SURFACE MODIFICATION OF SILICATE SUBSTRATES

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ABSTRACT

Polymer chains tethered to a surface have been extensively studied in the area of surface modifications. Exploratory efforts on surface modification in this research have been focused on three areas: first, investigation of surface-grafted, Y-shaped, diblock copolymer thin films using a “grafting-to” method; second, a polymer brush grafted from a uniform initiator monolayer; and third, binary mixed homopolymer brush fabrication using a “grafting-from” technique.

Y-shaped diblock copolymers grafted onto a flat surface were predicted to give rise to a rich variety of novel patterns. However, there have been few experimental reports primarily because these systems require challenging synthetic approaches. We used a synthetically simple approach to produce a Y-shaped AB diblock copolymer brush. A polystyrene-\(b\)-poly(2-vinylpyridine) (PS-\(b\)-P2VP) block copolymer containing a methylhydridosilane linking group was chemically “grafted-to” an 8-trichlorosilyloctene monolayer via a 1-step hydrosilylation reaction. The resulting Y-shaped thin film exhibited a low grafting density, characteristic of the “grafting-to” technique. To further decrease the miscibility of the two arms, methyl iodide was reacted with the P2VP block to produce quaternary ammonium groups. The surfaces before and after quaternization exhibited surface compositional changes upon exposure to block-selective solvents.
To create the optimal surface for a “grafting-from” polymerization, a uniform initiator layer on the silicate substrate is important. However, uniformity is a persistent issue when multifunctional silanes are used because of side-reactions and moisture sensitivity. In an attempt to minimize these problems, an allylsilane was synthesized to functionalize our substrates. Using atomic force microscopy, the allylsilane monolayer was found to be more uniform than the monolayer prepared from a trichlorosilane. Atom transfer radical polymerization was applied to graft polystyrene brushes from the initiator-bound surface.

Mixed polymer brushes, consisting of diblock or triblock copolymer brushes, Y-shaped diblock copolymer brushes and mixed homopolymer brushes, have been extensively studied because of the potential for amplifying the combined effects of conformational changes and microscopic phase separation. Macroscopic phase separation is generally suppressed by the tethering of one chain end to the surface. Both theoretical and experimental work have indicated that symmetric mixed homopolymer brushes would be able to undergo a solvent-induced transition between lateral and perpendicular microphase separation. Therefore, we devised a simple approach for one-pot, controlled brush synthesis by combining nitroxide-mediated radical polymerization and living cationic ring-opening polymerization. We observed that the mixed homopolymer brush showed surface changes when subjected to different solvents.
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DEDICATION

To my loving, patient and supportive husband, Sinan Li.
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CHAPTER I

INTRODUCTION

Human beings have realized the importance of surfaces and interfaces for a long time, because they are so closely related to our everyday life. Seven thousand years ago, the ancient Chinese used lacquer generated from tree sap to protect wooden surfaces.¹ The detailed study of surfaces and interfaces became a bona fide scientific discipline during the 1970’s. Since then it has been playing a forefront role in science. Surface and interface science is truly interdisciplinary, comprising the fields of physics, chemistry and analytical chemistry. Besides traditional coating applications, surface and interface science also relates closely to other areas such as heterogeneous catalysis, microelectronics, aviation, and biomedical devices.

Compared with the self-assembly of low molecular weight thiols or disulfides, phosphoric or phosphonic acids, and organosilanes, polymer-coated surface play more versatile roles in surface modification field. Self-assembled monolayers can accommodate a more or less strict two-dimensional arrangement of terminal functionalities. Polymers add an additional vertical dimension, since polymers can carry functional groups along the chains.¹ Thus, polymers have attracted more
attention in more recent studies. Polymer chains can be fixed onto a surface by two main techniques: physisorption and covalent attachment. Physisorption involves the deposition of a preformed polymer chain with one end or one block, which interacts preferentially with the substrate surface out of physical interaction. Covalent attachment can be achieved by “grafting-to” and “grafting-from”. In the “grafting-to” technique, preformed polymer chains containing a functional end group are attached to a functionalized surface by covalent bonds formation, while “grafting-from” involves in-situ polymerization from an initiator functionalized surface. Physisorption and “grafting-to” used preformed polymer chains. Thus molecular weight (MW) and molecular weight distribution (MWD) can be well controlled. However, the tethering density is low because of steric hindrance in the grafting process. In physisorption, the brushes are thermally or sovolytically unstable. For “grafting-from,” most polymerization methods can be used and higher tethering density can be achieved. However, this method has less precise control over MW and MWD, and the uniformity of the tethering density is not known. Due to the higher grafting density the “grafting-from” method has been a preferred choice for surface modification. The “grafting-from” technique entails the immobilization of an initiator molecule onto a surface, followed by polymerization from that initiator functionalized surface.

The purpose of this research is to utilize multiple approaches for silicate surface modifications. Y-shaped diblock copolymers grafted onto a flat surface were
predicted to give rise to a rich variety of novel patterns. However, there have been few experimental reports primarily because these systems require challenging synthetic approaches. We used a synthetically simple approach to produce a Y-shaped AB diblock copolymer brush. A polystyrene-\textit{b}-poly(2-vinylpyridine) (PS-\textit{b}-P2VP) block copolymer containing a methylhydridosilane linking group in the middle was chemically “grafted-to” a 7-octenyltrichlorosilane (OTS) monolayer via a 1-step hydrosilylation reaction. The resulting “Y-shaped” thin film exhibited a low grafting density, characteristic of the “grafting-to” technique. To further decrease the miscibility of the two arms, methyl iodide was reacted with the P2VP block to produce quaternary ammonium groups. The surfaces before and after quaternization exhibited surface compositional changes upon exposure to block-selective solvents.

To create the optimal surface for a “grafting-from” polymerization, a uniform initiator layer on the silicate substrate is important. However, uniformity is a persistent issue when multifunctional silanes are used because of side-reactions and moisture sensitivity. In an attempt to minimize these problems, an allylsilane was synthesized to functionalize the flat silicate substrate surfaces. Using atomic force microscopy (AFM), the allylsilane-derived initiator monolayer was found to be more uniform than the initiator monolayer prepared from the corresponding trichlorosilane reagent. Atom transfer radical polymerization (ATRP) was applied to graft polystyrene brushes from the initiator-bound surface.

Mixed polymer brushes consisting of diblock or triblock copolymer brushes,
Y-shaped diblock copolymer brushes and mixed homopolymer brushes have been extensively studied because of the potential for amplifying the combined effects of conformational changes and microscopic phase separation. Macroscopic phase separation is suppressed by the tethering of one chain end to the surface. Both theoretical and experimental work have indicated that symmetric mixed homopolymer brushes would be able to undergo a solvent-induced transition between lateral and perpendicular microphase separation. Therefore, a very simple approach was devised for a one-pot, controlled homopolymer brush synthesis by combining nitroxide-mediated radical polymerization and living cationic ring-opening polymerization. We observed that the mixed homopolymer brush underwent a transition between a vertical microphase separation and a lateral microphase separation when subjected to different solvents.
CHAPTER II

HISTORICAL BACKGROUND

Polymer chains tethered to a surface or an interface have been the subject of extensive theoretical \(^{2-11}\) and experimental \(^{12-22}\) research. Potential applications for polymer brushes include colloidal stabilization, \(^{23}\) adhesion, \(^{24-25}\) lubrication, \(^{26}\) nanotechnology, \(^{27}\) microelectronics, \(^{28}\) and biology. \(^{29}\) Results have been reported for homopolymer brushes, binary mixed homopolymer brushes, random copolymer brushes, block copolymer brushes and functionalized polymer brushes.

Our exploratory efforts on surface modification have been focused on three areas: first, investigation of surface-grafted, Y-shaped, diblock copolymer thin films using a “grafting-to” method; second, a polymer brush grafted from a uniform initiator monolayer; and third, binary mixed homopolymer brush fabrication using a “grafting-from” technique. This chapter will review literature relevant to these three areas. The preparation of surface attached polymer thin films, the fabrication of initiator monolayer and binary mixed homopolymer brushes, and polymerization methods employed in this dissertation, such as atom transfer radical polymerization, nitroxide-mediated radical polymerization and cationic ring-opening polymerization, will be described in this chapter.
2.1 Polymer brushes

Polymer brushes refer to an assembly of polymer chains with one end tethered to a surface or an interface. Polymer brushes can correspond to adsorbed diblock copolymers, end-grafted polymers, polymer micelles, block copolymer melts, block copolymer at fluid-fluid interfaces and graft copolymers (see Figure 2.1).³

Surface-tethered polymer chains have been generically called polymer brushes. However, strictly speaking, depending on the tethering density and interaction between polymer chains and the substrate surfaces, surface-tethered polymer chains in the polymer films will assume different conformations which will be called either mushroom conformation, pancake-like conformation, or brush conformation (see Figure 2.2). If the distance between two anchoring sites is larger than the size of the surface-attached polymer molecule, the segments of individual polymer chains will not interact with each other and depending on the interaction between the polymer segments and the substrate surface, two cases must be distinguished. If the interaction is weak or even repulsive, the surface-attached polymer molecule will keep the unperturbed random coil conformation with one end linked to the substrate surface, and this conformation is called a mushroom conformation. However, if the polymer segments are adsorbed onto the substrate surface, the polymer molecule will have the pancake-like conformation. As tethering density increases, the polymer chains start to overlap and the polymer segments will try to avoid each other by stretching away from substrate surface, and this conformation is called a polymer brush.¹
Figure 2.1. Examples of polymer brushes.
Next, the preparation techniques for tethering polymer chains onto substrate surfaces will be described and some previous work representation of the numerous publications will be selectively chosen and briefly introduced.
2.1.1 Polymer brushes by the physisorption technique

Physisorption entails selective interaction of parts of the polymer chain with the substrate surfaces using physical attraction (see Figure 2.3). Physisorption is a reversible process and physisorbed chains lack thermal or solvolytical stability. A number of publications on physisorbed polymer chains were based on polystyrene-\textit{b}-poly(2-vinylpyridine) (PS-\textit{b}-P2VP) and polystyrene-\textit{b}-poly(ethylene oxide) (PS-\textit{b}-PEO), both of which were prepared by anionic polymerization.

![Figure 2.3. Polymer brush by physisorption technique.](image)

Parsonage \textit{et al.}\textsuperscript{30} studied the physisorption onto silicate surfaces of a series of PS-\textit{b}-P2VP block copolymers of various molecular weights in a selective solvent (toluene). The P2VP blocks are the anchoring blocks on the substrate surface, while the PS blocks form the bristles of the brushes. Hadziioannou \textit{et al.}\textsuperscript{31} reported
polymer brush formation by selective adsorption of PS-\textit{b}-P2VP block copolymers onto mica substrates. Fytas and coworkers\textsuperscript{32} adsorbed PS-\textit{b}-PEO block copolymers onto a glass prism surface to form a PEO anchor and PS brush in toluene, which is a good solvent for both blocks. There is a strong attraction between the substrate surface and the polar PEO block and the nonpolar PS block form a brush stretching away from the surface.

Due to the highly discriminating process in terms of copolymer structures, solvent qualities and substrate surface polarities, there are a limited number of systems studied and most reports were based on PS-\textit{b}-P2VP and PS-\textit{b}-PEO copolymers. To expand the scope of these studies, Stöhr and Rühe\textsuperscript{33} devised a macroinitiator-based physisorption method. Poly(\textepsilon-caprolactone) containing azo free radical initiating moieties was physisorbed onto a silicate substrate surface. After that, free radical polymerization of \textit{n}-alkyl methacrylates was conducted from the azo free radical initiating moieties in the physisorbed poly(\textepsilon-caprolactone).

There is more research interest in chemisorption (covalent attachment) than in physisorption, because of the higher thermal and solvolytical stability of chemisorbed layers. The covalent bond formation between substrate surfaces and polymer chains makes the polymer brushes more stable and robust. Chemisorption including “grafting-to” and “grafting-from” will be described in the following two parts.
2.1.2 Polymer brushes by “grafting-to” technique

In the “grafting-to” technique, preformed, end-functionalized polymer chains are reacted with a functionalized substrate surface under appropriate conditions to form the tethered polymer chains (see Figure 2.4). For this technique, end-functionalized polymer chains with a precisely controlled molecular weight and molecular weight distribution were prepared at first usually by living anionic, cationic, radical, group transfer or ring opening metathesis polymerizations. Living polymerizations were usually applied in order to afford narrow molecular weight distributions and control over molecular weight. Before grafting the polymer chains onto a surface, the synthesized polymer chains can be fully characterized.

![Figure 2.4. Polymer brush by “grafting-to” technique.](image)

Frank and coworkers\textsuperscript{34} grafted poly (γ-benzyl-L-glutamate) onto silicate substrate surfaces using two methods. In the first method, the N-terminus of each polymer chain was reacted with the chloroformate group in a self-assembled monolayer (SAM)
from 3-(trichlorosilyl)propyl chloroformate. In the second method, polymerization was initiated from (γ-aminopropyl)triethoxysilane. The polymer chains with triethoxysilyl terminal groups were subsequently grafted onto the silicate surface. Ebata and coworkers\textsuperscript{35} grafted polysilanyllithium made by anionic polymerization onto a (3-bromopropyl)dimethylchlorosilane SAM. Using an anionic polymerization, polystyrene terminated with a trichlorosilane end group was synthesized and deposited onto a silicate substrate surface by Tran and Auroy.\textsuperscript{36} Due to the steric hindrance involved in the “grafting-to” process, films obtained from solution chemisorption are limited to a dry film thicknesses of less than 5 nm. Both the Minko and Luzinov groups\textsuperscript{37,39} grafted carboxylic acid end-group functionalized polymer chains onto 3-glycidoxypropyltrimethoxysilane (GPS) modified silicate surfaces.

2.1.3 Polymer brushes by the “grafting-from” technique

The “grafting-from” technique has been an attractive approach for making dense and robust polymer brushes. It involves \textit{in-situ} polymerization from an initiator-functionalized surface (see Figure 2.5). The functionalized surface can be fabricated by plasma treatment or glow-discharge with the presence of a gas or by bonding small initiator molecules onto a substrate surface. Almost all polymerization techniques have been utilized in making polymer brushes via the
“grafting-from” technique, including conventional free radical polymerization, various controlled free radical polymerizations [atom transfer radical polymerization (ATRP), reverse atom transfer radical polymerization (RATRP), nitroxide-mediated radical polymerization (NMP), reversible addition-fragmentation transfer polymerization (RAFT)], ring-opening metathesis polymerization, anionic polymerization, and cationic polymerization.³

Figure 2.5. Polymer brush by “grafting-from” technique.

Using a cationic polymerization mechanism, Vidal and coworkers⁴⁰,⁴¹ successfully grafted polyisobutylene and poly (isobutylene-co-isoprene) from a silica gel surface containing cationic initiators. The cationic initiator surface was produced by depositing 2-(chloromethylphenyl)ethyl(dimethylchlorosilane onto the silica gel. Tsubokawa’s group⁴² grafted polystyrene brushes via cationic polymerization from a surface bound acylium perchlorate initiator, which was
generated from phthalic anhydride. Jordan and Ulman\textsuperscript{43} utilized the ring-opening
cationic polymerization of 2-ethyl-2-oxazoline from a triflate initiator surface, which
was obtained by reacting the SAM of 11-hydroxyundecanethiolate on gold with a
trifluoromethanesulfonic anhydride vapor. Zhao and Brittain\textsuperscript{44} synthesized
polystyrene brushes from (trichlorosilylphenyl)-2-methoxy-d_3-propane
functionalized silicate substrate surface via cationic polymerization with TiCl\textsubscript{4}
present as catalyst.

Jordan's group\textsuperscript{45} used anionic polymerization to synthesize polystyrene brushes.
The initiator surface was generated \textit{in-situ} by reacting a
4-bromo-4'-mercaptobiphenyl SAM on gold substrate surface with \textit{sec}-butyllithium
to form the initiatiating biphenyllithium monolayer. Utilizing a similar strategy,
Ingall \textit{et al.}\textsuperscript{46} reacted 3-bromopropylsilane with a silicate surface, which was then
lithiated with lithium di-\textit{tert}-butylbiphenyl to produce the initiator monolayer. After
that, acrylonitrile was added to start the anionic polymerization.

Conventional radical polymerization has long been used in making polymer
brushes from surfaces. Laible \textit{et al.}\textsuperscript{47,48} grafted styrene, methyl methacrylate
(MMA) and vinyl acrylamide from an azo free radical initiator bound to a silica gel
surface. In the first step, \textit{p}-nitrophenytrichlorosilane was reacted with silica gel.
Then the nitro groups were reduced to form amine functionalities. After that, the
amine functionality was reacted with sodium nitrite followed by sodium
naphthyl-2-thiol to form the phenyl-diazo-(naphthyl-2)thioether free radical initiator,
which was used to initiate polymerization under standard free radical conditions. Boven et al. 49 first treated glass beads with 3-aminopropyltriethoxysilane to introduce amino functional groups onto the surface. The azo initiators were then immobilized onto the surface through amide bond formation between the modified surface and an acid chloride functionalized azo initiator. From the surface bound azo initiator, a poly(methyl methacrylate) (PMMA) layer was fabricated. Sugawara and Matsuda 50 grafted polystyrene from a poly (vinyl alcohol) film and polyacrylamide from a poly(ethylene terephthalate) PET film. First, polyallylamine, which had been partially derivatized with photoreactive phenylazido, was coated onto substrate thin film surfaces. The aminated polymer was covalent bonded onto the surface from the reactive phenylnitrene generated from UV irradiation. An azo initiator was then immobilized onto the thin film surface via a condensation reaction. Finally, polymerization was initiated from the surface-bound azo free radical initiator to generate polymer layers. Velten and coworkers 51-52 prepared polystyrene layers from a peroxide-functionalized mica surface, which was prepared via ion exchange between 1-(trimethylamino)-6-({\(t\)}-butyldioxy)hexyl bromide and a mica surface. After that, free radical polymerization was conducted from the mica surface. Via photoemulsion polymerization, Ballauff and coworkers 53 successfully prepared spherical polyelectrolyte brushes. Polystyrene emulsion was prepared by conventional emulsion polymerization techniques, followed by a seeded emulsion polymerization using 2-\([p\)-(2-hydroxy -2-methylpropiophenone)]-ethylene
glycol-methacrylate photoinitiator. After that, photoemulsion polymerization of acrylic acid was initiated from emulsion particle surfaces. This “grafting from” process generated polystyrene cores with a shell of poly(acrylic acid) brushes. Tsubokawa\(^54\) grafted polyacrylamide by a redox process from silicate surfaces. The surfaces were treated with propyltrimethoxysilane derivatives that gave hydroxyl, amino and thiol functional surfaces as reducing groups, which were then utilized in combination with ceric ammonium nitrate to initiate radical polymerization. From the same group, polystyrene brushes were prepared from a surface-bound perester radical initiator, which was obtained by reacting a 4-trimethoxysilyl-1,2,5,6-tetrahydrophthalic anhydride functionalized surface with \(\alpha,\alpha\)-dimethyl(4-isopropylbenzyl) hydroperoxide to form the peroxystyler initiator.\(^42\) A similar strategy was also applied to modify the surface of carbon black particles using various monomers. They also reported similar work on the surface of carbon black particles with many different monomers.\(^55\text{-}56\)

Minko and coworkers\(^57\text{-}60\) have reported the results of considerable research on surface-initiated radical polymerization. A macroinitiator from copolymerization of acrylic acid, butyl acrylate, and 5-hydroperoxy-5-methyl-1-hexen-3-yne was physisorbed onto a silicate substrate, followed by initiation of styrene and MMA. They concluded that the propagating surface-initiated radical chains terminate only by reaction with bulk free radicals or chain transfer to solvent or monomer. Rühe and coworkers\(^61\text{-}67\) formed an azo SAM (see Figure 2.6) followed by radical
polymerization from the surface. The initiator SAM contained a cleavable group; thus tethered polymer chains could be degrafted and characterized. Polyelectrolyte brushes have attracted a lot of the attention due to their interesting properties. Using the same Rühe initiator, Biesalski and Rühe\textsuperscript{64, 68} prepared polyelectrolyte brushes by the surface-initiated polymerization of sodium \textit{p}-styrene sulfonate or 4-vinylpyridine. The poly(4-vinylpyridine) brushes were then quaternized with \textit{n}-butylbromide in nitromethane to afford the polyelectrolyte brushes.
Figure 2.6. Schematic description of polymer brush grafted from Rühe’s initiator.61
Rühe's initiators:

![Chemical structure of initiators](image)

R: Me, Cl

Figure 2.6. Schematic description of polymer brush grafted from Rühe’s initiator.\(^{61}\)

(continued)

Controlled radical polymerizations can give better control over molecular weight and molecular weight distribution, compared with conventional radical polymerizations. Controlled radical polymerizations have been utilized extensively in making well-defined polymer brushes. Typical controlled radical polymerization techniques utilized for surface-initiated polymerization include iniferter polymerization, ATRP, NMRP, and RAFT. In the iniferter polymerization technique, an iniferter molecule decomposes into a highly reactive initiating radical and a stable counter radical as a chain transfer agent and terminating agent. de Boer and coworkers\(^{69}\) immobilized a photoinitiator onto silicate substrate surfaces, followed by photoinitiation of various monomers. Huang and Wirth\(^ {70-72}\) reported the surface initiated polymerization of acrylamide by the ATRP method. The ATRP initiator 1-(trichlorosilyl)-2-[\(m/p\)-(chloromethyl)phenyl]ethane was reacted with a substrate
surface. ATRP was conducted using CuCl and 2,2’-bipyridine ligand. Ejaz et al.\textsuperscript{73} grafted MMA from an ATRP initiator functionalized surface. This ATRP initiator functionalized surface was prepared by a Langmuir-Blodgett technique in which 2-(4-chlorosulfonylphenyl) ethyltrimethoxysilane was deposited onto a silicate substrate surface. Either CuCl or CuBr was used as catalyst and 4,4’-di-n-heptyl-2,2’-bipyridine as ligand. For better control over polymerization, the addition of free initiator \( p \)-toluenesulfonyl chloride was necessary. A linear relationship was found between the \( M_n \) of the free polymer and the polymer brush film thickness. Using a similar strategy, Husseman and coworkers\textsuperscript{74} grafted MMA from an ATRP initiator functionalized surface. The ATRP catalyst was bis(triphenylphosphine) nickel(II) bromide. Free initiator, 2-bromo-2-methylpropionate, was added to ensure better control over polymerization. Ohno and coworkers\textsuperscript{75} prepared a PMMA brush from gold nanoparticles, using the sacrificial initiator ethyl 2-bromoisobutyrate. Since the initiator monolayer was fabricated by self-assembly of thiols onto gold nanoparticles, the polymerization reaction was conducted at 40 °C. Rather than using sacrificial free initiator to better control the polymerization, deactivator can also be utilized to control polymerization. Jeyaprakash et al.\textsuperscript{76} grafted polystyrene brushes from a silicate substrate surface by changing the amount of \( \text{[styrene]}_0 / \text{[CuBr]}_0 \) and using CuBr\textsubscript{2} as the deactivator. The deactivator system resulted in a higher film thickness than the corresponding sacrificial free initiator system. However, the use of sacrificial initiator generates
free polymer, which can be fully characterized and has been shown to roughly correspond the molecular weight of the brush and correlates linearly with brush thickness. Baum and Brittain\textsuperscript{77} synthesized PMMA, polystyrene (PS) and poly($N,N$-dimethylacrylamide) (PDMA) brushes using RAFT. Rühe’s azo initiator\textsuperscript{61} was first immobilized onto a silicate substrate surface. The RAFT polymerization was initiated from the azo initiator functionalized surface with the addition of RAFT chain transfer agent 2-phenylprop-2-yl dithiobenzoate and the addition of AIBN (2,2'-azobis isobutyronitrile) free initiator to assist the polymerization. Free polymers generated in the solution were found to correlate well with grafted brush chains. Using the NMRP technique, Devaux \textit{et al.}\textsuperscript{78,79} synthesized polystyrene brushes using a surface-bound TEMPO (2,2,6,6-tetramethyl-1-piperidinyloxy) type NMRP initiator. The TEMPO type NMRP initiator monolayer was fabricated by the initiator with a triethoxysilane anchoring group, using a Langmuir-Blodgett technique. Husseman and coworkers\textsuperscript{74} also studied surface-initiated controlled radical polymerization by NMRP. An initiator monolayer was synthesized by self-assembly. Free initiator was added in order to better control the polymerization process. Without adding free initiator, attempts to control polymer growth failed. This was explained by the fact of the very low initiator concentration relative to monomer concentration. Lowering monomer concentration didn’t help to control the polymerization process since the polymerization rate was still very low at less than 25 % of monomer weight concentration.

21
Harada and coworkers$^{80}$ used ring-opening metathesis polymerization (ROMP) to synthesize polymer brushes from a silicate substrate surface. 7-Octenyltrichlorosilane was self-assembled onto a substrate surface followed by reaction of the terminal double bond with Grubbs’ catalyst to produce the appropriate ROMP surface immobilized catalyst. Juang and coworkers$^{81}$ reported surface initiated polynorbornene brush formation via the ROMP technique. The Ru catalyst functionalized surface was prepared in several steps: first, a hydrogen-terminated silicon surface was chlorinated; second, an alkene functionality was introduced by reacting the chlorinated surface with a Grignard reagent; and third, a Ru catalyst was reacted with the surface-bound vinyl group to produce the surface-bound ROMP catalyst. Polynorbornene brush was then synthesized from the functionalized surface.

Hertler et al.$^{82}$ grafted PMMA brushes from a surface via group transfer polymerization (GTP). Several types of sily ketene acetals were fixed onto chloromethylated divinylbenzene cross-linked PS beads. After that, MMA was polymerized from the surface-bound GTP initiator in the presence of tetrabutylammonium $m$-chlorobenzoate in tetrahydrofuran (THF) to produce PMMA brushes.

2.1.4 Mixed polymer brushes

Polymer brushes have been widely used for smart, responsive materials due to
their capability of undergoing large conformational changes in response to small external field perturbations.\textsuperscript{83} Mixed polymer brushes, consisting of diblock or triblock copolymer brushes, Y-shaped diblock copolymer brushes and mixed homopolymer brushes, have attracted attention since they could amplify the adaptive nature by combining both conformational changes and microscopic phase separation. Macroscopic phase separation was suppressed due to the tethering of one chain end to the surface. Thus, mixed polymer brushes were able to self-assemble into a rich variety of patterns on the nanoscale by tuning parameters such as composition, molecular weight, grafting density, solvent quality and temperature.

2.1.4.1 Linear block copolymer brushes

Using different living polymerization techniques, linear diblock and triblock copolymer brushes have been prepared and reported extensively. Zhao and Brittain\textsuperscript{14, 44, 84} combined cationic polymerization and atom transfer radical polymerization to generate PS-\textit{b}-PMMA diblock copolymer brushes from silicate substrates. The synthesis scheme is illustrated in Figure 2.7. A cationic initiator with a trichlorosilane anchoring group was self-assembled onto a silicate substrate surface. After that, cationic polymerization of styrene was initiated from the surface. ATR-FTIR study found that the initiation efficiency from the initiator-bound surface was only about 7%. This was followed by ATRP of MMA. The structures of the PS-\textit{b}-PMMA diblock copolymer brushes were confirmed using ellipsometry, x-ray
photoelectron spectroscopy (XPS), FT-IR and water contact angle measurements. However, the initiation efficiency of the second PMMA block was unknown. It’s highly possible that the brushes were a mixture of tethered PS homopolymer and PS-\textit{b}-PMMA diblock copolymer brushes. The diblock copolymer brushes showed “smart”, self-adapting behavior to environment changes and self-assembled into different nano-morphologies. After treatment with methylene chloride, which is a nonselective solvent (good solvent for both blocks), the surface was enriched with PMMA. When subjected to cyclohexane which is a selective solvent at 35 °C (good solvent for PS and poor solvent for PMMA), PMMA migrated to the inner core of the polymer micelles and PS would form the shell of the micelles (see Figure 2.8 a); an AFM study found that slowing tuning the solvent quality from nonselective to selective (PS favored), the surface nano-morphology would change slowly from smooth to regular micellar arrays (figure 2.8 b).
Figure 2.7. Synthesis of tethered PS-\textit{b}-PMMA on silicate surface.\textsuperscript{14}
Figure 2.7. Synthesis of tethered PS-b-PMMA on silicate surface.14 (continued)
Figure 2.8. Micelle formation from tethered PS-\textit{b}-PMMA and AFM image

(a) Scheme of the micelles from tethered PS-\textit{b}-PMMA; (b) AFM image

of the tethered PS-\textit{b}-PMMA brushes with 23 nm thick PS layer and 14 nm

thick PMMA layer after selective solvent treatment.\textsuperscript{84}
Sedjo et al.\textsuperscript{15} tethered diblock copolymer brushes from substrate surfaces by reverse atom transfer radical polymerization (RATRP). From a surface-bound azo free radical initiator, the first PS block was synthesized by RATRP using CuBr\textsubscript{2} and the PMEDTA ligand. The second PMMA block was prepared via ATRP using the first block as a surface tethered macroinitiator. The tethered PS-b-PMMA diblock copolymer brushes exhibited reversible water contact angle changes in response to different solvent treatments.

Boyes et al.\textsuperscript{85} prepared ABA triblock copolymers from a silicate substrate surface via ATRP. First a bromoisobutyrate initiator bearing a trichlorosilane anchoring group was self-assembled onto a silicate substrate surface. After that, PS-b-PMA-b-PS and PMA-b-PS-b-PMA triblock copolymer brushes were prepared, respectively, via sequential monomer addition. The surface properties and nanomorphological changes upon different solvent treatments for each ABA type brush were characterized by ellipsometry, tensiometry, ATR-FTIR, and AFM.

2.1.4.2 Y-shaped polymer brushes

Y-shaped diblock copolymer brushes refer to the structure shown in Figure 2.9 with two different homopolymer chains linked together to a short stem on the substrate surfaces. The very short tethering stem can be regarded as a tethering point. Therefore, the Y-shaped diblock copolymer brushes can be deemed as a special case of binary mixed
homopolymer brushes, for which there are always two different blocks tethered at the same point.

Figure 2.9. Y-shaped diblock copolymer brushes.

Zhulina and Balazs\textsuperscript{11} theoretically predicted that Y-shaped AB copolymers grafted onto a flat surface should give rise to a rich variety of well-defined lateral nanostructures and novel patterns. At low grafting density, in poor solvents, pinned micelles might form. The pinned micelles could be mixed micelles, internally segregated micelles, or split micelles depending on the interaction parameter between
the two blocks (see Figure 2.10). While at higher grafting density, laterally microsegregated brushes were predicted (see Figure 2.11).

Figure 2.10. Pinned micelles formed by Y-shaped block copolymer: (a) mixed micelles; (b) internally segregated micelles; (c) split micelles.\textsuperscript{11}
Figure 2.11. Laterally microsegregated brush formed by Y-shaped block copolymers.\textsuperscript{11}

However, there have only been a few experimental reports on Y-shaped AB diblock copolymer films primarily because they offer a greater synthetic challenge. Long \textit{et al.}\textsuperscript{86} grafted central functionalized asymmetric triblock copolymers to a surface by chemical bond formation between the short central functionalized block and the substrate (see Figure 2.12). One disadvantage was the dispersity of the anchoring mid-block. Tsukruk and co-workers\textsuperscript{24} observed switchable surface nanopatterns by grafting Y-shaped molecules onto a glycidol propyl triethoxysilane
functionalized silicate substrate (see Figure 2.13). Direct, in-fluid observation of the surface morphology, nanomechanical and microtribological properties of the Y-shaped binary brushes were performed in different solvents.\textsuperscript{87}

Figure 2.12. Synthesis of Y-shaped diblock copolymer thin film by Long \textit{et al.}\textsuperscript{86}
Figure 2.12. Synthesis of Y-shaped diblock copolymer thin film by Long et al.\textsuperscript{86}

(continued)
Figure 2.13. Synthesis of Y-shaped diblock copolymer thin film by Tsukruk et al.\textsuperscript{24}
We devised a synthetically simple approach to produce a Y-shaped AB diblock copolymer brush. The terminal double bond of a SAM of 8-trichlorosilyloctene (OTS) was reacted under hydrosilation conditions with polystyrene-\(b\)-poly(2-vinylpyridine) (PS-\(b\)-P2VP) that contained a methylhydridosilane (SiMeH) group. We observed changes in surface properties upon treatment with block-selective solvents. To further decrease the miscibility of the two arms, the film was treated with methyl iodide to form quaternary ammonium groups on the P2VP block. After quaternization, the surface properties and morphologies under selective solvent treatments were also studied.

2.1.4.3 Binary mixed homopolymer brushes

Both theoretical and experimental work indicated that symmetric binary mixed homopolymer brushes would be able to undergo a solvent-induced transition between lateral and perpendicular microphase separation (see Figure 2.14). Selective solvents will favor one component at the top layer and the unfavored block will form clusters segregated near the bottom. This is called a “dimple-like” morphology. While in nonselective solvents, lateral microphase separation might occur and a “ripple-like” structure might result. However, an increase in chain length asymmetry or component incompatibility will lead to perpendicular rather than lateral microphase separation in nonselective solvents.$^{83}$
There have only been a few experimental reports on binary mixed homopolymer brushes primarily because of the synthetic challenges in producing well-defined brushes. “Grafting-to” was reported by Minko and coworkers in making binary mixed homopolymer brushes. Carboxylic acid end group functionalized PS and P2VP homopolymers were grafted onto a glycidol propyl triethoxysilane (GPS) functionalized surface. The glycidol propyl triethoxysilane functionalized surface provided a high concentration of many different types of functionalities for grafting.
The PS had to be grafted first followed by P2VP grafting. If the grafting sequence was reversed, the PS chains could not be grafted. This is explained by the fact that P2VP possesses a strong specific interaction with substrate surface. If P2VP is grafted first, it will occupy all the grafting sites and then PS will not able to penetrate and be grafted. However, if P2VP is grafted in the second step, the strong specific interaction between P2VP and the substrate surface provides a driving force for the grafting process to happen. The disadvantage of this work lies in the low brush thickness and low grafting density, which are typical of the “grafting-to” process.

Figure 2.15. “Grafting-to” technique in making binary mixed homopolymer brushes.

PS chains, dark; P2VP chains, gray. The GPS grafted layer offers many different functionalities.88
Figure 2.15. “Grafting-to” technique in making binary mixed homopolymer brushes.

PS chains, dark; P2VP chains, gray. The GPS grafted layer offers many different functionalities.88 (continued)

“Grafting-from” was also utilized in making binary mixed homopolymer brushes and it was preferred due to the high grafting density, brush thickness and stability.
Most of the synthetic “grafting-from” approaches involved conventional free radical polymerizations from a surface-bound azo initiator monolayer. One type of homopolymer was synthesized first. Then the second homopolymer was prepared from residual surface-immobilized azo initiator. This approach was illustrated in Figure 2.16. Characteristic of the conventional radical polymerization method, molecular weight and molecular weight distribution can’t be well controlled.\textsuperscript{83}

![Diagram](image)

Figure 2.16. “Grafting-from” technique in making binary mixed homopolymer brushes.\textsuperscript{83}
In order to fabricate well-defined binary mixed homopolymer brushes, controlled radical polymerization techniques, ATRP and NMRP, were performed sequentially from a binary mixed initiator monolayer\textsuperscript{89,90} or from a Y-shaped difunctional initiator monolayer.\textsuperscript{91,92} Fukuda and coworkers\textsuperscript{89} reported controlled radical polymerizations in making binary mixed homopolymer brushes. ATRP and nitroxide triethoxysilane initiators were coadsorbed onto a silicate surface along with an inactive species \textit{n}-hexyl triethoxysilane which was used in order to control the grafting density. ATRP of MMA was conducted at 60 °C followed by NMRP of styrene at an elevated temperature. The reaction scheme is illustrated in Figure 2.17. A similar strategy was reported by Zhao:\textsuperscript{90} the corresponding trichlorosilane ATRP initiator and nitroxide initiator were cofixed onto a substrate surface to make a binary initiator surface. ATRP of MMA was conducted first followed by NMRP of styrene at an elevated temperature. The synthesis scheme utilized by Zhao is illustrated in Figure 2.18.

![Silicon Wafer](image)

Figure 2.17. Fukuda \textit{et al.}'s\textsuperscript{89} approach in making binary mixed homopolymer brushes using a binary mixed initiator monolayer.
Figure 2.17. Fukuda et al.’s approach in making binary mixed homopolymer brushes using a binary mixed initiator monolayer. (continued)
Figure 2.18. Zhao’s approach in making binary mixed homopolymer brushes using a binary mixed initiator monolayer.
Figure 2.18. Zhao’s\textsuperscript{90} approach in making binary mixed homopolymer brushes using a binary mixed initiator monolayer. (continued)

To ensure molecular-level mixing of the two types of initiators in the initiator monolayer, a Y-SAM was devised by Zhao and coworkers\textsuperscript{91,92} (see Figure 2.19). ATRP of MMA was conducted first at 75 °C, followed by dehalogenation by tributyltin hydride to eliminate the possibility of bromine end group caused chain transfer reaction in the next step. Finally NMRP of styrene was performed at an elevated temperature.
Figure 2.19. Zhao’s\textsuperscript{91} approach in making binary mixed homopolymer brushes using a Y-SAM.
Sogah and coworkers\textsuperscript{93} performed a simultaneous one-pot, one-step diblock copolymerization by combining NMRP of styrene and living cationic ring-opening polymerization (CROP) of 2-phenyl-2-oxazoline (PhOXA). The one pot block copolymerization can be achieved for several reasons: first, the two types of polymerization mechanisms are compatible with each other; second, there is no
crossover propagation in the two types of polymerizations; third, the two types of polymerizations are conducted under similar reaction conditions. The reaction scheme is illustrated in Figure 2.20.

Figure 2.20. One-pot, one-step simultaneous diblock copolymerization via NMRP and living CROP.93
Enlightened by Fukuda, Bin Zhao and Sogah et al.’s work, we developed a synthetically simple approach for the one pot preparation of binary mixed homopolymer brushes by combining simultaneous NMRP and living CROP. The binary mixed homopolymer brushes were studied by ATR-FTIR, tensiometry, ellipsometry, XPS and AFM.
2.2 Initiator monolayer fabrication

As mentioned before, “grafting-from” involves in-situ polymerization from an initiator-bound surface. The initiator-bound surface can be fabricated in many ways, for example, adsorption from a Langmuir-Blodgette technique and self-assembly. Self-assembly includes organosilanes on a silicate substrate surface,\textsuperscript{94} thiols on gold,\textsuperscript{95-103} acids on alumina,\textsuperscript{104-106} alcohols and amines on platinum.\textsuperscript{94} Among those, organosilane-derived monolayers are probably the most widely used.

Self-assembly utilizes molecules with the following characteristics: the molecules have reactive head anchoring groups which will react with the substrate surfaces and this reaction between the anchoring groups and substrate surfaces provides the driving force for the self-assembly process; the molecules also contain long alkyl spacers to ensure close and orderly packing in the self-assembly; terminal topmost functional groups are the initiating moieties in the self-assembled initiator monolayer.

The initiator monolayer can be fabricated in many ways, of which self-assembly of trichlorosilanes on silicate substrate surfaces is widely used. However, McCarthy and Fadeev\textsuperscript{107} reported that self-assembly is not the only reaction possible between trichlorosilanes and surfaces. There are other possibilities such as vertical polymerization and covalent attachment (see Figure 2.21). Thus uniformity is always going to be an issue when using multifunctional silanes. Monochlorosilanes
are a better choice in terms of making more uniform initiator monolayers. However, they are still moisture-sensitive and hard to purify.

Figure 2.21. Possible reactions between chlorosilanes and silicate substrates.107
Shimada and coworkers\textsuperscript{108} reported the functionalization of silica gel with allylsilanes, which are stable toward hydrolysis and can be purified by silica gel chromatography. The authors suggested that the reaction proceeds as a protodesilylation of allylic silanes; a $\beta$-silyl cation intermediate is formed by the protonation of the allyl group with silanol on the silica surface and undergoes nucleophilic attack by the silanol oxygen leaving propene. In order to obtain a uniform initiator monolayer in our research, an allylsilane was used to functionalize the flat silicate substrate in this research. Using AFM, the initiator monolayer was found to be more uniform than the corresponding trichlorosilane functionalized one. ATRP was used to prepare polymer brushes because it can provide good control over brush thickness and polydispersity.

2.3 Atom transfer radical polymerization

Controlled radical polymerizations, including ATRP, NMRP and RAFT, have been an active research topic during the last decade. Living polymerization techniques have played an important role in macromolecular engineering to synthesize well-defined polymers with precise control over molecular weight, molecular weight distribution, and molecular architecture. Compared with living ionic (anionic and cationic) polymerization techniques, controlled radical polymerization requires less stringent reaction conditions and can polymerize a greater variety of monomers because the controlled radical polymerization techniques
are more tolerant of polar functional groups. Controlled radical polymerizations are possible through a reversible activation/deactivation equilibrium between dormant and active species. The general mechanism is illustrated in Figure 2.22. The exchange between the active and dormant species allows slow but simultaneous growth of all chains. The concentration of active species is kept low enough to minimize the termination process which is a second order reaction of radicals, while the rate of propagation is first order based on radical concentration. For both NMRP and ATRP, the persistent radical effect (PRE) must be considered. PRE helps establishing the reversible activation/deactivation equilibrium with rate of deactivation much larger than the rate of activation. Stable radicals, such as nitroxide radicals in NMRP, or metalloradicals [e.g. X-Cu(II) species] in ATRP are generated together with reactive alkyl radicals. The reactive alkyl radicals can undergo both homocoupling and cross-coupling, while the unreactive stable radicals can only undergo cross-coupling with reactive alkyl radicals. Thus the concentration of stable radicals will predominate over reactive alkyl radical. Then the kinetic effect takes place. The cross-coupling between stable radicals and alkyl radicals becomes much faster than the homocoupling of alkyl radicals due to the predominance of stable free radicals. Thus, the rate of deactivation is much faster than the rate of activation. Also most of the chain ends are kept “alive” by the cross-coupling since the chain ends can be reversibly activated and deactivated.
Cross-coupling is a reversible reaction, unlike the homocoupling between alkyl radicals.

$$
P \xrightarrow{K_{act}} X \xleftarrow{K_{deact}} P^* \xrightarrow{k_p} +M$$

(Dormant)  (Active)

Figure 2.22. General mechanism of controlled radical polymerization.109

The general mechanism of ATRP is depicted in Figure 2.23.110 Radicals are generated through a reversible redox process catalyzed by a transition metal complex. Radicals react reversibly with the oxidized metal complexes (deactivator) to reform the dormant species and the original metal complex (activator). Polymer chains grow by the addition of monomer to the free radicals in the activation cycle, meanwhile some degree of termination also occurs although the concentration of reactive alkyl radicals is kept low due to the PRE. A number of monomers such as styrenes, (meth)acrylates, (meth)acrylamides, and acrylonitrile have been successfully polymerized via ATRP. Alkyl halides are typical ATRP initiators and the rate of polymerization is first order with respect to the initiator concentration. The ATRP catalyst plays a key role in determining the position of the dynamic ATRP equilibrium. To be an ATRP catalyst, the metal must have at least two oxidation states separated by one electron. In addition, the metal center should have reasonable affinity toward the halogen, the co-ordination sphere around the metal should be expandable upon
oxidation to selectively accommodate the (pseudo)halogen, and the ligand molecules should strongly complex with the metal. ATRP can be carried out either in bulk, in solution, or in a heterogeneous system such as emulsion or suspension.\textsuperscript{110}

\[ \text{R} \rightleftharpoons \text{X} + \text{M}^n_t \rightleftharpoons \text{Y / Ligand} \]

\[ K_{\text{deact}} \quad K_{\text{act}} \]

\[ \text{R} \quad + \quad \text{X} \rightleftharpoons \text{M}^{n+1}_t \rightleftharpoons \text{Y / Ligand} \]

\[ k_p \quad k_t \]

\text{monomer} \quad \text{termination}

Figure 2.23. General mechanism of ATRP.\textsuperscript{110}

2.4 Nitroxide-mediated radical polymerization

Both ATRP and NMRP proceed with reversible termination, while RAFT proceeds with reversible chain transfer. The basic mechanism and the PRE of NMRP have been introduced in section 2.3. The cyclic nitroxide radical 2,2,6,6-tetramethyl-1-piperidinoxy (TEMPO) has been extensively studied and primarily used for styrene controlled radical polymerization. NMRP can be initiated by either a bimolecular process or a unimolecular process.
The bimolecular process utilizes a mixture of conventional radical initiator (such as AIBN (2, 2’-azobis(2-methylpropionitrile)) and BPO (benzoyl peroxide)) and a stable nitroxide radical. Georges and coworkers\textsuperscript{111} reported NMRP using this methodology for PS block copolymers with low polydispersity (PDI = 1.20). The reaction scheme for making low PDI PS is illustrated in Figure 2.22. The polymerization was conducted at 130 ºC in bulk with BPO and TEMPO radical in the molar ratio of 1.3 to 1.
The unimolecular initiation process involves the thermal decomposition of an alkoxyamine compound such as 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine.
into a reactive alkyl radical and a stable TEMPO radical. Figure 2.25 is one example of this unimolecular process.

Figure 2.25. Unimolecular process in NMRP.\textsuperscript{112}
Compared with ATRP, NMRP with TEMPO radical requires higher reaction temperatures (125 – 145 °C) and longer reaction times (1-3 days), and the monomers are limited to styrene and 4-vinylpyridine. Adding a slowly decomposing conventional free initiator or acylating agents to reduce the nitroxide radical concentration helps improve the control over NMRP. New nitroxide stable radicals other than TEMPO radical have been devised. Figure 2.26 shows two examples of new nitroxide radicals.
2.5 Cationic ring-opening polymerization of 2-oxazolines

The polymerization of 2-oxazolines has been widely studied since the 1960s. 2-Substituted 2-oxazoline polymerizations are the most extensively reported.\textsuperscript{114-122} Unsubstituted 2-oxazoline polymerization produces crystalline poly(N-formylethylenimine) which is insoluble in common organic solvents but soluble in water. A lot of research work has been done on mechanistic studies of cationic 2-oxazoline polymerizations. It has been reported that cationic 2-oxazoline polymerizations proceed via two different types of propagating species, either ionic or covalent, depending on the ring size, substituents, and initiator types. Here unsubstituted 2-oxazoline polymerizations using different initiator types are utilized to illustrate the two different types of polymerizations (see Figure 2.27). When the polymerization is initiated by methyl tosylate, the chain will propagate via an ionic species. However, if the polymerization is initiated by methyl iodide, the propagating species
is covalent. In this case, the ring of the generated oxazolinium salt is rapidly opened by the attack of the iodide counteranion.\textsuperscript{124-132}

![Chemical structure](image)

Figure 2.27. Two types of cationic ring opening polymerizations of 2-oxazoline.\textsuperscript{133}
CHAPTER III

EXPERIMENTAL

3.1 Y-shaped diblock copolymer thin film preparation

3.1.1 Materials

ATR crystals (25×5×1 mm) were purchased from Harrick Scientific. Silicon wafers were obtained from The Polishing Corporation of America. 7-Octenyltrichlorosilane (OTS, 95%) was purchased from Gelest, Inc. and distilled prior to use. Anhydrous toluene (99.8%), dichloromethane (ACS grade), absolute ethanol and iodomethane (99%) were obtained from Aldrich and were used as received. Styrene (99%) and 2-vinylpyridine (97%) were purchased from Aldrich and purified by distillation under vacuum after removal of inhibitor by passing through basic alumina column. The PS-\(b\)-P2VP diblock copolymers containing a methylhydridosilane group (Figure 3.1) were obtained from two sources. PS-\(b\)-P2VP (1) was purchased from Polymer Source, Inc.; for the PS block, \(M_n=23,100\) g/mol and \(M_w/ M_n =1.06\); for the P2VP block, \(M_n =20,000\) g/mol and \(M_w/ M_n =1.07\); for the PS-\(b\)-P2VP, \(M_n =47,000\) g/mol and \(M_w/ M_n =1.06\). The other PS-\(b\)-P2VP (2) was synthesized anionically; for the PS block, \(M_n=5,400\) g/mol and \(M_w/ M_n =1.06\); for the P2VP block, \(M_n =5,300\) g/mol and \(M_w/ M_n =1.05\); for the PS-\(b\)-P2VP, \(M_n =11,000\) g/mol and \(M_w/ M_n =1.07\).
3.1.2 Characterization methods

Film thicknesses were determined by ellipsometry using a Gaertner model L116C ellipsometer. The light source was a He-Ne laser ($\lambda=632.8$ nm) at a fixed incident angle of 70°. Refractive indices of $n = 1.455^{134}$ (for silicon oxide), $n = 1.589^{135}$ (for PS) and $n = 1.595^{136}$ (for P2VP) were used. For the PS-$b$-P2VP copolymer, a weight average of the refractive indexes was used. Water contact angles were determined using a Ramé Hart NRL-100 goniometer with a controlled environment chamber and a tilting base mounted on a vibrationless table. The relative humidity in the chamber was maintained by adding two drops of water in the wells of the chamber. Advancing and receding angles were determined using the tilting stage method. ATR-FTIR spectra were obtained using a Nicolet System 730 spectrometer with a modified 4XF beam condenser (Harrick Scientific). A total of five hundred scans
was collected and spectral resolution was 2 cm$^{-1}$. To study surface topography, AFM studies were made at ambient conditions on a multimode scanning probe microscope (Digital Instruments) in the tapping mode with a silicon tip (Multi-75) that was purchased from NanoDevices, Inc. Tapping mode AFM was performed in order to minimize the damage to the samples. Using a standard grid, the scanner was calibrated in both lateral and vertical directions.

3.1.3 Preparation of OTS-SAM

Silicon wafers were cut into 3 cm × 1 cm strips. ATR crystals and silicon pieces were cleaned using a ‘piranha’ solution (70/30, v/v, concentrated H$_2$SO$_4$/30% H$_2$O$_2$). It should be noted that the “piranha” solution is extremely reactive and should be handled with care. After heating at 90°C for 1 h, the samples were cooled to room temperature and immediately rinsed with distilled water repeatedly. The cleaned silicate substrates were dried by a stream of air, followed by characterization using ATR-FTIR and ellipsometry. The samples were stored for no longer than 30 min before use.

The ATR crystal and silicon wafer samples were placed into a dried round-bottom flask that was flushed with nitrogen for 15 min. A 20 mL solution of 1mM OTS in anhydrous toluene was added to the flask via syringe. The flask was heated at 60 °C for 4 h; after removal from the deposition solution, the substrates were rinsed in 15 mL of methylene chloride, followed by ethanol washing and drying.
in a stream of air. The samples were characterized by water contact angles, ellipsometry and ATR-FTIR.

3.1.4 Control experiment

Before using the PS-\textit{b}-P2VP diblock copolymer and to test the viability of the surface confined hydrosilation reaction, triocetylsilane (TOS) was reacted with the terminal double bonds in an OTS-SAM in anhydrous toluene using the Speier’s catalyst at 80 °C for 10 h. The reaction scheme of the control experiment is shown in Figure 3.2.

![TOS reaction scheme](image)

**Figure 3.2.** Control experiment on surface-confined hydrosilation reaction.
Figure 3.2. Control experiment on surface-confined hydrosilation reaction.

(continued)
3.1.5 Synthesis of PS-b-P2VP diblock copolymer

The PS-b-P2VP (2) diblock copolymer was prepared anionically involving the following steps: (i) synthesis of end-functionalized polystyrene I, (ii) synthesis of poly(2-vinylpyridine) lithium II, (iii) synthesis of PS-b-P2VP III. The three-step reaction process was illustrated schematically in Figure 3.3

Synthesis of end-functionalized polystyrene I. Styrene (11.0 mL, 10.0 g) was polymerized under vacuum-line conditions with sec-butyllithium (2.0 mmol) as the initiator in benzene (100 mL) at room temperature. The reaction was allowed to proceed for 18 h. Then excess diphenylethylene (0.50 mL, 2.8 mmol) was added using vacuum-line techniques, and then the reaction was allowed to proceed for 4 h to complete the “capping”. After the “capping”, excess dichloro(methyl)silane (0.90 mL, 8.6 mmol) was added to terminate the reaction. Then the reactor was reconnected onto the vacuum line to remove the remaining dichloro(methyl)silane in vacuo. After that, 100 mL of THF was distilled into the reactor to form a homogeneous solution. Based on SEC data of polymer I (a small portion was taken out and terminated by methanol for characterization), the dimer content was less than 1%, and the number average molecular weight was 5.4 kg/mol (PDI was 1.06).

Synthesis of poly(2-vinylpyridine)lithium II. 2-vinylpyridine (11.2 mL, 10.5 g) was polymerized under vacuum-line conditions with n-butyllithium (2.1 mmol) as the initiator in THF (50 mL) at -78 °C. The reaction was allowed to proceed for 3 h. Based on SEC data of polymer II (a small portion was taken out and terminated by
methanol for characterization), the number average molecular weight was 5.3 kg/mol (PDI was 1.05).

*Synthesis of PS-b-P2VP III.* The THF solution of II (dark red) was used to titrate the THF solution of I (colorless) at -78 °C, until a steady light red color persisted in solution. Then the solution was treated with 1.0 mL of methanol. After that, the polymer solution (200 mL) was added to hexane (5-fold volume, 1000 mL) dropwise to effect precipitation of the polymer. Based on SEC data of polymer III, the content of polymer I and II was very small (less than 5%) and the number average molecular weight was around 11.0 kg/mol (PDI was 1.07).

![Figure 3.3. Synthesis of PS-b-P2VP diblock copolymer.](image)
Figure 3.3. Synthesis of PS-\textit{b}-P2VP diblock copolymer. (continued)
Figure 3.3. Synthesis of PS-\textit{b}-P2VP diblock copolymer. (continued)
3.1.6 Preparation of Y-shaped diblock copolymer thin film

An OTS-SAM modified ATR crystal and a silicon wafer were placed into an oven-dried, two-necked, 50-mL flask equipped with a reflux condenser fitted a calcium chloride drying tube. The other neck of the two-necked flask was sealed with a rubber septum. The flask was purged with nitrogen gas for 15 min using a needle through the rubber septum. To 0.5 g of PS-\(b\)-P2VP in 15 mL of anhydrous toluene, 0.5 mL of 5% hydrogen hexachloroplatinate hydrate in anhydrous 2-propanol (or in anhydrous THF) was added. The hydrosilylation reaction was allowed to proceed at 80°C for 24 h, after which the ATR crystal and silicon wafer were removed and rinsed with THF. To remove physisorbed free polymer chains, the ATR crystal and silicon wafer were exhaustively extracted with THF in a Soxhlet extractor for 48 h followed by repeated sonication in THF until there was no appreciable thickness change as deduced by ellipsometry. Samples were characterized by water contact angles and ATR-FTIR. The silicate substrate was subjected to different selective solvent treatments and surface morphologies were studied by AFM.

3.1.7 Solvent treatments of unquaternized Y-shaped thin film

The sample was immersed in THF (a good solvent for both blocks) at room temperature overnight. After drying with a stream of clean air, the sample was characterized by AFM and contact angles. The sample was immersed again in THF overnight to recover its original state. Half of the solvent in the vial was replaced by
cyclohexane (which is a selective solvent for PS) each time. This process was repeated until the composition of the THF/cyclohexane mixture was 95/5 (v/v) cyclohexane/THF. For each step, the sample was heated in the new solvent mixture at 40°C for 30 min. After each compositional change, AFM and contact angle measurements were performed after drying by a stream of air.

In a second set of experiments, the sample was immersed in THF overnight to recover the original state. The same procedure was then repeated as described above but used 2-propanol was added (which is a selective solvent for P2VP) until the solvent composition was 95/5 (v/v) isopropanol/THF. For each step in solvent mixture composition, the sample was treated at room temperature for 30 min. AFM and contact angle measurements were again performed.

3.1.8 Quaternization of P2VP block in the Y-shaped thin film

The diblock copolymer modified ATR crystal and silicon wafer were put into a scintillation vial. Ethyl methyl ketone (15 mL) and excess CH₃I (5 mL) were added to the vial. The reaction was allowed to proceed for 5 days at room temperature followed by Soxhlet extraction with heptane for 48 h and sonicication in toluene. Contact angles, ATR-FTIR and ellipsometry measurements were performed. The quaternized substrate was treated with block-selective solvents and studied by AFM.
3.1.9 Solvent treatments of quaternized Y-shaped thin film

The sample was immersed in water overnight. After drying with a stream of clean air, it was characterized by AFM and contact angles. The sample was placed in cyclohexane at 40 °C overnight. AFM and contact angle measurements were performed after drying.

3.2 Polymer brush grafted from an allylsilane-functionalized surface

3.2.1 Materials

10-Undecen-1-ol, 2-bromoisobutryl bromide, t-butylidimethylsilyl chloride, imidazole, allylmagnesium bromide $N,N,N',N''$-pentamethyldiethylenetriamine (PMDETA, 99%), ethyl 2-bromoisobutyrate (98%), anhydrous anisole and anhydrous dimethylformamide (DMF) were obtained from Aldrich and used as received. Chlorodimethylsilane and trichlorosilane were from Gelest. Styrene (Aldrich) was passed through a column of activated basic alumina. Silicon ATR crystals were obtained from Harrick Scientific. Silicon wafers were purchased from Polishing Corporation of America. All other reagents were purchased from Aldrich. Cuprous bromide (CuBr) (Aldrich, 98%) was purified as described in the literature. Slightly greenish CuBr (15 g) was mixed with just enough 1N sulfuric acid to make a paste, to which 500 mL of 1N sulfurous acid was added. The mixture was stirred for about half an hour and filtered through a sintered glass filter funnel while making sure that there was always a layer of liquid covering the CuBr salt in the funnel.
Then the CuBr salt was washed four times with 25 mL of glacial acetic acid, followed by 3×30 mL of absolute ethanol and 6×15 mL of anhydrous diethyl ether. After that, the diethyl ether was removed by water pump suction for about 30 s. Finally the purified CuBr salt was transferred into a clean and oven-dried round bottom flask, which was then connected to the vacuum line overnight.

3.2.2 Characterization methods

Film thicknesses were determined by ellipsometry using a Gaertner model L116C ellipsometer as described before. For the initiator monolayer, the refractive index was taken as $n = 1.42-1.44$. Altering this value by 0.05 resulted in less than a 1-Å change in the calculated thickness of the monolayer. For the polystyrene layers, $n=1.589$. Water contact angles were determined using a Ramé Hart NRL-100 goniometer with a controlled environment chamber and a tilting base mounted on a vibrationless table as introduced before. ATR-FTIR spectra were obtained using a Nicolet System 730 spectrometer with a modified 4XF beam condenser (Harrick Scientific). To study surface topography, AFM studies were made at ambient conditions on a multimode scanning probe microscope (Digital Instruments) in the tapping mode with a silicon tip (Multi-75) that was purchased from NanoDevices, Inc. The molecular weights of free soluble polymers were measured in THF by gel permeation chromatography (GPC) using a Waters 501 pump, Waters HR4 and HR2
styrigel columns, a Waters 410 differential refractometer and a Viscotek 760A dual light scattering and viscosity detector.

3.2.3 Control experiment

To test if allylsilane could be deposited onto a flat silicate substrate surface or not, before starting this project, allyltriisopropylsilane purchased from Aldrich was reacted with the silanol groups on flat silicate substrate surfaces by heating under reflux in toluene for 15 h. The reaction scheme is shown in Figure 3.4.

![Reaction Scheme](image)

Figure 3.4. Control experiment for allylsilane deposition
3.2.4 Initiator monolayer preparation from allylsilane

Initiator monolayer preparation involves the following steps: (i) reaction of 10-undecenyl alcohol and t-butyldimethylsilyl chloride to give the protected product undec-10-enyl t-butyldimethylsilyl ether (1); (ii) hydrosilation reaction of (1) with chlorodimethylsilane to afford 1-(t-butyldimethoxysiloxy)-11-(chlorodimethylsilyl) undecane (2); (iii) Grignard reaction of (2) with allylmagnesium bromide to produce the allylsilane 1-(allyldimethylsilyl)-11-(t-butyldimethoxysiloxy) undecane (3); (iv) deposition of the prepared allylsilane onto a silicate surface to afford (4); (v) deprotection of the t-butyldimethylsilyl group in the organic monolayer on the silicate substrate to give a hydroxyl group terminated monolayer (5); and (vi) reaction of terminal hydroxyl groups with bromoisobutyryl bromide to prepare the ATRP initiator monolayer (6). The six-step immobilization process is illustrated schematically in Figure 3.5.

\textit{Undec-10-enyl t-butyldimethylsilyl ether (1).} Undec-10-enyl t-butyldimethylsilyl ether (1) (6.40 g; 90% yield) was prepared according to the procedure of Keinan and co-workers.\textsuperscript{138}

\textit{1-(t-Butyldimethoxysiloxy)-11-(chlorodimethylsilyl)undecane (2).} To a solution of 3.2 g (11.25 mmol) of (1) in 15 mL of anhydrous toluene were added 2.5 mL (22.5 mmol) chlorodimethylsilane and 1 mL of an 2-propanol solution of chloroplatinic acid, H\textsubscript{2}PtCl\textsubscript{6} (5 mg). The mixture was heated at 80 °C for 5 h. The solution was then filtered through a short column of silica gel to remove the catalyst. The excess
trichlorosilane and toluene were removed under reduced pressure. The product (2) (4.2 g) was used without further purification. $^1$H NMR (300 MHz) in CDCl$_3$, $\delta$ (ppm): 3.64 (t, 2H), 1.48 (m, 2H), 1.30 (br s, 18H), 0.98 (s, 9H), 0.40 (s, 6H), 0.08 (s, 6H); $^{13}$C NMR (75.5 MHz) in CDCl$_3$, $\delta$ (ppm): 63.45, 33.70, 32.87, 29.88, 29.61, 26.18, 22.89, 19.22, 16.60, 14.30, 0.60, -5.09.

1-(Allyldimethylsilanyl)-11-(t-butyldimethylsilanyloxy)undecane (3). Into a dry 250-mL two-necked flask equipped with a dropping funnel, a stirring bar, and a condenser to which was attached a guard-tube filled with anhydrous calcium chloride, was added 12 mL of 1 mol/L diethyl ether solution of allylmagnesium bromide. (2) (4.2 g; 11 mmol) in 20 mL dry diethyl ether was added drop-wise to the flask. The addition is complete after 30 min followed by heating at reflux for 2 h. After cooling, 40 mL of water was added slowly into the reaction flask followed separation of the layers and two additional ether (2×30 mL) extractions. The combined ether extracts were dried over anhydrous magnesium sulfate. The ether was removed on a rotary evaporator and the product was purified by silica gel column chromatography (hexanes/ethyl acetate 3:1, v/v) to give 4.0 g of (3). $^1$H NMR (300 MHz) in CDCl$_3$, $\delta$ (ppm): 5.80 (m, 1H), 4.84 (m, 2H), 3.61 (t, 2H), 1.52 (m, 2H), 1.28 (br s, 16H), 0.91 (s, 9H), 0.52 (m, 2H), 0.06(s, 6H), -0.01 (s, 6H); $^{13}$C NMR (75.5 MHz) in CDCl$_3$, $\delta$ (ppm): 135.59, 112.71, 63.59, 33.85, 33.14, 29.94, 29.88, 29.82, 29.69, 29.59, 26.23, 26.04, 23.97, 23.55, 18.61, 15.06, -3.50, -5.01. Elemental analysis: calculated C 68.67, H 12.57; found C 68.71, H 12.72.
Deposition of (3) onto silicate substrates. The cleaned ATR crystal and silicon wafer pieces were placed into a dried round-bottomed flask that was flushed with nitrogen for 15 min. Allylsilane (0.1 g) in 15 mL of anhydrous toluene was added to the flask via syringe. The reaction was conducted by heating under reflux in toluene for 15 h; after removal from the deposition solution, the substrates were rinsed in 15 mL of CH$_2$Cl$_2$ followed by ethanol washing and drying in a stream of clean air. The samples (4) were characterized by water contact angles, ellipsometry and ATR-FTIR.

Deprotection of the t-butyldimethylsilyl group. The t-butyldimethylsilyl groups were deprotected from the allylsilane (3) functionalized ATR crystal and silicate substrates in a neutral medium. ATR crystal and silicate substrates were placed in a rubber-septum sealed dry flask which was flushed with nitrogen for 15 min, to which water (2.76 mmol) and dry LiCl (25 mmol) in 7 mL of anhydrous DMF were added. The reaction was carried out at 90 °C for 24 h. After rinsing the solid substrates with copious water and dichloromethane, the dried samples (5) were characterized by water contact angle measurement, ellipsometry and ATR-FTIR.

ATRP initiator monolayer preparation. Hydroxy terminated substrates (5) were dried by connection to a vacuum line followed by addition of 20 mL of 0.1 M bromoisobutyryl bromide in THF (anhydrous) solution and 2 mmol of anhydrous pyridine. The reaction was allowed to proceed at room temperature for 10 min. Then the substrates (5) were taken out and rinsed with copious water and methylene
chloride. Water contact angle measurements, ellipsometry, and ATR-FTIR were performed.

\[(\text{CH}_2)_9\text{OH} + \text{Cl} - \text{Si} - \text{C} \]

Imidazole, DMF

\[(\text{CH}_2)_9\text{O} - \text{Si} - \text{C} \quad (1)\]

H - Si - Cl, "Pt"

\[\text{Cl} - \text{Si} - (\text{CH}_2)_{11}\text{O} - \text{Si} - \text{C} \quad (2)\]

MgBr, Dry ether

\[\text{Si} - (\text{CH}_2)_{11}\text{O} - \text{Si} - \text{C} \quad (3)\]

Figure 3.5. Reaction scheme for allylsilane synthesis, deposition, introduction of ATRP initiator and ATRP of styrene from silicate substrates.
Figure 3.5. Reaction scheme for allylsilane synthesis, deposition, introduction of ATRP initiator and ATRP of styrene from silicate substrates. (continued)
Figure 3.5. Reaction scheme for allylsilane synthesis, deposition, introduction of ATRP initiator and ATRP of styrene from silicate substrates. (continued)
3.2.5 Initiator monolayer preparation from corresponding trichlorosilane

To make a comparison, a corresponding trichlorosilane (8) functionalized surface was prepared. The synthesis and self-assembly of the trichlorosilane were performed according to Matyjaszewski and coworkers. The reaction scheme is shown in Figure 3.6.

Figure 3.6. Reaction scheme for trichlorosilane (8) synthesis.
3.2.6 Surface initiated ATRP

The initiator bound solid substrates were placed into a 100 mL Schlenk flask which was sealed with a rubber septum. The flask was degassed and back-filled with nitrogen three times and left under a nitrogen atmosphere. Styrene (13.5 mL), CuBr (55 mg) and anhydrous anisole (16.5 mL) were added to another 100 mL Schlenk flask which was equipped with a stirrer bar and sealed with a rubber septum. This flask was degassed by purging with nitrogen for 1 h. PMDETA (157 µL) was added to the mixture via a syringe and the solution was stirred at 100 °C for about 10 min until it became homogeneous. The solution was cannulated to the flask containing the solid substrates, followed by the addition of free initiator, ethyl 2-bromoisobutyrate (23 µL), via a syringe. The polymerization proceeded at 100 °C for 12 h, after which the ATR crystal and silicon wafer were removed and rinsed with CH₂Cl₂. To remove physically absorbed polymer chains, the solid substrates were placed into a Soxhlet extractor and extracted with THF for 24 h. Free polymer from the polymerization solution was isolated by evaporating residual monomer and solvent first, then dissolving in THF and passing through a short column of activated basic alumina to remove any residual catalyst.

3.3 Simultaneous binary mixed homopolymer brush formation

3.3.1 Materials

Styrene (99%, Aldrich) and 2-phenyl-2-oxazoline (PhOXA) (99%, Aldrich) were
distilled over CaH₂ under reduced pressure and stored in a refrigerator prior to use. Anhydrous triethylamine, 4-(chloromethyl)benzoyl chloride (97%), trichlorosilane (99%), 4-vinylbenzyl chloride (95%), 2,2,6,6-tetramethylpiperidinoxy (TEMPO) (98%), benzoyl peroxide (97%) and allylmagnesium chloride (2.0 M solution in THF) were obtained from Aldrich and used without further purification. Platinum-divinyl tetramethyl-disiloxane complex in xylene (2.1~2.4% Pt concentration in xylene) (Karstedt’s catalyst) was purchased from Gelest Inc. and used as received. All other chemical reagents were purchased from Aldrich and used as received.

3.3.2 Characterization methods

Ellipsometry, goniometry, ATR-FTIR, AFM and GPC studies were conducted as described in previous sections.

3.3.3 Preparation of difunctional Y-SAM

The Y-SAM was prepared according to Figure 3.7. 4-Vinylbenzyl chloride (4VBC) was reacted with benzoyl peroxide (BPO) and TEMPO radical to afford compound 1. Compound 1 then was reacted with allylmagnesium chloride to give compound 2. Compound 1 and 2 were synthesized by following Zhao et al.’s work. Compound 3 was prepared in the following manner: To a three-necked flask, anhydrous methylene chloride (10 mL), triethylamine (0.30 g, 3.0 mmol) and compound 2 (0.77 g, 2.3 mmol) were added. The flask was then cooled
in an ice bath, followed by the addition of a solution of 4-(chloromethyl)benzoyl chloride (0.57 g, 3.0 mmol) in 5 mL methylene chloride in a dropwise manner. The reaction was allowed to proceed at room temperature overnight. Then the mixture was washed with ammonium chloride (3×20 mL). Next the organic phase was dried over anhydrous sodium sulfate. After filtration and removal of methylene chloride using a rotary evaporator, the crude product was purified by column chromatography using 3:1 (v/v) hexanes/ethyl acetate as eluent to afford 3 (0.89 g, 80%). $^1$H-NMR (300 MHz) in CDCl$_3$, δ (ppm): 0.74, 1.06, 1.19, 1.35 (each s, 12 H, CH$_3$), 1.27-1.56 (m, 6H, -CH$_2$CH$_2$CH$_2$-), 2.35 (q, 2H, -CH$_2$-CH=CH$_2$), 2.69 (t, 2H, Ar-CH$_2$-CH$_2$-), 4.51 (dd, 1H, 1H, -OCH/H-), 4.84 (dd, 1H, -OCH/H-), 4.60 (s, 2H, Ar-CH$_2$-Cl), 4.95 (t, 1H, -CH-), 4.97 (m, 2H, -CH=CH$_2$), 5.82 (m, 1H, -CH=CH$_2$), 7.11-7.26 (dd, 4H, ArH), 7.41-7.94 (dd, 4H, ArH). $^{13}$C NMR (75.5 MHz) in CDCl$_3$, δ (ppm): 17.37, 20.58, 30.71, 34.29, 35.32, 35.67, 40.65, 45.61, 60.31, 67.10, 83.86, 115.12, 127.80, 128.33, 128.60, 130.23, 130.47, 138.21, 138.25, 141.43, 142.30, 166.04. After that, a hydrosilation reaction was conducted to afford the anchoring molecule 4. Compound 4 was prepared in the following manner: compound 3 (0.89 g, 1.84 mmol) was added to a 50 mL flask. Then 15 mL of trichlorosilane was injected into the flask under nitrogen protection. After that, 4 µL of Karstedt’s catalyst was added. The reaction was allowed to proceed at room temperature overnight. Excess trichlorosilane was removed by bulb-to-bulb distillation and the product was used without further purification. $^1$H-NMR (300 MHz) in CDCl$_3$, δ (ppm): 0.72, 1.05,
1.17, 1.33 (each s, 12H, $CH_3$), 0.89 (t, 2H, Si-$CH_2$), 1.35-1.71 (m, 10H, $-CH_2CH_2CH_2$ and Si-$CH_2$-$CH_2$-$CH_2$), 2.70 (t, 2H, Ar-$CH_2$-$CH_2$), 4.50 (dd, 1H, -OCHH-), 4.83 (dd, 1H, -OCHH-), 4.60 (s, 2H, Ar-$CH_2$Cl), 4.95 (t, 1H, -$CH$-), 7.11-7.26 (dd, 4H, ArH), 7.41-7.94 (dd, 4H, ArH). $^{13}$C NMR (75.5 MHz) in CDCl₃, δ (ppm): 17.37, 20.58, 21.27, 22.88, 30.71, 34.29, 35.32, 33.90, 40.65, 45.61, 60.31, 67.10, 83.86, 128.33, 128.60, 130.23, 130.47, 138.25, 141.43, 142.30, 166.04. Then the trichlorosilane 4 was deposited from anhydrous toluene at 40 °C onto a “piranha” solution treated clean silicate surface to give the difunctional initiator monolayer Y-SAM 5.
Figure 3.7. Synthesis of difunctional initiator monolayer Y-SAM.
Figure 3.7. Synthesis of difunctional initiator monolayer Y-SAM. (continued)
Figure 3.7. Synthesis of difunctional initiator monolayer Y-SAM. (continued)
3.3.4 Free difunctional initiator synthesis

For better control over the polymerization, a free difunctional initiator with the same asymmetric difunctional initiating moieties was synthesized using styrene as a starting material in a similar synthetic strategy (Figure 3.8). Styrene was reacted with benzoyl peroxide (BPO) and TEMPO radical in the first step. Then the first step product was hydrolyzed under basic conditions. After that, the hydroxy functionality was reacted with 4-chloromethylbenzoyl chloride to give the free difunctional initiator 6. This step was performed in the same manner as the synthesis of compound 3. $^1$H NMR (300 MHz) in CDCl$_3$, δ (ppm): 0.75, 1.07, 1.20, 1.36 (each s, 12 H, $CH_3$), 1.26-1.57 (m, 6H, -C$H_2$CH$_2$CH$_2$-), 4.54 (dd, 1H, 1H, -OCH$_2$H-), 4.82 (dd, 1H, -OCH$_2$H-), 4.60 (s, 2H, Ar-C$H_2$-Cl), 5.06 (t, 1H, -CH$_2$-), 7.26-7.39 (m, 5H, ArH), 7.41-7.93 (dd, 4H, ArH). $^{13}$C NMR (75.5 MHz) in CDCl$_3$, δ (ppm): 17.37, 20.64, 29.93, 34.33, 40.66, 45.62, 60.34, 67.09, 84.13, 127.81, 127.86, 128.29, 128.64, 130.23, 130.41, 140.84, 142.34, 166.01.

![Figure 3.8. Synthesis of free difunctional initiator.](image)

BPO TEMPO
Figure 3.8. Synthesis of free difunctional initiator. (continued)
3.3.5 Simultaneous binary mixed homopolymer brush preparation

The simultaneous living CROP and NMRP were accomplished by following Sogah et al.'s work. The reaction scheme is depicted in Figure 3.9. The simultaneous CROP and NMRP were accomplished in the following way: first the initiator-bound silicate substrate and free initiator were treated with silver triflate followed by addition of excess PhOXA at room temperature. This led to the formation of the corresponding triflate salt in the presence of excess PhOXA. Second, styrene was added to the mixture followed by heating the mixture at 125 °C for 44 h. Simultaneous polymerization of both monomers occurred to give free diblock copolymer and the binary mixed homopolymer brush. Finally, the reaction was quenched with methanol.

Figure 3.9. One-pot, one-step simultaneous living CROP and NMRP.
Figure 3.9. One-pot, one-step simultaneous living CROP and NMRP. (continued)
CHAPTER IV

RESULTS AND DISCUSSION

4.1 Y-shaped diblock copolymer thin film

4.1.1 Control experiment

Before using the PS-b-P2VP diblock copolymer, and to test the viability of the surface confined hydrosilation reaction, trioctylsilane (TOS) was reacted with the terminal double bonds in the self-assembled monolayer which is prepared from 7-octenyltrichlorosilane in toluene using the Speier’s catalyst at 80 °C for 10 h. The success of control experiment was confirmed by ATR-FTIR, ellipsometry and contact angle measurements.

As observed by ATR-FTIR (Figure 4.1), the bottom spectrum is for OTS-SAM, and the upper one is after hydrosilation. The spectra show some slight differences in the aliphatic C-H stretching region below 3000 cm\(^{-1}\). After hydrosilation, a new peak at 2960 cm\(^{-1}\) appeared which was assigned to the introduced methyl end group. Advancing and receding water contact angles were 95° and 85° for OTS-SAM, respectively. After hydrosilation the contact angles increased to 100° and 87°, respectively. This is consistent with the knowledge that saturated hydrocarbon surface has a higher contact angle than does an unsaturated hydrocarbon surface.\(^{137}\)
The OTS-SAM had a thickness of 1.3 nm. After hydrosilation the film thickness increased by 1.1 nm (± 0.2 nm). All these three measurements confirmed the success of the surface-confined hydrosilation reaction.

Figure 4.1. ATR-FTIR for control experiment (a) Si/SiO$_2$/OTS-SAM; (b)Si/SiO$_2$/OTS-SAM/TOS.

4.1.2 Thin film of Y-shaped molecule before and after quaternionzation

The general synthesis scheme is outlined in Figure 4.2. Each step was confirmed by ATR-FTIR (Figure 4.3). For the OTS-SAM, the ATR-FTIR spectrum shows peaks between 2925 cm$^{-1}$ for aliphatic C-H stretching and 2853 cm$^{-1}$ for the CH$_2$ stretching. The grafting of PS-\textit{b}-P2VP was confirmed by the characteristic
bands at 1568 and 1590 cm\(^{-1}\) which are assigned to aromatic C-C stretching, and 3026, 3060 and 3082 cm\(^{-1}\) which are assigned to aromatic C-H stretching. The extent of quaternization was nearly complete, as evidenced by the disappearance of the peak at 1435 cm\(^{-1}\) shown in Figure 4.3 (c).\(^{136}\)

\[
\text{\begin{align*}
 & \begin{array}{c}
 \text{Cl} \\
 \text{C} \end{array} \\
 & \begin{array}{c}
 \text{Si} \\
 \text{C} \end{array} \\
 & \begin{array}{c}
 \text{Cl} \\
 \text{Cl} \\
 \text{C} \end{array} \\
 & \text{+} \\
 & \text{OH}
\end{align*}
\]

\text{Anhydrous toluene} \rightarrow 4 \text{h} \quad 60^\circ \text{C}

\[
\begin{array}{c}
\{ \text{O} \text{Si} \text{O} \} \\
\text{O}
\end{array}
\]

\[
\begin{array}{c}
\text{CH}_2\text{CH}_3
\end{array} \\
\text{Si} \\
\begin{array}{c}
\text{CH}_3 \\
\text{H}
\end{array} \\
\begin{array}{c}
\text{CH}\text{CH}_2
\end{array} \\
\text{N} \\
\begin{array}{c}
\text{H}
\end{array}
\]

\text{"Pt"} \quad \text{Anhydrous toluene} \rightarrow 24 \text{h} \quad 80^\circ \text{C}

Figure 4.2. Surface modification steps in making the Y-shaped diblock copolymer thin film
Figure 4.2. Surface modification steps in making the Y-shaped diblock copolymer thin film. (continued)
Figure 4.3. ATR-FTIR spectra of (a) Si/SiO$_2$//OTS-SAM, (b) Si/SiO$_2$//Y-shaped PS-$b$-P2VP and (c) Si/SiO$_2$//Y-shaped PS-$b$-(quaternized P2VP)

The OTS-SAM exhibited a thickness of 1.3 nm and advancing ($\theta_a$) and receding ($\theta_r$) contact angles of 95° and 85°. The properties of the copolymer films before and after quaternization are listed in Tables 4.1 and 4.2, respectively. For PS-$b$-P2VP (1), the dry film thickness changed from 3.0 nm (before quaternization) to 4.3 nm (after quaternization); for PS-$b$-P2VP (2), the dry film thickness increased from 3.3 nm (before quaternization) to 4.8 nm (after quaternization). This film thickness increase after quaternization is typical of the polyelectrolyte effect due to the salt formation. The electrostatic repulsion caused the chains to become more rigid and thus the film thickness increased. The low film thickness for the copolymer film is
typical for films made by the “grafting to” technique. To estimate the grafting density, we used a method reported by Tsukruk and co-workers. The density of the Y-shaped polymer on the surface was assumed to be 1.1 g/cm$^3$. The density of PS is 1.05 g/cm$^3$, and the density of P2VP is 1.15 g/cm$^3$. The density of the block copolymer PS-$b$-P2VP is calculated to be 1.10 g/cm$^3$ by taking the weight average of the densities of PS and P2VP. Furthermore, it was assumed that the density of the grafted polymer is the same as that of the free polymer. For PS-$b$-P2VP (1), the calculated grafting density is 0.04 chain/nm$^2$ and the grafting distance (the distance between two tethering points) is 5.6 nm; for PS-$b$-P2VP (2), the calculated grafting density is 0.19 chain/nm$^2$ and the grafting distance is 2.6 nm. This calculation indicated that the Y-shaped molecules were sparsely grafted and existed in the mushroom regime. Thin film prepared from PS-$b$-P2VP (2) showed a higher grafting density, which can be explained by the fact that PS-$b$-P2VP (2) has a lower molecular weight and thus lower steric hindrance in the grafting process.
Table 4.1 Properties of Y-Shaped copolymer modified surface before quaternization

<table>
<thead>
<tr>
<th></th>
<th>Contact angle(^a) after THF treatment</th>
<th>Contact angle after isopropanol treatment</th>
<th>Contact angle after cyclohexane treatment</th>
<th>Film thickness(^b) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/SiO(_2)/Y-shaped PS-(b)-P2VP(1)</td>
<td>80° 64° 75° 62° 80° 63°</td>
<td>3.0</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Si/SiO(_2)/Y-shaped PS-(b)-P2VP(2)</td>
<td>86° 70° 73° 60° 88° 75°</td>
<td>3.3</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The standard deviation of contact angles was < 2°. \(^b\) Film thickness was determined from ellipsometry and the uncertainty was ± 0.2 nm.

Table 4.2 Properties of Y-Shaped copolymer modified surface after quaternization

<table>
<thead>
<tr>
<th></th>
<th>Contact angle after water treatment</th>
<th>Contact angle after cyclohexane treatment</th>
<th>Film thickness (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si/SiO(_2)/Y-shaped PS-(b)-(quaternized P2VP) (1)</td>
<td>52° 43° 75° 60°</td>
<td>4.3</td>
<td></td>
</tr>
<tr>
<td>Si/SiO(_2)/Y-shaped PS-(b)-(quaternized P2VP) (2)</td>
<td>50° 40° 80° 68°</td>
<td>4.8</td>
<td></td>
</tr>
</tbody>
</table>

\(^a\) The standard deviation of contact angles was < 2°. \(^b\) Film thickness was determined from ellipsometry and the uncertainty was ± 0.2 nm.
4.1.3 Molecular weight effect

Since the lower molecular weight PS-b-P2VP (2) faces less steric hindrance in the deposition process, a slightly thicker film was obtained. For PS-b-P2VP (1), the dry film thickness was 3.0 nm before quaternization and 4.3 nm after quaternization; for PS-b-P2VP (2), the dry film thickness was 3.3 nm before quaternization and 4.8 nm after quaternization. Due to the smaller steric hindrance in the “grafting-to” process, higher grafting density and a thicker film should result for PS-b-P2VP (2). Just as the calculation mentioned before, for PS-b-P2VP (1), the calculated grafting density is 0.04 chains/nm$^2$ and the grafting distance is 5.6 nm; for PS-b-P2VP (2), the calculated grafting density is 0.19 chain/nm$^2$ and the grafting distance is 2.6 nm.

AFM studies were performed on both PS-b-P2VP (1) and PS-b-P2VP (2) copolymer films before and after quaternization. RMS roughness in AFM is defined as the root-mean-square of height deviation taken from the mean data plane. Detailed RMS data was listed in the next section 4.1.4. Systematically, PS-b-P2VP (1) thin films exhibited higher roughness values than the corresponding PS-b-P2VP (2) thin films. This is probably because PS-b-P2VP (2) has a higher grafting density and more complete coverage of the surface.

4.1.4 AFM morphologies of the unquaternized sample

The morphology of polymer thin films results from a complicated mixture of many variables that include molecular weight, composition, grafting density,
miscibility of component polymers (χ parameter), architecture of polymers at surfaces and the interacting environment.

The unquaternized sample was subjected to different solvent treatments as described in the experimental section and the results are shown in table 4.1. According to the prediction of Zhulina and Balazs,11 the single grafting site of the diblock copolymer will impose a spatial constraint; mixed, internally segregated (weakly incompatible blocks) or split micelles (highly incompatible blocks) are predicted to form in the mushroom regime. The solubility parameter134 of PS was calculated to be 19.1 (J/cm³)¹/², and for P2VP was 20.6 (J/cm³)¹/². They are weakly incompatible blocks and we have speculated that mixed or internally segregated micelles would form.

The THF treated surface morphology is shown in Figure 4.4. After treatment with a non-selective solvent (THF), the observed contact angles for PS-b-P2VP brushes [the contact angle θa of 80° (Table 4.1) for PS-b-P2VP (1) and θa of 86° (Table 4.1) for PS-b-P2VP (2)] were intermediate between the contact angles for PS (θa = 92°) and P2VP (θa = 73°) as measured from spun-cast films. THF is a good solvent for both PS and P2VP, thus a smooth morphology is expected. Roughness analysis from AFM study indicated an RMS roughness of 1.0 nm for PS-b-P2VP (1), and of 0.6 nm for PS-b-P2VP (2). PS-b-P2VP (2) thin films exhibited a lower roughness probably because they have higher grafting density and more complete surface coverage. Although the P2VP block has a stronger affinity for the silicate substrate144 and the PS block favors the air interface, the outermost air
interface is not composed completely of PS. We concluded this because the observed contact angles for the PS-\textit{b}-P2VP thin film are intermediate between the contact angles for PS and P2VP, which suggested a mixed composition. The contact angle $\theta_a$ of 80 ° (Table 4.1) for PS-\textit{b}-P2VP (1) and $\theta_a$ of 86 ° (Table 4.1) for PS-\textit{b}-P2VP (2) suggested a mixed surface of PS and P2VP.

After cyclohexane treatment, the surface exhibits a different morphology (Figure 4.5). Cyclohexane (40 °C) is a block-selective solvent for PS. Increasing cyclohexane concentration should promote PS migration to the solvent interface while P2VP will try to avoid contact with the solvent and migrate to the bottom. However, contact angle measurements (Table 4.1) suggested a binary mixed surface. Again, this is probably due to the Y-shaped architecture effect as mentioned before. According to the prediction of Zhulina and Balazs,\textsuperscript{11} mixed or internally segregated micelles are probably formed. The surface RMS roughness was 1.1 nm for PS-\textit{b}-P2VP (1) and 0.9 nm for PS-\textit{b}-P2VP (2). The surfaces exhibited slightly rougher morphologies than nonselective solvent THF treated ones, which is consistent with the theoretical speculation that nonselective solvent treatment would result in smoothest morphologies.

The surface topography after 2-propanol treatment is shown in Figure 4.6. Isopropanol is block-selective solvent for P2VP, so P2VP should migrate to the solvent interface. However, solvent induced rearrangement will compete with the attraction between the silicate surface and P2VP. The small decrease in contact
angle measurement suggests that more P2VP exists at the air interface in the mixed or internally segregated micelles. Surface roughness after 2-propanol treatment increased to 1.8 nm for PS-b-P2VP (1) and to 1.4 nm for PS-b-P2VP (2).

Figure 4.4. AFM images of the unquaternized samples after THF treatment. Vertical scale is 20 nm/div.
Figure 4.5. AFM images of the unquaternized samples after cyclohexane (40 °C) treatment. Vertical scale is 20 nm/division.
Figure 4.6. AFM images of the unquaternized samples after 2-propanol treatment.

Vertical scale is 20 nm/division.
4.1.5 AFM morphologies of the quaternized surface

To further decrease the miscibility of the two blocks in the Y-shaped polymers, the P2VP block was quaternized by reaction with iodomethane. In this regime, it was predicted that split micelles might form. The quaternized sample was treated with water and cyclohexane and changes were monitored by AFM and contact angles. The surface morphology after water treatment is illustrated in Figure 4.7. Water is a block-selective solvent for quaternized-P2VP. Distinct domains or surface features are observed in the AFM. The roughness of the water treated sample was 6.2 nm for PS-\textit{b}-P2VP (1) and was 2.6 nm for PS-\textit{b}-P2VP (2). The water contact angles were relatively low [$\theta_w = 52^\circ$ for PS-\textit{b}-P2VP (1) and $\theta_w = 50^\circ$ for PS-\textit{b}-P2VP (2)], suggesting a significant amount of the polar quaternized-P2VP at the air interface. After treatment with cyclohexane at 40°C, the advancing contact angle ($\theta_a$) increased to 75° for quaternized PS-\textit{b}-P2VP (1) and to 80° for quaternized PS-\textit{b}-P2VP (2). The contact angle indicated a higher proportion of PS at the air interface. AFM (Figure 4.8) analyses showed that quaternized PS-\textit{b}-P2VP (1) had an RMS roughness of 6.9 nm and quaternized PS-\textit{b}-P2VP (2) had an RMS roughness of 3.3 nm. The PS-\textit{b}-P2VP (2) sample has more densely grafted chains and more complete surface coverage than the PS-\textit{b}-P2VP (1) sample as evidenced by the AFM studies on quaternized samples. The lower grafting density and less complete surface coverage might be the reason for the observed high RMS roughness for the quaternized PS-\textit{b}-P2VP (1) thin film.
Figure 4.7. AFM images of the quaternized samples after water treatment. Vertical scale is 50 nm/division.
Figure 4.8. AFM images of the quaternized samples after cyclohexane treatment.

Vertical scale is 50 nm/division.
4.2 Polymer brush grafted from an allylsilane-functionalized surface

4.2.1 Control experiment

To graft polymer chains from the surface, a uniform and dense initiator layer on the silicon substrate is important. Self-assembly of trichlorosilanes\textsuperscript{137} is widely used for that purpose. However, McCarthy and Fadeev\textsuperscript{107} demonstrated that self-assembly is not the only reaction possible between trichlorosilanes and surfaces and that uniformity is always going to be an issue when multifunctional silanes are used.

Shimada and coworkers\textsuperscript{108} reported an interesting method for the modification of the silica gel surface by using allylorganosilanes. In toluene under reflux, deallylation of the allylsilane takes place to form the Si-O-Si bond with the silica surface. This new method of surface functionalization has the merit that allylsilanes are stable toward hydrolysis and can be purified by silica gel chromatography. Figure 4.9 presents an example of a reaction used in Shimada et al.’s work.
Shimada used silica gel in his work; to test the method on a flat substrate, we performed a control reaction using allyltriisopropylsilane. The reaction scheme is shown in Figure 3.4. ATR-FTIR analysis (Figure 4.10) showed peaks characteristic of aliphatic C-H stretching. Advancing and receding water contact angles of 80° and 65° confirmed the formation of a hydrocarbon functionalized surface. An
ellipsometry thickness of 0.8 nm also verified the existence of the monolayer. All these results were consistent with a successful deposition.

Figure 4.10. ATR-FTIR result for control experiment

4.2.2 Initiator monolayer preparation and characterization

In this research, an allylsilane (3) was synthesized and deposited (Figure 3.5). The presence of the monolayer was confirmed by ATR-FTIR, which showed peaks for the aliphatic C-H stretching [Figure 4.11(a)]. The water advancing and receding contact angles were 87° and 76°, respectively, and the film thickness measured from ellipsometry was 2.3 nm. The t-butyldimethylsilyl groups in the organic monolayer
(4) were deprotected to afford terminal hydroxyl groups as evidenced by the appearance of a peak at 3400 cm\(^{-1}\) in the ATR-FTIR [Figure 4.11(b)]. The advancing and receding water contact angles decreased to 65° and 52°, respectively. The film thickness measured from ellipsometry was 1.5 nm. To introduce an ATRP initiator onto the surface, the terminal hydroxyl groups were reacted with bromoisobutyryl bromide. This step was verified by the disappearance of the hydroxyl peak at 3400 cm\(^{-1}\) and the appearance of a peak at 1740 cm\(^{-1}\) which was assigned to the carbonyl adsorption [Figure 4.11(c)]. The advancing and receding water contact angles were 82° and 70°, respectively, and the film thickness was 1.8 nm. The contact angle and ellipsometry data are listed in Table 4.3.

Figure 4.11. ATR-FTIR spectra for each surface modification step: (a) sample 4 obtained by depositing allylsilane (3), (b) deprotected monolayer (5), (c) ATRP initiating monolayer (6), and (d) Si/SiO\(_2\)/polystyrene (7).
Table 4.3 Properties of each surface modification step

<table>
<thead>
<tr>
<th></th>
<th>Contact angle(^a)</th>
<th>Film thickness(^b)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>(\theta_a)</td>
<td>(\theta_r)</td>
</tr>
<tr>
<td>(4)</td>
<td>87°</td>
<td>76°</td>
</tr>
<tr>
<td>(5)</td>
<td>65°</td>
<td>52°</td>
</tr>
<tr>
<td>(6)</td>
<td>82°</td>
<td>70°</td>
</tr>
<tr>
<td>Si/SiO(_2)/polystyrene (1(^{st}) layer)</td>
<td>92°</td>
<td>73°</td>
</tr>
<tr>
<td>Si/SiO(_2)/polystyrene (2(^{nd}) layer)</td>
<td>92°</td>
<td>73°</td>
</tr>
</tbody>
</table>

\(^a\) The standard deviation of contact angles was <2°. \(^b\) Film thickness was determined from ellipsometry and the uncertainty was ±0.2 nm.

4.2.3 Initiator monolayer uniformity

The main purpose of this research was to obtain a uniform initiator monolayer from which polymer chains could be grafted. AFM was used to study the uniformity of the ATRP initiator monolayer [Figure 4.12(a)]. The organic initiating monolayer (6) exhibited good uniformity and the rms roughness from AFM was 0.3 nm.

In comparison, AFM was performed on the trichlorosilane (8) functionalized surface. The synthesis and self-assembly of trichlorosilane was conducted by following the work of Matyjaszewski et al.\(^{145}\) AFM analysis [Figure 4.12(b)] indicated significant aggregation on the surface and the rms roughness increased to 0.7 nm, which was consistent with the work of McCarthy and Fadeev.\(^{107}\)
Figure 4.12. AFM 3D plots of (a) initiator monolayers (6) and (b) initiator monolayer from trichlorosilane (8).
4.2.4 Surface initiated ATRP

Living polymerization techniques are preferred for making polymer brushes since they can afford better control over brush thickness and polydispersity. The advantage of ATRP over other living polymerizations lies in its tolerance to impurities and polar functionalities in the monomers.

The ATRP of styrene from the modified silicon wafers was conducted. After a 12 h reaction, the film thickness increased by 10 nm and the advancing and receding water contact angles were 92° and 73°, respectively, which are characteristic of a polystyrene film. Molecular weight analysis (GPC) of the free polymer indicated $M_w = 10,400$ g/mol and $M_w/M_n = 1.07$. The existence of polystyrene polymer brush was also verified by ATR-FTIR analysis [Figure 4.11(d)]. To test if most chain ends were still “alive” after the polymerization, the same substrates were subjected to the same polymerization conditions again; after 12 h, the film thickness increased by another 10 nm and showed the same water contact angle values. The free polymer displayed $M_w = 10,500$ g/mol and $M_w / M_n = 1.08$. This result suggested that most chain ends remain active and were capable of successfully reinitiating additional monomer.

4.3 Simultaneous binary mixed homopolymer brush

4.3.1 Simultaneous binary mixed homopolymer brush synthesis

Enlightened by the work of Fukuda$^{89}$, Bin Zhao$^{90-92}$ and Sogah$^{93}$, a synthetically
much simpler approach was derived for a one-pot preparation of binary mixed homopolymer brushes combining simultaneous NMRP and living CROP. In the next step, the self-adapting behavior of the binary mixed homopolymer brushes to environmental changes was also studied.

The difunctional Y-SAM, free difunctional initiator and one-pot polymerization were synthesized according to the reaction schemes shown in Figures 3.7, 3.8 and 3.9. The simultaneous living CROP and NMRP gave free diblock copolymer and the binary mixed homopolymer brush.

The $^1$H NMR (300MHz) spectrum (Figure 4.13) of the free polymer in deuterated chloroform showed the presence of styrene and phenyloxazoline (PhOXA) monomer units in an approximately 1:1 ratio. GPC measurement showed a number average molecular weight of about 20,000 and PDI of 1.34. Combined with NMR integration, each diblock free polymer contained about 80 styrene monomer units and 79 PhOXA monomer units.
The asymmetric difunctional initiator monolayer had a thickness of 0.8 nm and its presence was verified by ATR-FTIR (Figure 4.14). The absorption at 1731 cm$^{-1}$ was characteristic of the carbonyl group stretching in the ester. The mixed homopolymer brush had a thickness of 8 nm and its presence was confirmed by ATR-FTIR. The absorption at 1643 cm$^{-1}$ was characteristic of the carbonyl group.
stretching in the amide linkage of poly(PhOXA). The Y-SAM had advancing and receding water contact angles of 70° and 58°, respectively.

Figure 4.14. ATR-FTIR results: (a) Si/SiO₂//Y-SAM; (b) Si/SiO₂//Y-SAM/binary mixed homopolymer brush.

4.3.2 Solvent treatments on binary mixed homopolymer brushes

The binary mixed homopolymer brush exhibited “smart,” reversible self-adapting behavior to environmental changes. This reversible self-adapting behavior was studied by contact angle measurement, XPS and AFM. AFM images were obtained
using a Multimode Scanning Probe Microscopy (Digital Instruments) in tapping mode with a silicon tip. XPS was performed on a Perkin-Elmer instrument using Al Kα radiation at the MATNET Surface Analysis Center at Case Western Reserve University. The incidence angle of X-rays was 45° with respect to surface normal. Survey spectra were taken after the sample was treated with cyclohexane, methanol and chloroform. The sampling depth of the XPS experiments is about 5-10 nm depending on the core level binding energy and takeoff angle.\textsuperscript{146} The XPS and tensiometry results indicated large compositional changes on the topmost layer upon different solvent treatments. Generally speaking, lateral microphase separation gives lower RMS roughness than vertical microphase separation.\textsuperscript{83} Cyclohexane at 40 °C is selective solvent for PS.

After cyclohexane treatment, the advancing and receding water contact angles were 92° and 73°, respectively, which suggested more PS component at the air interface. XPS indicated a N\textsubscript{1s} peak intensity corresponding to 0.3 % nitrogen in the at least half of the binary mixed polymer brush layer. The RMS roughness from AFM was 0.8 nm (see Figure 4.15).

Methanol is selective solvent for poly(PhOXA). After methanol treatment, the advancing and receding water contact angles decreased to 62° and 50°, respectively, suggesting a PPhOXA-enriched surface. XPS indicated 3.3% nitrogen in the at least half of the binary mixed polymer brush layer. The rms roughness from AFM was 1.2 nm (see Figure 4.16).
Chloroform is a nonselective solvent. After chloroform treatment, the advancing and receding water contact angles were 80° and 67° respectively, indicating a binary mixed composition at the top layer. XPS showed an intermediate N$_{1s}$ intensity of 1.0 %, also suggesting a binary mixed composition. The RMS roughness from AFM was 0.6 nm (see Figure 4.17).
Figure 4.15. AFM images of the binary mixed brush after cyclohexane (40 °C) treatment. Vertical scale is 10 nm/division.
Figure 4.16. AFM images of the binary mixed brush after methanol treatment.

Vertical scale is 10 nm/division.
Figure 4.17. AFM images of the binary mixed brush after chloroform treatment.

Vertical scale is 10 nm/division.
CHAPTER V

SUMMARY AND CONCLUSIONS

The purpose of this research was to utilize multiple approaches for silicate surface modifications. This research contained three projects: the first project was the preparation and characterization of a “switchable” Y-shaped thin film surface prepared via a simple “grafting-to” method using a polystyrene-$b$-poly(2-vinylpyridine) copolymer; the second project was to achieve the grafting of a polymer brush from an allylsilane-functionalized surface; and the third project addressed the simultaneous synthesis of binary mixed homopolymer brushes by combining NMRP and CROP in a “grafting-from” approach.

A simple method for preparing a ‘Y-shaped’ polymer brush has been devised. The procedure involved a one-step hydrosilylation of a SiHMe-functionalized PS-$b$-P2VP diblock copolymer to a 7-octenyltrichlorosilane functionalized SAM. This “grafting-to” technique produced a thin film with low grafting density. We observed changes in contact angles and nanomorphology after treating this brush with block-selective solvents. The largest effects were observed for the ‘Y-shaped’ brush that had been derivatized with methyl iodide to create a quaternized P2VP block. Due to lower steric hindrance in the “grafting-to” process, lower molecular weight PS-$b$-P2VP diblock copolymers afforded a higher grafting density and more complete surface coverage.
To graft polymer chains from the surface, a uniform and dense initiator layer on the silicate substrate surface is preferred. The initiator monolayer can be fabricated in many ways, of which self-assembly of trichlorosilanes on silicate substrates is widely used. In order to obtain a uniform initiator monolayer, an allylsilane was synthesized and used to functionalize a flat silicate substrate surface. Using AFM, the initiating monolayer derived from allylsilane was found to be more uniform than the corresponding layer made from the corresponding trichlorosilane. Atom transfer radical polymerization was used to prepare polystyrene brushes from the allylsilane-derived initiator surface. Evidence for a living polymerization was demonstrated by sequential monomer addition. Tensiometry, ellipsometry, ATR-FTIR, and AFM were used to characterize the surface modification steps for this project.

Mixed polymer brushes, consisting of diblock or triblock copolymer brushes, Y-shaped diblock copolymer brushes and mixed homopolymer brushes, have been extensively studied because of the potential for amplifying the combined effects of conformational changes and microscopic phase separation. Macroscopic phase separation is suppressed by the tethering of one chain end to the surface. Both theoretical and experimental work has indicated that symmetric binary mixed homopolymer brushes would be able to undergo a solvent-induced transition between lateral and perpendicular microphase separation.

In order to obtain a binary mixed brush with high grafting density, a very simple
approach was devised for simultaneous controlled mixed homopolymer brush synthesis by combining nitroxide-mediated radical polymerization and living cationic ring-opening polymerization. It was observed that the mixed homopolymer brush showed “smart” behavior to environment changes. And these reversible, self-adapting changes were observed using XPS, AFM and water contact angle measurements.
REFERENCES


