 Synthesis of Bolaamphiphilic Silicone-Boronic Acid Esters

NMR demonstrated that both internal and terminal isomers were formed during the initial hydrosilylation of vinylphenylboronic esters (Figure 6.6).

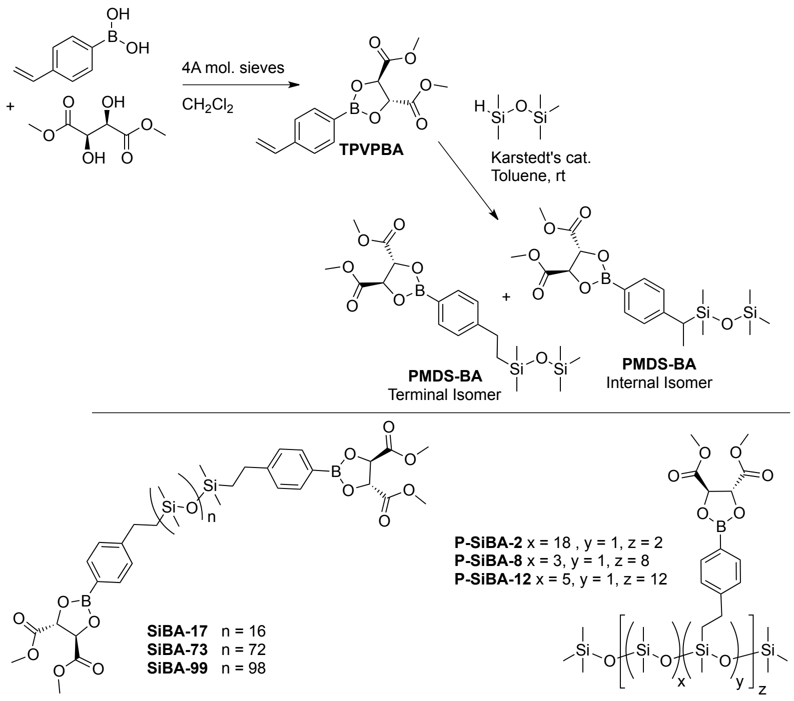


Figure 6.6: Formation and general structure of silicone boronic acids

6.3.3.1 Hydrosilylation of hydride-terminated polysiloxanes: General procedure using DMS-H25 HMe$_2$SiO(Me$_2$SiO)$_{97}$SiMe$_2$H (SiBA-99)

Approximate molecular weight determined by ^{1}H NMR end group analysis (ratio of terminal to internal SiMe$_2$ groups) ≈ 7327 g/mol. 4-vinylphenylboronic acid dimethyl-L-tartrate ester (TPVPBA)[ii] (1.66 g, 5.72 mmol) was added to a 100 mL round-bottomed flask containing a magnetic stir bar. After addition of 30 mL dry toluene to the reaction flask, a solution of DMS-H25 (19.06 g, 2.60 mmol) in 10 mL dry toluene was added using a Pasteur pipette. At that point, the reaction mixture was a clear, colorless solution. Karstedt's catalyst (25 μL, 2% solution in xylenes) was added to the reaction, causing the solution to immediately turn bright yellow. The reaction was stirred at room temperature for 20 h, during which time the yellow color faded considerably. The reaction was then stirred with activated carbon (~2 g) for 24 h prior to filtration through a fritted funnel containing ~10 g Celite, eluting with hexanes. The volatile solvents were removed via distillation on a rotary evaporator, giving the product as a clear, colorless oil. Yield: 19.8 g (96 %); ratio of products (terminal: internal) was 5:4. Note that it is not possible to quantify polymers with a,w-diterminal vs diinternal vs internal/terminal end groups, or pendant-functional polymers.

Terminal Isomer: (55%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.9 Hz, 4H), 7.22 (d, *J* = 7.9 Hz, 4H), 5.07 (s, 4H), 3.83 (s, 12H), 2.67 (m, 4H), 0.89 (m, 4H), 0.2 to -0.05 (m, ~600H).

Internal Isomer: (45%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 7.9 Hz, 4H), 7.11 (d, *J* = 7.9 Hz, 4H), 5.06 (s, 4H), 3.83 (s, 12H), 2.22 (m, 2H), 1.37 (d, *J* = 7.4 Hz, 6H), 0.2 to -0.05 (m, ~600H).

$HMe_2SiO(Me_2SiO)_{71}SiMe_2H$ DMS-H21 (SiBA-73): Approximate molecular weight determined by ^{1}H NMR end group analysis (ratio of terminal to internal $SiMe_2$ groups) ≈ 5399 g/mol. Following the general procedure, TPVPBA (1.17 g, 4.03 mmol) and DMS-H21 (8.18 g, 1.52 mmol) were combined with 10 µL of Karstedt's catalyst solution (~9 x 10^{-4} mmol Pt) in dry toluene. Yield: 9.05 g (97 %). Ratio of products (terminal : internal) was 10:9.

Terminal Isomer: (55%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.78 (d, *J* = 7.9 Hz, 4H), 7.23 (d, *J* = 8.0 Hz, 4H), 5.07 (s, 4H), 3.83 (s, 12H), 2.66 (m, 4H), 0.89 (m, 4H), 0.2 to -0.05 (m, ~400H).

Internal Isomer: (45%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.74 (d, *J* = 8.0 Hz, 4H), 7.11 (d, *J* = 8.0 Hz, 4H), 5.06 (s, 4H), 3.83 (s, 12H), 2.23 (m, 2H), 1.37 (d, *J* = 7.4 Hz, 6H), 0.2 to -0.05 (m, 400H).

$HMe_2SiO(Me_2SiO)_{15}SiMe_2H$ DMS-11 (SiBA-17): Approximate molecular weight determined by ^{1}H NMR end group analysis (ratio of terminal to internal $SiMe_2$ groups) ≈ 1246 g/mol. Following the general procedure, TPVPBA (4.70 g, 16.2 mmol) and DMS-H11 (9.62 g, 7.7 mmol) were combined with 25 µL of Karstedt's catalyst solution (~2.25 x 10^{-3} mmol Pt) in dry toluene. Yield: 12.0 g (85 %). Ratio of products (terminal : internal) was 10:9.

Terminal Isomer: (56%): ^{1}H NMR (600 MHz, acetone-*d_6*): δ = 7.76 (d, *J* = 7.9 Hz, 4H), 7.32 (d, *J* = 7.9 Hz, 4H), 5.18 (s, 4H), 3.81 (s, 12H), 2.75 (m, 4H), 0.98 (m, 4H), 0.2 to 0.0 (m, ~110H).

Internal Isomer: (44%): ^{1}H NMR (600 MHz, $CDCl_3$): δ = 7.73 (d, *J* = 8.0 Hz, 4H), 7.22 (d, *J* = 7.9 Hz, 4H), 5.17 (s, 4H), 3.81 (s, 12H), 2.33 (q, *J* = 7.4 Hz, 2H), 1.43 (d, *J* = 7.5 Hz, 6H), 0.2 to 0.0 (m, 110H).

$Me_3SiO[(Me_2SiO)_{17}(Me(H)SiO)_1]_2SiMe_3$ HMS-071 (P-SiBA-2): Approximate equivalent weight determined by ^{1}H NMR analysis (ratio of Si-H to internal $SiMe_2$ groups integration) ≈ 1318 g/mol. Mn = 2744 g/mol, Mw = 3808 g/mol and PDI = 1.388 by GPC

(5mg/mL in toluene). Following the general procedure, TPVPBA (2.30 g, 7.93 mmol) and HMS-071 (9.08 g, 3.31 mmol) were combined with 10 µL of Karstedt's catalyst solution (~9 x 10^{-4} mmol Pt) in dry toluene. Yield: ~10 g (88 %). Reaction progress was monitored by ^{1}H NMR (observation of starting material peak disappearance) however subsequent product spectral analysis was too complex to determine ratio of isomers.

$Me_3SiO[(Me_2SiO)_3(Me(H)SiO)_1]_8SiMe_3$ HMS-301 (P-SiBA-8): HMS-301 was distilled under vacuum (0.5 mmHg) at 180 °C for 2h to remove low molecular weight oligomers. Approximate equivalent weight determined by ^{1}H NMR analysis (ratio of Si-H to internal $SiMe_2$ groups integration) ≈ 283 g/mol. Mn = 2342 g/mol, Mw = 4859 g/mol and PDI = 2.075 by GPC (5mg/mL in toluene). Following the general procedure, TPVPBA (5.2 g, 17.9 mmol) and HMS-301 (5.0 g, 2.13 mmol) were combined with 15 µL of Karstedt's catalyst solution (~1.35 x 10^{-3} mmol Pt) in dry toluene. Yield: ~8 g (78 %). Reaction progress was monitored by ^{1}H NMR (observation of starting material peak disappearance) however subsequent product spectral analysis was too complex to determine ratio of isomers.

$Me_3SiO[(Me_2SiO)_5(Me(H)SiO)_1]_{12}SiMe_3$ HMS-151 (P-SiBA-12): Approximate equivalent weight determined by ^{1}H NMR analysis (ratio of Si-H to internal $SiMe_2$ groups integration) ≈ 430 g/mol. Mn = 5403 g/mol, Mw = 6349 g/mol and PDI = 1.175 by GPC (5mg/mL in toluene). Following the general procedure, **TPVPBA** (4.05 g, 13.96 mmol) and HMS-151 (6.0 g, 1.11 mmol) were combined with 15 µL of Karstedt's catalyst solution (~1.35 x 10^{-3} mmol Pt) in dry toluene. Yield: ~8 g (80 %). Reaction progress was monitored by ^{1}H NMR (observation of starting material peak disappearance)

however subsequent product spectral analysis was too complex to determine ratio of isomers.

Nomenclature: Abbreviated five-digit labels are used to represent each formulation, e.g., **17-A-25**. The first two digits **99**, **73**, and **17** represent the approximate siloxane length of the bolaamphiphilic silicone-boronic acid **SiBA**, or **2**, **8**, and **12** represent the approximate number of pendant boronate esters per siloxane chain used in the formulation, the central letter (**A**-**F**) represents the amino compound used in the formulation where **A** is 6-7% aminopropylmethylsiloxane – dimethylsiloxane copolymer (APS) and **B** is 2-4% aminoethylaminopropylmethylsiloxane – dimethylsiloxane copolymer (AEAPS), **C** is aminopropyl terminated polydimethylsiloxane (low molecular weight ~ 840 g/mol), **D** is aminopropyl terminated polydimethylsiloxane (high molecular weight ~ 7150 g/mol), **E** is polyethylenimine, ethylenediamine copolymer, **F** is TAEA and the last two digits represent the percent by weight of silicone-boronic acid present in the formulation, or the molar equivalents of boron in TAEA samples.

6.3.4 Synthesis of Physically Crosslinked PDMS Elastomers

6.3.4.1 General procedure using SiBA-73:APS 1:1 composition (73-A-50)

Liquid APS (2 g) and liquid SiBA-73 (2 g) were placed in a plastic Petri dish (internal diameter = 3.5cm) lined with Teflon and immediately mixed by stirring with a plastic rod. A loose-fitting lid was placed over the Petri dish and the sample was left on a flat surface exposed to ambient conditions for at least 1 week before any testing was performed. The resulting material was a transparent and colorless rubber.

6.3.4.2 General procedure using SiBA-73:TAEA 0.5 composition (73-E-0.5)

TAEA (21 mg) was dissolved in a small amount of dichloromethane (~0.5 mL) and added to SiBA-73 (2.0 g) inside a polypropylene Speed Mixer^{TM} container. The container was then capped and mixed in a Speed Mixer^{TM} DAC 150 FVZ-K for 30 seconds at a speed of 3000 rpm. The sample was placed on a flat surface without a lid for at least 1 week before any testing was performed. The resulting material was a transparent and colourless rubber.

Table 6.9: Formulations of amino/boronic ester elastomers

Product Name	Boronate	Amino Compound	Molar Ratio BA/NH2	Shore OO[a]	% Swelling	Relaxation Time (s)[b]
99-A-25	SiBA-99	APS	1 to 9.5	29.3 ± 1.7	dissolved	1.25
99-A-50	SiBA-99	APS	1 to 3.2	55.7 ± 3.9	1328	>6.28
99-A-75	SiBA-99	APS	1 to 1.1	36.7 ± 1.2	dissolved	1.58
99-B-25	SiBA-99	AEAPS	1 to 4.8	28.0 ± 0.8	2926	>6.28
99-B-50	SiBA-99	AEAPS	1 to 1.6	56.0 ± 0.8	1339	>6.28
99-B-75	SiBA-99	AEAPS	1 to 0.5	47.0 ± 0.8	dissolved	1.25
99-E-0.5	SiBA-99	TAEA	1 to 0.5	64.7 ± 2.1	dissolved	15.78
99-E-1.0	SiBA-99	TAEA	1 to 1	67.3 ± 1.7	dissolved	>62.83
99-E-1.5	SiBA-99	TAEA	3 to 2	69.3 ± 1.2	dissolved	>62.83
73-A-25	SiBA-73	APS	1 to 7.2	24.0 ± 1.4	dissolved	0.50
73-A-50	SiBA-73	APS	1 to 2.4	51.7 ± 1.2	1284	>6.28
73-A-75	SiBA-73	APS	1 to 0.02	33.3 ± 1.2	dissolved	0.16
73-B-25	SiBA-73	AEAPS	1 to 3.6	41.7 ± 0.9	2091	>6.28
73-B-50	SiBA-73	AEAPS	1 to 1.2	60.3 ± 0.5	1033	>6.28
73-B-75	SiBA-73	AEAPS	1 to 0.4	18.3 ± 0.5	dissolved	0.40
73-E-0.5	SiBA-73	TAEA	1 to 2	81.7 ± 2.9	dissolved	>6.28
73-E-1.0	SiBA-73	TAEA	1 to 1	68.3 ± 1.2	dissolved	4.99
73-E-1.5	SiBA-73	TAEA	3 to 2	76.7 ± 0.5	dissolved	too brittle
17-A-25	SiBA-17	APS	1 to 2.2	86.7 ± 0.5*	537	>6.28

17-A-50	SiBA-17	APS	1 to 0.7	40.7 ± 3.3	507	≈0
17-A-75	SiBA-17	APS	1 to 0.2	liquid	dissolved	liquid
17-B-25	SiBA-17	AEAPS	1 to 1.1	73.7 ± 0.9**	717	>6.28
17-B-50	SiBA-17	AEAPS	1 to 0.4	56.3 ± 2.6	dissolved	0.50
17-B-75	SiBA-17	AEAPS	1 to 0.1	liquid	dissolved	≈0
17-E-0.5	SiBA-17	TAEA	1 to 2	74.3 ± 1.7	dissolved	0.79
17-E-1.0	SiBA-17	TAEA	1 to 1	85.7 ± 1.2	485	too brittle
17-E-1.5	SiBA-17	TAEA	3 to 2	80.3 ± 1.2	526	too brittle
2-C-25	P-SiBA-2	DMS-A11	1 to 11.8	liquid	dissolved	liquid
2-C-50	P-SiBA-2	DMS-A11	1 to 4.0	49.7 ± 2.5	dissolved	0.84
2-C-75	P-SiBA-2	DMS-A11	1 to 1.3	72.7 ± 1.2	dissolved	0.63
2-D-25	P-SiBA-2	DMS-A21	1. to 1.4	too soft	dissolved	0.43
2-D-50	P-SiBA-2	DMS-A21	1 to 0.5	too soft	dissolved	≈0
2-D-75	P-SiBA-2	DMS-A21	1 to 0.15	liquid	dissolved	liquid
8-C-25	P-SiBA-8	DMS-A11	1 to 4.2	liquid	dissolved	liquid
8-C-50	P-SiBA-8	DMS-A11	1 to 1.4	NH[d]	NH	NH
8-C-75	P-SiBA-8	DMS-A11	1 to 0.5	72.3 ± 1.7***	361	too brittle
8-D-25	P-SiBA-8	DMS-A21	1 to 0.5	63.7 ± 0.4	dissolved	≈0
8-D-50	P-SiBA-8	DMS-A21	1 to 0.2	67.7 ± 0.5	dissolved	9.22
8-D-75	P-SiBA-8	DMS-A21	1 to 0.05	too soft	dissolved	13.62
12-C-25	P-SiBA12	DMS-A11	1 to 5.3	NH	NH	NH
12-C-50	P-SiBA12	DMS-A11	1 to 1.8	NH	NH	NH
12-C-75	P-SiBA12	DMS-A11	1 to 0.6	76.3 ± 1.2	336	29.16
12-D-25	P-SiBA12	DMS-A21	1 to 0.6	71.7 ± 0.5	dissolved	0.63
12-D-50	P-SiBA12	DMS-A21	1 to 0.2	61.3 ± 0.5	dissolved	1.35
12-D-75	P-SiBA12	DMS-A21	1 to 0.07	68.0 ± 0.8	dissolved	0.92

[a] Nomenclature is explained above; [b] Values for Shore hardness reflect averages of 3 readings on 1 sample for each formulation. Measurements were taken after samples were aged for 2-7 weeks. *Shore A = 22.3 ± 0.5. ** Shore A = 26.3 ± 0.5. *** This is the Shore A value. [c] Values for relaxation time are calculated from the average G'/G" crossover frequencies found for 3 experiments on 3 samples for each formulation. A relaxation time value of >6.28 or >62.83 indicates that the crossover frequency fell below the observed frequency range for the experiment (1-100 or 0.1-100 rad/s, respectively, too hard for the instrument to measure) and a value of ≈0 indicates that there was no

observable crossover frequency (indicating viscous, non-elastomeric fluids); [d] NH = non-homogenous (solid/liquid).

6.3.5 NMR Experiments

6.3.5.1 Small molecule test reaction

A standard glass NMR tube was charged with **PMDS-BA** (50 mg) and deuterated chloroform (approx. 0.6 mL). A ^{11}B NMR spectrum was recorded and calibrated according to a boron-trifluoride diethyletherate (BF_3-OEt_2) external standard. Ethylenediamine (7 mg) was then added to the sample. The sample was mixed thoroughly by inverting the capped NMR tube. A second ^{11}B spectrum was recorded and calibrated as before. In order to reduce interference from background signals, a linear back prediction was performed on all ^{11}B NMR data.

6.3.5.2 Polymer reaction

A standard glass NMR tube was charged with **SiBA-17** (100 mg) and deuterated chloroform (approx. 0.6 mL). A ^{11}B NMR spectrum was recorded and calibrated according to a BF_3-OEt_2 external standard. **APS** (100 mg) was then added to the sample. The sample was mixed thoroughly by inverting the capped NMR tube. A second ^{11}B spectrum was recorded and calibrated as before. In order to reduce interference from background signals, a linear back prediction was performed on all ^{11}B NMR data.

6.3.5.3 TAEA binding to TPVPBA

A standard glass NMR tube was charged with **TPVPBA** (24 mg) in deuterated chloroform (approx. 0.6 mL). A ^{1}H NMR spectrum was recorded as a reference spectrum to the unbound material. Subsequent samples were prepared containing the quantities of **TPVPBA** and **TAEA** listed in Table 6.10 below. Upon mixing, ^{1}H NMR spectra were recorded within 1 hour. The diagnostic aromatic proton signals were monitored for changes due to binding of nitrogen to boron. The observed chemical shifts are listed in Table 6.10 with δ_1 referring to the signal produced by two equivalent protons *meta* to boron, while δ_2 refers to the signal produced by two equivalent protons *ortho* to boron.

Table 6.10: Sample compositions for **TAEA** binding to **TPVPBA**

TPVPBA (mg)	TAEA (mg)	Ratio B : NH_2	δ_1 (ppm)	δ_2 (ppm)
10	--	--	7.42	7.83
10	0.5	1 : 0.3	7.40	7.75
10	1.3	1 : 0.75	7.35	7.61
10	1.7	1 : 1	7.33	7.56
10	2.52	1 : 1.5	7.31	7.53
10	3.36	1 : 2	7.31	7.53
10	3.8	1 : 2.25	7.30	7.53
10	5.0	1 : 3	7.30	7.52
10	10.1	1 : 6	7.30	7.53

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[i] a) M. Barlkanl; C. Hepburn, *Iranian J. Polym. Sci.* **1992**, *1*, 1. b) B. B. S. T. Boonstra; E. M. Danenberg, *Rubber Chem. Technol.* **1959**, *32*, 839.

[ii] M. A. Brook, L. Dodge, Y. Chen, F. Gonzaga, H. Amarne, *Chem. Commun.* **2013**, *49*, 1392.