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Spread and Set Silicone-Boronic Acid Elastomers

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The ability of boronic acids to form complexes with a variety of ligands, including other boronic acids, has been utilized to crosslink polymers and to chromatographically separate saccharides, among other applications. It was anticipated that the formation of such complexes could be used to pin boronic acids to aqueous interfaces. Silicone-boronic acid polymers, protected as esters, were synthesized using hydrosilylation. Exposure to moisture led to deprotection of tartrate- and, at a slower rate, catechol-protected silicone boronates to give the free silicone boronic acids. Surprisingly, this deprotection was accompanied by the transformation of the silicone polymer from a liquid to a soft, elastic film (Young's modulus 70-250 kPa). Protected silicone boronates were found to be extremely efficient at rapidly spreading across water: partial hydrolysis anchored the robust, thin (<2 μm) film to the interface, which led to the formation of strong, thin silicone elastomer films. Film stability was decreased in the presence of competitive ligands in the aqueous subphase, including glycerol, phosphate, Tris, or higher pH, all of which disrupted the boronic acid: boronic acid complexation. Newly introduced water droplets on top of the film were encapsulated by the highly mobile tartrate-protected silicone boronic acid, permitting the formation of stable, stacked water droplets. The strength and behavior of self-assembled stimuli-responsive silicone materials could be tailored through a combination of boronic acid density on the silicone and the use of various analytes and conditions known to impact the coordination and ionization state of boronic acids.

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, 2] analytical devices,[3 4] microfluidic devices,[5] and switchable surfaces[6, 7] among many 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,[8] as well as their ability to selectively and reversibly bind to 1,2- and 1,3-diols.[9] In order to affect the desired response in biological environments, boronic acids may be appended to or included in polymers that are partially[10] or fully water-soluble:[11] hydrophobic polymers containing boronic acids may also find utility at certain interfaces.

Poly(dimethylsiloxane) (PDMS) is a mixed organic/inorganic hydrophobic polymer with a variety of useful properties including a high degree of oxygen permeability,[12] thermal and electrical resistance, as well as being considered biocompatible.[13] Silicones are exceptionally surface active.[14] 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 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, 15] **SiBA**s with varied three-dimensional structures and molecular weights have demonstrated selective saccharide sensing abilities in solution,[15] as well as providing a mechanism for the production of novel thermoplastic silicone elastomers.[16]

PDMS oil, similar to other hydrophobic liquids, will spread on water with a rate proportional to its viscosity.[17] Surprisingly, during initial studies with protected silicone boronates on water, it was discovered that very rapid spreading of **SiBA**s was accompanied by the formation of responsive, elastomeric films that self-assembled at the aqueous interface. The unusual formation of elastomeric films from **SiBA**s at the air/water interfaces, as well as the response of those films to chemical changes in the sub-phase, including pH and the presence of competitive boronic acid-binding molecules, is reported below.

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† Electronic Supplementary Information (ESI) available: Rate of protecting group hydrolysis by ^{1}H NMR; ^{1}H NMR of **TSiBA** (solution) and **TSiBA** (solution and solid state); photo sequence showing i) placement of **TSiBA** on water (4 s); demonstration of supported water droplets on the formed viscoelastic films; the elastomeric film with constrained water droplets is readily removed. Video showing generation of thin, supportive silicone elastomer films on water. See DOI: 10.1039/x0xx00000x

Results

Two types of silicone-boronic acids were prepared for this study: a monofunctional silicone-boronic acid of molecular weight 296 g/mol **PMDS-BA** and α,ω-telechelic polymers with molecular weights (M_n) of up to ~7600 g/mol. The compounds were prepared by hydrosilylation of the appropriate Si-H functional silicones with (protected) 4-vinylphenyl boronic esters: both terminal and internal isomers resulted, which were not separated (only the terminal product is shown, Figure 1).

Hydrolysis and Crosslinking of the Silicone Boronic Acids

Protected **SiBA**s were found to be liquids with approximately the same low viscosities as their α,ω-hydridosilicone precursors. The most labile esters of those tested, derived from dimethyl-L-tartrate **TSiBA**, hydrolyzed essentially on contact with water, such that viscoelastic films formed at the water interface at a rate essentially concomitant with interfacial area. While water vapor rapidly diffuses through silicones, bulk water is essentially insoluble in silicone oil. Therefore, complete hydrolysis in water took from minutes to hours, depending on the thickness of the bulk silicone sample. Under the same conditions, catecholate-protected boronic acids **CSiBA** hydrolyzed slowly, over about 1 day: pinacol boronate esters **PSiBA** did not undergo measurable hydrolysis over several days.

NMR spectroscopy was used to confirm the rates of boronate ester hydrolysis under optimal conditions (ESI†). ^1H NMR of D_2O beneath of a film of the silicone boronate ester was used to follow release of the protecting group. The experiment thus measured the faster rate of boronate ester hydrolysis on contact with water and the slower rate associated with diffusion of water into and liberated protecting group out of the silicone. The data demonstrated efficient hydrolysis of dimethyl-L-tartrate, much slower hydrolysis of catechol, and negligible hydrolysis for pinacol under the experimental conditions tested.

Viscoelastic materials formed once the protecting groups were removed by hydrolysis. The Young's modulus of the materials depended, as expected, on the chain length of the telechelic silicone boronic acids, which determined the spacing between crosslinks (Table 1). **TSiBA-99** formed a more viscous fluid than its protected precursor, while the other two materials were soft elastomers: **TSiBA-17** was much harder than **TSiBA-73** once the tartrate protecting groups were removed. Under force of gravity, deprotected **SiBA** slowly flowed to conform to the shape of the container in which they were held, while the substance would fracture and break apart under sudden stress (e.g., hitting it with a hammer): after removing the layer from water, the silicone boronic acid could be rolled into a ball, bounced, and stretched (Figure 4B,C).

It was initially proposed that crosslinking either originated from phase separation of boronic acids to give clusters/star crosslink sites or the formation of dimers.[8, 18] This question was examined by titrating a monofunctional boronic acid **PMDS-BA** into **SiBA-73**. If crosslinking was a consequence of simple aggregation of boronic acids, little effect of the presence of the monofunctional boronic acid would be 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**) to give **1** (Figure 2),[19] confirming that the primary interaction responsible for viscoelasticity of **SiBA**s arises from boronic acid dimers. Note that the presence of competing ligands for boron in the aqueous subphase can compromise the ability of boronic acids to dimerize.[2]

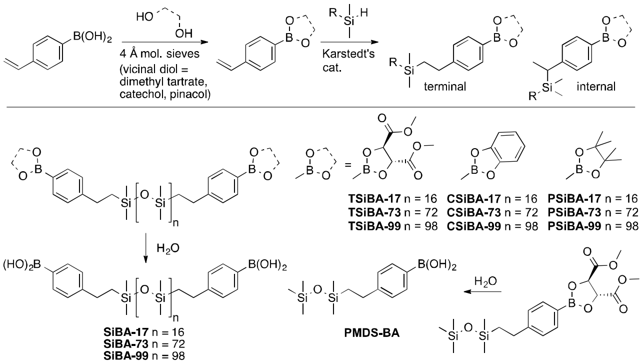

Figure 1. Synthesis and hydrolysis of protected silicone-boronic acids

Table 1. Compressive Strength Measurements of TSiBA films

Sample	Silicone Molecular Weight (g/mol)	Young's Modulus (MPa)	Shear Modulus (MPa)
TSiBA-17	1135	0.1702 ± 0.0177	0.0654 ± 0.0068
TSiBA-73	4512	0.1536 ± 0.0270	0.0590 ± 0.0104
TSiBA-99	7485	N/A[a]	N/A[a]

[a] Exposure **of TSiBA-99** to water did not result in film formation; mechanical strength measurements are therefore not possible.

An alternative explanation for the crosslinking involves the formation of boroxines, which was a helpful suggestion by a referee. Boroxines are B-O trimers resulting from the dehydration of boronic acids.[8] Normally, the equilibrium lies far to the side of boronic acids in the presence of water but, of course, many of the boronic acid groups will reside within a silicone environment, which could have a very low water content. Boroxines derived from phenyl boronic acids exhibit a notable shift of the ortho to boron aryl protons in the ^1H NMR spectrum, from about 7.7 to 8.1 ppm.[20] As noted in the experimental section, all the ortho proton signals exhibited at about 7.7 ppm, with no signal near 8.1 consistent with free boronic acids (ESI†).

The concept of 1:1 boronic acid complexation was further supported by the use of solvents known to interrupt hydrogen bonding.[21] When **SiBA-17** was exposed to DMF, a solvent well known to interrupt H-bonding, the elastomeric nature was lost and a viscous oil resulted. These data are consistent with boronic acid dimerization via hydrogen bonding being the key intermolecular interaction in the elastomers.

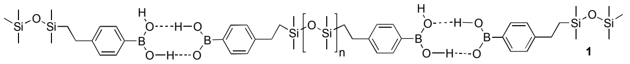

Figure 2. Hydrogen bonded boronic dimer **1** formed from the reaction of **PMDS-BA** with bolaamphiphilic **SiBA-73**.

The formation of boronic acid dimers, of course, would only lead to chain extension of telechelic polymers, not elastomers. Crosslinks require higher order interactions, which must be available in addition to the chain extension caused by dimerization of α,ω-telechelic silicone boronates. The physical properties of **SiBA** are very similar to those of Silly Putty, a copolymer of dimethylsiloxane fluids and boric oxide.[22] Dynamic crosslinking in Silly Putty arises from Lewis acid/Lewis base interactions between oxygen atoms and the vacant site on boron. We ascribe the elastomeric properties of **SiBA** to the analogous combination of Lewis acid/base interactions plus boronic acid dimerization.

Spreading of Protected and Unprotected SiBAs

A very unusual feature of the protected **SiBA**s was their ability to spread extremely efficiently, particularly across water/air interfaces (a 10 µL drop dispersed over 60 cm^2 during ~ 1 s (Figure 3, see video in Electronic Supplemental Information). By contrast, pure, deprotected **SiBA-73** (obtained by liquid extraction of a THF/water solution of **TSiBA-73** with hexanes) did not efficiently spread on water, but produced a low surface area silicone domain that covered only a few percent of the available surface area. When a quantity (similar to spreading experiments with **TSiBA** described above) of **SiBA-73** in hexanes was dropped onto an identical water interface, discrete, non-uniform 'islands' were observed that covered, at most, 10% of the available surface (Figure 4A): the deprotected boronic acid was not an efficient spreader. We elected to characterize in more detail the thin films formed after spreading the protected **SiBA**s on water. One simple method to test the mechanical strength of the film involved placing droplets of water onto the film, and determining if the film was strong enough to prevent passage of the droplet into the aqueous subphase.

A film of created from protected **SiBA**s floating on water, just like low or high molecular weight non-functional silicones or functional polymers such as α,ω-aminopropylsilicones, could not support water droplets on the surface (Figure 3, Figure 4). This was always true for **PSiBA**s with which hydrolysis was extremely slow, and **CSiBA** in the first few hours after spreading on water, until hydrolysis and crosslinking to produce a viscoelastic film had occurred. **TSiBA**s, by contrast, immediately formed a robust film on water contact (Figure 4B,C). Further investigation of the characteristics of the viscoelastic films was undertaken using the rapidly film forming **TSiBA**s.

The extremely efficient spreading of **TSiBA**s could be observed using water droplets placed on a **TSiBA** film. When water droplets were sequentially placed on a **TSiBA**-derived film, they did not coalesce, as each droplet became spontaneously enveloped by a silicone film faster than a second drop could be added (water on submicron-thick films of **TSiBA** on water, Figure 3B, Figure 4). Furthermore, each water droplet became pinned to the viscoelastic film on which it rested. When the surfaces were tilted, there was no movement of the droplets due to gravity. The cohesive strength of the film is apparent from Figure 4B,C in which a **TSiBA** layer dotted with several blue and red colored water droplets is being lifted from the surface of water upon which it was originally produced: the colored water droplets neither dripped or rolled off the silicone/water film, but eventually burst without mixing during manipulation and folding of the film (Figure 4C).

It was possible to push this process further. A film of **TSiBA** was placed on water in a Petri dish, and then two drops of differently colored water were placed one after the other on top of the film to give water-on-water-on-water sandwiches with silicone boronic acid films between. Thus, the **SiBA** surrounding the first drop migrated to surround the second drop without allowing the drops to merge. The images in Figure 5 demonstrate both the efficiency of **TSiBA** spreading across the air water interface and the strength and resilience of the subsequently formed elastomeric film.

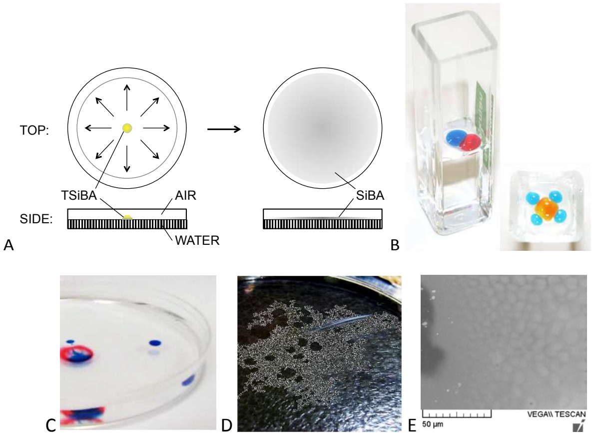

Figure 3. A) Schematic showing spreading of **TSiBA** on distilled water in a Petri dish. B) colored water droplets, added one-by-one, supported on the same film in a 1 x 1 cm cuvette: note, the drops do not merge. C) After resting on the surface for ~ 3 minutes, the red water droplet generated a defect and penetrated the silicone film: this rarely occurred. 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). E: SEM image showing cracks between silicone domains (scale bar 50 µm).

Effects of the Subphase on Film Stability

The stability of **SiBA** elastomer layers could 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, to give an film thickness of approximately 1.7 µm. The impact of various solutes or changes in pH of the aqueous sub-phase and on the **SiBA** layer stability is summarized in Table 2.

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 location where the **SiBA** was initially deposited. The rate of loss of elasticity was affected by the original crosslink density and rate of change of crosslink density for materials: it was thus affected by the **SiBA** molecular weight. At low pH, **TSiBA-17** was not as effective at producing stable layers as **TSiBA-73**. The complete hydrolysis of boronic ester to boronic acids and (over)crosslinking of the short silicone chains in the former case gave brittle, cracked layers through which the water could penetrate. By contrast, **TSiBA-17** performed better than **TSiBA-73** at mid-pH values because the only 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 in both cases (Table 2).

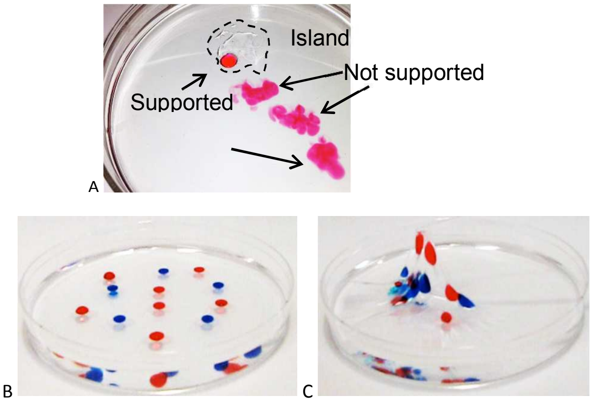

Figure 4. (A) Island of (unprotected) **SiBA-73** produced on water sub-phase using solvent evaporation; red-colored water drops were only supported where islands were located. Photos demonstrating the stability of **SiBA** on water. (B) Colored water drops supported on top of the entire surface area of a ~1.7 µm thick film of **SiBA-73** (from **TSiBA-73**) on water. (C) Silicone layer and accompanying droplets being lifted from the sub-phase: note, the drops do not coalesce (see also a video, ESI†).

Other moieties that bind to boronic acids[8] inhibited boronic acid/boronic acid crosslinking when present in the sub-phase. Compounds including 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 2). Tris(hydroxymethyl)aminomethane and tris(aminoethyl)amine, in addition to increasing the solution pH, also behave as Lewis basic molecules that competitively bind to boronic acids.[16] These too will inhibit crosslinking. Phosphate anions are known to form complexes with boronic acids and boronate esters[23] and account for the losses in **SiBA** layer stability when produced on a pH 7.00 buffer compared to pure water. Note that the concentration of competitive binder in solution was much higher than that of the boronic acids, such that crosslinking via boronic acid dimerization will be ineffective.

Increasing the quantity of **SiBA** initially dispensed onto an aqueous solution to give thicker layers increased the film stability of the layers: their ability to support water droplets of larger size and for longer time periods increased (Table 2). However, the stability of the layers changed over time irrespective of thickness. For example, after a few minutes, defects in thin **TSiBA**-derived films beneath supported droplets could develop, leading the droplet to breach the silicone layer. Once a defect formed, it did not heal at ambient temperature: subsequent droplets placed at the same location appeared to penetrate the silicone and bleed into the aqueous sublayer below without resistance (Figure 3C). After aging overnight, films derived from **TSiBA** could no longer support water droplets anywhere on the surface irrespective of film thickness; they passed straight through because defects/cracks had developed in the film (Figure 3C-E). The process was mirrored with **CSiBA**-derived films but over much longer time periods because of the slower hydrolysis process leading to elastomeric films.

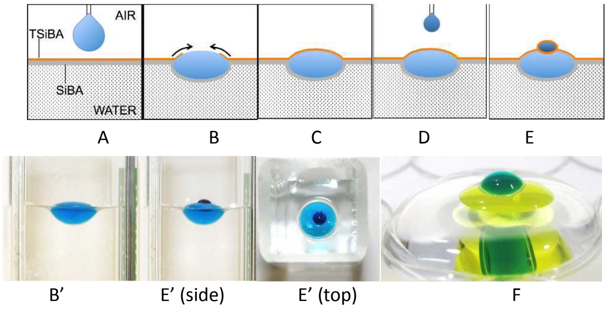

Figure 5. Stacking water droplets on **SiBA**; (A) **TSiBA** hydrolyzes partially on contact with water to form a viscoelastic film. (B, B') A water droplet (light blue) is supported by the **TSiBA**: unhydrolyzed **TSiBA** spreads around the water droplet. (C) New **SiBA** film formed on light blue 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.

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, 50,000 cSt) led to only marginal changes in the ability of water droplets to penetrate the silicone film (Table 2) supporting this proposal: the crosslink density remained high with this shortest oligomer.

Discussion

Spreading across water is typical behavior for hydrophobic, non-functional silicones, but also end-functional silicones that bear hydrophilic groups including amines/ammonium ions or carboxylic acids/carboxylates.[24] Deprotected **SiBA** bola-amphiphiles performed similarly to other end-functional silicones in that they produce high molecular areas at low surface pressures.[2] Silicone-based materials that do not undergo covalent crosslinking do not create viscoelastic films on water/air interfaces, at least not of the strength to also support water drops (> ~ 50 kPa, Table 1. 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 elastomeric 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,[15] and it is known that free boronate anions are preferred over their boronate ester counterparts at high pH.[25] 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 to a ball, and would shatter when subjected to a sharp, compressive force. Thus, it seems reasonable given their chemical similarities 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,[22] a network structure arises from condensation B-OH and Si-OH groups to give B-O-Si linkages as well as transient Lewis acid/Lewis base interactions between the open valence on boron and the oxygen atoms in the backbone of PDMS.[26] Boric acid provides the necessary linkages to observe the dual properties of viscosity at low shear rates and elasticity at high shear rates. In our case, free boronic acids, like partly condensed boric acid, appear to be able to crosslink through coordination B-O 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).

Table 2. Water penetration times through viscoelastic films formed from **SiBA** for various sub-phases, pH values and from various quantities of spread **TSiBA-73** and **TSiBA-17** with diluents

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[c]
1M HCl	40 ± 23	122 ± 35	27 ± 16
1M NaOH	-	-	-
10% glycerol	-	-	-
10% TRIS[d]	-	-	-
10% tris(2-aminoethyl)-amine	-	-	-

SiBA	Amount dispensed [μL][a]	Thickness [μm][b]	Penetration time[c] [s]	Diluent (volume)
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	12 ± 3	none
	10	1.70	13 ± 4	D_4 (2.5 μL)[e]
	10	1.70	26 ± 12	PDMS 50,000 cSt (2.5 μL)[f]

[a] Full details of sub-phase composition can be found in the Experimental section, phosphate buffers were used; [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] Removal of outlier (1 of 6 results) gives 29 ± 17 sec. [d] Tris(hydroxymethyl)aminomethane. [e] **TSiBA-73** was dispensed using an Eppendorf pipette; [f] Approximate thickness based on volume of **SiBA** dispensed and an internal Petri dish diameter of 8.7 cm; [g] Time measured from placement of 100 μL water droplet until complete transfer through the **SiBA** layer was observed; average over 4-6 trials; [h] Water took more than 480 s to penetrate for all trials; [i] D_4 = octamethylcyclotetrasiloxane; [f] DMS-S45 hydroxyl-terminated PDMS, 110,000 g/mol.

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 **1** (Figure 6).[2] Although the experiments performed in this study can not determine 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.[16] 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.[27] 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[28] it is more likely that the combination of boronic acid dimers plus Lewis acid/Lewis base interaction possibilities give rise to the observed cohesiveness of **SiBA** layers on water.

Aging of the silicone films led to loss of cohesivity through shrinking and cracking, but other factors could also be used to disfavor film formation. The ability to chemically affect crosslink stability by adding competitive binders in the aqueous subphase 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.[8] It is not surprising, therefore, that there was a strong correlation between the pH of the sub-phase and elastomeric film strength (Table 2). At acidic pHs, 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**, however, tetracoordinate, anionic boron species will form and then be forced into the aqueous phase,[25] 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 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 seen in boronic acid block copolymers.[10] 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.[10] 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.[29] 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 thus represent a related class of pH responsive materials that are capable of boronic acid binding internally as well as toward external analytes such as diols.

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 vertically engulf small drops of water placed on the viscoelastic film that formed at the air/**SiBA**/water interface (Figure 5A and B): the process can be repeated to give water-on-water-on-water structures (Figure 5E,E' and F). Thus, the **SiBA**s are exceptional spreaders across water as long as the boronic acid protecting group remains intact. By contrast, without a protecting group, even in hexanes solution (normally an excellent solvent for spreading on water), the free silicone-boronic acid was not able to spread across a water interface: while a typical film layer produced from a given quantity of **TSiBA-73** extended to the edge of the vessels submicron thick films, only a small crosslinked silicone island was produced from the same quantity of **SiBA-73** spread from a solution of hexanes (Figure 4A).

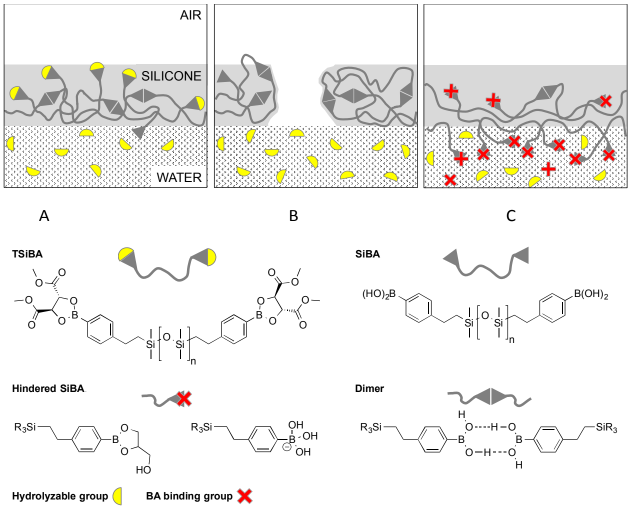

Figure 6. Spreading followed by hydrolysis and crosslinking of silicone-boronic acids on water: (A) Cartoon representing boronic acid interactions in silicone phase after partial hydrolytic deprotection of boronic acids, (B) defect formation caused by over-crosslinking of fully hydrolyzed SiBA layer, and, (C) disruption of crosslinking due to the presence of Lewis bases or competitive boronic acid binding molecules

Mechanistic Model for Film Formation

We can rationalize the behavior of silicone boronic acids by considering the efficiency of spreading, the rates of hydrolysis of protecting groups, and the ability of the resulting boronic acids to form 1:1 crosslinks, without which viscoelastic films could not form. After addition of a protected **SiBA** to a bulk water, the polymer effectively spreads 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 of ~ 1.7 μm thickness (Figure 3, Figure 4, Figure 5A). Prior to hydrolysis, the silicone films were not resilient: water droplets passed straight through them, similar to the case of non-functional and α,ω–functional silicone oils. However, as hydrolysis of the boronate ester occurred, a viscoelastic film was established through a combination of boronic acid/boronic acid dimer complexes and weaker interactions between boronic acids and silicone chains (Figure 5A, Figure 6A). Non-hydrolyzed materials were still mobile spreading agents, as shown by the ability engulf new water droplets (Figure 5B, C). Over time and with full hydrolysis of the protecting groups, further crosslinking led to shrinking of the film and cracking (Figure 3D,E, Figure 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 a mobile oil (Figure 6C).

Spread and set polymers are most effectively produced from boronic acids that possess a diol-based protecting group with a low association constant,[30, 31] like dimethyl-L-tartrate, rather than a strongly binding protecting group like catechol[30] or pinacol.[32] The precursors rapidly spread across water interfaces. Following hydrolysis, the physical properties of the resulting films can be quite robust, and tunable, depending on boronic acid density and film 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.

Conclusions

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 nearly competitive with, spreading (within seconds of contact with water) to rapidly form elastomeric films. The robustness of these films 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: this should be reversible. 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 completely surround a newly introduced water droplets permitting the preparation of water-on-water-on-water assemblies. These spread and set elastomers provide new opportunities for the physical structuring of silicones and water-containing fluids.

Experimental

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 = 110,000, 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.

Characterization

Crosslinking suppression

TSiBA-73 was hydrolyzed by dissolution in THF (2.0 g/ ~15.0 mL) then mixing with water (~15.0 mL). The mixture was then extracted three times with hexanes (3 x 15.0 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 (381.0 mg **SiBA-73** with 21.0 mg **PMDS-BA**) then the solvent was allowed to evaporate under nitrogen.

The addition of 3 parts of DMF to 1 part of deprotected **SiBA-73** led to conversion of the putty into a viscous oil, as a consequence of loss of boronic acid/boronic acid hydrogen bonding (ESI†).

Film Surface Characterization

Samples of **TSiBA-99**, **TSiBA-73**, and **TSiBA-17**, respectively, were added dropwise by Pasteur pipette to separate SEM stubs covered with a layer of carbon tape. The stubs were exposed to various atmospheric conditions (from 36-73% relative humidity at 20.6 - 23.0 °C) and the film were monitored under these conditions at 24 h using a Tescan Vega

II LSU scanning electron microscope (Tescan USA, PA) operating at 10 kV, using low vacuum mode.

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 500.0 mL): pH 3.0, potassium hydrogen phthalate (5.105 g, 25.00 mmol), HCl (0.1 M, 111.5 mL), actual pH 2.84; pH 4.0, potassium hydrogen phthalate (5.105 g, 25.00 mmol), HCl (0.1 M, 0.5 mL), actual pH 3.91; pH 5.0, potassium hydrogen phthalate (5.105 g, 25.00 mmol), NaOH (0.1 M, 113.0 mL), actual pH 4.93; pH 6.0, potassium dihydrogen orthophosphate (3.405 g, 25.02 mmol), NaOH (0.1 M, 28.0 mL 2.8 mmol), actual pH 5.99; pH 7.0, potassium dihydrogen orthophosphate (3.405 g, 25.02 mmol), NaOH (0.1 M, 145.5 mL), actual pH 7.00; pH 8.0, potassium dihydrogen orthophosphate (3.405 g, 25.02 mmol), NaOH (0.1 M, 233.5 mL), actual pH 7.84; pH 9.0, disodium hydrogen orthophosphate (6.78 g, 47.76 mmol), HCl (0.1 M, 22.5 mL), (actual pH 9.07); pH 10.0, disodium hydrogen orthophosphate (6.85 g, 48.25 mmol), NaOH (0.1 M, 16.8 mL), actual pH 9.96; pH 11.0, sodium bicarbonate (1.05 g, 12.50 mmol), 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 (25.0 g) in 18.1 MΩ-cm water (225.0 mL). A stock solution of hydrochloric acid (1.0 M) was produced by dilution of 2.7 M hydrochloric acid (58.0 mL) to a final volume of 156.0 mL using 18.1 MΩ-cm water. A stock solution of sodium hydroxide (1.0 M) was prepared by dissolving sodium hydroxide (10.0 g, 250.0 mmol) in 18.1 MΩ-cm water (250.0 mL). A stock solution of glycerol (10wt%) was prepared by dissolving glycerol (20.0 g) in 18.1 MΩ-cm water (180.0 mL). A stock solution of tris(hydroxymethyl)-aminomethane (10wt%) was prepared by dissolving tris(hydroxymethyl)-aminomethane (25.0 g) in 18.1 MΩ-cm water (225.0 mL). A stock solution of tris(2-aminoethyl)amine (10wt%) was prepared by dissolving tris(2-aminoethyl)amine (2.5 g, 17.1 mmol) 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 10.0 µL of **TSiBA-17**, **73** or **99**, respectively, was placed on the surface of the solution using an Eppendorf pipette. After 60 s, 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.

Mechanical Strength Characterization

To individual 350µL wells of a 96-well plate, 250µL samples of **TSiBA-99**, **TSiBA-73**, and **TSiBA-17** were added. The 96-well plate was exposed to 100% relative humidity at 25 °C in an environment controlled humidity chamber using an ESPEC ESL-2CA cold temperature and humidity chamber to allow the samples to cure. The plate was removed after 144 h exposure in the chamber. **TSiBA-99** remained a viscous oil; as a result no mechanical strength data could be gathered. Young's modulus and Shear modulus were measured in triplicate every 24 hours on a MACH-1 micromechanical system instrument using a 0.500 mm hemispherical indenter radius, and Poisson ratio of 0.3.

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Spread and Set Silicone-Boronic Acid Elastomers

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Graphical abstract

Silicone boronates efficiently spread on water and then form resilient elastomers as shown by the colored water-on-silicone-on-water films that form.