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The First Attachment and Post-Functionalization of Polybutadiene and Thio-Click Functionalized Polybutadiene on H-Terminated Si(111)

by

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A thesis submitted to the faculty of

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GRADUATE COMMITTEE APPROVAL

of a thesis submitted by

Todd D. Wickard

This thesis has been read by each member of the following graduate committee and by majority vote has been found to be satisfactory.

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BRIGHAM YOUNG UNIVERSITY

As chair of the candidate’s graduate committee, I have read the thesis of Todd D. Wickard in its final form and have found that (1) its format, citations, and bibliographical style are consistent and acceptable and fulfill university and department style requirements; (2) its illustrative materials including figures, tables, and charts are in place; and (3) the final manuscript is satisfactory to the graduate committee and is ready for submission to the university library.

Date	Matthew R. Linford Chair, Graduate Committee

Accepted for the Department

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ABSTRACT

The First Attachment and Post-Functionalization of Polybutadiene and Thio-Click Functionalized Polybutadiene on H-Terminated Si(111)

Todd D. Wickard

Department of Chemistry

Master of Science

I report the attachment of polymers with pendant vinyl groups to hydrogen-terminated silicon(111) (Si(111)-H) under mild conditions. 1,2-addition polybutadiene (M_w 3200-3500) was attached to Si(111)-H at room temperature with visible light. I also report the partial functionalization, in solution, of 1,2-addition polybutadiene with various thiols using thiol-click chemistry. These compounds bind to Si(111)-H via visible light activation. The partially functionalized polybutadienes allow further functionalization at the surface through unreacted carbon-carbon double bonds. Surfaces were characterized with contact angle goniometry, spectroscopic ellipsometry, X-ray photoelectron spectroscopy (XPS), time-of-flight secondary ion mass spectrometry (ToF-SIMS), and atomic force microscopy (AFM).

ACKNOWLEDGEMENTS

The author wishes to acknowledge his spouse, children, and recruiter; without whom this would have been less than the adventure it was. Thanks Sheri, Travis, Margaret, Matt, Helmut, Christina, Niels, Guarav, Lei, Li, and Feng. Thanks Murph.

Table of Contents

Chapter 1

Literature Review

From low friction nanocoatings on internal combustion engines, protective coatings on silica glass, to catalysis, surface modification has many applications and uses in research and industry.[1-3] Modifying a surface with specific coatings for a certain application is a complex undertaking. One goal of surface modification is to create tailored surfaces. In the case of silicon, many different methods have been employed to produce surface coatings; however, present research often attaches a monolayer to the silicon surface or grows a polymer on the silicon surface from an initiation site. These layers are typically covalently attached to a hydrogen-terminated silicon surface and sometimes have hetero atoms in their end-groups that allow further surface modification. These covalently attached monolayers usually consist of an alkyl chain smaller than 20 carbon atoms or a polymer grown from the silicon surface. Past research did not look at placing intact polymer molecules on the silicon surface. A possible reason for this oversight is the assumption that an entire polymer chain would not evenly coat or securely attach to the silicon surface. Since full polymer chain attachment to silicon has not been done and both the silicon surface and polymer chemistry have tremendous industrial importance, the potential and characteristics of direct binding of polymers to silicon need to be investigated. In this thesis, first, I review the preparation and characterization of hydrogen-terminated silicon (H-terminated silicon), organic monolayer and polymer growth on the silicon surface, photochemical attachment of alkene and alkyne moieties to the silicon surface, and thiol click chemistry, to provide a background for the significance of my work of 1,2-addition polybutadiene (M_w 3200-3500) attachment to H-terminated silicon(111).

H-Terminated Silicon

There are various known pathways for passivating the silicon surface with covalently attached organic compounds. These include cycloaddition,[4-15] condensation,[16,17] silanization of hydroxyl-terminated surfaces,[18-22] reversible addition-fragmentation chain transfer polymerization (RAFT),[22-24] atom-transfer radical polymerization (ATRP),[25-32] silanization of hydrogen-terminated surfaces,[33-38] arylation,[39-42] reaction with Grignard and lithium reagents,[43-47] chemomechanical scribing,[35,48-56] ring opening metathesis polymerization (ROMP),[57-60] and hydrosilylation.[61-63] A major contribution to silicon surface chemistry has been the availability of a variety of useful characterization methods. I will cover several of these techniques to better show the context of the present work.

The fledgling electronics industry's experimentation with silicon surface modification explored the conditions of surface modification and its effect on the silicon substrate.[64] The most commonly known method involved hydrogen passivation of the silicon surface, which is the Radio Corporation of America (RCA) cleaning method developed by Kern and Puotinen in 1965.[65] The RCA method was initially a cleaning step before the silicon substrate underwent thermal oxidation for metal-oxide-semiconductor technologies. It is a wet chemical approach and was not well characterized vis-à-vis surface roughening, chemical residues, and/or surface species. Another early report by Seager et al.[66] on silicon surface modification discussed the reduction of grain boundary potential barriers and the state density at twinned silicon junctions for substrates used in solar cells. These surface conditions lowered efficiency in early solar cells. The resulting research moved the industry toward hydrogen plasma passivation, which modified the silicon surface via a hydrogen plasma (10^{-1} Torr) created in a Tesla coil, generating temperatures of about 400° C. The ionized hydrogen attached to the silicon surface after reacting with the oxide layer. This experiment succeeded in making polycrystalline silicon more amenable to solar cell usage by increasing the efficiency of early solar cells, but it lacked characterization as to where and how the hydrogen bound in the silicon substrate. A year later, a group at Bell Labs reported the creation of electrically active surface defects when the substrate is laser melted.[67] Their method also employed passivation with monatomic hydrogen plasma at a relatively low temperature of 200° C, which was found to eliminate the electrical defects created by laser melting. The high-temperature method for passivating silicon was scrutinized in 1984 with the aid of electron-beam-induced current (EBIC) analysis and scanning electron microscopy to characterize the effect of hydrogen passivation at grain boundaries, which showed evidence for slow recombination velocities after photonic activation.[68] Bringans[69] heated the silicon substrate to 800 °C next to a hot filament in a diatomic hydrogen atmosphere in the presence of arsenic to induce a bonding competition between hydrogen and arsenic. These passivation methods resulted in a surface very susceptible to oxidation.

Oxygen is well known as an aggressive molecule in the atmosphere and can oxidize passivated silicon, rendering the devices produced in the early 1980s useless. Studies appeared starting in 1984 testing the stability of H-terminated silicon in the atmosphere. Yablonovitch, etal.,[70] conducted a surface-recombination velocity (SRV) study of the RCA clean step involving hydrogen-termination of the oxidized silicon wafer. They found evidence by means of contactless *in situ* electronic measurements of the charge carrier decay that the hydrogen-terminated silicon surface had the lowest SRV of any passivation technique reported up to that time. H-terminated silicon wafers produced with this method showed low SRV as evidenced by minutes-long manipulation in air without degradation.[5]

Burrows et al.[71] studied H-terminated silicon with infrared (IR) spectroscopy to identify the surface hydrides and thereby infer the morphology of the silicon surface after passivation. His group utilized hydrogen fluoride (HF) in D_2O (deuterium oxide, or heavy water) to create DF; which enabled deuterium to attach to the surface, providing differences in the IR signal from deuterium versus normal hydrogen. Their study concluded that the HF etched silicon surfaces were microscopically rough; however, it was inconclusive whether the roughness was due to the oxide layer. Later, Bringans[72] made a comparative study of hydrogen termination methods on silicon. These included H-termination studies of ultra high vacuum, wet chemical, ion sputtering, and spin etching conditions. Spin etching showed the best results for removing carbon residue from the silicon surface.

In 1990, Chabal et al.[73,74] published the ideal hydrogen termination of Si(111) utilizing a basic (*p*H = 9-10), buffered solution (7:1 NH_4F:HF with NH_4OH to adjust the *p*H) in a ten step process. IR measurements showed the hydrogen to be perpendicular to the surface, which inferred a monohydride silicon surface. His group next compared the surface effects of using HF versus NH_4F on Si(111).[75] They showed the utility of using NH_4F solutions to produce atomically flat surfaces. They also demonstrated that HF produces atomically rough surfaces. Additionally, they showed the surface roughening to be a completely reversible process. This research was extended by Dumas and Chabal[76] in 1991 with electron energy loss spectroscopy (EELS) characterization of both Si(111) and Si(100) surfaces etched in 40% NH_4F solutions to find the energy loss peak associated with this particular Si-H surface binding. They argued that a new loss peak found at approximately 330 cm^{-1} belonged to the silicon phonon. In 1990, Thornton and Williams[77] examined the silicon (111) and (100) surfaces prepared by chemical etching in various HF concentrations and analyzed them by means of X-ray photoelectron spectroscopy (XPS). Their XPS measurements showed the surface to contain very little carbon and oxygen after etching and was one of the first to utilize XPS analysis of the hydrogen–terminated silicon surface.

Jacob and Chabal[78] further investigated the dependence of surface structure on the *p*H of the etching solution. They used polarized infrared absorption spectroscopy to examine the silicon-hydrogen stretching vibrations as an aid of inferring the structure of the Si(111) stepped surfaces and the Si(111) flat surfaces. They achieved Si-H linewidths as narrow as 0.05 cm^{-1} by this method, indicating a very uniform arrangement of hydrogen on silicon by buffered HF solutions. The next study by Chabal et al.[79] involved examination of the steric hindrances and surface relaxation of stepped H-terminated silicon surfaces. Their research showed the flat Si-H surface to be nearly stress free, reporting 0.21 eV per unit cell with Raman analysis. Once the production of an ideal Si(111):H surface was made, modifications to the steps in the process were reported. Yang et al.[80] demonstrated that long etch times contributed to residue buildup on the silicon surface. Their method relied on a final etch step with a buffered HF solution and showed smoothing of the silicon surface even after etching with unbuffered HF.

Chabal et al.[81] followed up his hydrogen-terminated silicon studies by examining the oxidation of the hydrogen-terminated silicon surface. The results from this study showed the oxidation of the surface to occur by incorporating oxygen into the silicon bonds without necessarily breaking the hydrogen bonds, as observed by infrared absorption spectroscopy. Their proposed model stated that oxidation began with the attachment of oxygen at the steps of the silicon surface. Cerofolini et al.[82] also examined the oxidation of H-terminated Si(100) during exposure to air at room temperature with XPS. Their research demonstrated that oxidation first occurs at a surface feature then logarithmically grows over the rest of the surface. This research supported an improved method proposed by Kato et al.[83] which was an ultraclean and atomically controlled etching of the Si(111)-1 x 1 surface. Their method involved a cleaning step of sonication in trichloroethylene, followed by acetone, an oxidation step with hot (120 °C) 3:1 H_2SO_4:30% H_2O_2 (piranha) solution, followed by rinsing in Millipore™ water, an etch in NH_4F for 8 minutes, concluded with a rinse in Millipore™ water. The surface was characterized by high resolution electron energy loss spectroscopy (HREELS) and atomic force microscopy (AFM). They took AFM images at different etching times from 1-10 minutes to show a progression of the surface toward near ideal smoothness by 8-10 minutes, with 8 minutes showing the best combination of smoothness and HREELS hydrogen signal.

Alkyl Layers on Silicon

A number of surface scientists have explored organometallic chemistry on the crystalline silicon wafer surface. The first reports of organic molecule monolayer formation on silicon by Linford and Chidsey[61] showed a densely packed alkyl monolayer on hydrogen-terminated Si(111) and Si(100) surfaces utilizing diacyl peroxides heated to the melting point, backfilled with argon, then heated to 90-100 °C to pyrolyze the peroxide, thereby creating an alkyl monolayer. In 1995, Linford and Chidsey[62] cooperated with Eisenberger and Fenter to analyze alkyl monolayers of 1-alkenes on H-terminated silicon(111) produced by pyrolysis of 1-alkenes and alkynes with diacyl peroxides. They expanded their analytical tools to include contact angle goniometery, ellipsometry, infrared spectroscopy, XPS, and X-ray reflectivity. Their analysis showed the monolayers to be uniform, stable, and protective of the silicon substrate against oxidation. Their work further showed the monolayer to be tilted away from the surface normal. In 1997, Sung et al.[84] conducted a study of the thermal behavior of the monolayers produced by Linford, et al.[61,62] Their investigation found the monolayers to be stable up to 615 K before chemical decomposition fully took place at 785 K, as evidenced by HREELS.

In 1998, Effenberger et al.[85] demonstrated the photoactivated preparation and patterning of 1-alkenes and aldehydes on H-terminated silicon(111). Their work proceeded via melting the 1-alkene or aldehyde directly onto the surface and irradiation with a mercury vapor lamp to produce monolayers that could be prepared with masking methods. Theirs was among the early reports to create monolayers without a solvent and radical initiator. Later that same year, Sieval et al.[86] showed that a monolayer can form on H-terminated silicon through thermal activation. Their research utilized ω-functionalized 1-alkenes, using the ω-functionality on the 1-alkene to provide additional handles on the surface for further chemical modification/surface tailoring. Sieval et al.,[87] turned their attention to molecular modeling of the alkyl monolayer surface on Si(111) in 2000. This group also demonstrated the binding of various 1-alkynes to Si(100) through thermal reactions at the end of that same year.[88] The next year, this same group reported the formation of amino-terminated monolayers on H-terminated silicon and showed that the surfaces could be modified after monolayer formation.[89] At the end of the same year, they also published a molecular modeling study of octadecyl monolayers on the silicon surface,[90] showing that the model correlated best to the current empirical evidence for 50% surface substitution. Buriak et al.[91] showed the ability to nanopattern alkynes on H-terminated silicon via scanning probe-induced cathodic electrografting. The reaction was done under ambient conditions and presented the idea of hardwiring nanocircuits.

The new millennium brought more creativity to surface attachment. In 2003, Choi et al.[92] conducted a surface reaction through a Diels-Alder like fashion with 1,3-cyclohexadiene and acrylonitrile. The next year, Teague and Boland[93] conducted scanning tunneling microscopy (STM) studies of bonding conformations of 1,3-cyclohexadiene. Their research revealed the [2+2] and [4+2] interdimers, where the [2+2] interdimer belonged to two different conformers. Also in 2004, Boland et al.[94] investigated how density functional theory (DFT) applied to the product distribution of the 1,3-cyclohexadiene reaction on silicon, which demonstrated that the then current DFT did not match the actual product distribution. They concluded that DFT possesses gaps, which explains the inability of the theory to match observed results. In 2005, Wang and Buriak[95] showed how to drive the formation of an organic monolayer on silicon electrochemically. The reaction was done on H-terminated silicon(111) and silicon(100) with alkyl salts containing ammonium, phosphonium or pyridinium moieties. The AFM tip was positively biased and the surface was negatively biased. XPS, FTIR, and AFM scribing all showed the alkyl reagents to be covalently bonded to the silicon surface.

XPS was used by Cerofini et al.[96] in 2005 to quantitatively analyze the 1-alkene/1-alkyne monolayer on hydrosilylated silicon(100) by thermal reaction at 170 °C for two hours. Both films showed that oxygen was initially present in the XPS scan, but the surfaces suffered negligible oxidation over the timescale of one year. This same year, Grignard reagents were used to attach halo alkynes and alkenes to the surface of H-terminated Si(111).[97] The resulting surfaces were analyzed with HREELS, IR, and Auger electron spectroscopy, which showed that the surfaces retained the unsaturation in the hydrocarbon precursor. Conclusions from this research indicated that this surface could be used for further functionalization, but no experimentation was performed.

Polymer Growth on Silicon

The majority of the previously mentioned investigations involved multistep approaches to bind rather small organic molecules on the silicon surface. In 2000, a report demonstrated ring-opening metathesis polymerization (ROMP) on a silicon surface.[98] The researchers started with a hydroxyl-terminated silicon surface, then reacted norbornene-containing silanes with the surface, and opened the ring of the norbornene at the unsaturated bond with a ruthenium catalyst. The ruthenium catalyst further led to polymerization of a monomer. The polymer thickness could be controlled by varying the monomer concentration in solution and the reaction time. Surface patterning was also demonstrated. This work was followed up by Juang et al.[99] who also performed ROMP on a silicon surface, but started from a chlorinated surface and utilized Grignard reagents to attach a terminal olefin. They also claimed thickness control of the polymer layer as a function of solution concentration.

Xu et al.[100] published a method they called electroless "synthetic metal" deposition by grafting 4-vinylaniline to H-terminated silicon(100) through the photochemically reactive terminal alkene moiety. This method used UV radiation to initiate the covalent attachment of the 4-vinylaniline to the H-terminated surface. This group also employed masking methods to show the controlled deposition of the 4-vinylaniline onto the silicon surface, then subjected this surface to electroless copper plating, which was shown to be selective for the aniline moiety. A few months later, this same group published a paper presenting surface-initiated atom-transfer radical polymerization (ATRP) of poly(ethylene glycol) monomethacrylate (PEGMA), utilizing a surface tethered α-bromoester.[101] The research presented another method for tailored surface functionalization through the hydroxyl end groups of the PEGMA chains. Possible functionalities included chloride, amine, aldehyde, and carboxylic acid groups.

Effenberger et al.[102] conducted a detailed experiment to determine the electrical breakdown voltage, insulative capacity, and doping effects of functionally terminated alkyl monolayers on silicon (100). Their results showed a dual layer due to two different refractive indices as measured by grazing incidence x-ray reflectivity. The monolayers were well represented by a two-layer model. The electrical property studies gave interesting results. The breakdown voltage of a typical functionalized monolayer was 16 MV/cm. In addition, the researchers showed that a doped surface acted like an organic field-effect transistor, although a source-drain distance of nearly 30 nm was needed. Almost all of the previously mentioned alkyl layers were produced by a multi-step approach. In 2008, Blake et al.[103] presented a one-step method to produce controlled growth of polymer brush nano thin films on H-terminated silicon(100) and (111). The method required mixing an initiator, a monomer, and a crosslinking agent dissolved in toluene, heated to 70 °C for 10h (the half-life of the radical initiator). The results showed a range of thicknesses from 2-15 nm and provided a range of modifications that could be performed on the silicon surface with readily available chemicals.

Photoactivation

Photochemical attachment of organic moieties onto silicon surfaces is an attractive surface modification method. It eliminates the risk that is inherent in heating volatile solvents with volatile and/or sensitive organic reagent and eliminates the use of radical initiators and their associated risk of detonation. Indeed, photochemical attachment can often simplify the reaction to solvent, solvate, and substrate under ambient conditions. One of the first reports using visible light (447nm) as a radical initiator for a H-terminated silicon(100) surface was presented by Sun and coworkers[104] in 2004. In addition, earlier reports exist of photochemical attachment of alkanes on partially iodated silicon surfaces,[105] but these reactions are more step intensive and do not produce as uniform a passivated surface as hydrogen termination.[73] The research performed by Sun and coworkers showed that lightly doped silicon was easier to modify through their photo activation route than heavily doped silicon substrates. This initial study led to two other reports of photoinitiated radical chain propagation of organic monolayers on the silicon surface.[106,107] Zuilhof et al,[108] continued to study photochemical attachment by focusing on the kinetics of the reaction by attempting a reaction in the dark at room temperature, founded on an earlier report in 2005.[109] The group continued to refine the photochemical approach by introducing a one-step method for creating N-hydroxysuccinimide (NHS)-ester terminated monolayers on silicon that allowed additional functionalization of the coated surface through the substitution of the NHS moieties with amines.[110] At about the same time, Chabal and coworkers[111] showed the UV induced covalent binding of zirconocenes on the H-terminated silicon surface for application in customized catalytic surfaces with sub-micron structures.

Thiol Click Chemistry

Some of the original experimentation with thiol-ene coupling occurred around 1950.[112-118] These early experiments showed the thiol-ene reaction to be complete, versatile, and that it could be applied to thiol polymers, creating materials with high thermal stability. The area did not reach wide appeal until the 1970s when UV curing systems were designed to use difunctional thiols and multifunctional enes and high conversion was explored.[119-123] This area of research is currently being intensely investigated as click chemistry. This term was first coined by Kolb et al. in 2001.[124] The inspiration for click chemistry came from the modularity and efficiency of natural chemical reactions that go to completion under a very high energy driving force. An example of this is the reaction between olefinic π bonds and azides which react with high efficiency and do so irreversibly.

Schlaad and coworkers experimented with thio compounds by synthesizing a thioester-terminated poly[2-(acetoacetoxy)ethyl methacrylate] in 2003 with subsequent studies on the structural behavior of the polymer.[125,126] This initial research and experimentation with thio compounds led to the rediscovery of the radical addition of ω-functional mercaptans to terminal alkenes,[127] based on previous research,[128-141] but newly applied to the modular click modification of 1,2-polybutadienes (Fig. 1). His group expanded the capabilities of the radical reaction by demonstrating the thorough nature of

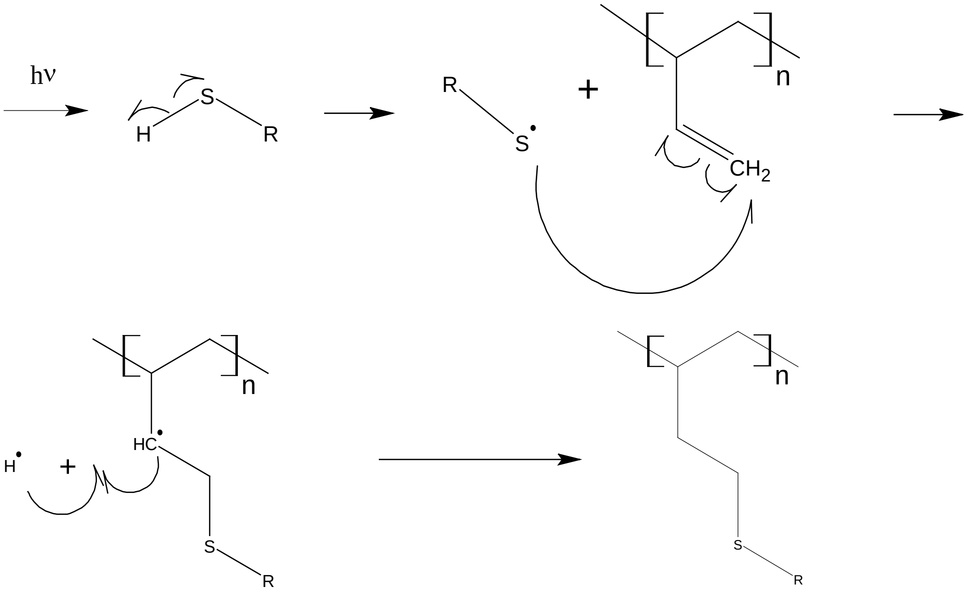


Figure 1. Schematic of a generic thiol click chemistry reaction involving the pendant alkene moiety of 1,2-addition polybutadiene. A propagation step is not shown whereby the carbon radical can abstract the thiol hydrogen creating another sulfur radical.

the chemistry, showing that it is a click type reaction. They further developed this chemistry by showing the conversion efficiency to be between 60 and 80%, depending on the type of functional ω-mercaptan.[141] The reaction of the polymer with ω-mercaptans resulted in a polydispersity index of 1.2, which demonstrated the narrow mass distribution of the functionalized polymer. The group successfully added amine and carboxylic acid functional groups in addition to ethylene glycol and fluorocarbons.[127,142] Other groups recognized the usefulness of this research and started to make even more diverse polymers through thiol-ene click chemistry, which included carbazole, dinitrobenzoate, phenol, pyridine, and 4-cyano-4-alkoxybiphenyl adducts on 1,2-polybutadiene.[143] Cesana et al.[144] reversed the chemistry and reacted alkenes with pendant thiols on 2-[2-(4-methoxybenzyl-sulfanyl)ethyl]-2-oxazoline, further expanding the utility of thiol-ene click chemistry. Thiol "click" chemistry was applied to nanocrystals and nanotubes,[145] poly[2-(3-butenyl)-2-oxazoline][142] and dendrimer synthesis.[146]

Initially, these reactions contained a radical initiator.[127,141] Roper et al.[147] demonstrated that the thiol-ene click reaction could be initiated by visible light. The study demonstrated that the light-initiated reaction achieved complete conversion, was independent of substituent length, and was less likely to react with internal trans enes. The modeling done by the group demonstrated that the cyclic enes can react, but ring strain and steric effects are considerations that reduce the efficiency of the reaction.

As has been demonstrated, no group has attempted to place a polymer directly on the silicon surface but instead has used polymerization techniques to grow them in situ. The aims of my research are to show attachment of 1,2-addition polybutadiene (modified and unmodified) to H-terminated silicon(111) with visible light activation. I show the influence of solution concentration on monolayer thickness and roughness. I report the partial functionalization of 1,2-addition polybutadiene by thiol-click chemistry and its subsequent attachment to hydrogen-terminated silicon with visible light. I also report the attachment of 1H,1H,2H,2H-perfluorodecanethiol onto 1,2-addition polybutadiene-passivated silicon surface through thiol "click" chemistry by visible light. I demonstrate that 1,2-addition polybutadiene can be partially functionalized, attached to the silicon surface, and then chemically modified after such attachment.

Experimental

Partial Functionalization. Industrially available 1,2-addition polybutadiene (PBd) (nominally 62 mole % 1,2-addition, Aldrich) was purchased and analyzed for actual 1,2-addition composition by fully functionalizing 1,2 PBd and submitting the resulting polymer for elemental analysis (EA) and ^{1}H NMR. The PBd was determined to be 87% 1,2-addition. The PBd was dissolved in purified THF, refluxed over LiNa, and then vacuum filtered through activated, basic Al_2O_3 (Aldrich) to remove any stabilizers in the solvent. Various thiols were proportionally added to the PBd/THF solution to prepare 25, 50, 75, and up to 100% functionalized 1,2-addition polybutadiene (PBd), including 11-mercaptoundecanoic acid (Aldrich), methyl-3-mercaptopropionate, 1H,1H,2H,2H-perfluorooctanethiol, and 1-octanethiol (Table 1). The thiol solution was frozen with liquid nitrogen, placed under vacuum, thawed, and then backfilled with argon. This was performed twice and the argon atmosphere was sealed in the Schlenk bomb after the last backfill. The solutions were placed in a UV chamber (Hearaeus, 303nm) for at least 22 hours. The contents of the reaction vessels were then placed in 1000 Dalton cutoff dialysis tubing (Spectrapor 6) and dialyzed for 3 days in THF, with the THF replaced daily. After the bulk of the solvent was evaporated, the polymers were dissolved in benzene (Aldrich, 99%) and freeze dried. Small quantities (< 20mg) of the resulting partially-functionalized polymers were submitted for elemental and NMR analysis. The methyl-3-mercaptopropionate was allowed to react in a vessel on a flat table under the UV exposure of sunlight on a day in summer in northern Europe. The reaction vessel received a total of 16 hours unobstructed light exposure (free from clouds, buildings, trees) in a 24 hour period. Most of the resulting polymers were obtained in quantities much less than one gram.

Polymer Analysis. Table 1 shows the functionalized PBd made by this method and the results from elemental analysis. NMR results correlated well with the elemental analysis results. For example, the double bond signals at ~5.0 ppm disappeared when the PBd was functionalized to 96% (Fig. 2). The 1H,1H,2H,2H-perfluorooctanethiol PBd samples were not analyzed due to the extremely limited quantity produced. The triisobutylsilane PBd samples were not analyzed for silicon content.

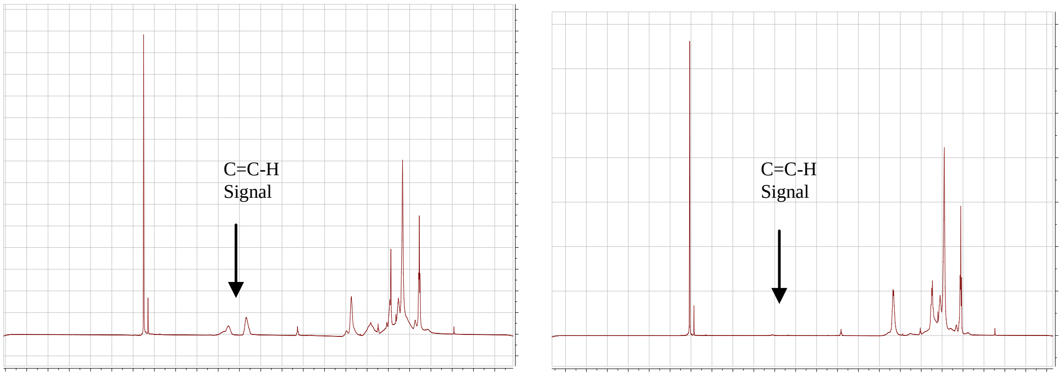
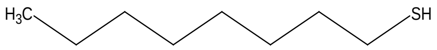
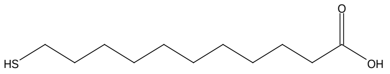
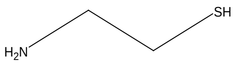
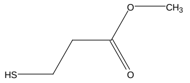
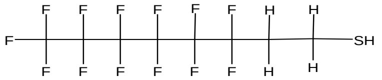
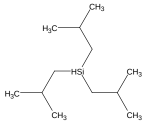
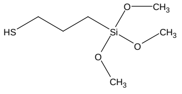


Figure 2. A comparison of the NMR signal reduction from double bonds at ~5.0 ppm of 20% octanethiol functionalized PBd on the left and 96% functionalized PBd on the right.

Hydrogen-terminated Silicon. Hydrogen-terminated silicon was made according to a literature method.[83] Silicon wafers (orientation 111, N doped, 585 μm thick) were obtained from Montco Silicon (Spring City, PA) and cleaved into ~1 cm^2 chips. The chips were placed in individual beakers with trichloroethylene (Mallinckrodt, 99.9%) and sonicated for 10 minutes. The chips were then placed in individual beakers of acetone (Fisher Spectrograde, 99.6%) and sonicated for 10 minutes. Next, the chips were soaked in filtered Millipore™ water for 20 minutes. The chips were immersed in a 3:1 solution of H_2SO_4 and 30% H_2O_2 at 120° C for 10 minutes. The chips were rinsed with Millipore™ water, placed in a Teflon chip container, and then submerged in 40%

ammonium fluoride (Ashland Chemical) at room temperature for 8 minutes. Next, the samples were removed and copiously rinsed with Millipore™ water, dried under N_2, and immediately placed in the solvated polymer for reaction. Reagents in this study were used as received unless otherwise noted.

Table 1
Reagents used, functionalization targets, and elemental analysis results for the thiol click reaction with PBd.

Reagent	Source	Target%	Elemental Analysis % Functionalization
1-Octanethiol 	Aldrich, 98.5%	25	20
		50	47
		75	70
		100	96
11-Mercaptoundecanoic acid 	Aldrich, 95%	25	6
		50	7
		75	10
2-Aminoethanethiol 	Acros, 98%	25	15
		50	31
		75	55
Methyl-3-mercaptopropionate 	Fluka, ≥98%	25	19
		50	44
		75	62
1H,1H,2H,2H-Perfluorooctanthiol 	Fluorochem, 99%	25	Not Analyzed
		50	Not Analyzed
Triisobutylsilane 	Aldrich, 99%	25	Not Analyzed
		50	Not Analyzed
3-Mercaptopropyltrimethoxysilane 	ABCR, 97%	25	16
		50	56

Surface Functionalization. Hydrogen-terminated silicon chips were placed in 10, 15, 20, 25, 33, and 40% w/w PBd solutions in mesitylene (Fisher, 99%) under N_2, then placed on a countertop under the fluorescent laboratory lights, and allowed to react for 24 hours. The partially functionalized polymers were dissolved in mesitylene to make ~15 w/w % solutions due to the limited quantities of the custom polymers on hand. They were then placed in scintillation vials filled with N_2, sealed, and then allowed to react under the fluorescent lighting for 24 hours. The chips were removed, rinsed with spectrograde acetone (Aldrich, 99.6%), sonicated in mesitylene for five minutes and dried under N_2. After analysis by water contact angle goniometry, ellipsometry, XPS and ToF-SIMS, four samples of PBd-coated silicon chips were coated with 1H,1H,2H,2H-perfluorodecanethiol (Oakwood Products, SC), placed in scintillation vials, sealed under N_2 atmosphere, and placed under the laboratory fluorescent lights for 24 hours. The four chips were then sonicated in spectrograde acetone (Aldrich, 99.6%) for two minutes and dried under N_2.

Characterization. The surfaces were subjected to sensitive surface analysis including contact angle goniometry, spectroscopic ellipsometry, XPS (X-ray photoelectron spectroscopy), and ToF-SIMS (time-of-flight-secondary ion mass spectrometry).

Results and Discussion

Section I

Partial Functionalization of Polybutadiene. The partially functionalized PBd samples were analyzed to determine the success of the reactions. EA was performed on most samples (Table 1). The two 1H,1H,2H,2H-perfluorooctanethiol and the two triisobutylsilane functionalized samples were not analyzed due to the limited quantity of product obtained. The 1-octanethiol-functionalized polymers were obtained closest to the targeted percentage. This is in contrast to the apparent failure of 1-undecanoic acid to functionalize the terminal alkenes on the PBd backbone (Fig. 1). It is proposed that the acid forms micelles in the THF solution, limiting the probability of reaction with PBd. This would limit the mobility of the individual molecules and not allow them to have the same reaction potential as solvated 1-octanethiol. This explanation could apply to the 2-aminoethanethiol reaction as well, though the smaller molecule would explain the greater success of the amine functionalization compared to the acid. The methyl-3-mercaptopropionate functionalized the PBd rather well as it was only exposed to the natural light occurring in one day. The 3-mercaptopropyltrimethoxysilane was added in slight excess to the 50% functionalization reaction, as shown in the end results. Overall, EA demonstrated that the attempted partial functionalization did occur, however, steric, solvent, and charge-based influences may have some effect on the extent of functionalization of polymers with 1-alkene functionality.

EA results were required before proton nuclear magnetic resonance (^{1}H NMR) measurements could provide information concerning the success of the partial functionalization of the base polymer. The pure polymer NMR spectrum was compared to the partially functionalized polymers to identify the signal corresponding to the alkene moiety. The signal correlating to the pendant alkene at ~5.0 ppm did decrease as higher percent functionalization was achieved (Fig. 2). In the case of the 96% octanethiol functionalization of PBd, the signal corresponding to the terminal double bond was almost completely gone, suggesting that the reaction had essentially gone to completion. Additionally, the spectra provided information concerning the added thiol. In the case of the methyl-3-mercaptopropionate, the ^{1}H signal of the terminal methyl group gave a characteristic signal shifted downfield by about 3.5 ppm (Fig. 3). Functionalization of PBd with triisobutylsilane was attempted to produce a bifunctional polymer which could

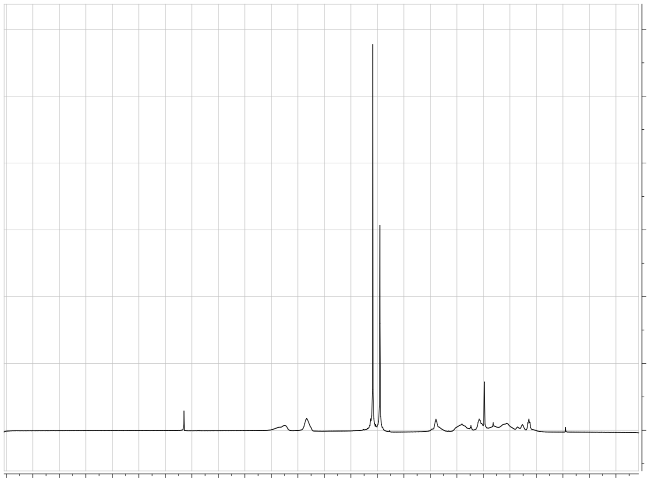


Figure 3. NMR of 16% Mercaptopropionate functionalized PBd and the characteristic downfield shifted methyl signal.

attach to an oxide or H-terminated silicon surface and was not a thiol. The thiol-click chemistry is well established in the literature[142] but upon comparing the bond strength between a thiol and the triisobutylsilane, it was surmised that the difference in the bond strength was close enough to attempt the reaction. This line of reasoning led me to attempt to use the thiol-click chemical environment to see if the silane would link to the terminal alkene as the thiols routinely do to create a silicon carbon bond.

Section II

Surface Attachment Results and Discussion. Hydrogen-terminated silicon(111) was prepared according to the procedure of Kato et al.[83] and then analyzed by AFM and XPS. AFM analysis resulted in an rms roughness of 0.71 Å after the piranha cleaning step and 0.91 Å after the fluoride etch. The images obtained from AFM are very flat, though some small surface defects do appear in the Si(111)-H image as compared to the SiO_2 surface image (Figure 1 in appendix). XPS showed the surface to be nearly free of oxide and carbon contamination (Fig. 4). These results show that the method of Kato et al.[83] produced a high-quality substrate for subsequent surface modification studies.

Contact angle goniometry showed a change from the hydrogen-terminated silicon surface to the PBd coated surface through an increase in the water contact angle, including an increase in water contact angle as solution concentration increased (Fig. 5). The trend these results suggest is that a higher solution concentration would produce a more uniform surface coating. The increase in the C1s/Si2p ratio as the solution concentration increased supports the contact angle goniometry results of the surfaces, which appeared to approach a maximum contact angle at full surface coverage.

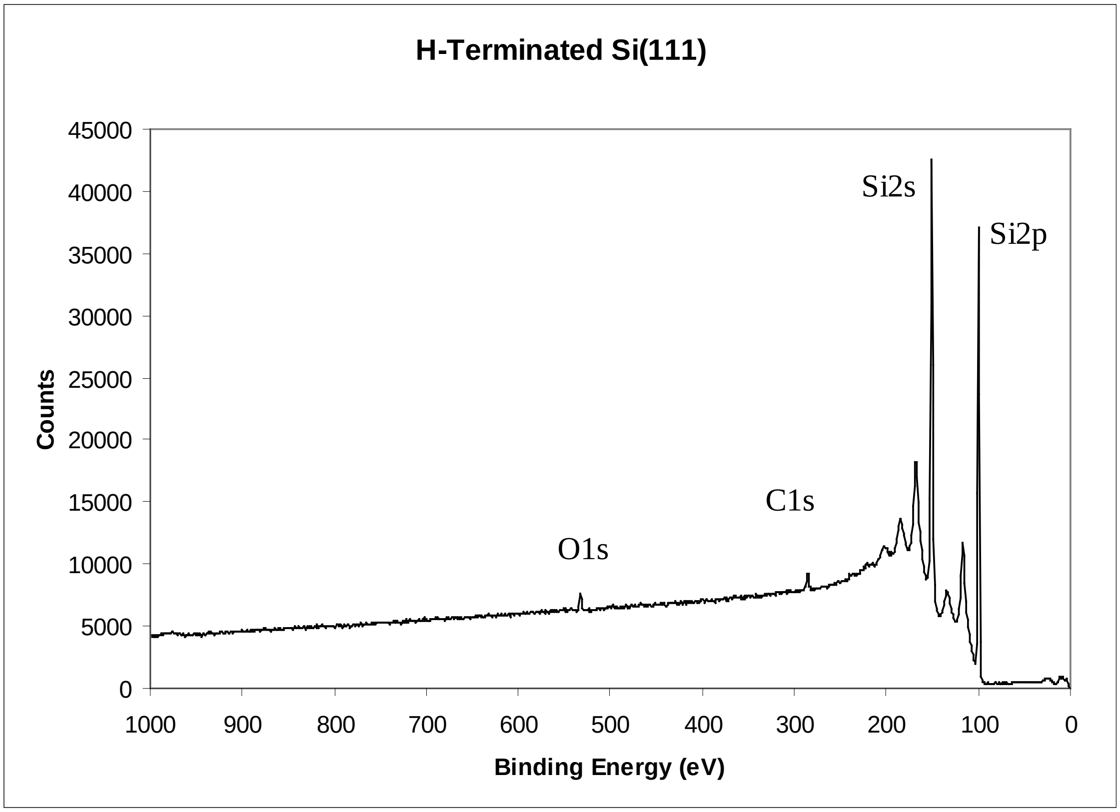


Figure 4. XPS survey scan of H-terminated silicon(111) immediately after etching. The C1s/Si2p ratio is less than 0.04.

Ellipsometry has some difficulty accurately determining film thicknesses below 10 nm; however, I used this method to show the thickness changes from the oxide, to the H-termination, to surface functionalization. A comparison of the PBd solution concentration to the thickness of the monolayer obtained by ellipsometry showed a general layer thickness between two and three nanometers. When this data is correlated to the AFM surface roughness calculations, it indicates that the surface becomes more evenly coated at higher concentrations since the surface shows lower surface roughness in AFM at higher concentrations for the methyl-3-mercaptopropionate PBd, but the unmodified PBd surfaces seem to fluctuate around some average roughness except for the lowest solution concentration (Table 1 in appendix).

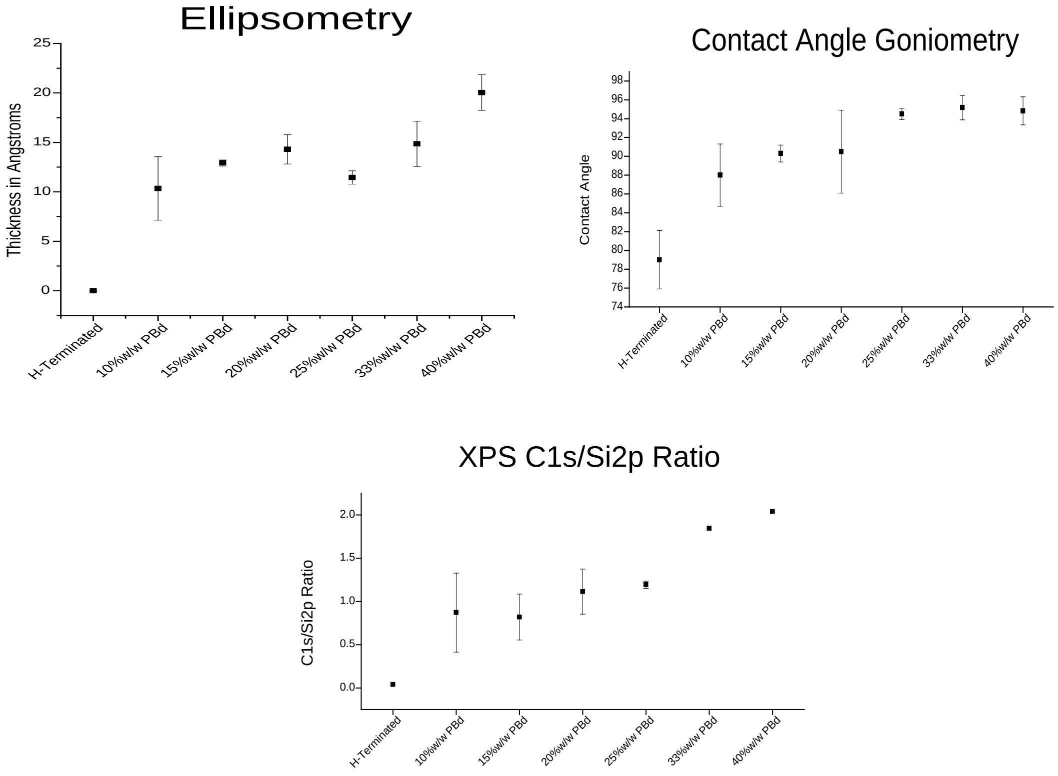


Figure 5. H-terminated Si(111) compared to various PBd weight percent solutions used to create PBd passivated surfaces in thickness (top left), water contact angle goniometry (top right), and XPS carbon 1s to silicon 2p ratio (bottom). The trend toward more uniform surface coverage at higher solution concentration is evident by the increase in each of these analyses and the solution increased in PBd content.

Polymer theory states that the size of a polymer coiled in solution is approximately the square root of the number of monomer units (mers) times the length of each monomer unit. The polybutadiene used was approximately 3200-3500 MW, the mass of one mer is about 52 AU, which would mean there are about 64 mers per polymer. The length of the polymer in solution would be the square root of 64, or about 8 mers. The length of the mer across the 1,2-addition bonds is approximately 2.5 Å (the length of two carbon-carbon bonds). The length of the individual mer times the number of mers in the polymer length should be about 20 Å in solution, which is very close to the ellipsometry value we obtain for the surfaces. The surface thickness results concur reasonably well with standard polymer theory.

ToF-SIMS indicates that the polymers are covalently attached to the silicon surface. A spectrum for unmodified 1,2-addition PBd was used from a reference book[148] due to the difficulty of ToF-SIMS analysis of a sticky, slightly viscous polymer (Fig. 6). The fragmentary pattern of the reference spectrum was used to aid in the identification of peaks though the intensities would vary based on the ion source. The comparison of ToF-SIMS spectra of the reference and 20 w/w % PBd solution in Figure 6 demonstrate the fragmentary pattern similarities, but differing peak intensities of a covalently attached PBd thin film. This result is reasonable since the polymer is attached to the silicon surface through the pendant alkene moieties on the backbone. The covalent attachment of PBd to silicon would suppress formation of larger fragments. Also, the layer is thin enough that having a significant silicon ion peak is expected. The ToF-SIMS results

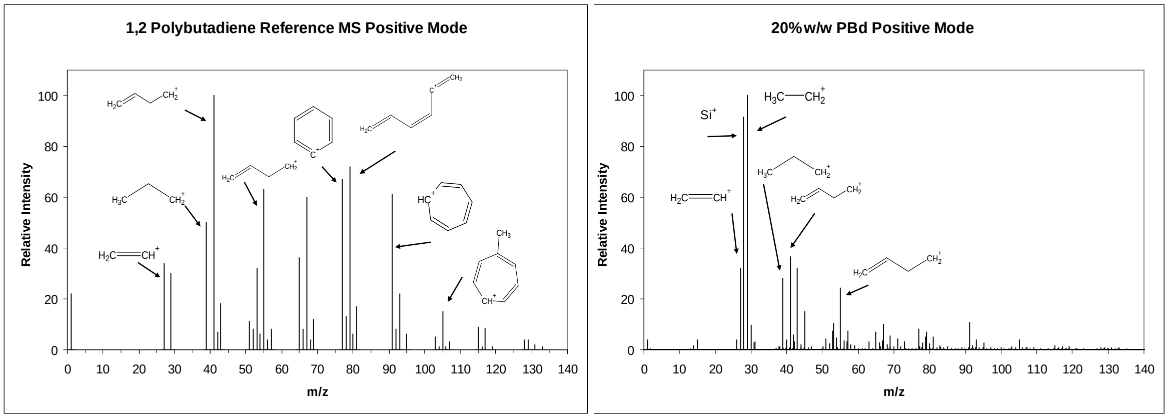


Figure 6. On the left is a static SIMS reference spectrum for 1,2 PBd and on the right is the 20%w/w PBd spectrum with specific fragments identified.

suggest that not all double bonds are covalently attached to the surface since larger polymeric fragments are still seen in the spectra, just at a lower intensity. Also, the ToF-SIMS spectra in negative ion mode show very limited fluorine from the hydrogen passivation method for those polymers without attached fluorine moieties (Fig. 7).

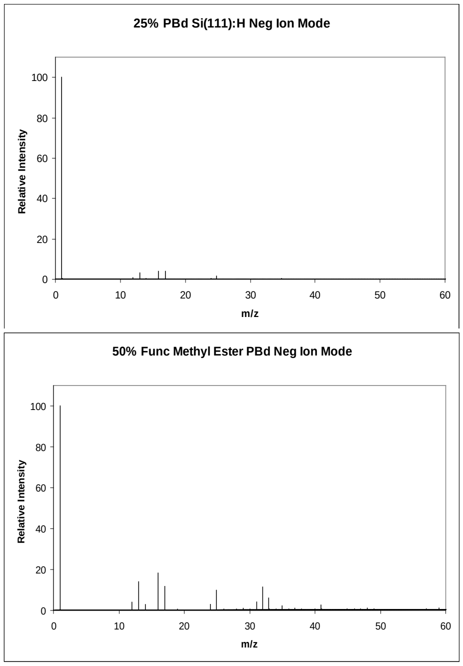


Figure 7. Negative ion mode mass spectra of 20%w/w PBD (top) and 50% methyl-3-mercaptopropionate PBD (bottom). The fluorine signal is nearly absent. The maximum ratio of F^-/H^- for non-fluorinated polymers was less than 0.01.

XPS analysis of PBd concentration differences gave clear indication of increased surface coverage with increased PBd concentration. Figure 5 shows a correlation in the C1s/Si2p ratio to polymer solution concentration, which is supported by the increase in thickness at higher concentration levels. Narrow scans of the C1s peak show the smooth, near Gaussian curve expected of unmodified organic molecules (Fig. 8).

The mercaptopropionatethiol functionalized PBd attached to Si(111)-H was analyzed with XPS. A comparison of the narrow scan carbon 1s peak of the PBd and the thiol functionalized PBd shows a split in the carbon peak (Fig. 8). The split corresponds to the effect three oxygen bonds have on the carboxyl carbon on the propionate. A single oxygen on carbon shifts the carbon signal 1.2-1.5 eV toward higher energy. As seen in the spectrum comparison, the shift in the carbon signal correlates well to the carbon having three oxygen bonds and having each oxygen bond shifting the C1s electron by approximately 1.5 eV. The trend of the C1s/Si2p ratio for the mercaptopropionate samples is similar to the surface thickness in ellipsometry; more polymer is attached to the surface at higher percent functionalization. The increase in thickness may be attributed to the additional alkene functionalities attached to the polymer backbone and higher packing densities.

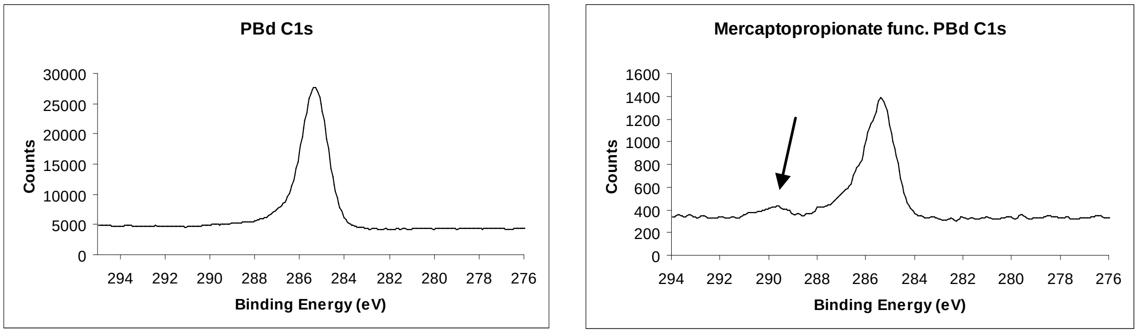


Figure 8. Comparison of C1s the signal of unmodified PBd (250 scans) and 16% Methyl-3-mercaptopropionate functionalized PBd on Si(111) (100 scans). The split peak in the right figure is marked with an arrow.

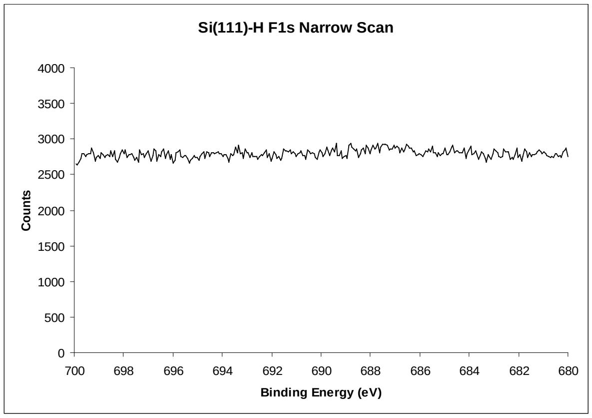


Figure 9. Narrow scan of the F1s binding energy region. This demonstrates the minimal fluorine left on the surface after the last rinse.

XPS also gave evidence for the effectiveness of the final rinsing step after NH_4F etching. The XPS narrow scan of H-terminated Si(111) demonstrates the effectiveness of the final rinse step of reducing fluorine contamination (Fig. 9). The survey spectrum includes 150 scans. Signal averaging would show a fluorine 1s photoelectron signal if it were present. The lack of a significant fluorine peak at 686 eV clearly shows the near absence of fluorine on the surface, supported by ToF-SIMS analysis, and proves the efficiency of the final rinse and drying before polymer surface passivation. Figure 1 in the appendix shows two negative ion mode ToF-SIMS spectra of 20%w/w PBd and 44% methyl-3-mercaptopropionate

PBd which provide further evidence for limited fluorine remaining on the surface before polymer attachment.

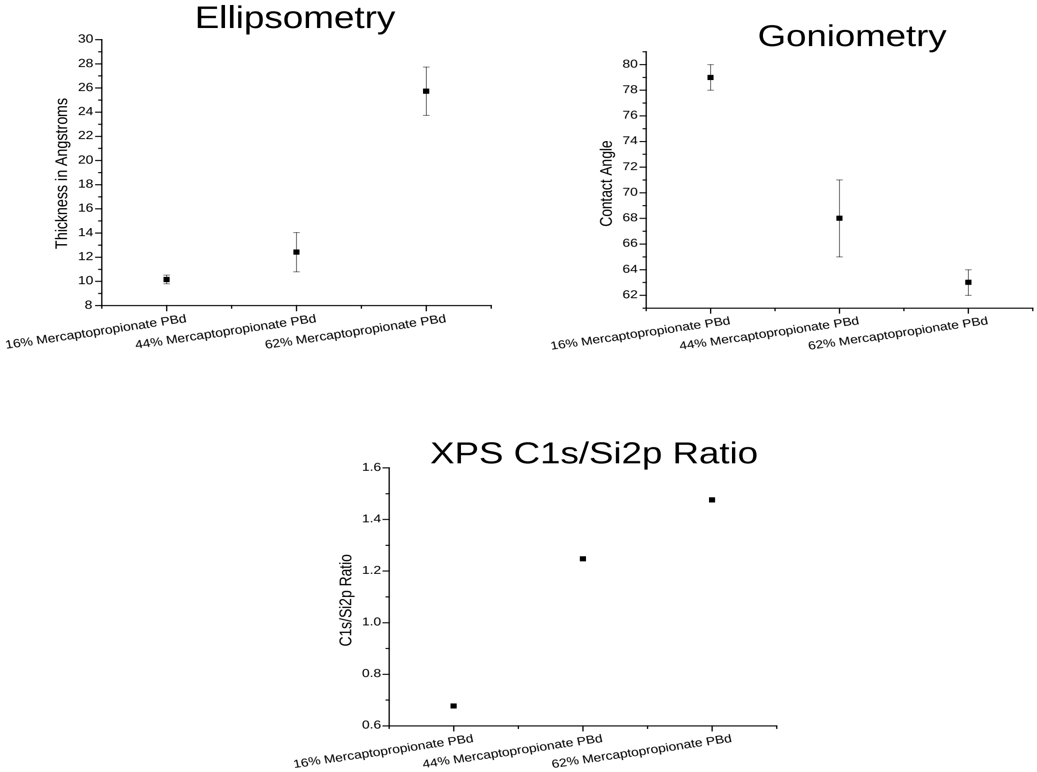


Figure 10. Ellipsometry, contact angle goniometry, and XPS C1s/Si2p ratio demonstrating mercaptopropionatethiol functionalized PBd increased in thickness at higher percent functionality, the greater methyl ester character of the surface led to a decrease in contact angle, and XPS confirmed more carbon on the surface at higher functionality.

With ToF-SIMS and XPS analysis, the partially functionalized polymers demonstrated the effectiveness of the thiol click chemistry. Surface immobilized mercaptopropionate functionalized PBd analysis by ellipsometry, goniometry and XPS indicated that the polymer did attach to the surface. Ellipsometry demonstrated thickness increase as percent functionalization increased (Fig. 10). Goniometry results showed an increased surface interaction at increased percent functionalization. The terminal group of the mercaptopropionate is a methyl ester. Methyl esters are known to be relatively hydrophilic and the decrease in contact angle at higher percent functionalization verifies

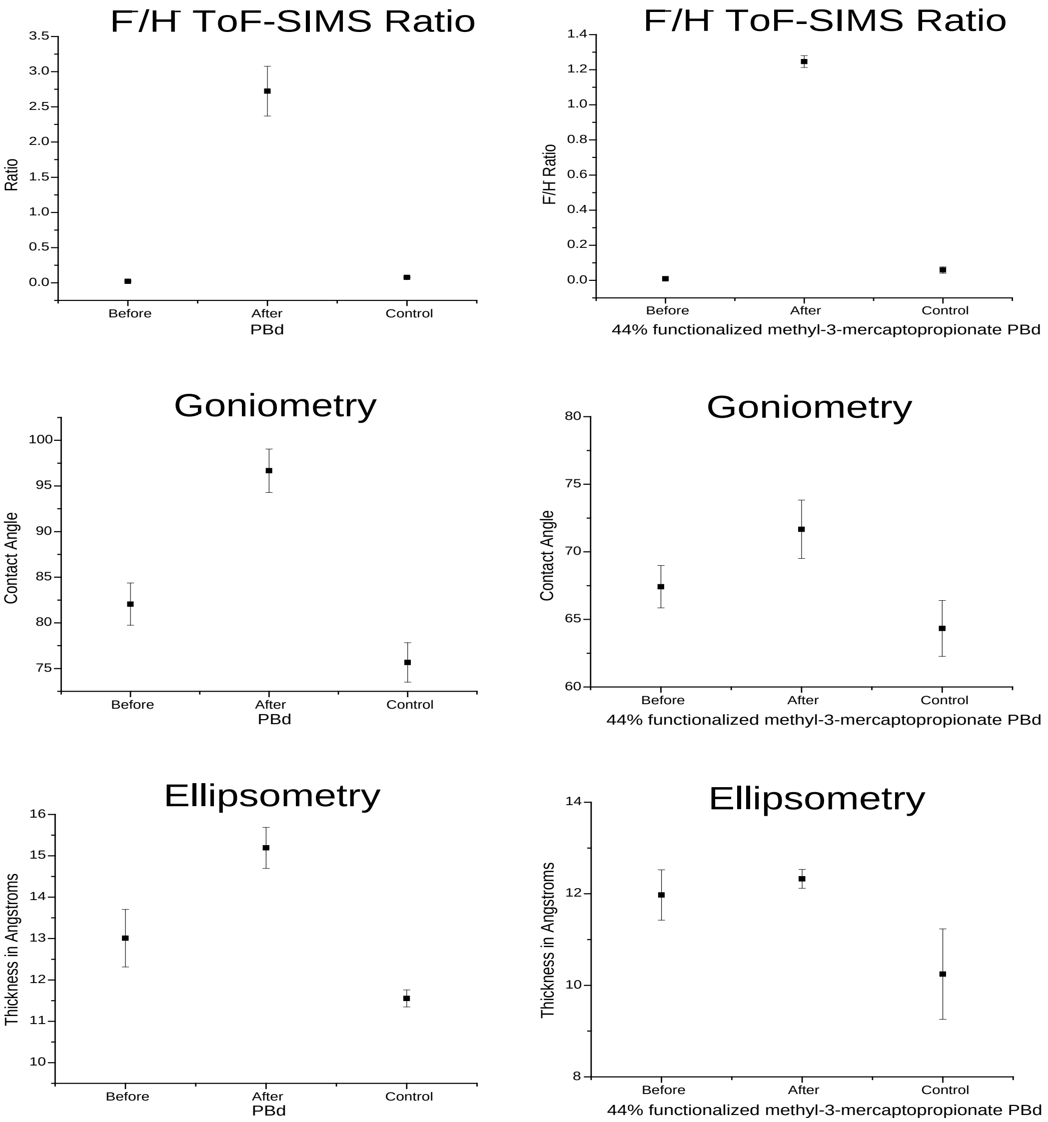


Figure 11. Before and after results of post surface attachment thiol click chemistry with PBd control.

the EA results and confirms the functionalized polymers' attachment to the surface. The XPS C1s/Si2p signal ratio comparison confirms ellipsometry results that more polymer is on the surface at higher percent functionalization.

To verify the presence of residual pendant alkenes and their availability for further attachment, a 44% mercaptopropionate functionalized PBd and a separate PBd passivated silicon(111) chip were reacted with 1H,1H,2H,2H-perfluorodecanethiol under laboratory light for 24 hours and the surface were characterized prior to and after the reaction. To ensure only bound species remained on the surface, the chips were sonicated in acetone (Aldrich, ≥99.9%) for 5 minutes after the perfluorooctanethiol reaction. Results showed a contact angle goniometry increase, an ellipsometry surface thickness increase (Fig. 11), a significant increase in the F^-/H^- ratio in negative ion mode ToF-SIMS (Fig. 6). As a control, PBd and 44% mercaptopropionate PBd passivated chips was reacted with neat octadecafluorooctane (Aldrich, 98%) and analyzed by the same methods as the perfluoro reaction. The results in Figure 9 show that virtually no adsorption occurs on the control surface and that the thiol does bind to the surface as evidenced by the surface thickness increase and F^-/H^- ratio increase in ToF-SIMS, which is very sensitive to the fluorine ion.

Time appeared to influence the thickness of the polymer layer on silicon. A reaction that was left for two months had a thickness of almost 40 Å. The resulting XPS data showed a significant C1s/Si2p ratio well beyond all other experiments lasting about 24 hours (Figure 2 in appendix). This result requires further study to confirm the time effect on the layer thickness. The octanethiol functionalized PBD tests gave conflicting results and require further study. Additional investigation is required to test the effect that attached functionalities have on surface attachment and post surface functionalization.

AFM roughness measurement of the Si(111)-H surface showed that the etching process was relatively gentle. Figure 11 is an image of the Si(111)-H surface immediately after etching compared to 44% methyl-3-mercaptopropionate functionalized PBd. The interesting feature of many of the functionalized PBd passivated surfaces is the apparent clustering. The height of these clusters in this study has remained below 10 nm.

The clustering behavior could be the attached thiol moieties demonstrating higher affinity for themselves than for PBd.

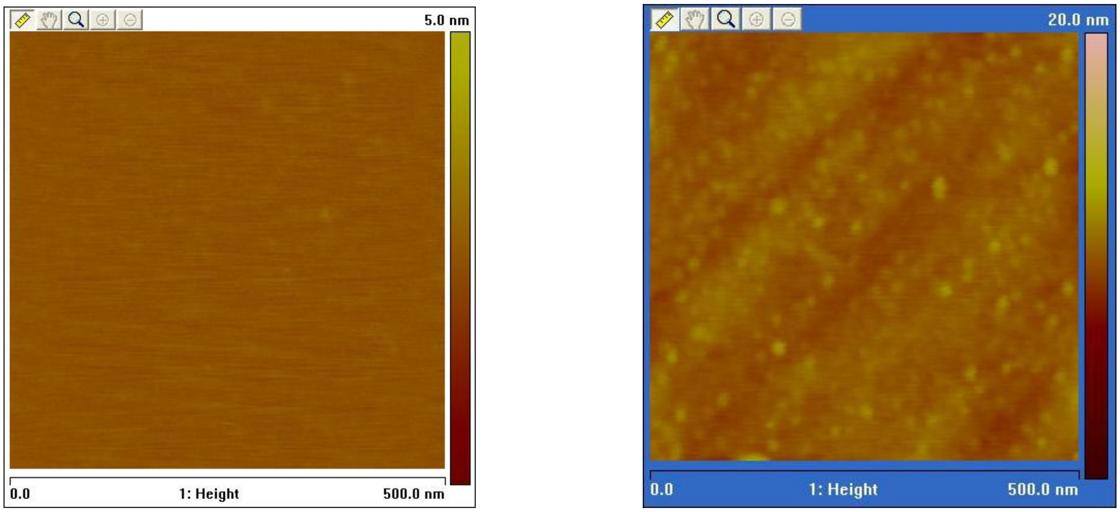


Figure 12. AFM images of Si(111)-H surface (left, white frame) compared to 44% methyl-3-mercaptopropionate functionalized PBd (right, blue frame).

Conclusions

Thiol click chemistry is a viable method to efficiently control functionalization of pendant alkene moieties on a polymer backbone. Thiol click chemistry also provides a pathway to multiply functionalize a polymer with various thiolated compounds while still leaving unreacted double bonds to produce polymers of unique characteristics and chemical handles for further modification. Silicon surface attached functionalized PBd demonstrated sufficient residual pendant alkenes for further surface modification through thio click chemistry.

Analysis showed 1,2-addition polybutadiene covalently attaches to hydrogen terminated silicon(111) surface through visible light activation. More material was attached to the surface when PBd solution concentration was increased. Unreacted pendant alkenes of 1,2-addition polybutadiene can be further functionalized after surface attachment with simple thiol click chemistry through visible light activation. This research provides surface scientists an almost limitless scaffold for custom surface functionalization both prior to and post H-terminated surface passivation.

Future Work

There are many areas of experimentation for this particular chemistry of thiol click polymer functionalization with surface attachment. Future work with this chemistry includes functionalizing PBd with mercaptosilanes. This particular functionalization would allow possible attachment of the polymer to an oxide substrate. This would allow the further functionalization of surfaces for nano circuits with carbon nanotubes used as field effect transistors since a thick oxide is required to prevent the field from being collapsed by a conducting substrate or thinly coated conducting substrate.

Thiol terminated DNA oligomers could be attached to PBd to create bio-compatible polymers and surfaces. A possible application for a DNA thiol functionalized polymer is in DNA origami surface attachment and metalized DNA nanowires. If the PBd is partially DNA functionalized, some of the residual pendant alkenes can be modified with a dithiol for possible attachment to a gold surface, if the dithiol will only react with one thiol and not form dithiol rings with the PBd. The dithiol reaction needs specific focus to find out if there would be ring formation and how this can be avoided by concentration or other solution manipulation.

A third area of work is in surface coatings. Polybutadiene has shown itself to be a durable surface coating on silicon. I reanalyzed some samples after months of handling and storage and found the surface characterization methods return data within experimental error of the initial measurements performed when the surfaces were newly made. This experience coupled with further study could lend itself to forming a modified

PBd for glass and polycarbonate coatings. Performance tests need to be made determining durability, wear resistance and decomposition of PBd on various surfaces.

Appendix

Figures

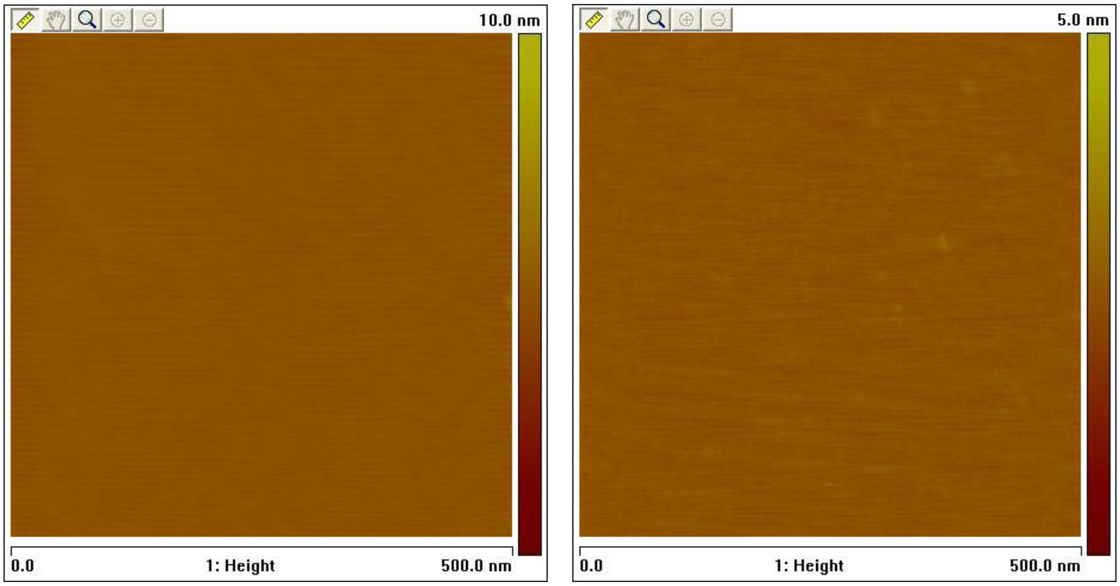


Figure 1. Two images showing the relative atomic flatness of the substrate after the piranha cleaning step (left) and after NH_4F etching (right). The rms roughness values for the surfaces were 0.7 Å (oxide, left) and 0.9 Å (H-terminated, right).

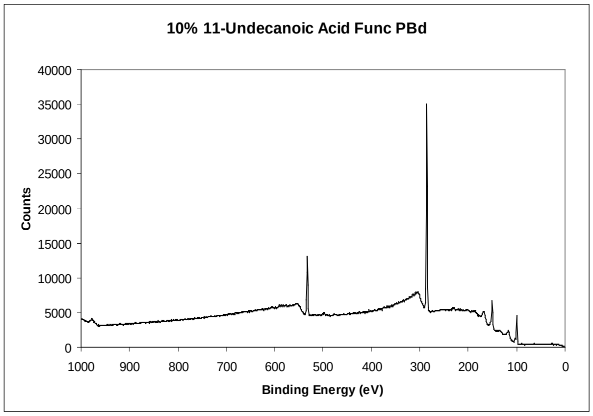


Figure 2. XPS survey scan of 10% 11-undecanoic acid functionalized PBd. The image is with 20 scans. The surface was under reaction for 2 months and shows the C1s/Si2p ratio is significantly greater than 24 hour reaction times.

Tables

Table 1
Surface analysis results for Si(111)-H, various PBd solution concentrations, and partially functionalized PBd

	Water Contact Angles	Ellipsometry (Å)	XPS C1s/Si2p	AFM Roughness (Å)
Hydrogen Terminated Si(111)	79±3	0	0.04	0.94
10%w/w PBd	88±3	10.34±3.21	0.87	1.85
15%w/w PBd	90.3±1	12.92±0.30	0.82	3.60
20%w/w PBd	90.5±4	14.30±1.48	1.11	3.58
25%w/w PBd	94.5±1	11.45±0.67	1.19	2.18
33%w/w PBd	95.2±1	14.85±2.29	1.85	2.05
40%w/w PBd	94.8±1	20.04±1.81	2.04	3.90
19% Mercaptopropionate PBd	79±1	10.16±0.36	0.68	10.90
44% Mercaptopropionate PBd	69±4	13.76±3.48	0.75	4.97
62% Mercaptopropionate PBd	63±1	25.73±2.00	1.26	2.43

Table 2
ToF-SIMS F^-/H^- and S^-/H^- ratios before and after reacting 44% methyl-3-mercaptopropionate functionalized PBd with perfluorinated thiol

	F^-/H^-	S^-/H^-
Before	0.011±0.0063	0.12±0.013
After HSR_F	1.24±0.034	0.12±0.018
Control	0.059±0.019	0.12±0.018

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