

**Synthesis, Characterization, and Reactive Modification of
2-Vinyl-4,4-dimethyl Azlactone Polymers**

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Degree

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Dedication

I dedicate this work to my family. Their encouragement and support has been a great influence on my personal and academic strengths.

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Abstract

Polymeric materials possessing specific functionality have been designed for use in applications such as membranes, biocompatible coatings, lubricants, and tissue engineering. Because the chemical nature of the repeat units set the properties offered by the polymer, the ability to reactively modify polymer chains to integrate specific functionality expands the range of potential applications. Thus, reactive modification of polymer thin films provides a useful route to confer new properties to the underlying material, with the range, strength and type of interaction across the interface dictated by the display of functional groups decorating the surface. To address the links between design, *in situ* functionalization, and properties, layers of end-tethered polymer chains, or polymer brushes, were created by grafting chains of poly (2-vinyl-4,4-dimethyl azlactone) (PVDMA) onto silicon substrates. The pendant azlactone rings of PVDMA readily react with nucleophiles, allowing *in situ* functionalization to be studied through the use of ellipsometry and neutron reflectivity measurements as a function of parameters that affect brush structure. The results indicate that the grafting density of chains and size of the functionalizing agent govern the extent of functionalization. In addition to an average view of the *in situ* functionalization process gained through ellipsometry measurements, the sensitivity of neutron scattering methods to isotopic substitution (of D for H) provides detailed insight into the location and amount of functional groups installed within the PVDMA brush by reactive modification. The resulting design-structure-property relationships provide a systematic basis for creating polymeric materials with desired properties, and this theme is advanced by the

development of surface gradients. Designing and using gradient surfaces is an efficient approach for screening a wide variety of conditions and optimizing the extent of chemical functionality, which alters surface properties delivered by reactive modification. All of these studies yield relationships between extent of reaction in the confined environment (in a brush or thin film), the spatial display of functional motifs, and the swelling properties of the interfacial layer, as well as insight into general strategies that can be used to tailor frictional, adhesive, or biomimetic properties of polymer interfaces.

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Chapter 1

Introduction

1.1 Polymer Brushes

Polymer brushes are layers of polymer chains that are covalently attached by one end to an interface or solid substrate. The characteristic feature of a polymer brush is that the chains are stretched because grafting creates a crowded layer.¹ As the grafting process begins and polymer chains are tethered, the grafting density is not high enough for the chains to overlap; therefore chains adopt a random coil conformation, and the characteristic size in this “mushroom” regime is the radius-of-gyration, R_g , of the chain.² As the grafting density on the surface increases, the polymer chains overlap, which increases the lateral interactions between neighboring chains. When those interactions are strong enough, the chains will stretch normal to the surface and balance the repulsive interaction energy with the elastic free energy that resists chain stretching.³ This balance between repulsive intermolecular forces between chains at the cost of the elastic free energy to stretch the chains from the surface results in a layer of chains having a stretched conformation, as shown in Figure 1-1.⁴

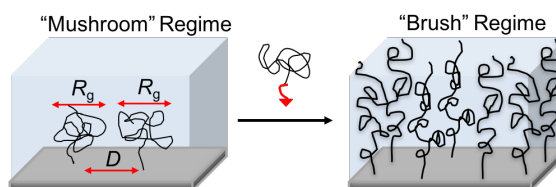


Figure 1-1. Polymer brush formation as grafting of polymer chains proceeds from a few chains on the surface to a densely grafted system in which the chains are stretched, forming a polymer brush.

Polymer brushes are created in the melt and solution. Polymer chains in the melt are forced to stretch away from the surface to minimize overfilling space.¹ When polymer brushes (uncharged) are exposed to a good solvent, excluded volume interactions are present and cause the brush to stretch in order to minimize interactions between chains and maximize interactions with the solvent. The equilibrium that is reached between the resistance to chain stretching and repulsive interactions results in a layer thickness that scales linearly with the degree of polymerization of the polymer.^{3,5} Thus, grafting of polymer chains changes the conformation and properties.¹ Once a polymer brush is created, the system responds differently than when the coils are free in solution: They have only one dimension in which they can expand or contract, and they have no freedom to move laterally. These features make polymer brushes unique and motivate various studies.

As shown in Figure 1-2, the chains of a polymer brush change their conformation in response to changes in the external environment.² Polymer brushes respond to different stimuli, such as changes in temperature, pH, solvent type, and electrical field.⁶ Depending on the change in interaction energy caused by application of the stimulus, the polymer brush chains will either expand or collapse. The degree of response of the polymer brush also depends on the grafting density and degree-of-polymerization.² As a result, it is important to understand how parameters varied in synthesis or in the grafting process impact the behavior and properties of a polymer brush. Understanding design-structure-property relationships of polymer brushes allows the system to be tailored toward specific applications.

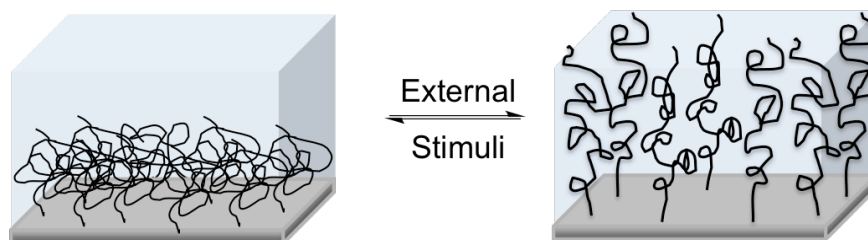


Figure 1-2. Schematic displaying conformations (collapsed and stretched) of grafted chains. Reversible conformation changes are triggered by a stimulus, such as a change in pH, temperature, or solvent quality.

Polymer brushes with reactive functional groups located within the brush layer are conceptually useful in various applications such as purification and chromatography processes, peptide and protein binding, coatings, adhesives, and “smart” materials for biosensing and detection that is triggered in response to external chemical or physical stimuli.⁷ Because of their reactivity and the steric bulk of pendant reactive groups, functional polymers often are difficult to end-graft to a surface. As a result, functional polymer brushes are frequently created by reactive modification of precursor (or protected) polymers using various post-polymerization modification strategies.^{8–15} Post-polymerization modification expands the tailorability for specific chemical and physical properties. In Section 1.2.1 of Chapter 1, progress related to reactive modification of polymer brushes is highlighted. Polymer brushes are created by either “grafting to” or “grafting from” processes, and because of distinct attributes of those grafting processes, different polymerization methods are chosen based on the monomer. The advantages of the grafting processes and different polymerization techniques to create polymer brushes

will be discussed in Section 1.3. Characterization techniques, concepts and research objectives for this dissertation work are described in Sections 1.4, 1.5 and 1.6.

1.2 Motivation

There has been an ample amount of research completed on post-polymerization modification of various polymer brush systems containing hydroxyl, carboxylic acid, carboxylic ester, and epoxide groups.¹³⁻¹⁸ Post-polymerization modification introduces specific functionality to provide particular properties that suit the polymer film for applications such as membranes and barrier layers,¹⁹ sensors,²⁰ anti-fouling coatings,^{9,21} anti-bacterial surfaces,²² and cell scaffold and protein separation.^{23,24} Although there have been a wide number of brush systems studied involving post-polymerization modification, detailed and systematic studies to determine quantitative relationships and quantify the extent of reactive modification have not been undertaken. R  he *et al.* synthesized reactive ester polymer brushes and then modified the brush via post-polymerization modification using n-alkylamines and monoamino-poly(ethylene glycol)s (PEGs). Analyses based on Fourier Transform Infrared (FTIR) spectroscopy assumed complete conversion of the amine-modified brushes. However, this study did not investigate how the extent of functionalization is affected by the amine size, or the grafting density of the brush.¹⁴ Klok *et al.* attempted to investigate the ability of small and large molecules to penetrate and react with a poly(glycidyl methacrylate) brush system. However this system was ineffective because the epoxide groups caused various side reactions and the large molecules were not able to penetrate into the brush.¹¹

Therefore it is imperative to choose a polymer brush system and set of model molecules that will answer fundamental questions and provide insights that

systematically address how varying the polymer brush structure and size of functionalizing agent affect post-polymerization modification. Varying the size of the functionalizing agent will provide insight into the penetration and reaction of molecules in the crowded environment of a polymer brush. Varying the molecular weight of the polymer chains will yield relations between polymer brush structure (thickness and grafting density) and its ability to be reactively modified (in my work, by a set of model amines). By addressing these, my dissertation research delivers important fundamental knowledge describing design-structure-property relationships of polymer brushes that undergo reactive modification. Specifically, I have studied poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) chains that were grafted to a substrate. “Grafting to” allows grafting density to be easily varied and also allows the molecular weight and dispersity ($\bar{D}$) of the brush chains to be known. Varying the grafting density of the PVDMA brush and different size primary amines were used to understand the reaction with the azlactone rings and penetration within the polymer brush scaffold. In addition to studies of functionalization of PVDMA brushes, some of the modified brushes were re-functionalized. The measurements taken after each functionalization reaction allow the extent of the reaction to be determined. Refunctionalization studies provide insight into whether PVDMA chains are completely modified when exposed to small molecules. This topic is not settled by previous studies.^{11,14} To expand beyond a “one sample at a time” approach, I also explored the use of surface gradients to probe large parameter spaces, where exposure time, concentration, or refunctionalization could be examined easily. The information learned from these studies is used to design and test functional

brushes for bio-inspired applications, such as scaffolds for liver cell growth or matrices for the simulation of bone growth (i.e., growth of inorganic CaCO_3 in a polymer matrix).

1.2.1 Reactive Modification of Polymer Brushes

The “grafting from” method, which uses surface-initiated controlled radical polymerizations methods, such as surface-initiated atom transfer radical polymerization (SI-ATRP), surface-initiated nitroxide mediated polymerization (SI-NMP), and surface-initiated reversible addition fragmentation chain transfer (SI-RAFT) polymerization, provides the advantages of precise control over thickness and composition, and offers some ability to tune the grafting density of the polymer brush by varying the surface density of initiator molecules.¹⁵ Barbey *et al.* used SI-ATRP to control the thickness of reactive brushes based on poly(glycidyl methacrylate) (PGMA). Post-polymerization modifications with either propylamine or bovine serum albumin (BSA) were investigated as a way to tether biomolecules to the brushes. Depth profiling X-ray photoelectron spectroscopy (XPS) studies showed that propylamine diffused and reacted throughout the PGMA brush. However, the propylamine-functionalized PGMA brushes experienced various side reactions, such as cross-linking of some of the remaining epoxide groups with secondary amines. On the other hand, BSA proteins were immobilized only at the top of the brush due to the steric hindrance of the large molecule, which prevented its penetration into the brush.¹¹ This research is important because it suggests that the size of the molecule reacting with the brush controls its distribution in the interfacial layer.

Rühe *et al.* are interested in development of functionalized self-assembled polymer monolayers in which probe molecules are attached to chains grafted on sensor

chips. These systems could be used for biomedical implants or bio-analytical purposes.¹⁴ In their approach, surface-initiated polymerization is used to generate thick polymer brushes. This chemistry involves using tethered azo-initiators, which are thermally activated in the presence of an active ester modified methacrylate monomers. The ester linkages of these methacrylate monomers can participate in reactions such as aminolysis, adding functionality onto the monomer. 1-propylamine, 1-dodecylamine, and 1-octadecylamine were chosen as model primary amines to react with the active ester polymer brush. Surface plasmon resonance (SPR) measurements showed that the thickness of the functionalized polymer brush changes, which indicates that the amines react within the polymer brush,¹⁴ and FTIR spectroscopy studies imply complete chemical conversion. A mathematical expression relating extent of functionalization, f , to ellipsometric thickness was developed for modification with PEGs. This expression assumed a constant mass density and grafting density upon functionalization in order to calculate the degree-of-conversion of polymer chains upon reactive modification.¹⁴ Using this model, they determined that the grafting density and size of the molecule affect the extent of functionalization, with large molecules resulting in a low degree-of-conversion of reactive groups along the brush chains (lower f). However, the assumptions of constant mass density and grafting density are questionable, given that mass is added to the chains, causing changes in interchain interactions. My dissertation research directly addresses and sheds light on these issues.

Thiol-click reactions, such as thiol-ene, thiol-yne, and thiol-isocyanate, are another method by which polymer brushes are reactively modified after polymerization. Thiol-click reactions have several advantages: They proceed at room temperature, take

place in aqueous environments and in the presence of oxygen, and the necessary functional groups (thiol, alkene, alkyne, or isocyanate) are found in a wide range of molecules.⁸ Rahane *et al.* synthesized poly(propargyl methacrylate) (PgMA) homopolymer brushes containing alkyne groups using surface-initiated photopolymerization (SIP), and modified them by orthogonal thiol-yne “click” reactions. The synthesis of PgMA required protection of the alkyne to limit radical-mediated side reactions. Because these reactions were successful, other polymer brushes containing isocyanates, epoxides, and alkylhalides pendant groups were synthesized via SIP and reacted with thiol molecules. The functionalization reactions (and the deprotection of the alkynes) were observed by ATR-FTIR spectroscopy, and they also confirmed that multifunctional polymer brushes were created when more than one type of functional thiol was used during reactive modification. These studies also show that thiol-click reactions take place in confined environments under mild conditions, and that this strategy can be used to tailor the surface properties by controlling the composition of the “thiol-clicked” surface and altering the concentration of the comonomers.⁸

These works demonstrate the potential for modifying surface properties and for creating multicomponent surfaces, which are prevalent in nature. Multicomponent surfaces are important because of their sensitivity to more than one type of analyte or “trigger” in solution. They also offer potential advantage of placing various chemical functionalities on surfaces, either by bottom-up or top-down processes. Such surfaces may be useful mimics of biological systems and give rise to applications in biosensors and regulation of cell adhesion, for example.⁷

1.2.2 Gradient Brushes: Research Review and Application

Beyond preparing “single sample” surfaces by either “grafting to” or “grafting from” approaches, it may be useful to assemble gradient substrates that span a range of conditions. Gradients are directional, allowing chemical or physical properties to change gradually and continuously over one or more directions along the substrate.²⁵ Orthogonal gradients vary two different properties independently and perpendicularly to one another.²⁶ In addition to thinking about creating gradients on a surface in two orthogonal directions, it is possible to create a two-dimensional gradient by controlling the penetration of a species into a thin film (vertical dimension) on a surface that contains a gradient in one direction along the film surface. This strategy can be extended to construct a three-dimensional gradient: First, an orthogonal gradient is installed in the plane of the film, and then this film is immersed in chemical solution containing macromolecules or nanoparticles that enter the film and reactively modify the interfacial layer in the thickness dimension. This type of gradient can be created when polymer brushes are functionalized via post-polymerization modification.^{25,26} A combination of different techniques may be applied to design a surface with gradual changes, for example, in thickness, grafting density, or chemical composition.⁷

Genzer’s group, perhaps, are the leaders in designing brush-based gradients. For example, they synthesized a gradient surface decorated with poly(2-hydroxyethyl methacrylate) (PHEMA) brushes via SI-ATRP. The gradient in grafting density was achieved by depositing a molecular gradient of n-octyltrichlorosilane (OTS), then immersing the OTS-modified wafer into a solution of 11-(2-bromo-2-methyl)propionyloxy undecyltrichlorosilane (BMPUS), an initiator used for SI-ATRP.

The wafer was then dipped vertically (slowly immersed) into a solution containing monomer and the catalyst complex. This slow immersion varies the polymerization time, and therefore changes the brush thickness. After polymerization, lysozyme solutions were prepared in a pH 10 buffer solution, which is the optimal condition for maximizing protein adsorption because it minimizes charge repulsion between protein molecules. Scanning probe microscopy was used to determine that as the grafting density of PHEMA chains increased, the amount of adsorbed protein decreased on the gradient substrate.¹⁸

Luzinov and coworkers developed a temperature gradient stage and used it to create a gradual change in polymer layer thickness, which affected grafting density of chains along the substrate. End functionalized polystyrene (PS) and poly(ethylene glycol) (PEG) chains were tethered to the poly(glycidyl methacrylate) (PGMA) layer, and AFM and ellipsometry were used to examine the topography and thickness along the gradient direction. Varying the annealing temperature for the carboxylic acid-terminated PS and PEG chains resulted in gradation of wettability.⁶ Ionov and coworkers continued this work with the use of PGMA as a primer layer and grafted PEG-NH₂ chains to the polymer-modified surface using a temperature gradient stage.²⁷ Kinesin motor molecules tagged with green fluorescent proteins were adhered to the surface and fluorescent images were taken to determine the optimal grafting density for protein adsorption. Gliding microtubules were also adhered on the PEG-Kinesin modified surface, and it was determined that longer microtubules have a lower probability of leaving the surface and tended to migrate toward the end of the substrate with a high grafting density of chains.²⁸

These works are highlighted because they clearly show the importance of grafting density of the polymer chains on surface properties. Being able to create a gradient that depends on the grafting density aids in understanding how the spatial distribution of molecules affects interfacial properties.²⁹ Perhaps as important, the use of post-polymerization modification reactions of brushes can be used to create interfaces that have physical and chemical properties or chemistries not present in the polymer brush chains. In addition to being fundamentally intriguing, these polymer-modified interfaces may find utility in applications such as biocidal surfaces, tissue engineering scaffolds, sensors, coatings and other diagnostic devices.²⁵

1.3 Strategies for Synthesizing Polymer Brushes

As implied by the works of Genzer, R  he, Rahane, and Luzinov, there are two main synthetic strategies for creating polymer brushes, and they are commonly called “grafting to” and “grafting from”.^{4,30} Each has variables that are adjusted to create polymer brushes, and each has advantages and limitations. In the grafting to method, polymer chains with a specific end group are polymerized independently, allowing the chains to be fully characterized before constructing the brush. The polymer chains are subsequently tethered to the substrate by reaction with a complementary group on the surface. “Click” chemistry reactions are one such example.³¹ The disadvantage of the grafting to approach is a limitation in the grafting density of chains due to the increasing steric repulsion as chains are attached to the interface.⁴ In the grafting from strategy, the polymer brush is synthesized from an initiator that has been attached/adsorbed on the substrate. The chains are grown from these surface-anchored initiation sites. The main advantage of grafting from is greater grafting densities and brush thicknesses are

achieved compared to grafting to methods. The main disadvantage of grafting from is that the polymer chains cannot be characterized, leading to incomplete information about the brush structure.⁷ Namely, because the degree-of-polymerization (molecular weight, M_n) of brush chains is unknown, it is also not possible to determine the grafting density of chains, σ , because they are related by $\sigma = H\rho N_A/M_n$. In this expression, H is the brush layer thickness, ρ is the mass density, and N_A is Avogadro's number.

Grafting polymer chains to the surface is an easy, controllable process that creates stable thin films, and the use of premade chains allows the molecular weight and polydispersity of the polymer chains to be known before they are tethered to the solid substrate.¹⁶ This grafting to method provides a way to modify the interface in order to produce a responsive system that alters surface properties such as friction, colloidal stability, adhesion, wettability, and biocompatibility.⁶ More specifically, polymer brushes are often useful in biomedical applications, including tissue engineering, biosensors, and the development of cell scaffolds used to repair and regenerative cell growth.³² In these areas, important design objectives are to increase compatibility with living tissue or generate a specific affinity (targeting) by surface modification via immobilization of biomolecules on the brush chains. The expectation is to increase biocompatibility by choosing the right biomolecule and make it available at the proper concentration and conformation at the polymer/fluid interface.³³ This represents a substantial challenge because polymer brushes do not always contain particular moieties that promote biocompatibility or mimic biological functions. Thus, learning how to properly incorporate these molecules into the polymer brush system via post-polymerization modification is essential.

All of my dissertation research involves the grafting to approach to attach polymer chains to substrates. Conventional free radical polymerization and reversible addition-fragmentation chain transfer (RAFT) polymerization were the polymerization techniques used to synthesize polymer chains. Conventional free radical polymerization was used for the synthesis of poly(glycidyl methacrylate) (PGMA). Luzinov and coworkers developed a novel method to attach polymer chains to surfaces by reacting end-functional (carboxylate or amine groups) polymers with surface-anchored PGMA films.³⁴ In this approach smooth, homogenous thin PGMA films are first attached to substrates with hydroxyl groups by thermal annealing, which leaves unreacted epoxy groups that serve as tethering points for end-functionalized chains.³⁵

RAFT polymerization is a “living”/controlled free radical polymerization method that allows control of the molecular weight of the polymer chains and low dispersity ($\mathcal{D} < 1.2$).³⁶ RAFT polymerization requires a chain transfer agent (CTA) that has a dithioester or trithiocarbonate group. The CTA includes an “R” and “Z” group that are essential to achieving control. The R group is the free radical leaving group that must be able to reinitiate the polymerization. The Z group affects the rate of addition and fragmentation and stabilizes the radical intermediate to maintain the living character.³⁷ There have been many CTAs synthesized, which is why RAFT polymerization can be used to polymerize a diverse assortment of monomers under a variety of experimental conditions.³⁸

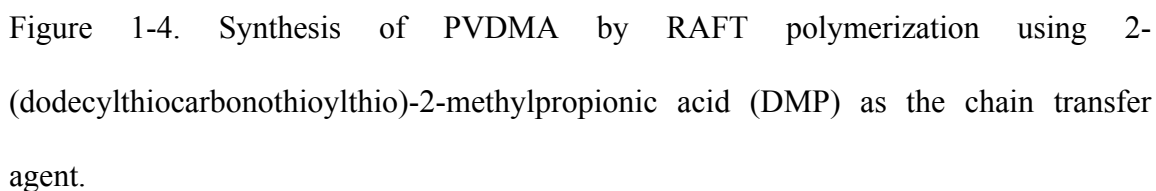
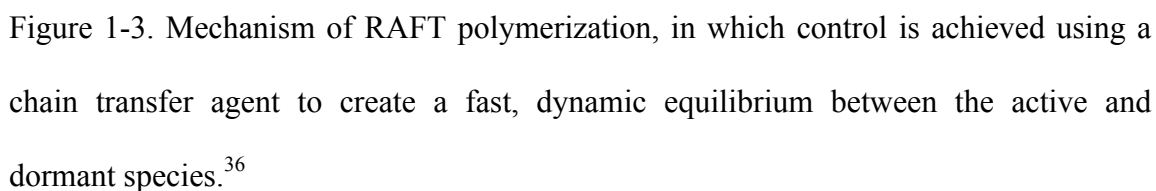
AIBN is a typical initiator used in RAFT polymerization and was chosen to initiate the reaction. After the initiator creates a polymer radical through monomer addition, the radical species will reversibly add to the CTA, forming a fast, dynamic

equilibrium between the active (growing chains) and dormant (stable radical) species. The polymerization reaction proceeds when a new dormant chain is formed from the R group that reinitiates and polymerizes the monomers, as shown in Figure 1-3. The fast, dynamic equilibrium enables control over the molecular weight and molar mass distribution of the polymer chains, allowing all chains to grow at the same rate.

As shown in Equation 1-1, the target molecular weight can be set by controlling the concentration of monomer, $[M]$, and chain transfer agent, $[CTA]$. This expression assumes 100% conversion and that direct initiation is minimal.³⁹

$$M_{n, \text{Theoretical}} = \frac{[M]m_0}{[CTA]} + m_{\text{CTA}} \quad (1-1)$$

In Equation 1-1, the molecular weight of the monomer and CTA are defined as m_0 and m_{CTA} , respectively. Polymer chains with narrow dispersity are important for the design of a polymer brush so that the structure contains chains of nearly the same length to avoid effects of polydispersity. A polydisperse brush results in the segment density profile deviating from being step-like, a feature that would hinder our investigation of post-polymerization modification reactions. In my dissertation research, VDMA is polymerized using RAFT polymerization with 2-(dodecylthiocarbonothioylthio)-2-methylpropionic acid (DMP) as the CTA, as shown in Figure 1-4. This polymerization will synthesize well-defined polymers with specific chain end chemistry (carboxylic acid end group) that can be used subsequently to tether the polymer chains to the substrate by one end. RAFT polymerization also facilitates the design of multiple architectures. This dissertation work includes homopolymers and block-copolymers that were synthesized using RAFT polymerization.



In order to understand the functionalization behaviors of poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) brushes, various molecular weights were synthesized using RAFT polymerization, as shown in Figure 1-5. The PVDMA chains were tethered to a solid substrate, either by the carboxylic acid end group of the CTA or by reaction (grafting) of the PGMA blocks with the surface. Grafting density was manipulated by changing chain molecular weight or grafting time. PVDMA brushes were extensively characterized before and after functionalization by ellipsometry, atomic force microscopy (AFM), ATR-FTIR spectroscopy, UV-Vis spectroscopy, and neutron reflectivity. Ellipsometry measurements yield the thickness of the layer, which gives the information about the height and extent of functionalization. AFM studies complement ellipsometry measurements, providing topographical height and phase images that provide insight into the homogeneity of the as-made and functionalized PVDMA brushes. ATR-FTIR spectroscopy was utilized to examine the disappearance of the azlactone ring upon functionalization with various amines. Neutron reflectivity (NR) was used to determine the segment density profile of the functionalized brushes. The resolution of NR and sensitivity to isotopic contrast allows the distribution of amines within the brush to be measured, which provides more detailed information than ellipsometry and AFM measurements.

1.4 Prior Work on PVDMA: Reactivity, Modification, and Fabrication

2-vinyl-4,4-dimethyl azlactone (VDMA) is an attractive and suitable monomer because it can be polymerized by different controlled (free) radical polymerization techniques, such as RAFT polymerization.¹⁶ RAFT polymerization uses a chain transfer

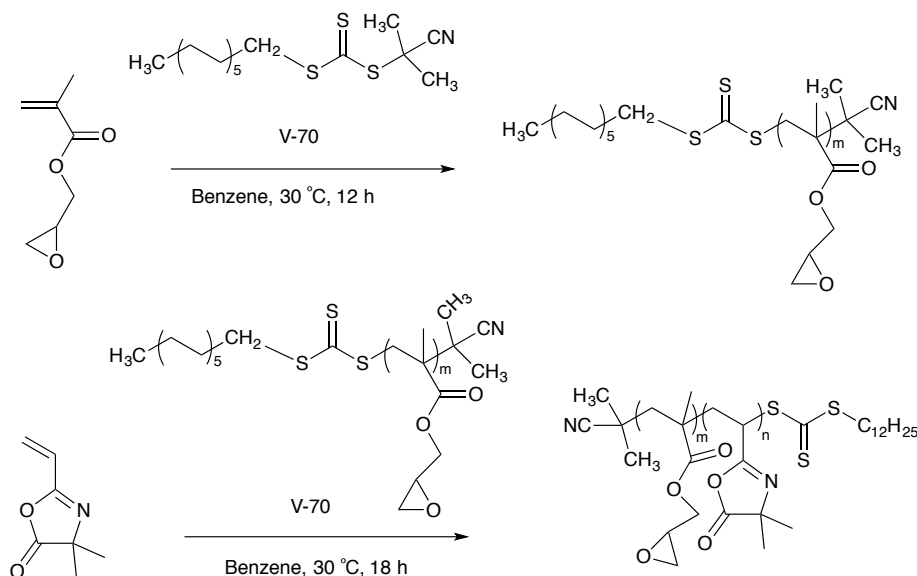


Figure 1-5. Macro-CTA of PGMA synthesized using 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT) as the CTA and 2,2-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70) as the initiator. Polymer chain extension with VDMA yields PGMA-b-PVDMA diblock copolymers.

agent to control the molecular weight of the polymer chain.⁴⁰ CTAs provide variation and control of the end-functional groups on the chains. Another reason that PVDMA is of interest is because it contains reactive azlactone rings along the polymer backbone. The azlactone ring is hydrolytically stable, but undergoes controlled, ring-opening reactions at room temperature when exposed to nucleophilic reagents, such as primary amines, alcohols, and thiols.⁴¹ The variety of functional amines and alcohols provides opportunities to create systems having a wide range of properties, which inspires a variety of applications, including biotechnology and biomaterial surface coatings.³³ Reactions between VDMA and amines or thiols are also important because these

functional groups are found in biomolecules, such as enzymes and proteins.⁴¹ Modification of PVDMA brushes with biomolecules may be used to design a model system that senses and detects or participates in biological processes.⁴¹ Changing the design of the polymer or enchainning different monomers opens possibilities for optimizing the response or functioning of the brush-based system. Not only can these efforts give a better understanding of interaction across interfaces, but they also may improve cell or protein adhesion, for example.¹¹

One of the best examples of the ability to reactively tailor VDMA or PVDMA is demonstrated by the work of Messman *et al.*¹⁷ They synthesized PVDMA and copolymers of VDMA and 1-vinyl-2-pyrrolidone (VP) by free radical polymerization. These polymers were reactively modified with nucleophiles, such as n-hexylamine, dansylcadaverine, and N_ω,N_α-bis(carboxymethyl)-l-lysine. The monomer could also be reactively modified: For example, they demonstrated the addition of an ethylene oxide oligomer to the monomer. ATR-FTIR spectroscopy was used to show that the nucleophiles do open the azlactone ring, as evidenced by the disappearance of the signal associated with the carbonyl of the azlactone at 1825 cm⁻¹ and the appearance of an amide peak at 1537 cm⁻¹.¹⁷ These studies of free PVDMA chains in solution show that various nucleophiles are capable of reacting robustly with the azlactone ring to modify polymer functionality and without any byproducts.

Conditions for creating PVDMA brushes of controlled thickness by reacting end-functionalized PVDMA chains with ultrathin PGMA films attached to silicon substrates were examined by Lokitz *et al.* RAFT polymerization using 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (DMP) as the CTA yielded

PVDMA chains having a carboxylic acid end group, which allows covalent attachment of the PVDMA chains to surfaces modified with a thin PGMA layer. (The $-\text{COOH}$ end group reacts with an epoxy ring of the surface attached PGMA layer.) Their work shows that the grafting to process yields sufficient densities resulting in PVDMA brushes.¹⁶ As suggested by Figure 1-1, grafted chains are considered to be in the brush regime when $D < 2R_g$. In other words, when the distance between two grafted chains, D , is less than twice the radius-of-gyration of the solvated polymer chain, R_g . D is calculated from the grafting density, σ , assuming that the polymer chains occupy a circular area on the surface: $D = 2(\pi\sigma)^{-1/2}$.

Additional studies by Lokitz *et al.* demonstrate that annealing temperature, annealing time and polymer concentration have an impact on PVDMA brush thickness. It was shown that the thickness of the polymer brush layer is directly proportional to the concentration of polymer in the solution used for spin coating. In addition, while PVDMA is stable, excessive heating can cause crosslinking of the PGMA, which affects the film thickness as well as its roughness.⁴¹ Because it is important for the PGMA to attach to the silicon surface and create a uniform layer, it was concluded the optimal annealing temperature for PGMA is 80 °C. This particular finding is applicable to my research because PGMA is applied to the silicon substrate before carboxylic acid-functionalized PVDMA chains are deposited by spin coating and covalently attached by annealing. Once deposited by spin casting, PVDMA is annealed at 110 °C for a minimum of 12 h in order to promote reaction between the carboxylic acid end-group on the chains with epoxy groups, creating a thin PVDMA brush.

The work by Lokitz *et al.* is significant because it establishes reaction conditions whereby smooth and homogenous polymer brushes are made. This is important for analysis of brush characteristics and post-polymerization modification by exposure to functionalizing reagents. In other words, well-prepared reactive polymer brushes are essentially 1-D systems: when the reagents are added, they can diffuse into the polymer brush, and modify the layer along its thickness dimension. I was able to learn how small molecules, added as reagents, diffused into and react within the polymer brush layer, leading to a variety of design-structure-property relationships and new insights into *in situ* chemical modification of reactive brushes.

1.5 An Overview of Neutron Reflectivity

Neutron reflectivity is a powerful characterization technique for studying reactive modification of thin films because of its ability to probe the structure of thin films and buried interfaces.⁴² Neutrons have wave-like properties and they non-invasively interact with the nucleus of the scatterer.⁴³ The wavelength of neutrons is on the order of 1 Å, resulting in the ability to probe structure on the molecular level.⁴⁴ Another advantage of neutrons is their low absorption allows buried interfaces to be investigated. Neutrons will reflect and refract as they pass through a thin film sample or through different mediums, as shown in Figure 1-6.⁴⁵ Specular reflection occurs when the surface is flat and smooth. In specular reflectivity, the scattered intensity is measured as a function of the wave vector transfer, Q , which is defined in Equation 1-2.⁴²

$$Q = \frac{4\pi}{\lambda} \sin \theta \quad (1-2)$$

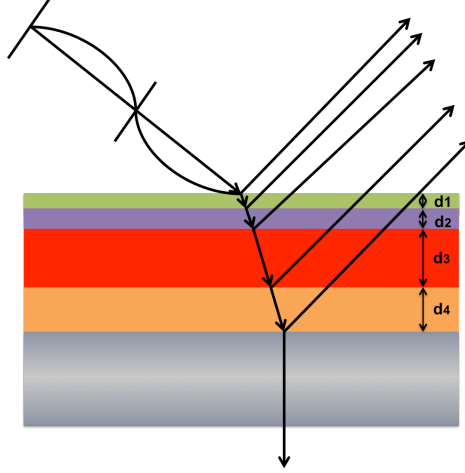


Figure 1-6. Illustration of how the neutron beam non-invasively interacts with the nuclei in a thin film. Some neutrons are reflected and some neutrons are refracted. The refracted beam probes the buried interfaces of each thin film. The reflected neutrons coherently add, and when detected and fit, yield structural information describing the film.

The reflectivity profile — reflected intensity as a function of Q — is related to the segment density profile normal to the surface, which contains structural information represented in the depth-dependent composition and mass density. The segment density profile contains composition b (per unit volume), calculated by equation 1-3.

$$N_b = \sum_{i=1}^J \frac{b_i}{V} \quad (1-3)$$

In this expression N_b is the scattering length density and b is the scattering length of j atoms that occupy the molecular volume, V .⁴³ The scattering length of each nucleus, b_j , is unique and varies arbitrarily across the periodic table. The SLD is sensitive to nuclear

isotopes and isotopic substitution of deuterium for hydrogen is a simple strategy for creating neutron scattering contrast in polymer materials because of the significant difference between the scattering length of H ($b_H = -3.74 \times 10^{-5} \text{ \AA}$) and D ($b_D = 6.67 \times 10^{-5} \text{ \AA}$).⁴⁴ Polymer brushes containing deuterium are important for quantitative determination of the effects of reactive modification because the relative ratio of D/H changes upon modification (with the addition of hydrogen rich amines), and measurements of the change in scattering length density are used to establish a depth-dependent profile. Analyzing neutron reflectivity data is tedious, and to accurately model NR data it is best to run replicate measurements and use complementary characterization techniques to resolve ambiguities. Reflectivity data is fit using a slab-like model consisting of multiple layers to build a realistic profile of the entire film.⁴² Each layer is described by its scattering length density (SLD), film thickness, and interfacial roughness of the film, which describes the width of the interface between two “slabs” of material. The SLD of the film (or layer) yields important information about the mass density and composition of the film. Comparing experimental measurements of SLD to calculated values enables the volume fraction of polymer components to be determined (if there is mixing between polymer layers within the film). NR can be used to determine the thickness of a film up to ~350 nm in thickness. Interfacial roughness provides information on the transition from one layer to the next: low interfacial roughness denotes a sharp interface, usually represented by a step-function profile, and a large interfacial roughness suggests that the interface is diffuse and material from two contacting layers is intermixed.⁴²

The types of systems I have studied in my dissertation research have been examined previously by neutron reflectivity. Soto-Cantu *et al.* completed neutron reflectivity measurements on PGMA modified surfaces. The NR measurements of the PGMA-modified surface indicated a layer thickness of 135 Å, an SLD of $8.3 \times 10^{-7} \text{ Å}^{-2}$, and a low interfacial roughness. These surfaces were reactively modified with propargylamine or 5-hexynoic acid.³⁵ Propargylamine-modified surfaces increased in thickness to 190 Å with slight increase in interfacial roughness, and the SLD slightly decreased to $8.2 \times 10^{-7} \text{ Å}^{-2}$. PGMA films modified with 5-hexynoic acid resulted in a thickness increase from 135 Å to 193 Å; however the SLD remained the same after functionalization. Both of the modified films were well-fit by a single layer model. A two-layer model was also examined to fit the data, but improvement in the “goodness-of-fit” parameter was not dramatic enough to support a two-layer model. Because these films were “hydrogen rich” (not deuterated), there were no significant changes in contrast to distinguish differences between the PGMA layer and the reactively modified layer. Perhaps most important about these studies, based on the measured SLD values, they determined that grafting of the thin film to a substrate does not result in the PGMA film reaching its bulk mass density.

Lokitz *et al.* used a grafting to approach to construct a PVDMA brush. A PGMA thin film was grafted first, followed by end-tethering of PVDMA chains. The NR data was fit to a three-layer model.¹⁶ The outer layer of PVDMA had a SLD of $1.47 \times 10^{-6} \text{ Å}^{-2}$, the SLD of the PGMA “base layer” was $1.35 \times 10^{-6} \text{ Å}^{-2}$, and between these slabs there was an interphase layer with an SLD of $1.43 \times 10^{-6} \text{ Å}^{-2}$, due to mixing of PGMA and PVDMA. Because the bottom layer and interphase layer had higher SLDs than what is

calculated for PGMA, it was assumed that some PVDMA chains were able to penetrate into and mix with the PGMA layer, resulting in this gradation of SLDs, as shown in Figure 1-7. Additionally, ellipsometry was used to measure the thickness of the film. The total ellipsometric thickness was comparable to the thickness determined through analysis of NR data; however if ellipsometry was used alone, the interphase region would not have been revealed. It should be noted that isotopic contrast enabled by the use of deuterated material would have enhanced the information obtained from these studies. In particular, greater detail of the width and intermixing in the interphase layer could have been revealed.

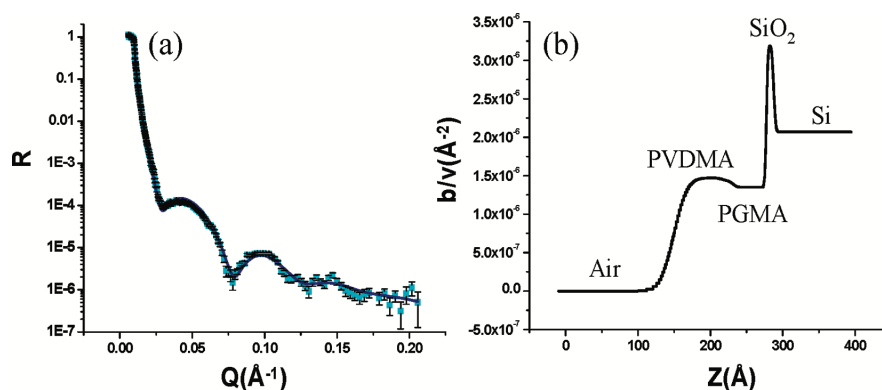


Figure 1-7. (a) Reflectivity as a function of wavevector transfer, Q . The data are shown as solid squares and the model as a dark blue line. (b) Scattering length density profile as a function of thickness, Z , used to generate the model reflectivity curve. Reprinted (adapted) with permission from Lokitz *et al. Macromolecules* 2009, 42 (22), 9018–9026. Copyright (2009) American Chemical Society.

Perhaps motivated by the recognition that deuteration was necessary, Lokitz *et al.* examined PVDMA brushes made by grafting PGMA-b-PVDMA chains. The methyl groups of PVDMA repeat units were isotopically substituted (D for H) to enhance the contrast between layers.⁴¹ Again, the NR data were fit using a three-layer model in which the layers were PVDMA (top), PVDMA-PGMA mix (middle), and PGMA (bottom), as shown in Figure 1-8.⁴¹ They determined the volume fraction profile of the film, characterized the composition of the interphase layer, and concluded that while PGMA prefers the solid/film interface and PVDMA preferentially segregates to the air/film interface, they do not completely phase separate.

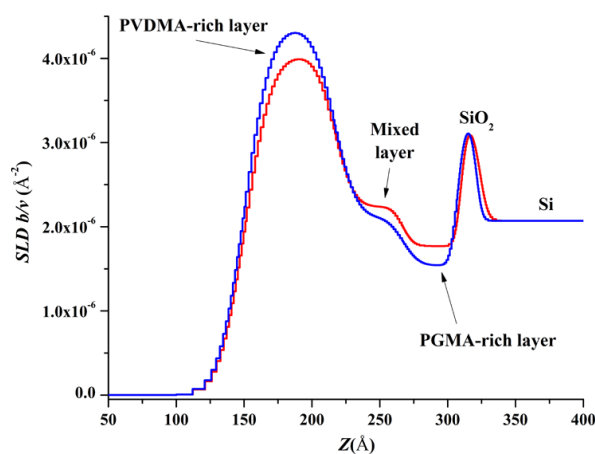


Figure 1-8. SLD profiles for the films annealed 25 °C (red) and 80 °C (blue) as a function of thickness, Z , used to generate the model reflectivity curves. Reprinted (adapted) with permission from Lokitz, *et al.* *Macromolecules* 2012, 45, 6438–6449. Copyright (2012) American Chemical Society.

1.6 Research Objectives

The main objective of my research is to understand the process of *in situ* modification of polymer brushes. To accomplish this, I will use poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) brushes because PVDMA is a useful, reactive polymer that can be modified by nucleophilic addition without producing byproducts. Furthermore, brushes are model systems because they organize at the solid/fluid interface. My main research tasks are to

1. Synthesize 4,4-dimethyl-d₆-2-vinyl-oxazolone (VDMA-d₆), poly(2-vinyl-4,4-dimethyl azlactone) and poly(glycidyl methacrylate)-block-poly(2-vinyl-4,4-dimethyl azlactone) diblock copolymers of different molecular weights;
2. Create well-defined PVDMA brushes of different molecular weights using a grafting to technique and characterize brush structure using ellipsometry, neutron reflectivity, spectroscopy, microscopy, and contact angle measurements. Within these studies I also will investigate the extent of functionalization and refunctionalization of brushes using model primary amines to understand penetration and reaction as a function of the size of the reactive species, grafting density (σ) of brush chains, and their molecular weight; and
3. Design a gradient system and investigate the effect of functionalization time and concentration along the polymer substrate using contact angle measurements, microscopy, and spectroscopy to examine changes in surface properties along the substrate.

In this dissertation, Chapter 2 describes the synthesis of PGMA homopolymers and end-functionalized PVDMA, which are grafted to a thin layer of PGMA to create PVDMA brushes. Different molecular weights were synthesized in a controlled manner, which allows the grafting density of the brush to be manipulated over a narrow range. The PVDMA brushes are used to address fundamental questions such as how the size of amine, concentration of amine, and functionalization time affect the extent of functionalization of the PVDMA chains. This chapter has scientific impact because of the insights obtained using NR, including confirmation that polymer chains are cleaved from the polymer brush. The results show that small amines can penetrate homogeneously throughout the brush, but larger amines result in a stratified, modified brush. The small layer thicknesses of the grafting to approach motivated the work described in Chapters 3 and 4, which rely on well-defined PVDMA brushes made by assembly of PGMA-*b*-PVDMA (or PGMA-*b*-PVDMA-*d*₆) diblock copolymers.

Chapter 3 describes neutron reflectivity studies aimed at understanding how grafting density affects the extent of functionalization of azlactone-containing polymer brushes. This reflectivity study delivers important fundamental insight into how grafting density of the polymer brush scaffold as well as the differences in size of the functionalizing agent (small primary amines) influence penetration of small molecules into the PVDMA brush and affect extent of modification. The sensitivity of NR to isotopic contrast is a key-enabling feature. Reflectivity measurements were made on the as-made PVDMA-*d*₆ films, the modified polymer films, and the re-functionalized polymer films. Re-functionalization studies provide clear insight as to whether PVDMA chains are completely modified. The fitting of the neutron reflectivity data yields

thickness, extent of functionalization, and amount of PVDMA chains that are cleaved from the substrate. From this data, depth-dependent scattering length density profiles, SLD (Z), are generated and compared.

The work described in Chapter 4 is motivated by results from work described in Chapters 2 and 3. Because there is “entropic death” of polymer brush chains during functionalization, designing a gradient system is a useful strategy to identify the best reaction conditions for a specific brush design (polymer, thickness and grafting density). Gradients allow a wide range of conditions to be explored in a single sample. PGMA-*b*-PVDMA block copolymer chains are used to in this effort, and controlled immersion creates a gradient in functionalization of the azlactone moieties of the brush along the substrate, which progressively changes the properties along the surface. I specifically investigate the change in wettability, topography, and extent of functionalization as a function of reaction time. Ellipsometry, AFM imaging, spectroscopy, and contact angle measurements are used to generate a complete picture of the position-dependent reactive modification.

Chapter 5 provides a simple summary of my dissertation work and what was learned. Through the completion of work, I have contributed fundamental knowledge for understanding reactive modification of polymer brushes, which enables numerous applications. In this final chapter, I will discuss the ideas for future research involving polymer materials based on 2-vinyl-4,4-dimethyl azlactone.

Chapter 2

Assessing Chemical Transformation of Reactive, Interfacial Thin Films Made of End-Tethered Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) Chains

A version of this chapter was originally published by Bethany Aden in *Macromolecules* 50, 2017, 618-630. Other co-authors include Camille M. Kite, Benjamin W. Hopkins, Anna Zetterberg, Bradley S. Lokitz, John F. Ankner, and S. Michael Kilbey II. For the work described in Chapter 2, I completed all of the polymer synthesis and characterization. Support from the National Science Foundation (Awards # 152221 and 133320) is gratefully acknowledged.

2.1 Abstract

Designing thin films or surface scaffolds with an appropriate display of chemical functionality is useful for biomedical applications, sensing platforms, adhesives, and barrier coatings. Relationships between the structural characteristics of model thin films based on reactive poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) brushes and the amount and distribution of primary amines used to chemically functionalize these layers *in situ* are quantitatively detailed via neutron reflectometry and compared with results from ellipsometry. After functionalization, the PVDMA brush thickness increases as a result of the primary amines reacting with the azlactone rings. Both techniques show that the extent of functionalization by small molecule amines depends on the size of the amine, the grafting density of brush chains and their molecular weight. However, constrained analysis of neutron reflectivity data predicated on that technique's sensitivity to isotopic substitution and its ability to resolve structure at the nanoscale shows that the extent of functionalization is not accurately represented by the average extent of functionalization determined from ellipsometric thickness: reactive modification is not uniform, even in modestly dense brushes, except when the penetrant is small. In

addition, there appears to be a loss of PVDMA chains during functionalization, attributed to chain scission resulting from additional stretching brought about by functionalization. These findings provide unprecedented insight into the alteration of surface properties by reactive modification and broadly support efforts to produce tailored surfaces in which properties such as friction, colloidal stability, adhesion, wettability, and biocompatibility can be modulated *in situ* by chemical modification.

2.2 Introduction

Surface and interfacial properties play an important roles in materials science and engineering, impacting such areas as wettability, adhesion, lubrication, optics, sensor technology, and nanopatterning.⁶ Tethering polymer chains to a surface by one end is an easy, controllable process that creates stable films. As a result, end-grafted layers that straddle the fluid/solid interface can confer new and useful properties to the surface. Above a critical grafting density, typically defined as the condition at which repulsive inter-chain interactions arise because of lateral crowding, the chains of the layer stretch away from the surface, creating a polymer “brush”.¹ While brushes are made by grafting pre-made chains to a substrate or by growing chains from it, with particular trade-offs resulting from the approach taken,^{3,7} the range and strength of the interaction potential is basically set by the molecular weight (or degree-of-polymerization, DP) of the chains and their grafting density,⁴⁷ while the choice of monomer (or co-monomers) and their topological arrangement sets the nature of the inter-surface potential.

Although there are a tremendous number of monomer types that can be used to create polymer brushes,⁷ post-polymerization modification is a useful and versatile strategy for designing “soft” surfaces with tailored interfacial properties. The use of

chemical transformations overcomes concerns with cross-reactivity between propagating chains and functional groups of the monomers, alleviates problems with increased steric bulk of pendant reactive groups, and reduces material demand when precious monomers are used.^{11,12,14,16,41} For post-polymerization modification to be successful, it is important to choose a monomer having a functional “handle” (reactive group) that is stable under polymerization conditions but is synthetically accessed with ease. There are numerous reports describing functionalization of pre-made brushes comprised of monomers having pendant hydroxyl, carboxylic acid, epoxy groups or functionalities that participate in orthogonal “click” reactions.^{13-17,29,48-50} Hydroxyl-containing polymer brushes, such as poly(2-hydroxyethyl methacrylate) (PHEMA) and poly(poly(ethylene glycol) methacrylate) (PPEGMA), have been acylated to alter the wetting characteristics of membranes and barrier coatings, to create smart surfaces, and to immobilize biomolecules.^{7,9,10,20,21,51,52} Carboxylic acid-functionalized polymer brushes have been transformed by a variety of post-polymerization modification reactions, yielding brushes that mediate protein binding or immobilization, and cell adhesion.^{23,24,53} Thiol-click reactions, such as thiol-ene, thiol-yne, and thiol-isocyanate reactions, have been used to reactively modify polymer brushes.^{8,54} For example, Rahane *et al.* synthesized polymer brushes containing alkyne groups using surface-initiated photopolymerization (SIP) and modified them via orthogonal thiol-yne “click” reactions. Other types of reactive brushes containing isocyanates, epoxides, and alkylhalides as pendant groups also were synthesized via SIP and reactively modified with dodecanethiol or thiolglycerol as model thiol molecules. Sequential or orthogonal functionalizations of copolymer brushes containing trimethylsilyl-protected propargyl methacrylate repeat units and co-

monomers containing other pendant groups also have been used to tailor surface properties by controlling the relative proportions of the co-monomers.⁸ Because functionality and surface properties are widely elaborated by *in situ* chemical transformation, well-defined polymer brushes are excellent model systems to quantitatively understand links between design and functionalization. However, to our knowledge there are only a few reports that systematically investigate the efficiency of reactive modification processes.

Rühe *et al.* used surface-initiated (SI) free-radical polymerization to create brushes comprising N-methacryloyl- β -alanine succinimide, a reactive ester, and functionalized those interfacial layers via aminolysis reactions using various n-alkyl amines and protected amino acids. FTIR and surface plasmon resonance (SPR) measurements suggest chemical conversion is nearly complete.¹⁴ The extent of functionalization, f , which reflects the conversion upon functionalization, was determined from the pre- and post-functionalization layer thicknesses, assuming no change in grafting density after aminolysis and that the mass density remains constant, even when the repeat units are reactively modified. By functionalizing using amino-terminated poly(ethylene glycol) (PEG), they also determined that as the molecular weight of the PEG increases, the extent of functionalization decreases, resulting in a lower degree of conversion due to the barrier for diffusion (penetration) established by the brush chains and the entropic penalty for additional stretching as PEG chains are added to the brush.¹⁴

Schüwer *et al.* used surface-initiated atom transfer (free) radical polymerization, or SI-ATRP, to synthesize PHEMA brushes and transformed them via a 2-step process.

First, a good leaving group was installed by reacting the PHEMA brushes with *p*-nitrophenyl chloroformate (NPC), then the resultant brushes were reactively modified using deuterated amino acids, which enabled neutron reflectometry to be used to study the penetration and reaction of deuterated “tags” in the NPC-modified PHEMA brush. Although the conversion of PHEMA with NPC was examined only qualitatively with FTIR and UV-vis spectroscopies, the grafting density of chains in brushes formed by SI-ATRP was not assessed. Furthermore, the scattering length densities (SLDs) of the amino acid-functionalized brushes used to fit reflectivity data (and extract a degree-of-functionalization) were assumed constant for all functionalization conditions at a value that implies mass densities are equal to ~75% of the bulk density. Despite these deficiencies, a variety of important observations were made. Results indicate that the types of amino acids used, D-10 leucine and D-3 serine, impact functionalization. In cases where D-10 leucine was used, the grafting density of the PHEMA chains, which was indexed only to the proportion of initiator molecules in the mixed self-assembled monolayer on the surface, played an important role: at a grafting density of 100%, functionalization by D-10 leucine appeared to be restricted to the peripheral region of the brush at the film/fluid interface, but as the grafting density decreased, more D-10 leucine was able to modify the brush, as evidenced by an increase in brush thickness after post-polymerization modification. However, behavior differed when D-3 serine was used: the distribution was inhomogeneous and no direct relationship between extent of functionalization and chain grafting density (proportion of initiators in the monolayer) was observed.⁵⁵ Given these unusual dependencies, it is also reasonable to wonder whether NPC-functionalization was consistent and uniform.

Perhaps to alleviate any complexity due to the formation and contribution of a leaving group, Barbey *et al.* used XPS and FTIR to examine the extent of post-polymerization modification of reactive poly(glycidyl methacrylate) (PGMA) brushes with propylamine and bovine serum albumin (BSA). XPS depth profiling and FTIR spectroscopy suggested the propylamine diffused and reacted homogeneously throughout the PGMA brushes; however, the instability of the epoxy group led to various side reactions. In contrast, the BSA protein (molecular weight ~66 kDa) was immobilized only at the top of the brush surface due to the steric hindrance of the large molecule, which prevented its penetration into the brush.¹¹

These works of Klok and coworkers^{11,55} and R  he and coworkers¹⁴ are important because they establish through quantitative measures, albeit with simplifying assumptions to facilitate analyses, that the size of the functionalizing agent and grafting density of chains influence the *in situ* reactive modification processes used to chemically transform the brush chains. However, the conclusion that functionalization of brushes with small molecules proceeds to completion, resulting in a uniformly modified brush remains unsettled. Also, the role of grafting density seems understood mostly in a conceptual sense. In that regard, it seems germane to also point out that the constructions of brushes in those works relied on surface-initiated polymerizations, which generally result in brushes of higher grafting density in comparison to brushes made by attaching premade chains by one end to a surface and rely on chains polymerized in solution as proxies for the molecular weight and dispersity of the brush chains. As will be demonstrated in the work described in this chapter, grafting density is an important variable that affects *in situ* brush functionalization. As a result, we revisit the effect of

the penetration and reaction of small molecules on the structure and composition of thin films with the anticipation of clarifying behaviors, elucidating links between brush structure and reaction conditions, and identifying key challenges remaining.

Our efforts focus on reactive, well-defined brushes of poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA). We have a long-standing interest in PVDMA that originates in the fact that VDMA can be polymerized by controlled (free) radical techniques, generating polymers and copolymers having reactive azlactone rings along the polymer backbone that are (relatively) hydrolytically stable but able to undergo ring-opening nucleophilic addition reactions (with primary amines, alcohols, and thiols) with no by-product formation.^{16,56–61} Messman *et al.* synthesized PVDMA copolymers that were reactively modified in solution with n-hexylamine, dansylcadaverine, and N_{α},N_{α} -bis(carboxymethyl)-L-lysine hydrate, and demonstrated “pegylation” of VDMA monomers.¹⁷ Lokitz *et al.* synthesized PVDMA block copolymers by reversible addition fragmentation chain-transfer (RAFT) polymerization and used those to create smooth and homogenous polymer brush scaffolds that were functionalized *in situ* by exposure to biotin-poly(ethylene glycol) amine.⁴¹

Herein we utilize carboxylic acid terminated, perdeuterated PVDMA chains grafted onto epoxy functionalized silicon substrates. The PVDMA brush layers were functionalized *in situ* with n-alkyl amines (hexyl, tetradecyl, or octadecyl). Along with investigations using FTIR spectroscopy and ellipsometry, which produce an “average” picture of the brushes and brush modification, we use neutron reflectivity and extract, from highly constrained fits of reflectivity data that incorporate both changes in structure (thickness and interfacial roughness) and composition (manifest in scattering length

density) indexed to the parent (unmodified) brush, quantitative descriptions of the distribution and amount of functionalizing agent in the modified PVDMA brush. In so doing, this rigorous analysis provides unparalleled insight into reactive modification that goes beyond previous reports. Specifically, our results reveal how the size of the functionalizing agent, chain molecular weight, and grafting density impact *in situ* modification.

2.3 Experimental Section

2.3.1 Materials

Silicon wafers of size 1.0 cm $\times$ 1.2 cm were purchased from Silicon Quest International. Glycidyl methacrylate (GMA, 97%, Aldrich) and 2-vinyl-4,4-dimethyl azlactone (VDMA) monomers were distilled under reduced pressure and the middle fractions (~70%) reserved for use. Azobisisobutyronitrile (AIBN, 98%, Aldrich) was recrystallized from methanol and dried under vacuum. 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (DMP) was synthesized following procedures described by Gondi *et al.*⁶² Benzene (99.9%, Aldrich), tetrahydrofuran (THF, 99.9%, Aldrich), chloroform (99.8%, Fisher), n-hexane (95%, Fisher), tetradecylamine (95%, Aldrich), octadecylamine (95%, Aldrich), and hexylamine (99%, Aldrich) were used as received. For neutron reflectivity studies, a perdeuterated variant of VDMA in which the 6 hydrogens of the methyl groups are isotopically substituted with deuterium, 4,4-dimethyl-d₆-2-vinyl-oxazolone (VDMA-d₆), was synthesized according to prior reports⁴¹ and used to provide isotopic contrast. Neutron reflectivity studies required the use of larger silicon substrates (50 mm diameter, 5 mm thickness) obtained from El-Cat (Waldwick, NJ, USA).

2.3.2 Instrumentation and Analysis

Gel Permeation Chromatography (GPC). Polymer molecular weights were measured using gel permeation chromatography (GPC) with a Tosoh EcoSEC GPC fitted with two Tosoh TSKgel SuperMultiporeHZ-M columns 4 μ (4.6 $\times$ 150 mm) and a TSKgel SuperMultiporeHZ-M guard column. Measurements were made at 40 °C using THF as the mobile phase. Molecular weights were determined using the EcoSEC Data Analysis software (version 1.04) relative to poly(methyl methacrylate) standards.

Ellipsometry. The thickness of thin films was determined using a variable-angle Beaglehole Picometer Ellipsometer that uses a He-Ne laser light source (λ = 632.8 nm). The thickness of each polymer-modified surface was measured in air at multiple angles, ranging from 80° to 60° in 1° steps, using previously published protocols.⁶³ The angularly-dependent data were co-fit using a model that treats each layer in the polymer film as a uniform slab. A refractive index of 1.46 was used for PGMA films and a refractive index of 1.50 was used for PVDMA layers.¹⁶ The slab-like model allows the thickness of each layer to be determined by optimizing goodness of fit. Multiple measurements were made on each surface and replicate samples were also used.

Fourier Transform Infrared Spectroscopy (FTIR). Polymer thin films and brushes were characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy using a Bruker Optics Vertex 70 spectrometer equipped with a Harrick Scientific VariGATR accessory, which has a germanium hemisphere internal reflection element. ATR-FTIR measurements used the narrow-band mercury-cadmium-telluride (MCT) detector, and at least 128 scans were collected.

Atomic Force Microscopy (AFM). The topography of polymer-modified surfaces was imaged using a Veeco Instruments Nanoscope IIIa MultiMode SPM atomic force microscopy (AFM) in tapping mode using a silicon cantilever.

Neutron Reflectivity (NR). Neutron reflectivity measurements were performed using the Liquids Reflectometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. The reflectivity data were collected using a sequence of 3.25-Å-wide continuous wavelength bands (selected from $2.63 \text{ \AA} < \lambda < 16.63 \text{ \AA}$) and incident angles (selected between $0.6^\circ < \theta < 2.71^\circ$) that together cover a range of momentum transfer wavevector, Q , where $Q = 4\pi \sin \theta / \lambda$, from $0.008 \text{ \AA}^{-1} < Q < 0.22 \text{ \AA}^{-1}$. For each sample, a single reflectivity curve was assembled by combining data acquired using seven different wavelength and angle data sets while maintaining a constant relative instrumental resolution of $\delta Q / Q = 0.023$ by varying the incident-beam apertures.

2.3.3 Synthetic Procedures

Synthesis of PGMA by conventional free radical polymerization. GMA (6.54 g, 4.60×10^{-2} mol) was combined with AIBN (228 mg, 1.39×10^{-3} mol) (that had been recrystallized) and benzene in a 50 ml round bottom flask, sealed with a rubber septum, and sparged with dry nitrogen for 30 minutes. The vessel was placed in an oil bath at 65 °C and allowed to react for 1 h while stirring. A typical polymerization uses AIBN and GMA in a molar ratio of 1:33 and a GMA concentration of 2.3 M. The free radical polymerization of GMA was quenched by immersing the flask in liquid nitrogen until frozen. After allowing the contents to thaw, the reaction mixture was precipitated into cold hexanes. PGMA was isolated by decanting and then dried under vacuum overnight.

Synthesis of PVDMA by RAFT polymerization. VDMA (2.78 g, 2.00×10^{-2} mol) (or the equivalent molar amount of VDMA-d₆) was combined with DMP (20.3 mg, 5.56×10^{-4} mol), AIBN (18.3 mg, 1.11×10^{-4} mol), and benzene in a 50 mL round bottom flask, sealed with a rubber septum, and sparged with dry nitrogen for 30 minutes. As an example, a RAFT polymerization was conducted using ratios of 1:180 of AIBN:VDMA and 15:539 of DMP:VDMA and a [VDMA] of 0.99 M to set the theoretical molecular weight to be 5,000 g mol⁻¹. This solution was immersed in an oil bath and stirred at 65 °C for 18 h, after which time the reaction was quenched by submerging the flask in liquid nitrogen until frozen. After warming the reaction mixture to room temperature, PVDMA was precipitated into cold hexanes, isolated by decanting, and then dried overnight under vacuum.

2.3.4 Sample Preparation

Wafer cleaning. Silicon wafers were cleaned prior to use in a piranha acid solution (3:1 v/v H₂SO₄/30% H₂O₂) at 80 °C for 30 minutes. After cleaning, the wafers were rinsed with deionized water and dried using a stream of nitrogen. Cleaned wafers were used immediately. Hydrogen peroxide (30%, Certified ACS, Fisher Chemical) and sulfuric acid (Certified ACS Plus, Fisher Chemical) were used as received. *Caution! Piranha acid is a strong oxidizer and a strong acid; it should be handled with extreme care, as it reacts violently with most organic materials.*

Formation of PGMA-modified silicon surfaces. Thin films of PGMA or PVDMA were deposited on silicon wafers by spin coating at 2500 rpm for 15 seconds using a Laurel Technologies Corporation spin coater (model WS-650MZ-23NPP). A 0.25 wt.% PGMA solution in chloroform was spin coated onto clean silicon wafers. After spin

coating, PGMA-modified substrates were annealed at 80 °C, which is above the glass transition temperature, but below temperatures at which PGMA rapidly crosslinks,⁴¹ for 30 minutes to promote reaction between the epoxy groups of PGMA and hydroxyl groups on the silicon substrate.⁴¹ Wafers were then sonicated in chloroform (CHCl₃) to remove any physisorbed PGMA chains. After sonication, the wafers were rinsed with chloroform and dried with a stream of nitrogen.

Formation of PVDMA brushes. A 0.25 wt.% solution of the carboxylic acid-terminated PVDMA in chloroform was made and used to deposit PVDMA chains onto PGMA-modified silicon wafers by spin coating. (The carboxylic acid end group comes from the use of DMP as the CTA.) After spin coating, the films were annealed at 110 °C for 18 h to provide mobility to the PVDMA chains and to promote reaction between remaining epoxy groups of the surface tethered PGMA film and the carboxylic acid end-group on each PVDMA chain. After cooling to room temperature while under vacuum, the wafers were sonicated in chloroform to remove non-covalently bound PVDMA chains, rinsed with chloroform, and then dried with a stream of dry nitrogen. Although the PVDMA chains are end-tethered to the surface-bound PGMA layer, and regardless of whether the chains were isotopically substituted or not, for convenience these structures are referred to as “PVDMA brushes”.

Post-polymerization modification of PVDMA brushes. PVDMA-modified wafers were submerged for 2 h in 0.25 wt.% solutions of either 1-hexylamine (HA), 1-tetradecylamine (TDA), or 1-octadecylamine (ODA) in chloroform. After this reaction time, the wafers were removed and sonicated in pure CHCl₃, rinsed with CHCl₃, and then dried with a stream of dry nitrogen. To explore whether functionalization (of the

azlactone rings) of the PVDMA brushes was exhaustive, some of the functionalized polymer brushes were refunctionalized by immersion in a 0.25 wt.% solution of 1-hexylamine for 1 h. After this second reactive modification, the wafers were sonicated, rinsed with chloroform, and then dried with a stream of dry nitrogen.

The concentration used for functionalization studies was deduced from a variety of parametric studies that explored functionalization time and concentration. Concentrations from 0.25 wt.% to 0.75 wt.% were investigated, and ellipsometry measurements showed negligible variation across this range;⁶⁴ therefore 0.25 wt.% was chosen for all experiments.

2.4 Results and Discussion

2.4.1 Synthesis of PGMA and PVDMA

Poly(glycidyl methacrylate) (PGMA), synthesized by conventional free radical polymerization, had a number average molecular weight, $M_n = 25,100 \text{ g mol}^{-1}$ and a dispersity of 1.9. RAFT polymerization was used to synthesize carboxylic acid-terminated PVDMA chains of various molecular weights, which are listed in Table 2-1. The agreement between target and measured molecular weights and low dispersities confirms that the RAFT polymerization of VDMA using DMP is well-controlled, as demonstrated in prior reports.^{17,35,41}

2.4.2 PVDMA brush formation: Surface Attachment and Characterization

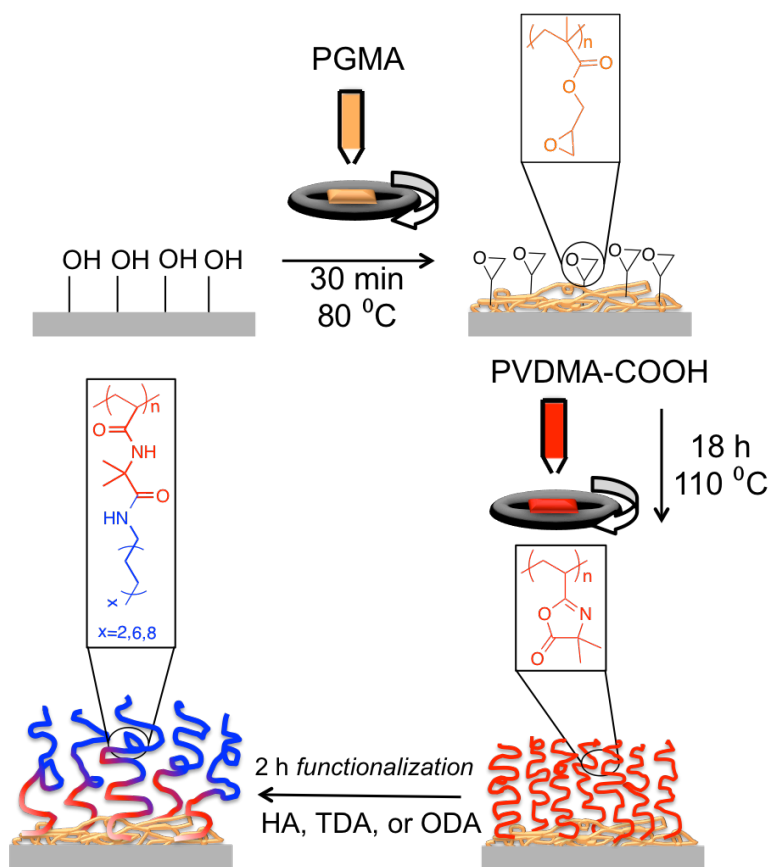
A “grafting to” approach is used to attach the pre-made PVDMA chains to PGMA-modified silicon substrates. As shown by Lokitz *et al.*, the terminal carboxylic acid end group of the CTA, 2-dodecylsulfanylthiocarbonylsulfanyl-2-methylpropionic acid (DMP), tethers the PVDMA chains by their end to the PGMA-modified substrate.⁴¹

Table 2-1. PVDMA Polymerization Conditions and Macromolecular Properties.

Target M_n (g mol ⁻¹)	AIBN:VDMA	DMP:VDMA	M_n (g mol ⁻¹)	$\bar{D}$
5K	1:180	15:539	4,800	1.13
10K	1:359	7:503	9,300	1.10
20K	1:719	4:575	17,300	1.09
30K	1:1078	2:431	29,400	1.15
35K ^a	1:1207	3:724	32,500	1.14

^a data for PVDMA-d₆

This approach follows reports by Luzinov *et al.*, who first demonstrated the use of PGMA as a “primer” layer onto which end-functionalized chains are easily grafted.^{34,65} Chloroform was used to deposit PGMA chains by spin coating, which yielded smooth, homogeneous thin films, as previously reported.³⁵ After spin coating, annealing, and removing non-bonded PGMA chains by sonication, the thicknesses of the surface-bound PGMA films were generally found to be 3 nm, as determined by multi-angle ellipsometry. PVDMA was then applied to the PGMA surface by spin coating from chloroform and annealing at 110 °C to covalently end-graft the PVDMA chains. This “grafting to” process, which is depicted in Scheme 2-1, results in PVDMA brushes that are end-tethered to a surface-bound PGMA primer layer, with the PVDMA brush layers measuring, on average, 5-7 nm by ellipsometry.



Scheme 2-1. Procedure used to create PVDMA brushes by attaching end-functional chains to a silicon substrate through a thin PGMA layer, and subsequent *in situ* functionalization by small molecule amines.

2.4.3 Physical Characterization of PVDMA Brush-Modified Surfaces

Grafting density is an important parameter that governs interactions and the extent of stretching of the brush chains and affects penetration of molecules into the brush layer.⁸ The ellipsometric thickness of PVDMA and chain molecular weight, determined by GPC, are used to calculate grafting density, σ , using the dimensional expression^{34,66}

$$\sigma = \frac{H\rho N_A}{M_n} \quad (2-1)$$

In this equation, H is the ellipsometric thickness of the dry layer, ρ is the mass density of the polymer brush layer, which is taken to be $1.05 \text{ g}\cdot\text{cm}^{-3}$ for PVDMA,⁴¹ N_A is Avogadro's number, and M_n is the number-average molecular weight of the polymer, which is given in Table 2-1. The calculated grafting densities are listed in Table 2-2, and the values confirm that as the molecular weight of the grafted PVDMA chains increases, H of the brush increases while σ decreases. These are not unexpected behaviors because as the molecular weight of the chains increases, the coil volume increases, which increases the “footprint” (the projected area) of the coil on the surface, which decreases the ability of tethered chains to pack closely.^{4,67,68} The distance between chains, D , where $D = 2(\pi\sigma)^{-1/2}$, is compared to the radius of gyration, R_g ($R_g = bN^{3/5}$, with $b = 0.15 \text{ nm}^{69}$ for PVDMA and $N = \text{degree of polymerization}$) to assess the degree-of-crowding of chains in the layer.

Grafted chains are considered to be in the brush regime when $D < 2R_g$.^{70,71} If $D/2R_g < 1$, then lateral crowding of the tethered chains causes them to stretch away from the surface when immersed in a good (or theta) solvent. The calculated grafting densities

Table 2-2. Characteristic Properties of Surface Grafted Layers made by Tethering PVDMA Chains of Different M_n .

M_n (g mol ⁻¹)	H (nm)	σ (chains/nm ²)	D (nm)	R_g (nm)	$D/2R_g$
4,800	5.2 ± 3.2	0.55	1.61	1.36	0.607
9,300	6.0 ± 1.8	0.45	1.77	1.74	0.510
17,300	6.1 ± 3.0	0.22	2.52	2.71	0.470
29,400	6.6 ± 2.3	0.14	3.08	3.70	0.424

confirm that the process used to graft the end-functional PVDMA chains results in layers that are in the brush regime. Characteristic values of H resulting from multiple measurements made on replicate samples are given in Table 2-2 (along with the standard deviation computed from those measurements); from those values, σ and D for PVDMA brushes of different molecular weights are calculated. These characteristic values are in good agreement with values reported in previous work by Lokitz *et al.*¹⁶

2.4.4 Functionalization of PVDMA Brushes with Primary Amines – An “Average” Picture

After characterizing the PVDMA brushes by ellipsometry, they were functionalized *in situ* by immersing each brush-modified substrate in a 0.25 wt.% solution of either 1-hexylamine (HA), 1-tetradecylamine (TDA), or 1-octadecylamine (ODA) in chloroform for a reaction time of 2 h. During this time, the azlactone rings of the PVDMA brush are reactively modified by nucleophilic addition of the amine. From various parametric studies, it was determined that a reaction time of 2 h is optimal in the

sense that it yields the largest increase in layer thickness. The change in ellipsometric thickness (before and after the functionalization reaction) is directly related to the extent of functionalization, f , which describes the fraction of azlactone rings that are consumed by nucleophilic addition:^{14,35}

$$f = \frac{[(H_{\text{PVDMA-Amine}} \cdot \rho_{\text{PVDMA-Amine}} \cdot M_V) - (H_{\text{PVDMA}} \cdot \rho_{\text{PVDMA}} \cdot M_V)]}{[H_{\text{PVDMA}} \cdot \rho_{\text{PVDMA}} \cdot (M_M - M_V)]} \quad (2-2)$$

In this expression, which is adapted from the work of Soto-Cantu *et al.*,³⁵ the subscripts on brush thickness, H , and mass density, ρ , denote the “parent” PVDMA brush or the modified PVDMA-amine conjugate, and M_V and M_M refer to the molar mass of the VDMA monomer and amine-modified conjugate, respectively. Values of M_V and M_M are 139.2 g mol⁻¹ for PVDMA, 240.4 g mol⁻¹ for PVDMA+HA, 352.6 g mol⁻¹ for PVDMA+TDA, and 408.7 g mol⁻¹ for PVDMA+ODA, respectively.⁶⁴ When calculating f from changes in ellipsometric thicknesses, it is assumed that the thickness increase is due to reactive modification of the PVDMA brush, while the PGMA layer thickness is fixed at its initial value.

Because the molecular weights of the monomer and functionalizing reagents are known, the main sources of uncertainty in applying Equation 2-2 originate from measurements of brush thickness as well as from the mass densities of surface tethered thin films (whether they are unfunctionalized or functionalized), which may differ from the bulk density.⁷² Dry layer thicknesses measured by ellipsometry are expected to be accurate within ± 1 nm; however, in thin films, thickness and refractive index, η , are coupled. Generally speaking, refractive indices are based on bulk systems or estimated for thin organic films to be $\eta = 1.5$. Thin film mass densities also are generally assumed

to be equivalent to the bulk values; however, because confinement to the surface distorts chain conformation and affects chain packing, the density of a polymer brush may not necessarily be equivalent to the bulk values, as rigorously proven by Deodhar *et al.* through neutron reflectivity measurements and analysis.⁷² Moreover, the density of the functionalized brush, here captured in $\rho_{\text{PVDMA-Amine}}$, is especially complicated because reactive modification changes the monomer mass and the volume occupied by the new repeat unit. The mass density of the reactively modified brush is not easily characterized because the chains are attached to the underlying PGMA film and, in turn, to the silicon surface. Additionally, the chains may not be uniformly functionalized because the segment density profile of a solvent-swollen brush is understood to be a smoothly decaying function, rather than “step-like”, with the segment density at the outermost periphery decaying to zero.^{70,71} Because of these complications, simplifying assumptions must be made. Prior work by Murata *et al.*¹⁴ and Soto-Cantu *et al.*³⁵ assumed that the density of the brush and the refractive index are not affected meaningfully by functionalization, and those simplifications also are invoked here as a starting point.

The extent of functionalization of PVDMA brushes of different molecular weights after modification with HA, TDA, and ODA as deduced from ellipsometry measurements are shown in Table 2-3. Ellipsometry measurements to determine the change in H result from making multiple measurements on at least 12 replicate samples. Chemical attachment of the amines increases crowding within the polymer brush, causing the chains of the brush to stretch, which manifests as an increase in thickness of the brushes. It is also observed that the extent of functionalization is affected by the size

Table 2-3. Extent of Functionalization Determined by Ellipsometry for PVDMA Brushes.

M_n^a (g mol ⁻¹)	H_{PVDMA}^b (nm)	σ (chains/nm ²)	FA ^c	$H_{\text{PVDMA-amine}}^b$ (nm)	f^d
5K	6.0 ± 0.9	0.64	HA	7.1 ± 0.6	0.429
	4.6 ± 1.2	0.44	TDA	6.0 ± 1.6	0.324
	4.6 ± 1.0	0.56	ODA	5.7 ± 1.2	0.157
10K	7.2 ± 2.6	0.52	HA	8.0 ± 2.6	0.174
	4.7 ± 0.7	0.36	TDA	5.8 ± 1.2	0.149
	6.2 ± 0.6	0.46	ODA	6.9 ± 0.8	0.061
20K	6.3 ± 3.8	0.24	HA	7.8 ± 3.9	0.378
	6.2 ± 4.1	0.23	TDA	7.2 ± 4.4	0.128
	5.7 ± 0.9	0.20	ODA	7.3 ± 1.9	0.111
30K	7.3 ± 2.9	0.16	HA	8.5 ± 1.2	0.316
	6.1 ± 1.7	0.12	TDA	8.1 ± 1.5	0.290
	6.3 ± 1.4	0.13	ODA	7.8 ± 1.7	0.160

^a M_n values are target M_n ; actual molecular weight values are given in Table 2-1

^b PVDMA thickness and PVDMA thickness after functionalization with the small molecule amine

^c FA refers to the functionalizing agent used: HA = hexylamine; TDA = tetradecylamine; ODA = octadecylamine ^d Extent of functionalization of the modified brush as determined via ellipsometry

of primary amine, with the smallest amine (hexylamine, HA) giving the greatest extent of functionalization, while the largest amine (ODA) results in the lowest f . These results also show that as the grafting density of chains increases, the extent of functionalization decreases, which is consistent with trends observed by R  he *et al.*¹⁴ and Klok *et al.*^{11,55} and is attributed to the crowding of the chains making it more difficult for molecules to penetrate into the brushes where they can react with functional groups.

In addition to steric crowding as a key factor prohibiting complete conversion, it is also possible that conjugation of the alkyl amine changes the solubility of the tethered chain. These two factors could work in concert to limit access to azlactone rings. It is conceivable that when the surfaces are submerged in the amine-containing solution, the most accessible azlactone rings located at the brush/solution interface are functionalized first. The addition of the amine by the ring-opening addition reaction causes a local increase in steric bulk, which, if coupled with a decrease in chain solubility, would limit access to reactive sites buried deeper in the brush layer. Such a scenario, if operative, would lead to a two-level (stratified) structure in which the outer portion of the brush is more highly functionalized than the strata closer to the substrate. However, ellipsometry measurements are incapable of detecting this structure in ultrathin films. Thus, the f values deduced from ellipsometry measurements are averages.

An additional effect, due to the conformational entropy of the brushes, also may be impacting the extents of functionalization determined from ellipsometry measurements. Notionally, thermodynamic equilibrium is achieved by a balance between swelling of the chains and the entropic penalty for stretching.^{3,5,68} Setting aside any change in solubility as the azlactone rings are reactively modified, the polymer

chains become increasingly stretched, taking the system further from the equilibrium established when the brush was originally formed. We posit that at some point, the thermodynamic penalty for additional stretching may become substantial, resulting in a “stretch-activated” scission of the chain. A loss of chains from the brush decreases the grafting density, thereby reducing the repulsive interchain interactions that cause swelling. This effect – so-called “entropic death” – was previously observed by Samancas and R  he.⁷³ Other works have also observed hydrolytic degrafting of chains of dense brushes created by surface-initiated polymerizations, ostensibly due to cleavage of siloxane bonds tethering the chains to the substrate or ester linkages within the surface-grafted initiator, both of which are labile in aqueous environments.^{74–78} While those works rely on optical imaging and ellipsometric measurements and do not assess areal density of chains (grafting density), the general phenomenon of a stretch-activated bond breaking is firmly established. While we revisit the concept of loss of chains later in the dissertation, we emphasize that all of these effects – additional crowding that stretches the layer; changes in chain solubility; and entropic death of chains – are likely to depend on the characteristic parameters of the brush, σ , M_n , and $D/2R_g$, as well as the solvent quality. For these reasons, direct comparisons of the extent of functionalization obtained for different brushes are tenuous.

In addition to ellipsometry, ATR-FTIR was used to qualitatively examine brush functionalization. Because the carbonyl of the azlactone ring at 1825 cm^{-1} is distinct, changes due to nucleophilic ring-opening of the azlactone ring are easily observed.¹⁷ As shown in Figure 2-1, PVDMA exhibits two distinct peaks: the carbonyl peak at 1825

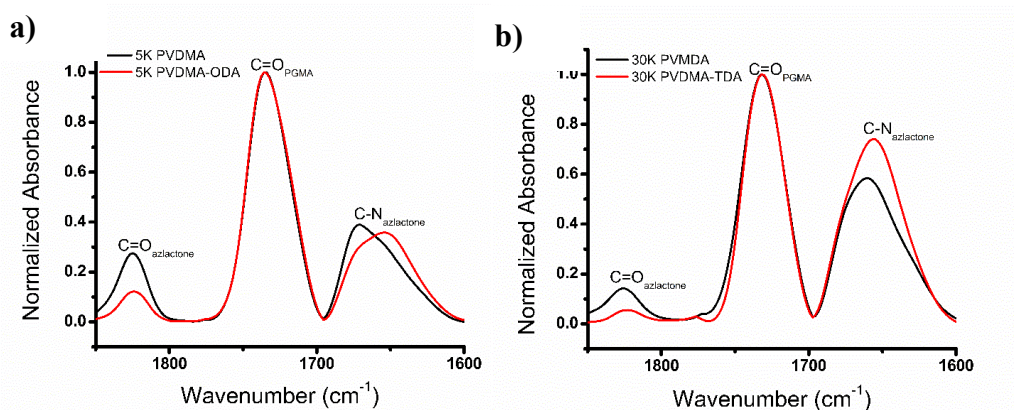


Figure 2-1. Partial ATR-FTIR spectra emphasizing the changes in modes associated with the azlactone rings of the (a) 5,000 g mol⁻¹ and (b) 30,000 g mol⁻¹ PVDMA brushes before and after exposure to an amine solution. The parent PVDMA films show peaks at 1825 cm⁻¹ due to the carbonyl of the azlactone ring and at 1660 cm⁻¹ due to the imine stretch (black lines). The PVDMA repeat units undergo ring-opening nucleophilic addition when exposed for 2 h to a 0.25 wt.% solution containing (a) octadecylamine or (b) tetradecylamine (red lines).

cm⁻¹ and the imine stretch at 1660 cm⁻¹. When the PVDMA brushes are exposed to a nucleophile, such as an amine or alcohol, a decrease in the carbonyl peak intensity at 1825 cm⁻¹ is observed along with a transformation of an imine stretch to an amide stretch, which is observed at 1650 cm⁻¹. While the ATR-FTIR spectra for ODA functionalization of a 5,000 g mol⁻¹ PVDMA brush (Figure 2-1a) and TDA functionalization for 30,000 g mol⁻¹ PVDMA brush (Figure 2-1b) appear to suggest a greater extent of functionalization as compared to that determined by ellipsometry, we found that the thinness of the samples complicated quantification. Nevertheless, both

spectra show that the PVDMA brushes are not exhaustively functionalized, which is consistent with extents of functionalization determined from the increase in ellipsometric thickness.

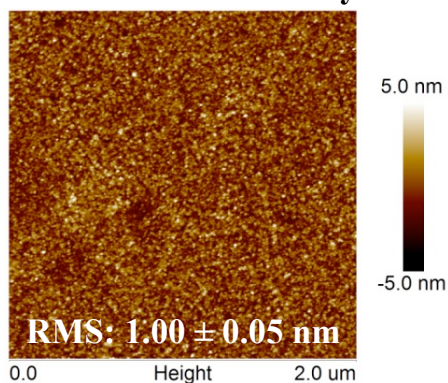
AFM was used to image the topography and quantify the roughness of the PVDMA-modified surfaces before and after functionalization. Images presented in Figure 2-2 confirm that the parent PVDMA brushes and the chemically modified brushes are smooth and homogenous, with RMS (root mean squared) roughness values of < 2 nm before and after functionalization.

Since I previously discussed that the brush refractive index may be affected by the functionalization and that the extent of functionalization is less than 100%, it is important to seek techniques that are sensitive enough to distinguish the parent film from the functionalized film and to determine the amount and distribution of the amines in the brush layer. For this purpose, I performed a series of neutron reflectivity measurements. Before presenting results, I first describe the qualities that suit neutron reflectivity for this task, then develop a model by which reflectivity data is interpreted to yield information on the extent of functionalization and the depth-dependent distribution of functionalizing agents in the film, as well as give insight into how loss of chains impacts functionalization.

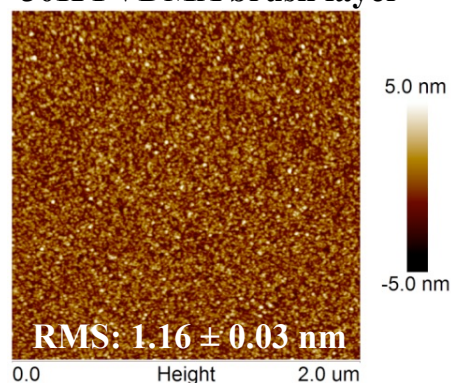
2.4.5 Functionalization of PVDMA Brushes with Primary Amines – Detailed Analysis via Neutron Reflectivity (NR)

The sensitivity of neutron scattering methods to isotopic substitution (of D for H) is used to provide insight into the distribution of functional groups bound to the PVDMA brush by reactive modification. Recall that in these experiments, methyl groups

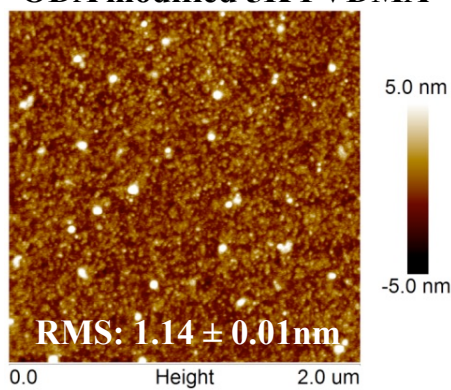
a) 5K PVDMA brush layer



c) 30K PVDMA brush layer



b) ODA modified 5K PVDMA



d) TDA modified 30K PVDMA

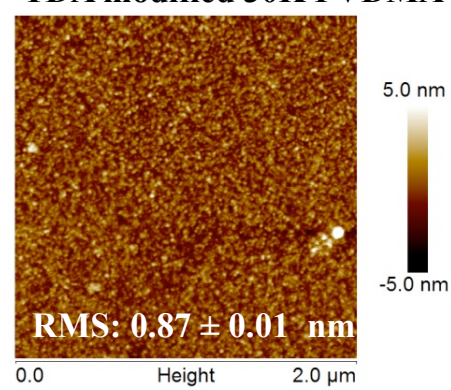


Figure 2-2. AFM height images acquired over $2.0 \mu\text{m} \times 2.0 \mu\text{m}$ regions of PVDMA brushes: (a) $5,000 \text{ g mol}^{-1}$ PVDMA brush, (b) ODA-modified $5,000 \text{ g mol}^{-1}$ PVDMA brush, (c) $30,000 \text{ g mol}^{-1}$ PVDMA brush, and (d) TDA-modified $30,000 \text{ g mol}^{-1}$ PVDMA brush.

of VDMA are isotopically substituted (D for H), giving VDMA-d₆. Thus, when PVDMA-d₆ is reactively modified with HA, TDA, or ODA, the relative ratio of D/H changes, (Hereafter, even though the polymer is perdeuterated, I simply refer to it as PVDMA.) The incident neutron beam noninvasively interacts with the PVDMA brush and is able to resolve structure in films of thicknesses ranging from 0.5 to 350 nm.⁴³ Reflected neutrons from the surface and from internal interfaces coherently combine to form a reflected beam that is then collected by the detector. A model is used to fit the neutron reflectivity data, providing insight into the structure of the layers in the film. The model yields the scattering length density (SLD) of the brush along with the thickness of the PGMA primer layer, and the thickness of the PVDMA brush. Neutron reflectivity is sensitive to the distribution of the functionalization molecule inside the brush and to the degree of mixing at the interfaces.

Density of PVDMA parent film: The scattering length density of the PVDMA parent film is given by

$$\Sigma_0 = \frac{\rho_0 N_A}{M_V} b_V = N_{V0} b_V \quad (2-3)$$

where ρ_0 is the mass density, N_A is Avogadro's number, M_V the VDMA monomer's molecular mass, b_V its scattering length, and N_{V0} the VDMA number density. Because we know the stoichiometry of PVDMA, we know b_V and M_V . These values are tabulated for the constituent repeat units under consideration. (See Table A-1 for tabulated values and Figure A-1 for ChemDraw structures representing repeat units in Appendix A.) By measuring the scattering length density Σ_0 of the parent film of known stoichiometry, we unambiguously measure its mass density:

$$\rho_0 = \frac{M_v}{b_v} \frac{\Sigma_0}{N_A} \quad (2-4)$$

Calculating the reacted fraction of modified films: After exposure of the brush to the amine solution, the mass density of the modified layer, ρ_M , as in the case of the parent film, is determined from the fitted SLD and the stoichiometry;

$$\rho_M = \frac{M_M}{b_M} \frac{\Sigma_M}{N_A} = \left(\frac{f_M M_{am} + M_v}{f_M b_{am} + b_v} \right) \frac{\Sigma_M}{N_A} \quad (2-5)$$

where Σ_M is the fitted SLD of the modified layer, M_M is its molecular mass, b_M is the aggregate scattering amplitude of the nuclei in the average repeat unit of the reactively-modified film, and f_M is the fraction of VDMA repeat units that are transformed by the ring-opening nucleophilic addition of the amine. The atomic mass and scattering amplitude of the modified layer are given by the f_M -weighted sums of the amine-modified (M_{am} and b_{am}) and VDMA (M_v and b_v) repeat units.

Two distinct modified layers: If, upon amine exposure, the film exhibits two distinct reacted layers, f_M is determined from the total thickness, d_M , and the thickness-weighted composite SLD, Σ_M :

$$d_M = d_{M1} + d_{M2} \quad (2-6)$$

$$\Sigma_M = \frac{d_{M1}}{d_{M1} + d_{M2}} \Sigma_{M1} + \frac{d_{M2}}{d_{M1} + d_{M2}} \Sigma_{M2} \quad (2-7)$$

where d_{M1} and d_{M2} are the fitted layer thicknesses of the two strata within the brush, identified as M1 and M2, and Σ_{M1} and Σ_{M2} are the fitted SLDs of those layers.

Ultimately, out of these relations, it would be useful to back out (calculate) the mass densities and converted fractions of the modified brush. Unfortunately, because

SLD is composed of the product of stoichiometry and mass density (see eq (2-3)), both chemical alteration of the repeat unit and change in density of the film contribute to the change in SLD. In short, the reactive modification changes the chemical nature of the repeating unit and that addition may bring steric effects that change the mass density of the functionalized polymer. If the film partitions into two reacted layers, the original population of parent VDMA monomers is distributed ambiguously into those two layers. It is possible to set limits on the reacted fraction by assuming that the SLD change is caused entirely by chemical reaction at constant mass density and performing the calculation over a physically reasonable range of mass densities. For the case of constant mass density, $\rho_M = \rho_{M1} = \rho_{M2}$, solving equation (2-5) for f_M for the two layers yields:

$$f_{Mi} = \frac{\rho_M N_A b_V - \sum_{Mi} M_V}{\sum_{Mi} M_{am} - \rho_M N_A b_{am}} \quad (2-8)$$

where subscript $i = 1,2$ denotes the two different constant mass-density strata and all other parameters are as defined above.

Accounting for loss of PVDMA chains: As described earlier, due to a stretching-activated entropic death from bond scission, PVDMA chains are lost during exposure to the amine solution. As with the partitioning of VDMA into two layers, loss of VDMA monomer during the reaction renders exact determination of mass density and reacted fraction infeasible. The fraction of PVDMA chains lost during reactive modification is therefore estimated by assuming a realistic mass density value $\rho_{M,est}$ (e.g. $1.0 \text{ g}\cdot\text{cm}^{-3}$) in equation (2-8) to obtain an estimated converted fraction $f_{M,est}$;

$$f_{M,est} = \frac{\rho_{M,est} N_A b_V - \Sigma_M M_V}{\Sigma_M M_{am} - \rho_{M,est} N_A b_{am}} \quad (2-9)$$

The development of equation (2-9) is important because if the amount of PVDMA that is lost is calculated, then it can be determined how much of the remaining PVDMA was modified by exposure to the amine. This gives clearer insight into the process of reactive functionalization under various conditions. To estimate the fraction of original VDMA monomers lost, equation (2-3) is recast to include the contribution of the added amines to the SLD of the modified film:

$$\Sigma_M = N_{V,est} b_V + N_{am,est} b_{am} \quad (2-10)$$

where $N_{V,est}$ and $N_{am,est}$ are the values of VDMA and amine number density for a film of mass density, $\rho_{M,est}$. Likewise, a more general expression for $f_{M,est}$ is captured by the ratio of number densities of amine-modified VDMA repeat units to all VDMA repeat units remaining postreaction:

$$f_{M,est} = \frac{N_{am,est}}{N_{V,est}} \quad (2-11)$$

Thus, equations (2-10) and (2-11) can be combined to eliminate $N_{am,est}$:

$$N_{V,est} = \frac{\Sigma_M}{b_{am} f_{M,est} + b_V} \quad (2-12)$$

and

$$\begin{aligned}
f_{\text{PVDMA-lost}} &= 1 - \frac{N_{\text{V,est}}}{N_{\text{V0}}} = 1 - \frac{\Sigma_{\text{M}}}{b_{\text{am}} f_{\text{M,est}} + b_{\text{V}} \Sigma_0} \frac{b_{\text{V}}}{\Sigma_0} \\
&= 1 - \frac{\Sigma_{\text{M}}}{\Sigma_0} \frac{b_{\text{V}}}{b_{\text{am}} f_{\text{M,est}} + b_{\text{V}}}
\end{aligned} \tag{2-13}$$

where equation (2-3) has been used to define N_{V0} . The quantity $f_{\text{PVDMA-lost}}$ thus represents our estimate of the fraction of VDMA repeat units lost during reaction with the amines.

Analysis of Reflectivity Data: Neutron reflectivity data was collected from surfaces consisting of “hydrogen-rich” PGMA as a thin film binding layer and PVDMA- d_6 for the brush layer. PVDMA- d_6 was synthesized as previously reported and had an $M_n = 32,500 \text{ g mol}^{-1}$ and $\bar{D} = 1.14$.⁴¹ The substrates for neutron reflectivity measurements were prepared exactly as the smaller substrates used in the ellipsometry measurements in terms of the wt.% of the polymer solutions and the solvent used in spin casting, annealing times, concentration of the functionalization reagent, and the time the brushes were exposed to the amine solution. Previous NR experiments revealed the SLD of the PGMA primer layer to be $9.0 \times 10^{-7} \text{ \AA}^{-2}$ and the average thickness of the PGMA layer to be $11.0 \text{ \AA}$. Because chloroform is a good solvent for PGMA, the covalently attached PGMA thin film will swell when exposed to the PVDMA- d_6 solution. This allows the PVDMA to penetrate into the PGMA thin film and covalently attach, resulting in brush formation. The presence of PVDMA within the nominal PGMA layer results in an increase in SLD of the PGMA primer layer. Therefore, the SLD of the PGMA primer layer in PVDMA-modified surfaces was found to have an average SLD of $2.2 \times 10^{-6} \text{ \AA}^{-2}$ and an average thickness of $31 \text{ \AA}$. From the measured SLD values for PGMA, we calculate the volume fraction of PVDMA that penetrates into the PGMA film during

attachment: $\phi_{\text{PGMA}} = 0.55$ and $\phi_{\text{PVDMA}} = 0.45$. All parameters for the PGMA layer found through model fitting were allowed to vary for the amine-modified films to observe if the PGMA primer layer could be modified by the amine because of the presence of PVDMA. It was confirmed that the thickness of the PGMA layer was consistent before and after functionalization and there was a slight decrease in SLD (decreases by $5.0 \times 10^{-7} \text{ \AA}^{-2}$) of the PGMA layer after functionalization. This slight alteration of the PGMA binding layer was not considered significant enough to affect the overlying PVDMA brush.

The SLD of the PVDMA layer was found to differ for each surface due to film-to-film variation in grafting density, with an average SLD measured for the PVDMA- d_6 layers of $\Sigma_0 = 3.7 \times 10^{-6} \text{ \AA}^{-2}$. This deviation of the SLD of the parent PVDMA layer from the expected bulk value for PVDMA- d_6 , $4.19 \times 10^{-6} \text{ \AA}^{-2}$, indicates a lower mass density for surface-tethered thin film systems. Consistent with results from ellipsometry, NR also shows a marked increase in layer thicknesses after the brush is exposed to a solution containing the primary amines. This is manifest in Figure 2-3, where the fringes in the reflectivity curve shift to lower Q with a decrease in spacing, both of which imply that the layer thickness increases upon functionalization of the PVDMA brush. The interfacial roughness (σ_R), which describes the width of the interface between two adjacent layers in the model used to fit the NR data, also shows a small increase upon functionalization. Because ellipsometry only determines the thickness of these layers, the change in neutron SLD before and after functionalization is crucial to understanding the extent of chemical reaction through its effect on both the layer thickness and the neutron SLD. Due to the isotopic substitution of the methyl groups, the SLD of the

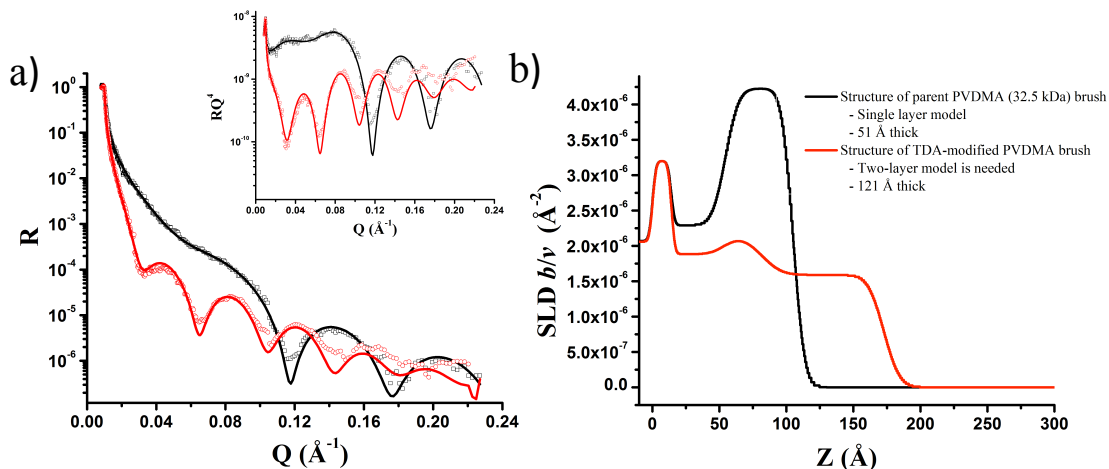


Figure 2-3. a) R versus Q and RQ^4 versus Q representations of neutron reflectivity data acquired for a 32,500 g mol⁻¹ PVDMA-d₆ brush: PVDMA-d₆ brush (black) and TDA-modified PVDMA brush (red). The data are shown as points and the best-fit model are represented by the solid lines; b) SLD profiles for a PVDMA-d₆ brush (black) and a TDA-modified PVDMA brush (red) as a function of thickness, Z . Analogous plots for all other samples are presented in *Appendix A*.

PVDMA layer decreases when reactively modified by hydrogen-rich amines. By measuring the exact decrease of the SLD and the increase in the thickness of the modified PVDMA, the extent of modification of the PVDMA brush (using the calculated values from Equation 2-7 to input into Equation 2-8) is determined. For this set of neutron reflectivity experiments, HA, TDA, and ODA were selected as the primary amines. PVDMA films were exposed to solutions of these amines for either 15 minutes or 2 h. This series of experiments answers important questions: Which amine functionalizes the azlactone brush to the highest extent? How much of the parent film is

lost due to entropic death of the brush chains? Do amines of different size penetrate into the polymer brush uniformly, or do they cause a stratification marked by different levels of functionalization?

As captured in Figure 2-3b, the SLD for the “parent” PVDMA layer was $4.225 \times 10^{-6} \text{ \AA}^{-2}$ and its thickness was 51 Å. Once the brush was exposed to the selected primary amine, tetradecylamine (TDA), for 2 h, the total film thickness increased to 121 Å. The thickness of the brush is consistent with measured values from ellipsometry. The addition of the hydrogen-rich amine to the PVDMA brush causes the SLD of the PVDMA- d_6 layer to decrease. The SLD profile (Figure 2-3b) reveals that there are two strata within the PVDMA brush. Through model fitting it was determined the top portion of the brush was 93 Å thick, 44% functionalized by TDA, and the measured SLD was $1.59 \times 10^{-6} \text{ \AA}^{-2}$. The bottom stratum of the brush had a thickness of 28 Å and was 37% functionalized, yielding an SLD of $2.135 \times 10^{-6} \text{ \AA}^{-2}$. The need for two distinct layers suggests the amines begin to react at the outer edge of the brush and then penetrate into the brush until the steric hindrance resulting from functionalization (and/or a decrease in solubility) prohibits modification, creating a stratified brush having a different extent of functionalization for each layer. The surface roughness for the parent PVDMA film is 16 Å at the film-air interface, and it increases to 50 Å after functionalization. These low roughnesses confirm that these are smooth, homogenous films.

Model fitting of the reflectivity measured for the modified films confirms the size of the amine used in modification has an effect on the extent of functionalization and the amount of PVDMA chains that are lost. The results presented in Table 2-4 reveal a few general trends: First, the SLD of the films decreases after functionalization due to

Table 2-4. Calculated Values from the Measured Σ_0 ($10^{-6} \text{ \AA}^{-2}$) Assuming $\rho_{M,est} = 1.0 \text{ g}\cdot\text{cm}^{-3}$.

Sample ^a - Modification	time	Σ_0^b ($10^{-6} \text{ \AA}^{-2}$)	ρ_0^c (g cm^{-3})	Σ_M^d ($10^{-6} \text{ \AA}^{-2}$)	f_{M1}^e	f_{M2}^e	$f_{M,est}^e$	$f_{PVDMA-lost}$
1. PVDMA-HA	15 m	3.835	0.96	2.505	0.51	—	0.73	0.31
2. PVDMA-HA	15 m	3.170	0.79	2.415	0.65	—	0.80	0.19
3. PVDMA-HA	2 h	3.630	0.91	2.680	0.47	—	0.61	0.23
4. PVDMA-HA	2 h	3.185	0.80	2.785	0.50	—	0.54	0.09
5. PVDMA-TDA	2 h	4.225	1.06	1.714	0.27	0.35	0.74	0.55
6. PVDMA-TDA	2 h	3.645	0.91	2.249	0.24	0.35	0.45	0.34
7. PVDMA-TDA	15 m	3.750	0.94	1.420	0.37	0.44	0.97	0.56
8. PVDMA-ODA	2 h	3.545	0.89	1.772	0.27	0.32	0.56	0.45
9. PVDMA-ODA	15 m	3.505	0.88	1.418	0.34	0.37	0.77	0.53

^a PVDMA-d₆ has an $M_n = 32,500 \text{ g mol}^{-1}$ and $D = 1.14$.⁴¹

^b Scattering length density of the PVDMA parent film

^c Mass density of the PVDMA parent film

^d Scattering length density of the PVDMA-modified layer

^e Extent of functionalization of each modified layer. $f_{M,est}$ is the estimated extent of functionalization that accounts for PVDMA chain loss ($f_{PVDMA-lost}$). f_{M1} and f_{M2} represent the actual extent of functionalization of each modified layer: layer 1 is the inner layer and layer 2 is the outer layer.

the addition of the amine to the perdeuterated azlactone ring and to loss of parent PVDMA. Second, the reflectivity curves acquired for PVDMA brushes exposed to the smallest amine, hexylamine (HA), are well-fit by a 1-layer model, suggesting that HA is able to penetrate into and react homogeneously with azlactone rings throughout the polymer brush. On the other hand, the fitting of reflectivity data of PVDMA brushes modified with tetradecylamine (TDA) and octadecylamine (ODA) required a 2-layer model, suggesting that as TDA and ODA react with the azlactone rings, steric hindrance or a change in solubility inhibits the ability of the larger amines to penetrate and uniformly react throughout the PVDMA brush. This results in two distinct layers of different SLD. The fits yield SLDs for the separate layers, which are then used to calculate reacted fractions, f_{M1} and f_{M2} , which quantify the extent of functionalization in each stratum. Note that the converted fractions, f_M , which are calculated in Equation (2-8), represent the fraction of reacted VDMA monomers *remaining* after accounting for the fraction lost. The fitted models confirm that the top stratum of the brush exhibits a larger decrease in SLD, corresponding to a greater degree-of-functionalization in comparison to the region buried within the bottom portion of the brush.

Finally, results shown in Table 2-4 indicate that as the size of the amine increases, the overall extent of functionalization decreases, which also might be anticipated and is fully consistent with insights derived from ellipsometry. Table 2-4 shows that samples 1-4 were modified with HA for either 15 min (samples 1 and 2) or 2 h (samples 3 and 4). The samples functionalized for 2 h result in a lower extent of functionalization compared to those functionalized for only 15 min, supporting our contention that PVDMA chains are cleaved from the surface once exposed to the

nucleophilic agent. Another trend observed involves the measured values of Σ_0 of the parent film. When Σ_0 is high, the film exhibits greater chain loss upon functionalization: brushes of higher Σ_0 have more chains per volume and, therefore, are more strongly stretched to alleviate the lateral crowding. Because the chains are more strongly stretched in the parent brush, additional steric stress resulting from functionalization and the increase in stretching that concomitantly ensues, is the impetus for the chains to cleave when decorated with amines. In a manner analogous to hydrolytic cleavage of siloxane bonds observed by others,^{74–78} it is possible that amidation of the ester bond (that results from reaction of the carboxylic acid end group of the CTA with an epoxide group of the PGMA layer) is occurring, which along with the tension of a stretched chain, facilitates bond breaking and loss of chains from the surface. This trend of greater loss of chains with increasing Σ_0 is also observed for the samples exposed to TDA and ODA. To determine how the size of the amine affects the extent of functionalization, it is important to compare results for brushes subjected to the same reaction times and similar Σ_0 . As stated previously, the HA modification resulted in a single functionalized layer, indicating the functionalization extended throughout the entire brush and was homogeneous. Comparison of the extent of modification of brushes exposed to HA to those modified using TDA and ODA (specifically, the topmost layer, f_{M2}) confirms that the size of amine does have an effect on the extent of functionalization: brushes modified with HA have the highest extent of functionalization, followed by TDA and then the largest amine, ODA. The fraction of VDMA monomers lost, however, is consistently larger for brushes exposed to the larger amine molecules, indicative of a more disruptive reaction process. The innermost portion of the modified PVDMA film

(layer 1 for TDA- and ODA-modified films) results in a smaller converted fraction of azlactone repeat units, which is consistent with impaired amine access. Although at this juncture we do not present values of $f_{\text{PVDMA-lost}}$ for each strata, instead expressing an overall $f_{\text{PVDMA-lost}}$ for the film. As will be shown later, a lower converted fraction correlates with a lower fraction of PVDMA repeat units lost.

As shown in Table 2-4, fits of the as-prepared PVDMA films exhibit mass density, ρ_0 , values ranging from 0.79–1.06 g·cm⁻³, which can be taken as typical for these films. While to this point the analyses assumed that $\rho_{\text{M,est}} = 1.0 \text{ g·cm}^{-3}$, it is possible and useful to estimate the uncertainty of the extent of functionalization and the amount of PVDMA lost after exposure to the amine by inserting these extreme values ($\rho_{\text{M,est}} = 0.79$ and $= 1.06 \text{ g·cm}^{-3}$) into equations (2-9) and (2-13) to determine $f_{\text{M,est}}$ and $f_{\text{PVDMA-lost}}$, respectively. Using these upper and lower limits allows a complete accounting of the fraction of VDMA monomers in the film, both modified and lost, as a function of depth. Calculated values are tabulated in Table 2-5 (lower limit using $\rho_{\text{M,est}} = 0.79 \text{ g cm}^{-3}$) and Table 2-6 (upper limit using $\rho_{\text{M,est}} = 1.06 \text{ g·cm}^{-3}$), and a visual representation is displayed in Figure 2-4 to provide a complete picture as to how this model was used to produced and express depth-dependent values.

Table 2-5 and Table 2-6 represent how the range of mass densities of the confined brush film, $\rho_{\text{M,est}}$, which is indexed to ρ_0 of the parent brush obtained by fitting (see Table 2-4, where $0.79 < \rho_0 \text{ (g cm}^{-3}\text{)} < 1.06$), affects the interpretations derived for the reactively modified brushes. As seen from these two tables and captured in corresponding plots for each system (Figure 2-4 and Figures A10-A16 in Appendix A), the main impact is in $f_{\text{M,est}}$, which as shown in Equation (2-9) takes into account

Table 2-5. Extent of Functionalization Using a Mass Density of the Modified Layer of $\rho_{M,est} = 0.79 \text{ g}\cdot\text{cm}^{-3}$.

Sample Modification	$f_{M,est}^a (\rho_{M,est} = 0.79)$	f_{M1}	f_{M2}	$f_{PVDMA-lost} (\rho_{M,est} = 0.79)$	$f_{PVDMA-lost1}$	$f_{PVDMA-lost2}$
1. PVDMA-HA	0.33	0.22	—	0.33	0.33	—
2. PVDMA-HA	0.39	0.30	—	0.22	0.22	—
3. PVDMA-HA	0.23	0.17	—	0.25	0.25	—
4. PVDMA-HA	0.17	0.15	—	0.11	0.11	—
5. PVDMA-TDA	0.49	0.15	0.23	0.56	0.47	0.59
6. PVDMA-TDA	0.24	0.09	0.20	0.36	0.27	0.43
7. PVDMA-TDA	0.69	0.23	0.30	0.58	0.50	0.60
8. PVDMA-ODA	0.36	0.15	0.21	0.47	0.39	0.50
9. PVDMA-ODA	0.55	0.22	0.26	0.55	0.51	0.57

^a Extent of functionalization of each modified layer assuming the given mass density of the modified layer, $\rho_{M,est}$. $f_{M,est}$ is the estimated extent of functionalization that accounts for PVDMA chain loss ($f_{PVDMA-lost}$). f_{M1} and f_{M2} represent the actual extent of functionalization of each modified layer: layer 1 is the inner layer and layer 2 is the outer layer.

Table 2-6. Extent of Functionalization Using a Mass Density of the Modified Layer of $\rho_{M,est} = 1.06 \text{ g}\cdot\text{cm}^{-3}$.

Sample Modification	$f_{M,est}^a (\rho_{M,est} = 1.06)$	f_{M1}	f_{M2}	$f_{PVDMA-lost} (\rho_{M,est} = 1.06)$	$f_{PVDMA-lost1}$	$f_{PVDMA-lost2}$
1. PVDMA-HA	0.85	0.59	—	0.31	0.31	—
2. PVDMA-HA	0.92	0.75	—	0.18	0.18	—
3. PVDMA-HA	0.72	0.56	—	0.22	0.22	—
4. PVDMA-HA	0.65	0.59	—	0.08	0.08	—
5. PVDMA-TDA	0.81	0.31	0.39	0.54	0.45	0.57
6. PVDMA-TDA	0.51	0.28	0.39	0.34	0.25	0.41
7. PVDMA-TDA	1.05	0.41	0.48	0.56	0.47	0.57
8. PVDMA-ODA	0.61	0.30	0.36	0.44	0.37	0.47
9. PVDMA-ODA	0.84	0.37	0.41	0.53	0.48	0.55

^a Extent of functionalization of each modified layer assuming the given mass density of the modified layer, $\rho_{M,est}$. $f_{M,est}$ is the estimated extent of functionalization that accounts for PVDMA chain loss ($f_{PVDMA-lost}$). f_{M1} and f_{M2} represent the actual extent of functionalization of each modified layer: layer 1 is the inner layer and layer 2 is the outer layer.

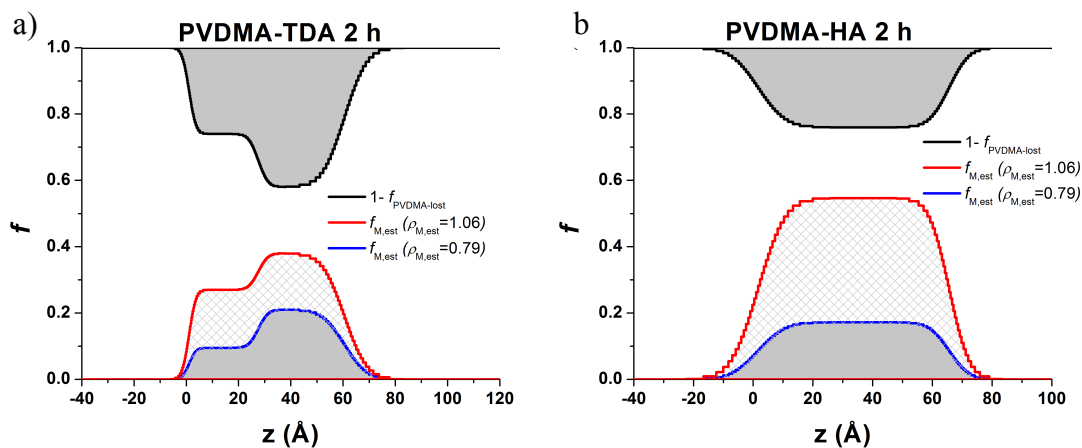


Figure 2-4. Converted fraction plots provide a complete accounting of reactive modification of PVDMA brushes, including how much PVDMA was lost, converted, or did not react, using the two extremes of mass density measured for the parent films. The amount of PVDMA available to be functionalized is represented by the fraction under the black line. If a mass density of $\rho_{M,est} = 0.79 \text{ g cm}^{-3}$ (blue line) or $\rho_{M,est} = 1.06 \text{ g cm}^{-3}$ (red line) is assumed, the proportion of the original film converted varies (a) between 0.2 and 0.4 for modification with TDA and (b) between 0.2 and 0.6 for modification with HA. The empty space between lower and upper bounded areas represents unreacted VDMA monomer.

PVDMA and the particular amine used for modification. Larger values of $\rho_{M,est}$ result in an increased extent of functionalization because there are more azlactone rings available to be functionalized. Again it is noted that the converted fraction, f_M , for a given layer represents the fraction of reacted VDMA monomers *remaining* after accounting for the fraction lost. The data presented in Tables 2-5 and 2-6 also show that the mass density range does not greatly impact the amount of PVDMA lost, $f_{PVDMA-lost}$, during the reaction, so it is assumed constant in constructing Figure 2-4 and analogous plots in the Appendix A. While $\rho_{M,est}$ does not show a significant effect on the amount of PVDMA lost due to functionalization, the results show that as the molecular weight of the amine increases, more PVDMA is lost. In addition, in cases where the reflectivity data is best modeled using two strata, lower extents of functionalization in a given stratum result in lower values of $f_{PVDMA-lost}$, ostensibly because lower steric crowding reduces stretch-activated scission of the chains.

The converted fraction plot, shown in Figure 2-4, represents the fraction of PVDMA lost, the fraction converted, and the fraction remaining that is neither lost nor functionalized. Figure 2-4a presents PVDMA modified with TDA for 2 h, where the data are best modeled using a 2- layer fit, while Figure 2-4b shows PVDMA modified with HA, which is well-described by a single-layer fit. Figure 2-4a corresponds to sample 5 from Tables 2-4, 2-5, and 2-6 and Figure 2-4b corresponds to sample 3 from Tables 2-4, 2-5, and 2-6.

2.4.6 Refunctionalization of PVDMA Brushes

Analyses of ellipsometry and reflectivity data are consistent insofar as showing that the extent of functionalization depends on the size of the functionalizing agent and

tethering densities, with smaller modifying agents and lower densities yielding higher conversion upon *in situ* modification. In addition, both sets of experiments show that functionalization is incomplete. To buttress this contention, sets of HA-, TDA-, and ODA-functionalized PVDMA brushes were refunctionalized by exposure to a 0.25 wt.% HA solution and thicknesses across the surfaces re-measured. Although sample-to-sample variations tend to mute the magnitude of the effect, as observed from Table A-4 in Appendix A, there are small but measureable increases in ellipsometric thickness upon refunctionalization for all but the HA-functionalized brushes. This is perhaps not unexpected, given that modification with HA yields the highest f_M .

2.5 Conclusions

Through neutron reflectivity measurements and the development of a model that allows the depth-dependent extent-of-functionalization to be computed, a complete and detailed picture of the reactive modification of confined thin film systems is provided, enabling comparison to findings from ellipsometric measurements. Analyses from both techniques demonstrate that reactive modification of poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) brushes by a series of small molecule amines is incomplete and that the extent of functionalization is strongly dependent on the size of the n-alkyl amine. While results are also consistent with trends from previous research,^{8,13,14} a variety of new and important insights surpassing current understanding are gained due to the sensitivity of neutron scattering to isotopic substitution enabled through the use of perdeuterated PVDMA. Most notably, it is found that end-tethered PVDMA brush chains do not achieve their bulk mass density and their functionalization is non-uniform for larger amines, ostensibly due to increased steric demand caused by addition of

amines to azlactone rings by ring-opening nucleophilic addition. That steric demand also appears to cause a scission of VDMA chains – an “entropic death” of chains due to the penalty for additional stretching – which may be aided by amidation of the ester bond linking the chains to the substrate. These findings are useful for situations in which the surface properties of interfacial thin films, not simply brushes, are altered *in situ* through reactive modification. Additional studies elucidating the effect of grafting density are presented in Chapters 3 and 4, where I used PGMA-*b*-PVDMA diblock copolymers to alter the areal density of chains. Furthermore, gradient surfaces described in Chapter 4 are used to assess changes in interfacial properties due to *in situ* modification.

Chapter 3

Neutron Reflectivity Study: Entropic Death from Chemical Transformation of End-Tethered Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) Thin Films via *in situ* Modification

3.1 Abstract

Structural properties of functional polymer brushes determine the amount of small molecules that can be incorporated into the brush system by chemical reaction. Therefore, physical and chemical properties of the modified brush are linked to the structure and properties of the parent polymer brush. The relationship between the structure of brushes created by preferential assembly of poly(glycidyl methacrylate)-block-poly(2-vinyl-4,4-dimethyl- d_6 azlactone) (PGMA-*b*-PVDMA- d_6) chains and the ability to chemically modify the PVDMA block *in situ* is examined to investigate how grafting density of chains affects the mass density of the thin film, amount of chains cleaved from the surface, and extent of functionalization. Brushes are reactively modified using a series of small molecule amines, and the amount of distribution of small molecules is determined through a highly constrained analysis of neutron reflectivity data. Brushes are uniformly modified by amines of different size except at high grafting density. The loss of PVDMA chains – “entropic death” – was previously established, however, here a relationship between the mass density of grafted chains and the amount of PVDMA chains that are cleaved from the brush is determined. Reactive modification is not complete and it is concluded that the PVDMA brush system can be further reacted. The ability to precisely alter surface properties of thin polymer films broadly supports efforts to produce tailored surfaces with desired properties, such as friction, adhesion, wettability, and biocompatibility.

3.2 Introduction

Because polymer brushes straddle solid/fluid interfaces, they are extensively explored for coatings. Examples include antibacterial coatings, functional membranes, and biointerfaces that resist non-specific protein adsorption or regulate cell adhesion. In all of these applications, polymer brushes are useful because of the ability to change surface properties by selecting monomers with specific thermal, mechanical or chemical properties. When producing such coatings, it is important to assess their stability and robustness. Klok *et al.* recently reviewed the stability and mechanochemical properties of polymer brush systems.^{74,79} It has been recently observed that when these coatings are placed in harsh environments, the mechanical stability of the film decreases and result in polymer chains degrafting from the substrate. In extreme environments, polymer brushes may be completely detached from the substrates to which they are attached.^{80,81} Therefore, it is important to understand the interplay between brush properties and solution conditions that cause this degrafting, so that stable, functional polymer brushes can be created.

Zhu *et al.* were the first to report degrafting of tethered chains.⁸² Zhu *et al.* and Zhang *et al.* studied copolymers of oligo(ethylene glycol) methacrylate (OEGMA) and hydroxyethyl methacrylate (HEMA) (Poly(OEGMA-r-HEMA)) that were synthesized by surface-initiated polymerization from an initiator-decorated gold substrate. To test their hypothesis of covalent bond breakage, these polymer chains were converted to weak polyelectrolytes by carboxylation. They observed that placing the polymer brush into a phosphate buffer saline solution caused the chains of the brush to swell, which

activated breakage of gold-thiol bonds holding the initiator to the surface. Quartz crystal microbalance (QCM) was used to measure the polymer composition and ellipsometry was used to determine the thickness of the polymer films.^{83–85} Their studies showed that films measured of higher thickness were more susceptible to bond breakage.

Bond tension in polymer chains attached to a substrate has been recently examined to determine the stability and mechanochemical properties of polymer brushes. Bond tension can be increased due to external forces such as salt content or pH, or self-generated due to intramolecular interactions between densely grafted polymer chains. Once a polymer brush is placed in a good solvent, the tension at the site where the polymer chain is attached to the substrate is decreased. However, circumstances where chains are tethered at a high grafting density, Deng *et al.* proposed that polymer-solvent interactions become stronger than the polymer-substrate interactions, and stretching due to solvation can induce the bond breakage.⁸²

Panyukov *et al.* and Sheiko *et al.* completed a range of investigations to determine the force required to cleave covalently attached chains from a solid substrate. They examined different molecular architectures and grafting densities that would strengthen conceptual understandings of bond tension and the force required to break a covalent bond. Panyukov *et al.* examined the role of bond tension in the polymer backbone of a molecular bottlebrush in a dilute solution, melt, and when adsorbed to a solid substrate. For each of these situations, the impact of solvent quality was examined.⁸⁶ Solution studies of densely grafted bottlebrushes determined that as the solvent quality increases, it alleviates the tension of the polymer chains. When the bottlebrush is placed in a poor solvent, the tension becomes strong enough to break

hydrogen bonds, but not covalent bonds. As the grafting density increases, the distance between chains decrease, and there is an increase in bond tension. This tension is not strong enough to detach grafted polymer chains from a polymer brush. However, bond tension of more complex architectures, such as star and molecular bottlebrushes, adsorbed to a substrate makes them susceptible to bond rupture.⁸⁷ Bottlebrushes adsorbed to a substrate increase the bond tension from picoNewton to nanoNewton range, which is strong enough to break the covalent bonds.^{86,88,89} They also determined that as the grafting density of the side chains increases, the adsorption-induced tension becomes high enough to break covalent bonds, thereby cleaving polymer side chains.⁸⁶ While these reports investigate mainly the degrafting of molecular bottlebrushes, these studies advance our understanding of bond tension of complex polymer systems where chains are grafted.

Schmidt *et al.* investigated the bond rupture forces using single molecule force spectroscopy with an atomic force microscopy (AFM) cantilever. Carboxymethylated amylose (CMA) polymer chains were covalently attached by one end to a surface treated with N-[3-(Trimethoxysilyl)-propyl]diethylenetriamine. They showed that after applying a force of 2.1 nN, a bond ruptured, releasing the chain. The rupture was attributed to bond scission of the weakest link, the Si-O-Si bond. Small microruptures indicated that this weakness occurs at the site where the chain is linked to the surface, which narrows the candidates for bond rupture to either the carboxylic acid amide bond (C(O)-N) or the siloxane bond (Si-O). It is known that siloxane linkages are susceptible to hydrolysis in aqueous environments and in harsh conditions, such as extremely high or low pH's and solutions of high salinity. The activation energy of the siloxane bond is lower than that

of the amide bond, and the siloxane bond length is longer (1.77 Å), which makes the siloxane bond more susceptible to mechanical stress.⁸⁰ This work is supported by conclusions from Panyukov *et al.* and Sheiko *et al.* in that they determined the bond that links the polymer chain to a substrate has the highest tension and most susceptible to being cleaved.^{81,86}

Tugulu *et al.* reported one of the first observations of degrafting of polymer brushes while studying long-term stability of poly(poly(ethylene glycol) methacrylate) (PPEGMA) brushes synthesized via surface-initiated atom-transfer radical polymerization (SI-ATRP). Contact angle, ellipsometry, and scanning electron microscopy were used to monitor the degrafting. Their results indicated that surfaces containing a grafting density greater than 70% allowed degrafting of chains from the polymer brush. (Here 70% refers to the percentage of molecules in the self-assembled monolayer that are initiator molecules – grafting density was not measured in these SI-ATRP studies.) Furthermore, their results showed higher grafting density accelerated the degrafting of the chains. They concluded the detachment occurred at the polymer/silicon interface because the polymer brush degrafted as a film. Degrafting did not occur when PPEGMA brushes were exposed to water. However, when the PPEGMA brush was placed in a cell culture media, an increased tension due to the osmotic stress, steric crowding, and buffer solution promoted degrafting.⁷⁶ Osmotic pressure introduced from the PPEGMA brushes swelling in cell culture media caused the chains to stretch, and the entropic penalty for stretching leads to detachment of polymer chains. They also examined cross-linked PHEMA systems. Huang *et al.* proposed that cross-linked polymers have more chemical and mechanical stability compared to linear polymer

brushes.⁹⁰ However, Tugulu *et al.* showed that cross-linking of PPEGMA chains did not enhance the stability. This work by Tugulu *et al.* is supported by conclusions from various authors who determined that the degrafting released the entire chain, not subunits, and degrafting of chains occurred in the presence of extreme pH and salt content.^{75,90–93}

Certain moieties in a polymer chain, such as esters or amides, and siloxane bonds are more susceptible to bond tension and hydrolysis.^{79,89,94} In an effort to decrease the amount of polymer chains cleaved from the surface, various groups have investigated approaches to increase brush stability by tailoring the chemistry of surface-initiator anchors and/or by adding hydrophobic polymers at the polymer/substrate interface to decrease the amount of cleaved polymer chains. Paripovic *et al.* focused on increasing the stability of hydrophilic polymer brushes. They examined how the chemical structure of the ATRP initiator and its hydrophobicity influenced the rate of polymer chain detachment. They tested the hypothesis that a more hydrophobic initiator anchoring the chains will protect against hydrolysis of the Si-O-Si linkage. Of the three initiators synthesized, the most hydrophilic contained an amide functional group and the other two initiators contained esters of different alkyl chain lengths. They showed that as the hydrophobicity of the initiator increased, the polymer brush was stable in a cell medium for longer times. Once again, the degrafting of polymer chains was observed in cell media but not in pure deionized water. This degrafting was attributed to the increase in osmotic stress on the brush system due to the presence of salt ions, which promotes cleavage of Si-O-Si bonds. To test their second hypothesis – that a thin hydrophobic layer at the brush/substrate interface would improve stability – a low molecular weight

hydrophobic block of either poly(methyl methacrylate) (PMMA) or poly(2-ethylhexyl methacrylate) (PEHMA) was first grown from the silicon substrate. Chain extension was used to add a hydrophilic and electrolytic block of poly(methacrylic acid) (PMAA). AFM imaging and ellipsometry measurements confirmed that the hydrophobic block enhances the stability of the polymer brushes.⁹⁵ There are more reports of different polymer brush systems exhibiting improved stability due to using a hydrophobic block as a “barrier” layer between the anchoring point and the brush chains.^{75,92}

Similarly, Bain *et al.* synthesized an initiator that did not have an ester linkage but could be used for surface-initiated free radical polymerization (SI-FRP).⁷⁷ They examined how changing the chemistry of the initiator could decrease the hydrolysis that led to degrafting. Their efforts were motivated by the desire to improve the stability of polymer brushes grown from surface-anchored initiators that would be exposed to cell culture media or other aggressive solution environments. Previous studies suggested that the reason for degrafting of polymer chains is due to the scission of labile bonds within the initiator. They created polystyrene (PS) brushes by growing from surfaces decorated with [11-(2-Bromo-2-methyl)propionyloxy]undecyltrichlorosilane (BMPUS), which is an initiator that contains an ester linkage. Their ellipsometry studies showed that all chains were degrafted, determined from ellipsometry, after being exposed overnight to p-toluenesulfonic acid (p-TsOH). They synthesized a new initiator, (R)-(2-((2-cyanopropan-2-yl)diazenyl)-2-methyl-6-(trichlorosilyl)hexanenitrile (BAIN), which did not have an ester linkage, and used it to synthesize PS or poly(dimethylaminoethyl methacrylate) (PDMAEMA) via SI-FRP and SI-ATRP. Ellipsometry measurements indicated a 20% decrease in PS brush thickness after overnight exposure to p-TsOH. The

PDMAEMA brushes grown from BAIN and BMPUS initiators were incubated in a phosphate-buffer solution (PBS) solution for 5 days. Ellipsometry confirmed that brushes grown from the initiator without the ester linkage are more stable, exhibiting only small changes in thickness, which suggests there is less chain degrafting compared to the brushes grown from BMPUS.⁷⁷

The work described in Chapter 2 used a grafting to approach to create a poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) brushes, which allowed fundamental questions to be answered. For instance, those studies addressed how the size of amine, concentration of amine, and functionalization time affect the extent of functionalization. This work also established that PVDMA chains were cleaved from the brush. Through neutron reflectivity we quantitatively determined the amount of chains lost during the functionalization, and showed that as the amine size increases, more chains were cleaved from the surface.

Herein, I devote additional focus to understanding why polymer chains are cleaved through post-polymerization modification using small primary amines. I present a neutron reflectivity study to specifically examine how the grafting density affects the extent of functionalization of azlactone-containing polymer films. This reflectivity study delivers important fundamental insight into how grafting density of the polymer chains, as well as the differences in size of the functionalizing agent (small primary amines), influence reactive modification of the PVDMA brushes and chain degrafting. Again, this study benefits from use of perdeuterated PVDMA chains and a change in scattering length density (SLD) when reactively modified with amines. Reflectivity measurements were made on the as-made PVDMA-d₆ film, the modified polymer film, and re-

functionalized polymer films. Refunctionalization studies provide clear insight as to whether PVDMA chains are exhaustively modified during the first step. Fitting of the neutron reflectivity data yields thickness, extent of functionalization, and amount of PVDMA chains that are cleaved from the substrate, which in concert allow the role of grafting density to be clearly understood.

3.3 Experimental Section

3.3.1 Materials

To provide isotopic contrast in neutron reflectivity studies, a perdeuterated variant of VDMA in which the 6 hydrogens of the methyl groups are isotopically substituted with deuterium, 4,4-dimethyl-d₆-2-vinyl-oxazolone (VDMA-d₆) was synthesized according to prior reports.⁹ Neutron reflectivity studies required the use of larger silicon substrates (50 mm diameter, 5 mm thickness), which were obtained from El-Cat (Waldwick, NJ, USA). Glycidyl methacrylate (GMA, 97%, Aldrich) and 2-vinyl-4,4-dimethyl azlactone (VDMA) were distilled under reduced pressure and the middle fractions (~70%) reserved for use. 2,2-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd.), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%, Aldrich), benzene (99.9%, Aldrich), tetrahydrofuran (THF, 99.9%, Aldrich), chloroform (99.8%, Fisher), n-hexane (95%, Fisher), tetradecylamine (95%, Aldrich), octadecylamine (95%, Aldrich), hexylamine (99%, Aldrich), hydrogen peroxide, 30% (Certified ACS, Fisher Chemical), and sulfuric acid (Certified ACS Plus, Fisher Chemical) were used as received.

3.3.2 Instrumentation and Analysis

Gel Permeation Chromatography (GPC). Polymer molecular weights were measured via gel permeation chromatography (GPC) using a Tosoh EcoSEC GPC fitted with two Tosoh TSKgel SuperMultiporeHZ-M columns 4 μ (4.6 $\times$ 150 mm) and a TSKgel SuperMultiporeHZ-M guard column. Measurements were made at 40 °C using THF as the mobile phase. Molecular weights were determined using the EcoSEC Data Analysis software (version 1.04) relative to poly(methyl methacrylate) standards.

Multi-angle Ellipsometry. The thickness of thin films was determined using a variable-angle Beaglehole Picometer Ellipsometer that uses a He-Ne laser light source (λ = 632.8 nm). The thickness of the polymer-modified surface was measured in air at multiple angles ranging from 80° to 60° in 1° steps, following previously published protocols.⁶³ The angularly-dependent data were co-fit using a model that treats the block copolymer layer as a uniform slab. A refractive index of 1.50 was assumed for the PGMA-b-PVDMA copolymer films.²¹ The slab-like model allows the thickness of the layer to be determined by optimizing goodness-of-fit. Multiple measurements were made on each surface and replicate samples also were measured.

Neutron Reflectivity (NR). Neutron reflectivity measurements were performed using the Liquids Reflectometer at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. Reflectivity data were collected over a range of momentum transfer wavevector, Q , where $Q = 4\pi \sin \theta / \lambda$, from $0.008 \text{ \AA}^{-1} < Q < 0.20 \text{ \AA}^{-1}$ using a sequence of 3.25- $\text{\AA}$ -wide continuous wavelength bands (selected from $4.25 \text{ \AA} < \lambda < 15.0 \text{ \AA}$) and incident angles (selected between $0.6^\circ < \theta < 2.34^\circ$). For each sample, a single reflectivity curve was assembled by combining data acquired using seven different

wavelength and angle data sets while maintaining a constant relative instrumental resolution of $\delta Q/Q = 0.023$ by varying the incident-beam apertures.

3.3.3 Synthetic Procedures

Synthesis of 4,4-dimethyl-d₆-2-vinyl-oxazolone. Because of the familiarity with the synthesis (from the work described in Chapter 2), a large scale synthesis was performed. Ammonium chloride (NH₄Cl) (87.2 g, 1.63 mol) and sodium cyanide (NaCN) (80.0 g, 1.63 mol) were dissolved in a stirring solution of methylene chloride and water (CH₂Cl₂/H₂O: 1/2). Acetone-d₆ (87.2 g, 1.36 mol) was added to the stirring solution. The flask was then sealed and allowed to react for 48 h at room temperature while stirring. The crude product mixture was extracted with CH₂Cl₂ (3×). The organic extracts were combined with MgSO₄, filtered, and the solvent evaporated under vacuum. The product was combined with 12 M hydrochloric acid (293.1 g, 8.04 mol) in a 1 L round bottom flask and sealed with a septum. The vessel was placed in an oil bath at 100 °C and allowed to react for 2 h while stirring in standard atmosphere conditions. After the reaction was complete, the solution was cooled to room temperature. Solvent was removed from the crude mixture under reduced pressure. The remaining product was rinsed with ethanol then filtered to remove ammonium chloride. The filtered product, 2-amino-3,3,3-trideuterio-2-trideuteriomethyl propionic acid (Aib-d₆), was concentrated under reduced pressure and then dried overnight under vacuum.⁹⁶ The isolated yield was 56%. Aib-d₆ (82.3 g, 0.75 mol) was combined with a stirring solution of NaOH (60.4 g, 1.5 mol) and H₂O (550 g, 30.5 mol) in a 2 L round bottom flask. Once cooled to 0 °C, acryloyl chloride (102.5 g, 1.1 mol) was added dropwise. The vessel was allowed to react overnight while stirring. “Vinyl Aib-d₆” was isolated by decanting, recrystallized

(3×) from a 3/1 mixture (v/v) of ethyl acetate/methanol and then dried overnight under vacuum.⁹⁷ My reaction resulted in an isolated yield of 34%. Vinyl Aib-d₆ (42.3 g, 0.26 mol) and ethyl chloroformate (28.2 g, 0.26 mol) were dissolved in 500 mL of anhydrous hexanes. Triethylamine (52.6 g, 0.52 mol) was added dropwise to the stirring solution to maintain a temperature of 45 °C. The reaction mixture was reacted for 2 h while stirring. Triethylamine hydrochloride was removed by filtration and hexanes were evaporated to yield VDMA-d₆ as an oil.⁹⁸ The isolated yield was 60%. ¹H NMR (500 MHz, CDCl₃, δ): 6.20 (m, 2H; CH), 5.85 (d, 1H; CH). The set of reactions are shown as Scheme B-1 in Appendix B.

Synthesis of PGMA Macro-CTA by RAFT polymerization. GMA (2.84 g, 1.0 mol) was combined with V-70 initiator (1.17×10^{-2} g, 1.89×10^{-3} mol), CPDT (6.55×10^{-2} g, 9.48×10^{-3} mol) and benzene in a 50 ml round bottom flask. The flask was sealed with a rubber septum and sparged with dry argon for 30 minutes. The vessel was placed in an oil bath set to 30 °C and allowed to react for 12 h while stirring. A typical RAFT polymerization consisted of using a CPDT:V-70 ratio of 5:1, a CPDT:GMA ratio of 2:211, and a [GMA] of 0.99 M; these conditions set the theoretical number-average molecular weight to be 15,000 g mol⁻¹. After a 12 h polymerization, the reaction mixture was quenched by immersing the flask in liquid nitrogen until the solution was frozen. After allowing the contents to thaw, the macro-CTA was precipitated into cold hexanes. The macro-CTA was isolated by decanting and then dried overnight under vacuum.

Synthesis of PGMA-b-PVDMA-d₆ by RAFT polymerization. VDMA-d₆ (2.90 g, 1.0 mol) was combined with macro-CTA (4.64×10^{-1} g, 2.90×10^{-3} mol), V-70 initiator (5.96×10^{-3} g, 9.67×10^{-4} mol), and benzene in a 50 ml round bottom flask. The flask

was sealed with a rubber septum, and sparged with dry argon for 30 minutes. As an example, a polymerization was prepared using a CPDT:V-70 ratio of 3:1, a PGMA macro-CTA:VDMA-d₆ ratio of 1:345, and a [VDMA-d₆] of 0.99 M; these conditions set the theoretical number-average molecular weight to be 50,000 g mol⁻¹. This solution was immersed in an oil bath and stirred at 30 °C for 18 h, after which time the reaction was quenched by submerging the flask in liquid nitrogen until the solution was frozen. After allowing the contents to thaw, PGMA-b-PVDMA-d₆ was precipitated into cold hexanes (3×), isolated by decanting, and then dried overnight under vacuum.

3.3.4 Sample Preparation

Wafer cleaning. Silicon wafers were cleaned prior to use in a piranha acid solution (3:1 v/v H₂SO₄/30% H₂O₂) at 80 °C for 30 minutes. After cleaning, the wafers were rinsed with deionized water and dried using a stream of nitrogen. Cleaned wafers were used immediately. *Caution! Piranha acid is a strong oxidizer and a strong acid; it should be handled with extreme care as it reacts violently with most organic materials.*

Formation of PGMA-b-PVDMA-modified silicon surfaces. Thin films of PGMA-b-PVDMA-d₆ were deposited on silicon substrates by spin coating a dilute solution at 1500 rpm for 15 seconds using a Laurel Technologies spin coater (model WS-650MZ-23NPP). For all spin coating preparations, a PGMA-b-PVDMA-d₆ concentration of 0.25 wt.% (in chloroform) was used. After spin coating, the films were annealed at 110 °C for 18 h, 24 h, and 30 h to promote reaction between the epoxy groups of the PGMA block and hydroxyl groups on the silicon substrate.⁴¹ Different reaction times were used to promote an increase in grafting density by increasing the anneal time. After cooling to room temperature while under vacuum, the substrates were sonicated in chloroform to

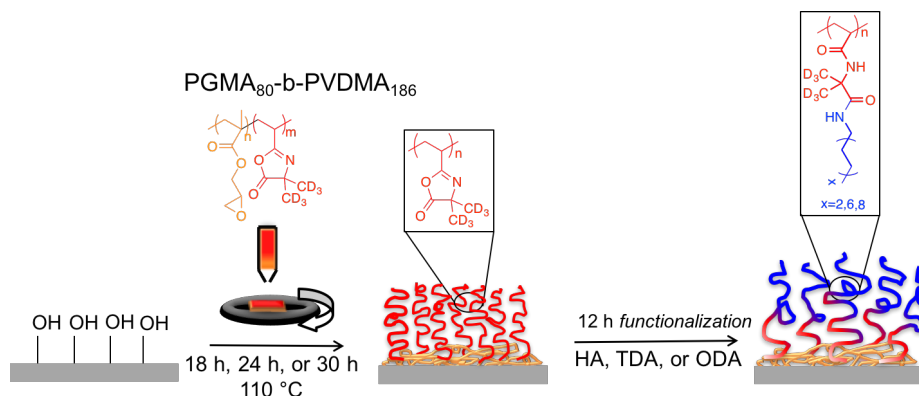
remove non-covalently bound PGMA-b-PVDMA-d₆ chains, rinsed with chloroform, and then dried with a stream of dry nitrogen. Although the PVDMA block is covalently connected by one end to the surface-bound PGMA block, for convenience I simply refer to these thin films as “PVDMA films”, as presented in Scheme 3-1.

Post-polymerization modification of PVDMA films. PVDMA-modified wafers were submerged for 12 h in 0.25 wt.% solutions of 1-hexylamine (HA), 1-tetradecylamine (TDA), or 1-octadecylamine (ODA) in chloroform. After this reaction time, the wafers were removed and sonicated in pure chloroform, rinsed with chloroform, and then dried with a stream of dry nitrogen. To explore whether the azlactone rings of the PVDMA chains were exhaustively reacted, the functionalized polymer films were refunctionalized by submerging the substrates in a 0.25 wt.% solution of 1-hexylamine for 1 h. After this second reactive modification, the wafers were sonicated and rinsed with chloroform, and then dried with a stream of dry nitrogen.

3.4 Results and Discussion

3.4.1 Synthesis of PGMA and PVDMA

A PGMA macro-CTA was synthesized by RAFT polymerization. The PGMA macro-CTA had a number-average molecular weight, $M_n = 11,800 \text{ g mol}^{-1}$ and dispersity of 1.25. This PGMA macro-CTA was used to create a PGMA-b-PVDMA-d₆ diblock copolymer by chain extension with VDMA-d₆ via RAFT polymerization. The diblock copolymer synthesized had an $M_n = 38,800 \text{ g mol}^{-1}$ and D of 1.18; the PVDMA block had an $M_n = 27,000 \text{ g mol}^{-1}$.



Scheme 3-1. Procedure used to create PVDMA brushes by selective assembly of PGMA-b-PVDMA diblock copolymers. PVDMA chains are end-attached to the silicon substrate through the surface-tethered PGMA blocks. These PVDMA brushes are modified *in situ* by exposure to small molecule amines.

3.4.2 PVDMA brush formation: Surface Attachment and Characterization

A “grafting to” approach is used to attach the premade PGMA-b-PVDMA-d₆ chains to a silicon surface. As shown by Lokitz *et al.*, increasing the concentration of the block copolymer solution, annealing temperature, and reaction time yields a linear increase in the thickness of the film.⁴¹ The PGMA block prefers the silicon surface, allowing epoxy groups to react with surface hydroxyl groups, creating covalent linkages to the substrate. Chloroform is used to spin-coat the PGMA-b-PVDMA, yielding smooth, homogeneous thin films as reported previously.^{35,99} After deposition by spin coating, the films are annealed at 110 °C for 18, 24, or 30 h to facilitate grafting. After that amount of time, the non-bonded chains are removed by sonication in CHCl₃. The thicknesses of the PGMA-b-PVDMA films were generally found to be 32.9 nm thick, as

determined by multi-angle ellipsometry and neutron reflectivity, and shown in Table 3-1. Because PGMA prefers the silicon substrate, this “grafting to” process results in the formation of a surface-anchored PVDMA film.^{41,98} The thickness of the layer is attributed to the PGMA block self-cross-linking, which results in additional chains farther from the polymer/silicon interface being incorporated into the film, as reported previously by Lokitz *et al.*⁴¹

Grafting density is an important parameter that governs interactions between the polymer chains and affects the penetration of small molecules into the brush system.^{30,33} Because the characteristics of the brush have been explained in depth in Chapter 2 (and are revisited again in Chapter 4), these details are omitted here.^{99,100} The focus of this Chapter is to explain the data collected from neutron reflectivity measurements and emphasize the physical picture that results.

Table 3-1. Characteristic Properties of PVDMA Films Made from Preferential Assembly of PGMA-b-PVDMA Diblock Copolymers.

<i>Anneal Time</i>	<i>H</i> (nm) ^a	σ^b (chains/nm ²)	<i>R_g</i> (nm)	<i>D^c</i> (nm)	<i>D/2R_g^d</i>
18 h	32.4 ± 3.1	0.758	3.45	1.30	0.19
24 h	31.1 ± 3.4	0.727	3.45	1.33	0.19
30 h	35.5 ± 3.1	0.822	3.45	1.25	0.18

^a Brush thickness of PVDMA film

^b Grafting density of brush chains is calculated by $\sigma = H\rho N_A/M_n$

^c Distance between grafted polymer chains

^d Values less than 1 confirms the grafted polymer chains form a polymer brush

3.4.3 Functionalization of PVDMA Brushes with Primary Amines

After characterization, polymer-modified surfaces were functionalized *in situ* by exposing the polymer-modified surfaces to a chloroform solution containing either 0.25 wt.% 1-hexylamine (HA), 1-tetradecylamine (TDA), or 1-octadecylamine (ODA) for 12 h. My previous work demonstrates that the reaction time for *in situ* modification should be increased as the thickness of the parent polymer film is increased.¹⁰⁰ Substrates that were annealed for 24 h or 30 h were exposed to a second functionalization for 1 h with a 0.25 wt.% HA solution to determine if the chains of the layer could be reacted further.

3.4.4 Detailed Analysis via Neutron Reflectivity (NR): Functionalization of PVDMA Brushes with Primary Amines

Neutron reflectivity data was collected from surfaces consisting of a block copolymer containing a “hydrogen-rich” PGMA segment that was the anchor layer. PVDMA-d₆ creates the brush layer that has been isotopically substituted to provide contrast of the brush layer. The perdeuterated block, PVDMA-d₆, was synthesized as described above and as previously reported and found to have an $M_n = 27,000 \text{ g mol}^{-1}$. The substrates for neutron reflectivity measurements were prepared exactly the same way as the smaller substrates used for ellipsometry measurements. The concentration of diblock copolymer solutions, the solvent used in spin coating, and the annealing times were the same for both sizes of substrates; the concentration of amine and reaction time in which the films were exposed to the functionalization agent were also fixed. Previous NR experiments revealed that the scattering length density (SLD) of the PGMA primer layer was $9.0 \times 10^{-7} \text{ Å}^{-2}$ and the average PGMA thickness was 11.0 Å. Also from our previous NR experiments (described in Chapter 2), it was determined that the SLD of the

PGMA “primer” layer had an average SLD of $2.2 \times 10^{-6} \text{ \AA}^{-2}$ and an average thickness of 31 Å after the process of end-grafting PVDMA chains to the PGMA layer, yielding a PVDMA- d_6 brush.⁹⁹ This increase in SLD was due to the PGMA and PVDMA mixing upon spin coating in a good solvent and annealing to attach the PVDMA chains, resulting in some penetration of PVDMA- d_6 into the thin PGMA layer.

To decrease this inter-mixing of the layers, a block copolymer was designed to have a short PGMA segment and a longer PVDMA block, creating the PVDMA layer. The average SLD measured for the PGMA layer in these PVDMA-modified surfaces is $7.2 \times 10^{-7} \text{ \AA}^{-2}$. This measured value is lower than the calculated SLD for the bulk value of PGMA, $9.1 \times 10^{-7} \text{ \AA}^{-2}$, a result that suggests that the process of tethering using a diblock copolymer creates a PGMA strata of lower mass density. (Recall that SLD is the product of composition and mass density.) As the annealing time used to tether the block copolymer is increased, the thickness of the PGMA layer increased. From analysis of the NR data, the average thickness of the PGMA layer was determined to be 4.6 Å, 5.4 Å, and 6.2 Å for the surfaces annealed for 18, 24, and 30 h, respectively. The self-cross-linking of PGMA results in the thickness increase for longer annealing times. To test the accuracy of the model used to fit NR data all parameters for the PGMA layer found through model fitting (SLD, thickness, interfacial roughness) were allowed to vary for the amine-modified films to observe if the PGMA primer layer was modified by the amine. Through these analyses, it was confirmed that both the thickness of the PGMA layer and the SLD was consistent before and after functionalization.

The SLD of the PVDMA layer was found to vary for each surface due to sample-to-sample variation in grafting density. Different annealing times of 18, 24, or 30 h were selected to create a range of grafting densities and examine how the grafting density affects *in situ* functionalization with small molecule amines. The scattering length density of the PVDMA parent film is given by

$$\Sigma_0 = \frac{\rho_0 N_A}{M_V} b_V = N_{V0} b_V \quad (2-3)$$

where ρ_0 is the mass density, N_A is Avogadro's number, M_V is the molecular mass of VDMA, b_V is the scattering length of the VDMA monomer, and N_{V0} is the VDMA number density. Because we know the stoichiometry of PVDMA and its repeat unit molar mass, b_V and M_V are known. (See Table A-1 for tabulated values and Figure A-1 ChemDraw structures representing repeat units.) By measuring the scattering length density, Σ_0 , of the parent film of known stoichiometry, we measure its mass density:

$$\rho_0 = \frac{M_V}{b_V} \frac{\Sigma_0}{N_A} \quad (2-4)$$

Parent PVDMA films were fit using a single layer model. Surfaces annealed for 18 h resulted in an average measured SLD of $\Sigma_0 = 2.8 \times 10^{-6} \text{ \AA}^{-2}$ and an average thickness of 333 Å for the PVDMA layer, as presented in Table 3-2. Surfaces annealed for 24 h resulted in a measured SLD either of $\Sigma_0 = 2.9 \times 10^{-6} \text{ \AA}^{-2}$ and an average thickness of 334 Å or $\Sigma_0 = 3.4 \times 10^{-6} \text{ \AA}^{-2}$ and an average thickness of 262 Å for the PVDMA surfaces. The two measured thickness differences of the parent PVDMA film is attributed to additional chains being incorporated into the layer due to crosslinking

Table 3-2. Effect of Annealing Time on the Measured Scattering Length Density, Σ_0 , Mass Density, ρ_0 , and PVDMA Film Thickness, d_0 .

Anneal time	Σ_0 ($10^{-6} \text{ \AA}^{-2}$)	ρ_0^c (g cm^{-3})	d_0 ($\text{\AA}$)
18 h	2.75 ± 0.11	0.687 ± 0.027	333 ± 15
24 h	2.87 ± 0.07	0.719 ± 0.017	334 ± 12
24 h	3.38 ± 0.19	0.845 ± 0.048	262 ± 27
30 h	2.84 ± 0.11	0.711 ± 0.026	366 ± 21
30 h	3.40 ± 0.08	0.849 ± 0.019	324 ± 23

between the epoxides of the PGMA blocks.⁴¹ This same phenomenon was observed for surfaces annealed for 30 h: the average SLD value measured for the PVDMA layer is $\Sigma_0 = 2.8 \times 10^{-6} \text{ \AA}^{-2}$ or $3.4 \times 10^{-6} \text{ \AA}^{-2}$ and an average thickness of 366 $\text{\AA}$ or 324 $\text{\AA}$, respectively, for the PVDMA surfaces. The deviation of the measured SLDs from the expected value for bulk PVDMA- d_6 , $4.19 \times 10^{-6} \text{ \AA}^{-2}$, indicates that the surface-tethered thin film systems have lower mass densities (lower than bulk). In addition, it is noted that the films created from the block copolymer has a lower SLD compared to those made using end-grafting of PVDMA homopolymers, which was presented and discussed in Chapter 2.⁹⁹ The lower mass density exhibited by these films is attributed to the increased molecular weight of the block copolymer (compared to grafting end-functional chains). As the molecular weight of the chains increases, the coil volume expands, which decreases the ability of chains to pack closely on the surface.^{4,67,68} Coupled with the

reactive process of tethering the chains, which is governed by kinetics, this limits the amount of polymer chains that are tethered to the surface.

Because ellipsometry can only determine the thickness of these layers, but not the amount and distribution of amines in the film, the changes in scattering length density before and after functionalization are crucial to understanding the functionalization of these films. Due to the isotopic substitution of the methyl groups on the azlactone ring, the SLD of the PVDMA-d₆ layer decreases when reactively modified by “hydrogen-rich” amines. By measuring the decrease in SLD of the layer and the increase in the thickness of the modified PVDMA, it is possible to determine the extent of functionalization of the PVDMA layer. For this set of neutron reflectivity experiments, HA, TDA, and ODA were selected as the primary amines. PVDMA films were exposed to dilute solutions of these amines for 12 h. This series of experiments answers important fundamental questions: Are there differences in functionalization of films made by preferential adsorption compared to those made by end-grafting of chains? How much of the parent film is lost due to entropic death of the modified polymer chains? Can the PVDMA film be further reactively modified via refunctionalization?

The results presented in Table 3-3 are derived from NR studies of the modified films, and they reveal a few general trends: First, the SLD of the films decreases after functionalization due to the incorporation of the hydrogen-containing amines in the perdeuterated azlactone layer. Second, the reflectivity curves acquired for PVDMA layers exposed to amines are well-fit by a single-layer model, suggesting that each amine is able to penetrate into and react homogeneously with azlactone rings throughout the

Table 3-3. Measured Scattering Length Density of Parent and Modified-PVDMA film.

Sample ^a Modification	Anneal time	Σ_0^b ($10^{-6} \text{ \AA}^{-2}$)	ρ_0^c ($\text{g}\cdot\text{cm}^{-3}$)	Σ_M^d ($10^{-6} \text{ \AA}^{-2}$)	$\rho_{M,\text{est}}^e$ ($\text{g}\cdot\text{cm}^{-3}$)
1. TDA-1	18 h	2.710	0.68	2.240	0.68
2. TDA-2	18 h	2.720	0.68	2.300	0.68
3. ODA-1	18 h	2.730	0.68	2.150	0.68
4. ODA-2	18 h	3.420	0.86	1.390	0.87
5. HA-1	18 h	2.930	0.73	2.470	0.74
6. HA-2	18 h	2.640	0.66	2.150	0.69
1. TDA-1	24 h	2.890	0.72	2.190	0.72
2. TDA-2	24 h	3.410	0.85	1.780	0.85
3. ODA-1	24 h	2.800	0.70	2.440	0.72
*4. ODA-2	24 h	3.550	0.89	1.870	0.90
5. HA-1	24 h	2.930	0.73	2.470	0.72
6. HA-2	24 h	3.170	0.79	2.150	0.85
1. TDA-1	30 h	2.850	0.71	2.450	0.71
2. TDA-2	30 h	2.980	0.75	2.130	0.76
3. ODA-1	30 h	2.800	0.70	2.190	0.71
4. ODA-2	30 h	3.340	0.84	1.890	0.85
5. HA-1	30 h	2.730	0.68	2.540	0.71
6. HA-2	30 h	3.450	0.86	2.100	0.85

^a PVDMA-d₆ has an $M_n = 27,000 \text{ g mol}^{-1}$ and $D = 1.18$.⁸

^b Scattering length density of the PVDMA parent film, best fit to a single layer film

^c Mass density of the PVDMA parent film

^d Scattering length density of the modified-PVDMA layer; best fit to a single layer film with the exception of Sample 4 (ODA-modified film) annealed for 24 h

^e Mass density of the modified PVDMA film

*Sample 4 ODA-modified is best fit using a two-layer model: $\Sigma_{M1} = 1.16 \times 10^{-6} \text{ \AA}^{-2}$ and $\Sigma_{M2} = 1.87 \times 10^{-6} \text{ \AA}^{-2}$; M1 is the outer most layer and M2 is the inner most layer

polymer layer. There was only one exception to this: the PVDMA film with high grafting density ($\rho_0 = 0.89 \text{ g cm}^{-3}$) that was modified with ODA required a two-layer fit, suggesting a stratified structure.

As shown in Table 3-4, the thickness of the parent layers determined by NR is consistent with values measured using ellipsometry. The parent and modified layer thicknesses resulting from fitting of NR data, d_0 and d_M , respectively, show an increase in layer thickness after the film is exposed to a solution containing the primary amines. This is also evident in Figure 3-1a where the fringes in the reflectivity curve of the modified layer (red data) shift to lower Q with a decrease in spacing with respect to the “parent” PVDMA film (black data). Both of these imply that the layer thickness increases upon functionalization of the PVDMA film. The interfacial roughness (σ_R), which describes the width of the interface between two adjacent layers in the model used to fit the NR data, also shows a small increase upon functionalization. As captured in Figure 3-1b, the SLD for the “parent” PVDMA layer was $2.72 \times 10^{-6} \text{ \AA}^{-2}$ and its thickness was 352 $\text{\AA}$. Once the film was exposed for 12 h to the selected primary amine, in this case tetradecylamine (TDA), the total film thickness increased to 420 $\text{\AA}$. Furthermore, the addition of the “hydrogen-rich” amine to the PVDMA film causes the SLD of the PVDMA- d_6 layer to decrease. Through analysis of model fitting it was determined that the film was 10% functionalized. The SLD profile (Figure 3-1b) reveals that only one layer was required to fit the PVDMA layer. This differs from my previous work on end-grafted chains (Chapter 2), which required two strata to fit the data when the larger amines, TDA and ODA, were used. We speculate that this difference is due to brushes formed by preferential adsorption of PGMA-b-PVDMA chains being less

Table 3-4 Parent and Modified-PVDMA-d₆ Films measured by Ellipsometry and Neutron Reflectivity.

Sample ^a	Anneal time	H_0^b (Å)	d_0^c (Å)	FA ^d	d_M^e (Å)
1	18 h	342.6	314.9	TDA	407.0
2	18 h	354.8	352.4	TDA	420.3
3	18 h	346.0	340.0	ODA	414.7
4	18 h	295.8	291.5	ODA	534.0
5	18 h	269.4	337.0	HA	385.8
6	18 h	332.5	322.7	HA	410.0
1	24 h	324.9	321.0	TDA	398.0
2	24 h	296.7	291.8	TDA	515.0
3	24 h	351.6	345.0	ODA	388.0
4	24 h	295.7	238.4	ODA	452.4
5	24 h	342.8	337.0	HA	385.8
6	24 h	251.8	254.9	HA	340.0
1	30 h	373.7	363.0	TDA	409.0
2	30 h	359.1	346.2	TDA	474.0
3	30 h	372.0	359.0	ODA	450.0
4	30 h	324.5	340.3	ODA	529.3
5	30 h	397.7	394.5	HA	425.0
6	30 h	306.0	308.3	HA	460.0

^a PVDMA-d₆ has an $M_n = 27,000 \text{ g mol}^{-1}$ and $\bar{D} = 1.18$

^b PVDMA film thickness measured by ellipsometry

^c PVDMA film thickness measured by neutron reflectivity

^d HA = hexylamine; TDA = tetradecylamine; ODA = octadecylamine

^e Modified-PVDMA film thickness measured by neutron reflectivity

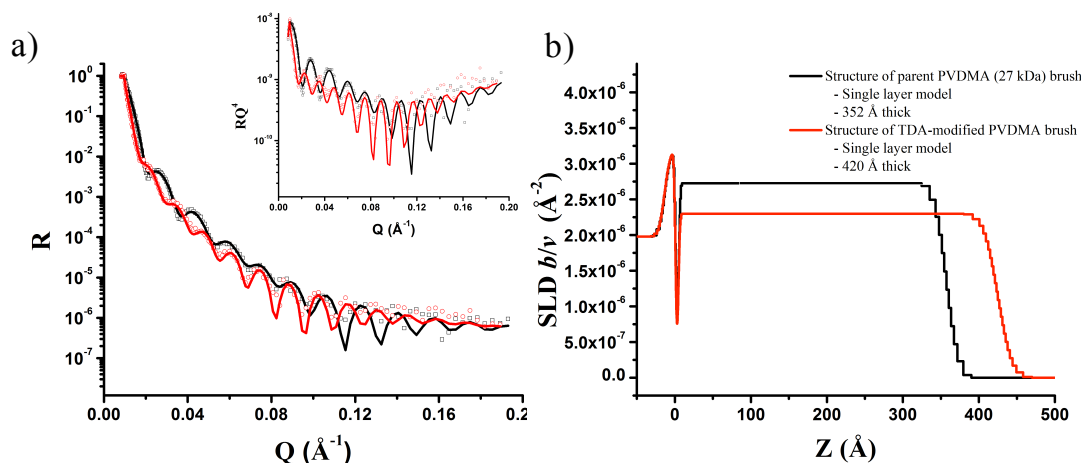


Figure 3-1. a) R versus Q and RQ^4 versus Q representations of neutron reflectivity data acquired for a 27,000 g mol⁻¹ PVDMA-d₆ film: PVDMA-d₆ film (black) and TDA-modified PVDMA film (red). The data are shown as points and the best-fit model is represented by the solid lines; b) SLD profiles for a PVDMA-d₆ film (black) and a TDA-modified PVDMA film (red) as a function of thickness, Z . Analogous plots for all other samples are presented in *Appendix B*.

crowded. As the degree of polymerization increases, the radius-of-gyration of the chain increases resulting in a lower grafting density. Thus, when grafting density is low, amines more easily penetrate into the polymer film, making *in situ* functionalization less affected by the steric crowding. This also results in a homogeneous distribution of the functionalizing agent that is described with a single-layer fit.

From the 18 surfaces that were prepared and examined by NR, only one surface had a high enough grafting density ($\rho_0 = 0.89 \text{ g} \cdot \text{cm}^{-3}$) that required a stratified (two-layer) fit. The SLD profile (Figure 3-2b) confirms there are two layers within the PVDMA

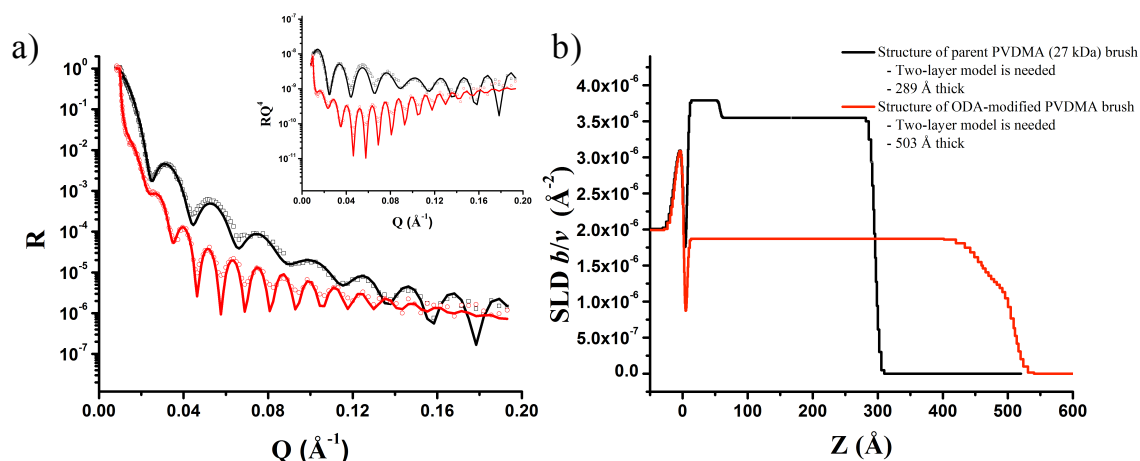


Figure 3-2. a) R versus Q and RQ^4 versus Q representations of neutron reflectivity data for a 27,000 g mol⁻¹ PVDMA-d₆ film: PVDMA-d₆ film (black) and ODA-modified PVDMA film (red). The data are shown as points and the best-fit model is represented by the solid lines; b) SLD profiles for a PVDMA-d₆ film (black) and an ODA-modified PVDMA film (red) as a function of thickness, Z .

film. The outer portion of the layer was 52 $\text{\AA}$ thick, and the measured SLD of 1.16×10^{-6} $\text{\AA}^{-2}$ suggested that 31% of the VDMA repeat units were functionalized by ODA. The bottom stratum of the layer had a thickness of 452 $\text{\AA}$ and an SLD of 1.87×10^{-6} $\text{\AA}^{-2}$ that equates to the chains being 24% functionalized. The surface roughness for the parent PVDMA film is 12 $\text{\AA}$ at the air/film interface, and it increases to 52 $\text{\AA}$ after functionalization. These low roughnesses confirm that these are smooth, homogenous films. The need for two distinct layers supports my contention that grafting density plays a crucial role in these reactive modification processes. When grafting density is high, the amines begin to react at the outer edges of the layer increasing the steric hindrance (and

potentially decreasing the solubility). As a result, the amines are not able to access the inner region of the polymer layer. This prohibits complete functionalization and creates a stratified layer having different extents of functionalization for each layer.

Through model fitting of the reflectivity measured for the modified films it is possible to calculate the amount of PVDMA chains lost, $f_{\text{PVDMA-lost}}$, and the reacted fraction of remaining VDMA monomers, f_{M} , to quantify the extent of functionalization of the films. The derivations of the relevant equations used in the calculations have already been discussed where they are originally presented as Equations (2-3) through (2-13) in Chapter 2.⁹⁹ Since the estimated mass density for each modified-PVDMA film was set to the parent PVDMA film, the estimated converted fraction, $f_{\text{M,est}}$ is given by

$$f_{\text{M,est}} = \frac{\rho_{\text{M,est}} N_{\text{A}} b_{\text{V}} - \Sigma_{\text{M}} M_{\text{V}}}{\Sigma_{\text{M}} M_{\text{am}} - \rho_{\text{M,est}} N_{\text{A}} b_{\text{am}}} \quad (2-9)$$

Once the converted fraction based on an estimated mass density is calculated, the estimated fraction of VDMA repeat units lost during reaction with amines, $f_{\text{PVDMA-lost}}$, can be calculated using Equation 2-13:

$$\begin{aligned} f_{\text{PVDMA-lost}} &= 1 - \frac{N_{\text{V,est}}}{N_{\text{V0}}} = 1 - \frac{\Sigma_{\text{M}}}{b_{\text{am}} f_{\text{M,est}} + b_{\text{V}} \Sigma_0} \frac{b_{\text{V}}}{\Sigma_0} \\ &= 1 - \frac{\Sigma_{\text{M}}}{\Sigma_0} \frac{b_{\text{V}}}{b_{\text{am}} f_{\text{M,est}} + b_{\text{V}}} \end{aligned} \quad (2-13)$$

Once again, because we do not know the mass density of the functionalized layer exactly, it is useful to estimate the range over which the extent of functionalization varies and the amount of PVDMA lost after exposure to the amine by using the lowest and highest mass densities of the parent film. Those extreme values were $\rho_{\text{M,est}} = 0.66$ and $\rho_{\text{M,est}} = 0.89 \text{ g}\cdot\text{cm}^{-3}$, and they can be inserted into equations (2-9) and (2-13) to

determine $f_{M,est}$ and $f_{PVDMA-lost}$, respectively. Table 3-5 presents the range of values based on estimated mass densities of the polymer layer, $\rho_{M,est}$, chosen based on the measured ρ_0 of the parent film. (See Table 3-4, where the range of densities are $0.66 < \rho_0 \text{ (g cm}^{-3}\text{)} < 0.89$.) These upper and lower limits yield a complete accounting of the fraction of VDMA monomers in the film, both modified and lost, as a function of depth. Calculated values of $f_{PVDMA-lost}$, $f_{M,est}$, and f_M are tabulated in Table 3-5 and a visual representation expressing the depth-dependent values is displayed in Figure 3-3.

Model fitting of the measured reflectivity for the modified films confirms the size of the amine used in modification has an effect on the extent of functionalization and the amount of PVDMA chains that are lost. The data presented in Tables 3-5 shows that the mass density range does not greatly impact the amount of PVDMA lost, $f_{PVDMA-lost}$, during the functionalization reaction, so it is assumed constant in composing Figure 3-3 and analogous plots for other samples, which can be viewed in Appendix B. While the value of $\rho_{M,est}$ does not have a significant effect on the amount of PVDMA lost during functionalization, the results support my previous conclusion on the impact of the size of amine; as the size of amine used in functionalization increases, the amount of PVDMA chains that are lost increases. As seen from Table 3-5, the main impact of different film mass densities is on $f_{M,est}$, which according to Equation (2-9) takes into account the specific amine used for modification. As discussed previously, larger values of $\rho_{M,est}$ require a higher extent of functionalization to obtain the same measured Σ_M . Results shown in Table 3-5 indicate that as the size of the amine increases, the overall extent of functionalization decreases, which also might be anticipated and is fully consistent with insights derived from ellipsometry and previously published results.

Table 3-5. Extent of Functionalization using a Mass Density Range of the Modified Layer of $\rho_{M,est} = 0.66\text{-}0.89 \text{ g}\cdot\text{cm}^{-3}$

Sample Modification	Anneal time	$f_{M,est}^a$ ($\rho_{M,est} = 0.66$)	$f_{PVDMA-lost}^b$ ($\rho_{M,est} = 0.66$)	f_M^c	$f_{M,est}^a$ ($\rho_{M,est} = 0.89$)	$f_{PVDMA-lost}^b$ ($\rho_{M,est} = 0.89$)	f_M^c
1. PVDMA-TDA	18 h	0.11	0.16	0.09	0.35	0.13	0.30
2. PVDMA-TDA	18 h	0.09	0.14	0.08	0.32	0.11	0.29
3. PVDMA-ODA	18 h	0.11	0.20	0.09	0.31	0.17	0.25
4. PVDMA-ODA	18 h	0.41	0.56	0.18	0.68	0.54	0.31
5. PVDMA-HA	18 h	0.09	0.15	0.07	0.55	0.12	0.48
6. PVDMA-HA	18 h	0.29	0.17	0.24	0.80	0.14	0.69
1. PVDMA-TDA	24 h	0.12	0.23	0.10	0.37	0.20	0.29
2. PVDMA-TDA	24 h	0.29	0.46	0.16	0.57	0.43	0.32
3. PVDMA-ODA	24 h	0.04	0.12	0.03	0.22	0.09	0.20
4. PVDMA-ODA	24 h	0.20	0.45	0.11	0.41	0.43	0.23
5. PVDMA-HA	24 h	0.09	0.15	0.07	0.55	0.12	0.48
6. PVDMA-HA	24 h	0.29	0.31	0.20	0.80	0.28	0.58
1. PVDMA-TDA	30 h	0.05	0.13	0.04	0.27	0.11	0.24
2. PVDMA-TDA	30 h	0.15	0.27	0.11	0.39	0.24	0.30
3. PVDMA-ODA	30 h	0.10	0.20	0.08	0.29	0.18	0.24
4. PVDMA-ODA	30 h	0.19	0.41	0.11	0.40	0.39	0.25
5. PVDMA-HA	30 h	0.05	0.07	0.05	0.50	0.04	0.48
6. PVDMA-HA	30 h	0.33	0.38	0.20	0.85	0.35	0.55

^a Estimated extent of functionalization

^b PVDMA chains lost

^c Extent of functionalization of each modified layer assuming the given mass density of the modified layer, $\rho_{M,est}$. f_M is the extent of functionalization after accounting for $f_{PVDMA-lost}$.

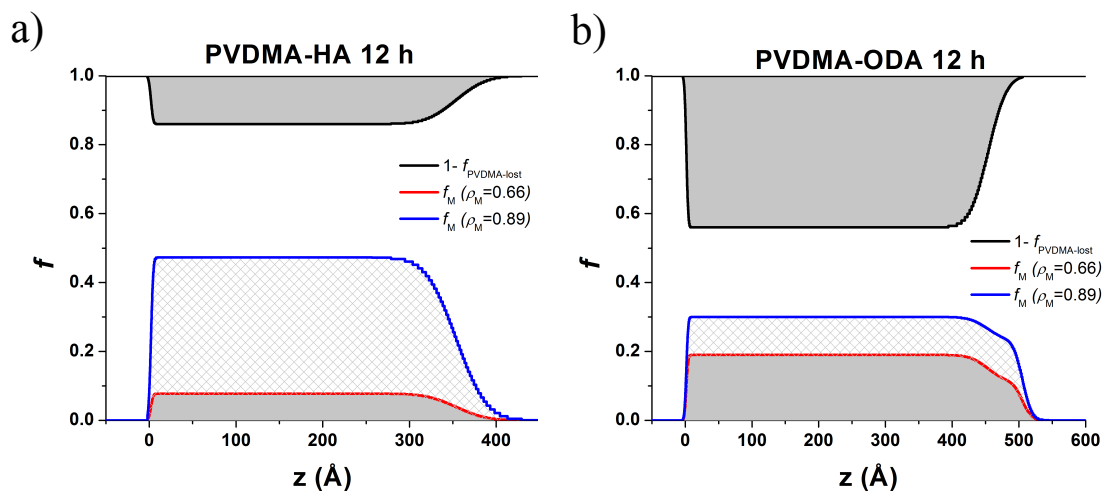


Figure 3-3. Converted fraction plots provide a complete accounting of reactive modification of PVDMA layers, including how much PVDMA was lost, converted, or did not react, using the two extremes of mass density measured for the parent films. The amount of PVDMA available to be functionalized is represented by the area beneath the black line. If a mass density of $\rho_{M,\text{est}} = 0.66$ (blue line) or $\rho_{M,\text{est}} = 0.89$ (red line) is assumed, the proportion of the converted film varies (a) between 0.07 and 0.48 for modification with HA and (b) between 0.11 and 0.23 for modification with ODA. The empty space between lower and upper bounded areas represents unreacted VDMA monomer.

Again it is noted that the converted fraction, f_M , is the fraction of reacted VDMA monomers *remaining* after accounting for the fraction that are lost. Figure 3-3a presents the depth-dependent profiles for PVDMA modified with HA for 12 h. Here the data is best modeled using a single-layer fit. Figure 3-3b shows depth-dependent profiles for a PVDMA layer modified with ODA for 12 h, which requires a two-layer fit of the measured reflectivity data. Figure 3-3a corresponds to sample 5 (annealed for 18 h) from Tables 3-3, 3-4, 3-5, and 3-6 and Figure 3-3b corresponds to sample 4 (annealed for 24 h) from Tables 3-3 through 3-6.

Due to having a number of replicate samples, I aim to reduce the number of assumptions made when analyzing NR data. More specifically, I attempt to resolve the issue of needing to assume an estimated mass density of the modified film because it affects calculations of the amount of chains lost and extent of functionalization. To address this, samples were first separated by their annealing time (18, 24, or 30 h), and then separated by their measured mass density of the parent film. As shown in Table 3-2 and discussed previously in this section, an estimated mass density for the modified film was selected from the parent mass density average and within its standard deviation for each anneal time. Although there is uncertainty, this process provides the best-estimate of mass density in calculating $f_{M,est}$, $f_{PVDMA-lost}$, and f_M compared to analyzing results within the limits of the mass density range ($\rho_{M,est} = 0.66 - 0.89$). The results presented in Table 3-6 reveal a few trends: As the mass density of the parent film increases, more PVDMA chains are lost. Because there are more chains grafted to the surface, the chains are more crowded and there is a higher entropic penalty for additional chain stretching in

Table 3-6. Calculated Values from the Measured Σ_0 and Σ_M ($10^{-6} \text{ \AA}^{-2}$).

Sample ^a Modification	Anneal time	ρ_0^b ($\text{g}\cdot\text{cm}^{-3}$)	$\rho_{M,\text{est}}^c$ ($\text{g}\cdot\text{cm}^{-3}$)	$f_{M,\text{est}}^d$	$f_{\text{PVDMA-lost}}^e$	f_M^f
1. TDA-1	18 h	0.68	0.68	0.19	0.16	0.12
2. TDA-2	18 h	0.68	0.68	0.12	0.14	0.10
3. ODA-1	18 h	0.68	0.68	0.17	0.19	0.11
4. ODA-2	18 h	0.86	0.87	0.65	0.54	0.30
5. HA-1	18 h	0.73	0.74	0.25	0.14	0.22
6. HA-2	18 h	0.66	0.69	0.43	0.16	0.29
1. TDA-1	24 h	0.72	0.72	0.20	0.22	0.15
2. TDA-2	24 h	0.85	0.85	0.56	0.44	0.29
3. ODA-1	24 h	0.70	0.72	0.09	0.12	0.08
*4. ODA-2	24 h	0.89	0.90	0.45	0.43	0.24
5. HA-1	24 h	0.73	0.72	0.30	0.14	0.18
6. HA-2	24 h	0.79	0.85	0.72	0.29	0.51
1. TDA-1	30 h	0.71	0.71	0.10	0.13	0.09
2. TDA-2	30 h	0.75	0.76	0.25	0.26	0.19
3. ODA-1	30 h	0.70	0.71	0.14	0.20	0.11
4. ODA-2	30 h	0.84	0.85	0.37	0.40	0.22
5. HA-1	30 h	0.68	0.71	0.15	0.06	0.14
6. HA-2	30 h	0.86	0.85	0.76	0.36	0.49

^a PVDMA-d₆ has an $M_n = 27,000 \text{ g mol}^{-1}$ and $D = 1.18$.⁸

^b Mass density of the parent PVDMA parent film

^c Estimated mass density of the modified-PVDMA film

^d Estimated extent of functionalization

^e PVDMA chains lost

^f Extent of functionalization of each modified layer assuming the given mass density of the modified layer, $\rho_{M,\text{est}}$. f_M is the actual extent of functionalization that accounts for $f_{\text{PVDMA-lost}}$.

*The table presents values from a single-layer fit for simplicity. The calculated values for a two-layer fit for Sample 4 are: $f_{M1,\text{est}} = 0.88$, $f_{M2,\text{est}} = 0.42$, $f_{\text{PVDMA-lost}1} = 0.65$, $f_{\text{PVDMA-lost}2} = 0.43$, $f_{M1} = 0.31$, $f_{M2} = 0.24$. M1 is the outer most layer and M2 is the inner most layer

a crowded layer, where the chains are already stretched during the grafting process. The size of amine also impacts the amount of PVDMA chains that are lost: as the molecular mass of the amine used for functionalization increases, the amount of chains that are lost increases. When PVDMA is functionalized, the added molecular mass of the amine (and volume of the modified repeat unit) produces additional crowding within the layer, causing chains to stretch farther from the surface. This increases the bond tension of the attached chain activates bond breaking that leads to more chains being cleaved from the substrate. Because the estimated mass density of the modified film varies, it is more difficult to interpret how the size of amine affects the extent of functionalization. For example, Table 3-6 shows that ODA-modified films annealed for 18 h have the highest extent of functionalization ($f_M = 0.30$). However, if we take a closer look at the characteristics of the films annealed for 18 h, it is clear that this film also has the highest mass density. Because there is more material on the surface, there is a larger fraction of azlactone rings available to be functionalized, which results in a higher extent of functionalization. When samples annealed for 18 h of the same mass density are compared, it is observed that as the size of amine increases, the extent of functionalization decreases: this is represented in Table 3-6 for Sample 2 (TDA-modified; $f_M = 0.10$) and Sample 6 (HA-modified; $f_M = 0.29$).

To simplify the analysis, an estimated mass density, $\rho_{M,est}$ of 0.703 g cm^{-3} was used to represent the mass density of the amine-modified films. The data presented in Table 3-7, which is analyzed using $\rho_{M,est} = 0.703 \text{ g cm}^{-3}$ is organized by annealing time with the size of the different amines used in functionalization increasing across the table (left to right). Because of the critical role grafting density plays, to determine how the

Table 3-7. Extent of f . Effect of Amine Size Using $\rho_{\text{est}} = 0.703 \text{ g}\cdot\text{cm}^{-3}$.

	Anneal Time	ρ_0 ($\text{g}\cdot\text{cm}^{-3}$)	f_{PVDMA} -lost	FA	f		ρ_0 ($\text{g}\cdot\text{cm}^{-3}$)	f_{PVDMA} -lost	FA	f		ρ_0 ($\text{g}\cdot\text{cm}^{-3}$)	f_{PVDMA} -lost	FA	f
1	18h	0.66	0.16	HA	0.33		0.68	0.16	TDA	0.13		0.68	0.19	ODA	0.12
2	18h	0.73	0.15	HA	0.15		0.68	0.14	TDA	0.12		0.86	0.56	ODA	0.20
3	24h	0.73	0.15	HA	0.15		0.72	0.22	TDA	0.13		0.70	0.12	ODA	0.07
4	24h	0.79	0.30	HA	0.27		0.85	0.47	TDA	0.19		0.89	0.45	ODA	0.13
5	30h	0.68	0.06	HA	0.13		0.71	0.13	TDA	0.08		0.70	0.20	ODA	0.11
6	30h	0.86	0.37	HA	0.27		0.75	0.27	TDA	0.14		0.84	0.41	ODA	0.14

size of the amine affects the extent of functionalization, it is important to compare results for films with similar mass densities, such as rows 1, 3, and 5 shown in Table 3.7. By comparing extents of functionalization as a function of amine size, it is seen that HA reacts to the highest extent, followed by TDA then ODA. Data in Row 5 also shows how the size of amine affects the amount of chains that are cleaved from the surface: as the amine size increases there appears to be more chains lost during reactive modification. The data in Table 3-7 also demonstrates that parent films of higher mass density result in a higher extent of functionalization, with the only exception being the pair of HA-modified surfaces annealed for 18 h. As explained before, layers having a higher areal density of chains provide more VDMA repeat units that can react with the amines present in solution.

From this NR study, I was able to establish a relationship between the parent mass density of chains on the substrate and the amount of chains that were lost. This is clearly shown in Figure 3-4, where it is seen that as the mass density of the film increases, the amount of PVDMA chains cleaved from the surface also increases. This result has scientific impact because while degrafting of chains has been reported for polymer brushes, this is the first report to show a quantitative relationship between extent of degrafting and grafting density of chains. Brushes of higher areal density have more chains per volume and, therefore, are more strongly stretched during the tethering process to relieve the lateral crowding between polymer chains. Because the chains are strongly stretched in the parent brush, additional steric stress resulting from functionalization causes an increase in stretching that drives the chains to detach when the chains are modified with amines. Therefore, the modified films cannot be assumed to

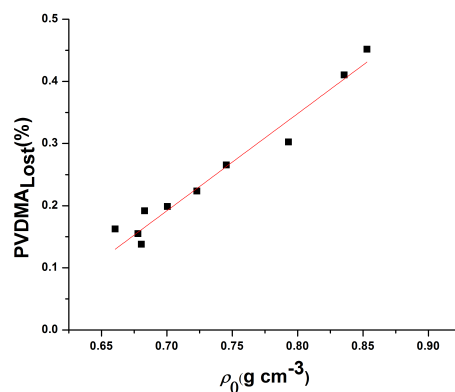


Figure 3-4. Relationship between mass density, ρ_0 , and the amount of PVDMA lost.

have constant mass density. For this reason, the previous NR study used an estimated mass density, $\rho_{M,est} = 1.0 \text{ g}\cdot\text{cm}^{-3}$ to calculate values for the amine-modified layers and a range of parent mass densities of the as-prepared brushes ($0.79 < \rho_0 \text{ (g}\cdot\text{cm}^{-3}) > 1.06$) was used to develop a complete accounting of the reactive modification of PVDMA chains.

In the previous results presented in Chapter 2, I theorized that polymer chains are cleaved from the surface by scission of the ester bond that resulted from the grafting reaction of the carboxylic acid end-functionalized PVDMA chain with an epoxide group of the surfaced-anchored PGMA layer. However, with the design of the PGMA-b-PVDMA diblock copolymer, this ester bond is eliminated. The epoxide groups from the PGMA block react with surface hydroxyls, resulting in the formation of siloxane (Si—O) bonds, which along with cross-linking of the epoxide groups, anchors chains to the substrate. Siloxane bonds have a low activation energy and are more susceptible to mechanical stress.^{80,81} Therefore, I theorize that when PVDMA chains are

functionalized, the added mass and volume of the repeat units increases the inter-chain crowding and causes the chains to stretch farther away from the surface. This additional stretching causes tension at the anchoring site. In order to decrease this tension, the block copolymer chain cleaves from the siloxane bond at the attachment site. Because the ester linkage was eliminated for this study, there is not as much scission of the carbon-carbon bonds that results in chain loss. This is to be expected because C-C bonds are stronger than ester linkages. This agrees with work published from Schmidt, Panyukov, and Sheiko, which demonstrates that bond breakage at the attachment point and loss of chains is facilitated by the tension of a stretched chain.^{80,81,95}

3.4.5 Refunctionalization of PVDMA Films

Analyses of reflectivity data consistently show that the extent of functionalization depends on the size of the amine modifier and grafting density. In addition, both NR studies (described in Chapter 2 and 3) show that functionalization is incomplete. To examine this further, sets of HA-, TDA-, and ODA-functionalized PVDMA films were refunctionalized by exposure to a 0.25 wt.% HA solution for 1 h. Those refunctionalized surfaces were remeasured by NR. In all cases, the fitted reflectivity data shows an increase in thickness upon refunctionalization and a further drop in SLD (from the original modification) for each of the amine-functionalized films. This is best shown in Figure 3-5, where an ODA-modified film (503 Å) shows an increase in thickness to 555 Å after it is refunctionalized with HA. Data for other amine refunctionalized films is presented in Appendix B. Collectively, this set of results support the conclusion that the modification of PVDMA films is not complete – they can be reacted further.

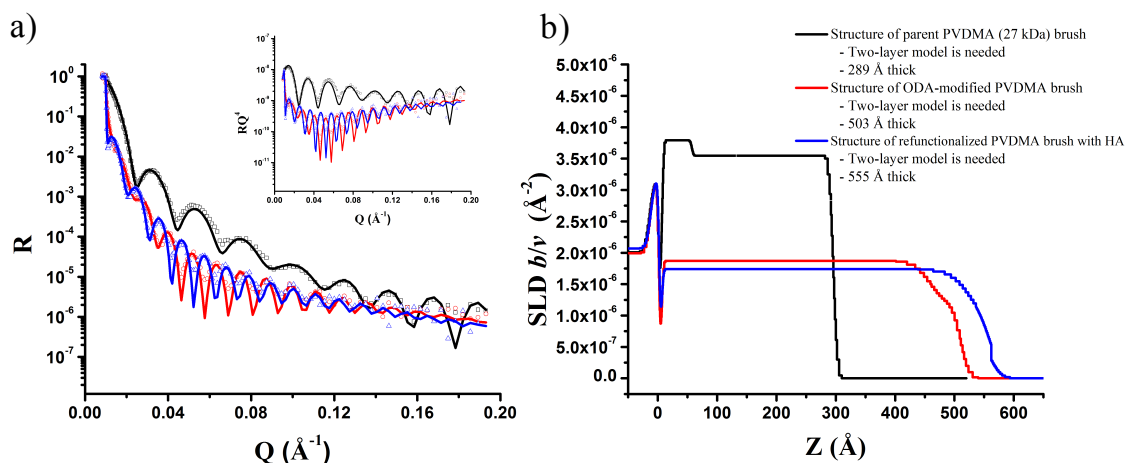


Figure 3-5. a) R versus Q and RQ^4 versus Q representations of neutron reflectivity data for a 27,000 g mol⁻¹ PVDMA- d_6 film: PVDMA- d_6 film (black), ODA-modified PVDMA film (red), and HA-modified PVDMA film (blue) (refunctionalized). The data are shown as points and the best-fit model is represented by the solid lines; b) SLD profiles for a PVDMA- d_6 film (black), an ODA-modified PVDMA film (red), and HA-modified PVDMA film (blue) (refunctionalized) as a function of thickness, Z .

3.5 Conclusions

Through neutron reflectivity measurements, the amount of PVDMA chains cleaved from the surface and the resulting extent-of-functionalization of the PVDMA layer is determined. The depth-dependent model yields a complete and detailed picture of reactive modification of an azlactone polymer system. Results from ellipsometry and findings from NR measurements deliver a more thorough understanding as to why PVDMA chains are cleaved from the film upon functionalization. The grafting density of chains and the type of chemical bond (ester or silanol linkages or carbon-carbon

bonds) fixing the chains to the surface play critical roles in degrafting. Analyses from ellipsometry and neutron reflectivity measurements demonstrate that reactive modification of poly(2-vinyl-4,4-dimethyl-d₆ azlactone) (PVDMA-d₆) films by small molecule amines is incomplete, and that the extent of functionalization is strongly dependent on the size of the n-alkyl amine. While results are consistent with trends from previous research,^{41,99} a variety of new and important insights surpassing current understanding are gained due to the sensitivity of neutron scattering to isotopic substitution enabled through the use of perdeuterated PVDMA. Most notably, results show that the extent of functionalization of the block copolymer containing PVDMA is uniform for films having a low mass density, despite increased steric demand caused by addition of amines to azlactone rings by ring-opening nucleophilic addition. That steric demand also appears to cause chain scission of the modified film – an “entropic death” of chains – due to the penalty for additional stretching. From this work, a relationship between mass density and amount of polymer chains that are cleaved is defined: as the mass density increases, more polymer chains are cleaved after functionalization. These insights into the role of chain grafting density and cleavage of chains during functionalization are generally useful whenever films are altered *in situ* through post-polymerization modification to change the resultant surface or interfacial properties.

Chapter 4

Functionality Gradients in Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) Thin Films Created by *in situ* Modification

4.1 Abstract

Generating physical or chemical gradients in thin film scaffolds is an efficient approach for screening and optimizing interfacial structure or chemical functionality to create tailored surfaces that are useful because of their wettability, antifouling or barrier properties. The relationship between the structure of poly(2-vinyl-4,4-dimethyl azlactone) brushes created by preferential assembly of poly(glycidyl methacrylate)-block-poly(2-vinyl-4,4-dimethyl azlactone) (PGMA-b-PVDMA) diblock copolymers and the ability to chemically modify the PVDMA chains *in situ* to create a gradient in functionality is examined to investigate how extent of functionalization affects the interfacial and surface properties. The introduction of a chemical gradient by controlled immersion allows reactive modification to generate position-dependent properties that are assessed by ellipsometry, ATR-FTIR spectroscopy, contact angle measurements, and AFM imaging. These are used to establish relationships between layer thickness, reaction time, position, and extent of functionalization. These findings provide unique insight into the alteration of interfacial and surface properties controlled *in situ* by chemical modification and broadly support efforts to produce tailored surfaces having application as tailored membranes, protein resistant surfaces, or sensors.

4.2 Introduction

Block copolymers (BCPs) consisting of chemically incompatible blocks undergo microphase separation in bulk and in thin films. Domain sizes on the scale of tens of nanometers and the ability to fine-tune the chemical and physical properties through the choice of monomeric building blocks diversify the range of potential applications for

these nanoscale systems. In thin film systems, BCPs can be used to pattern or template surfaces, inspiring applications as biomaterials, such as tissue engineering or cell culturing, bit-patterned media made through lithographic approaches, and functional materials.^{101–104} Varying the degree-of-polymerization (DP) and composition of the copolymer alters the phase behavior, affecting the size and shape of the microdomains.¹⁰⁵ In addition, to minimize the total free energy of a thin film, one block typically prefers the film/substrate interface because it has a lower interfacial energy while the other block prefers the air interface because it has a lower surface energy.^{104,106–109} Thin films have an additional parameter, thickness, that can be manipulated, which affects the microstructure.¹⁰² When spin coating is used, film thickness and roughness, which are directly related to the microstructure, are affected by spin speed, solution concentration, and solvent evaporation rate.^{110,111} These trade-offs between equilibrium, which set the microphase-separated morphology, and kinetically-governed processes linked to the deposition method lead to a particular display of interfacial properties and film structure.

Gradient surfaces with gradual and continuous changes in physical and/or chemical properties provide the ability to screen surface chemistry or tune specific interfacial characteristics in a facile manner. There are five characteristics of gradients that directly affect interfacial properties, including type, dimensionality, directionality, length scale, and time dependency.^{25,50} In addition, multiple gradients in orthogonal directions can be exploited to more widely alter the properties of the interface, and 3D gradients can be created by linearly varying the molecular weight or grafting density when tethering polymer chains by one end to the surface. Surface-bound gradients have

been fabricated in a variety of ways to develop interfaces with specific chemical and physical properties. Gradient polymer films are created by three main ways: Gradual immersion to alter surface chemistry, thermal gradients for spatial control of surface modification, and diffusion to control surface density of small molecules.²⁵ These designs have been investigated to explore how properties change along the substrate, but there are few systematic reports of how the molecular weight and grafting density of chains affect the extent of functionalization of these films, which sets the surface properties. Each of these approaches are highlighted in turn.

In an early example of an immersion process, Ueda-Yukoshi and Matsuda attached poly(vinylene carbonate) to a glass substrate and then gradually submerged the film in a NaOH solution at a controlled immersion rate.¹¹² Exposure to the strong base converted carbonate groups to hydroxyl groups, resulting in a responsive surface whose hydrophobicity and response depended on immersion time. Contact angle (CA) and X-ray photoelectron spectroscopy (XPS) measurements were performed to analyze changes in wettability of the polymer film. These gradient surfaces also were exposed to endothelial cells (ECs), and it was shown that the more hydrophobic region of the substrate exhibited the highest areal density of adhered ECs while the most hydrophilic area displayed the most migration and lowest surface density of adherent ECs.¹¹² In another example, Morgenthaler *et al.* used a controlled dipping process to adsorb poly(L-lysine)-graft-poly(ethylene glycol) (PLL-g-PEG) chains onto a substrate. (The PLL backbone adsorbed to the substrate through electrostatic interactions.) This procedure varied the density of chains along the substrate. These PLL-g-PEG modified substrates were then placed in a biotin solution. XPS, variable angle spectroscopic

ellipsometry, and optical wave-guide light mode spectroscopy were used to determine that biotin does not adhere in regions of low PEG chain density but biotinylation occurred where PEG chains were most dense.¹¹³

Shovsky and Schönherr used a liquid cell Peltier element to create a thermal gradient and studied the temperature dependence of the hydrolysis of self-assembled monolayers (SAMs) and wetting behavior.¹¹⁴ Specifically, XPS and CA measurements confirm that the extent of hydrolysis increases of the N-hydroxysuccinimide (NHS) ester groups decorating the periphery of the SAM as the temperature increases. CA measurements indicate that hydrolysis of the SAM in an NaOH solution is a function of time and is described by pseudo-first-order kinetics.¹¹⁴

PGMA has been used frequently as a “primer” layer,^{16,28,34,35,115,116} and it has been used to create gradients.^{28,34,65,116,117} Ionov and coworkers used a temperature gradient stage to create a gradual and directional change in the grafting density of end functionalized polystyrene (PS) or poly(ethylene glycol) (PEG) chains that were tethered to a PGMA layer. Atomic force microscopy (AFM) and ellipsometry were used to examine the topography and thickness along the gradient film. Variation in the annealing temperature affected the reaction kinetics between the carboxylic acid-terminated PS or PEG chains and surface-bound epoxides, resulting in gradation of wettability.¹¹⁷ Ionov and coworkers continued this strategy by using a thermal gradient to manipulate the grafting density of PEG-NH₂ chains on a PGMA-modified surface.^{28,34,65} The gradient surface was exposed to a solution containing kinesin motor molecules tagged with green fluorescent protein and fluorescent imaging was used to reveal how grafting density

affected protein adsorption. Their results indicate that as the grafting density of PEG chains increases, longer microtubules tend to migrate to the most dense region.²⁸

Ionov *et al.* additionally used a thermal gradient to control grafting of carboxylic acid-terminated poly(*tert*-butyl acrylate) (PBA-COOH) chains to a PGMA-modified substrate. End-functionalized poly(2-vinylpyridine) chains having a carboxylic acid end group (P2VP-COOH) were then grafted to the PBA-modified substrate. The PBA chains were hydrolyzed, forming a mixed film displaying poly(acrylic acid) and poly(2-vinylpyridine) chains. Because P2VP is a weak poly(base), it is charged positively at low pH, while the weak poly(acid) PAA is charged negatively at a high pH. The mixed system was then exposed to bovine serum albumin (BSA), which is amphoteric with an isoelectric point (IEP) at pH = 4.9. BSA is positively charged (cationic) below its IEP and negatively charged (anionic) above the IEP. Due to electrostatic interactions, the protein adsorption is the highest when the substrate has the opposite charge: in other words, protein adsorption to PAA is weaker at high pH because PAA is negatively charged but there is strong adsorption at low pH. Conversely, the opposite behavior is exhibited with P2VP, where strong adsorption occurs at high pH and weak adsorption at a low pH. (P2VP and BSA have positive charges.)¹¹⁵

A number of approaches have been used to tailor the density of small molecules. For example, Wang *et al.* applied an electrochemical potential across a gold substrate to create a gradient in hexadecanethiol (HDT) density. A disulfide atom-transfer radical polymerization (ATRP) initiator was backfilled into areas of low HDT density, and surface-initiated (SI)-ATRP was used to create a gradient in poly(*N*-isopropylacrylamide) (PNIPAM) grafting density along the substrate.¹¹⁸ Ellipsometry

measurements, AFM imaging, and surface plasmon resonance (SPR) spectroscopy were used to characterize the PNIPAM gradient, and changes in chain conformation from the “mushroom” regime to the “brush” regime were observed. They also showed that high grafting densities resulted in a smoother surface morphology.¹¹⁸ Coad *et al.* used a plasma deposition method to distribute 1,7-octadiene and allylamine across a substrate.¹¹⁹ The gradient was created by controlling the vapor composition, which was used to increase the amount of allylamine along the substrate. Post-deposition modification of the allylamine was used to install a SI-ATRP initiator, which allowed gradation in the grafting density and thickness of PHEMA brushes, as evidenced by XPS, AFM, and ellipsometry.¹¹⁹ Kim *et al.* used a corona-discharge process to vary the number density and type of functional groups (hydroxyls, ethers, ketones, aldehydes, carboxylic acids and carboxylic esters) present along the polyethylene (PE) films, with the gradients created by increasing the power as the corona discharge device was moved along the surface. ATR-FTIR spectroscopy, contact angle measurements, and AFM imaging were used to characterize the surface properties along the gradient PE film. The PE films were reactively modified with polyethyleneimine (PEI). After reaction, these surfaces were exposed to a biotin solution to yield a biotinylated PE surface that could bind a fluorescently-labeled streptavidin. It was determined a higher corona exposure resulted in a smaller water contact angle (more hydrophilic surface due to more PEI) and a stronger fluorescent intensity, indicating greater extent of conjugation of streptavidin.¹²⁰

Previous work on poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) has been focused on solution and thin film structure and properties.^{16,41} Lokitz *et al.* examined a

variety of deposition conditions for poly(glycidyl methacrylate)-block-poly(2-vinyl-4,4-dimethyl azlactone) (PGMA-b-PVDMA), varying the concentration of the block copolymer solution and the annealing conditions (time and temperature) to tether the films to the substrate through the PGMA blocks.⁴¹ They identified how thickness of the block copolymer is affected by those conditions and identified conditions that produced smooth, homogeneous thin films. Because PGMA prefers the silicon substrate and PVDMA prefers the film/air interface, these layers were assumed to be PVDMA brushes. Post-polymerization modification of the PVDMA brush with biotin-poly(ethylene glycol)amine was examined in a qualitative sense.

Our previous work demonstrates that functionalization of a PVDMA brush with small primary amines can be used to change interfacial characteristics. It was demonstrated that as the thickness of the PVDMA brush increases, longer reaction times are required in order to reach higher extents of functionalization of the azlactone rings of the PVDMA brush. I also determined that chains are degrafted from the substrate – an “entropic death” – caused by increased stretching upon modification of already dense brushes. This process is possibly activated by the amine used for the reactive modification.⁹⁹ That work focused on a single experiment per sample where different processes were used to change the film. In this work, I examine the feasibility of introducing a chemical gradient to achieve a range of film conditions and make multiple measurements from a single sample. In these studies, position along the brush-modified substrate is directly related to reaction time.⁹⁹

Here I present a systematic study using three PGMA-block-PVDMA block copolymers of different molecular weight (and composition) and select three simple

primary amines that are used as model compounds to investigate how the extent of functionalization depends on reaction time. A gradient is established by the use of post-polymerization modification of PVDMA, which provides an efficient way to screen a variety of conditions and supports efforts to create new or desirable surface properties without changing the base polymer. Gradient functionality is introduced to the parent film by a controlled immersion process. A solution containing the amine is injected continuously, creating directionality in the extent of chemical modification along the substrate as the liquid level “climbs” up the substrate. A relationship is established between immersion time and the functionality along the surface. Beyond demonstrating the robustness of this approach, specific attention is given to quantifying relations between extent of functionalization, molecular weight, grafting density, exposure time, and position along the gradient for each amine used.

4.3 Experimental Section

4.3.1 Materials

Silicon wafers of size 1.0 cm × 1.2 cm and 3.0 cm × 1.0 cm were purchased from Silicon Quest International. Glycidyl methacrylate (GMA, 97%, Aldrich) and 2-vinyl-4,4-dimethyl azlactone (VDMA) were distilled under reduced pressure and the middle fractions (~70%) reserved for use. 2,2-Azobis(4-methoxy-2,4-dimethyl valeronitrile) (V-70, Wako Pure Chemical Industries, Ltd.), 2-cyano-2-propyl dodecyl trithiocarbonate (CPDT, 97%, Aldrich), benzene (99.9%, Aldrich), tetrahydrofuran (THF, 99.9%, Aldrich), chloroform (99.8%, Fisher), n-hexane (95%, Fisher), tetradecylamine (95%, Aldrich), octadecylamine (95%, Aldrich), hexylamine (99%, Aldrich), hydrogen

peroxide, 30% (Certified ACS, Fisher Chemical), and sulfuric acid (Certified ACS Plus, Fisher Chemical) were used as received.

4.3.2 Instrumentation and Analysis

Gel Permeation Chromatography (GPC). Polymer molecular weight and dispersity were measured via gel permeation chromatography (GPC) using a Tosoh EcoSEC GPC fitted with two Tosoh TSKgel SuperMultiporeHZ-M columns 4 μ (4.6 $\times$ 150 mm) and a TSKgel SuperMultiporeHZ-M guard column. Measurements were made at 40 °C using THF as the mobile phase. Molecular weights were determined using the EcoSEC Data Analysis software (version 1.04) relative to poly(methyl methacrylate) standards.

Multi-angle Ellipsometry. The thickness of thin films was determined using a variable-angle Beaglehole Picometer Ellipsometer that uses a He-Ne laser light source (λ = 632.8 nm). Following previously published protocols, the thickness of each polymer-modified surface was measured in air at multiple angles ranging from 80° to 60° using 1° steps.⁶³ The angularly-dependent data were co-fit using a model that treats each layer in the polymer film as a uniform slab. A refractive index of 1.50 was assumed for the PGMA-b-PVDMA copolymer films.⁴¹ The slab-like model allows the thickness of each layer to be determined by optimizing goodness-of-fit. Multiple measurements were made at various positions along gradient surfaces and replicate samples were also prepared and measured.

Fourier Transform Infrared Spectroscopy (FTIR). Polymer-modified surfaces were characterized by attenuated total reflectance-Fourier transform infrared (ATR-FTIR) spectroscopy using a Bruker Optics Vertex 70 spectrometer equipped with a

Harrick Scientific VariGATR accessory, which has a germanium hemisphere internal reflection element. ATR-FTIR measurements used the narrow-band mercury-cadmium-telluride (MCT) detector, and at least 128 scans were collected. A blank silicon surface was used to acquire the background spectrum.

Atomic Force Microscopy (AFM). Polymer-modified surfaces were analyzed using Veeco Instruments Nanoscope IIIa MultiMode SPM atomic force microscopy (AFM) in tapping mode using a silicon cantilever.

Contact Angle (CA). A Krüss DSA30 Drop Shape Analyzer was used to measure water contact angles via the sessile drop method using deionized water as the probe liquid. Polymer-modified surfaces were rinsed with chloroform and dried with a stream of dry nitrogen before contact angle measurements. A 5 μ L drop of deionized water was placed on the surface using an automatic dosing via syringe. The water contact angle was measured at various positions along each polymer-modified surface and replicate samples were also prepared and tested.

4.3.3 Synthetic Procedures

Synthesis of PGMA Macro-CTA by RAFT polymerization. GMA (7.11 g, 5.00×10^{-2} mol) was combined with V-70 initiator (4.38×10^{-2} g, 1.42×10^{-4} mol), CPDT (2.46 $\times 10^{-1}$ g, 7.11×10^{-4} mol) and benzene in a 100 ml round bottom flask. The flask was sealed with a rubber septum and sparged with dry argon for 30 minutes. The vessel was placed in an oil bath set to 30 °C and allowed to react for 12 h while stirring. A typical RAFT polymerization consisted of using a CPDT:V-70 ratio of 5:1, a CPDT:GMA ratio of 3:211, and a [GMA] of 0.99 M; these conditions set the theoretical number-average molecular weight to be 10,000 g mol⁻¹. After a 12 h polymerization, the reaction mixture

was quenched by immersing the flask in liquid nitrogen until the solution was frozen. After allowing the contents to thaw, the macro-CTA was precipitated into cold hexanes (3x). The macro-CTA was isolated by decanting and then dried overnight under vacuum.

Synthesis of PGMA-b-PVDMA by RAFT polymerization. VDMA (2.78 g, 2.0×10^{-2} mol) was combined with the PGMA macro-CTA (3.09×10^{-1} g, 6.18×10^{-5} mol), V-70 initiator (6.36×10^{-3} g, 2.06×10^{-5} mol), and benzene in a 50 ml round bottom flask. The flask was sealed with a rubber septum and sparged with dry argon for 30 minutes. As an example, a polymerization was prepared using a CPDT:V-70 ratio of 3:1, a PGMA macro-CTA:VDMA ratio of 3:970, and a [VDMA] of 0.99 M; these conditions set the theoretical number-average molecular weight of the PVDMA block to be 45,000 g mol⁻¹. This solution was immersed in an oil bath and stirred at 30 °C for 18 h, after which time the reaction was quenched by submerging the flask in liquid nitrogen until the solution was frozen. After allowing the contents to thaw, PGMA-b-PVDMA was precipitated into cold hexanes, isolated by decanting, and then dried overnight under vacuum.

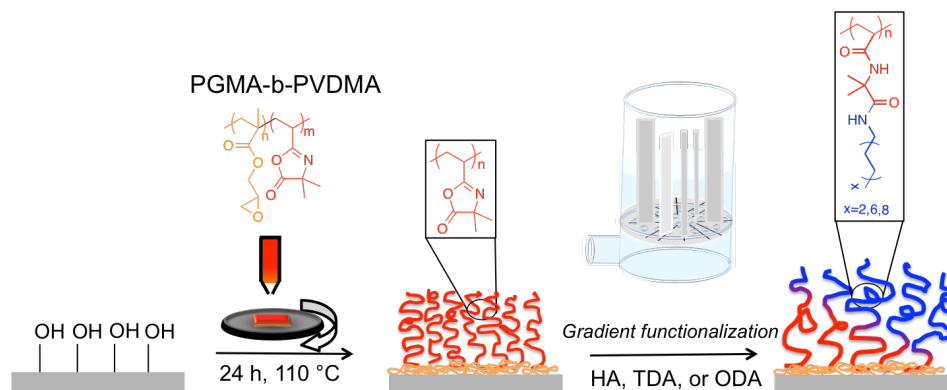
4.3.4 Sample Preparation

Wafer cleaning. Silicon wafers were cleaned prior to use in a piranha acid solution (3:1 v/v H₂SO₄/30% H₂O₂) at 80 °C for 30 minutes. After cleaning, the wafers were rinsed with deionized water and dried using a stream of nitrogen. Cleaned wafers were used immediately. *Caution! Piranha acid is a strong oxidizer and a strong acid; it should be handled with extreme care as it reacts violently with most organic materials.*

Formation of PGMA-b-PVDMA-modified silicon surfaces. Thin films of PGMA-b-PVDMA were deposited on silicon substrates by spin coating a dilute solution at 1500

rpm for 15 seconds using a Laurel Technologies spin coater (model WS-650MZ-23NPP). For all spin coating preparations, a PGMA-b-PVDMA concentration of 0.25 wt.% in chloroform was used. After spin coating, the films were annealed at 110 °C for 24 h to promote reaction between the epoxy groups of the PGMA block and hydroxyl groups on the silicon substrate.⁴¹ After cooling to room temperature while under vacuum, the substrates were sonicated in chloroform to remove non-covalently bound PGMA-b-PVDMA chains, rinsed with chloroform, and then dried with a stream of dry nitrogen. Although the PVDMA chains are end-tethered to the surface-bound PGMA layer, for convenience I simply refer to these thin films as “PVDMA brushes” or “PVDMA films”.

Post-polymerization modification of PVDMA brushes. Polymer-modified wafers were secured vertically in a custom-built Teflon holder designed to grip these substrates by their base edge. The substrate holder was placed inside a custom-built, cylindrical glass cell. A port located at the bottom, below where the substrate is held, allows fluid to be gradually added to (or removed from) the cell at a controlled rate. The New Era (NE)-1000 programmable single syringe pump was used to inject chloroform solutions containing either 1-hexylamine (HA), 1-tetradecylamine (TDA), 1-octadecylamine (ODA), or dansylcadaverine (DC) at 0.25 wt.% into the cell, as shown in Scheme 4-1. Previous work indicated the concentration of the functionalizing agent has a negligible effect on extent of functionalization over concentration range from 0.25 wt.% to 0.75 wt.%.⁹⁹ After the gradual immersion functionalization process, the substrates were removed from the cell and holder, sonicated in pure CHCl₃, rinsed with CHCl₃, and then dried with a stream of dry nitrogen.



Scheme 4-1. Procedure used to create PVDMA brushes by selective assembly of PGMA-b-PVDMA diblock copolymers. PVDMA chains are end-attached to the silicon substrate through the surface-tethered PGMA blocks. These PVDMA brushes are modified *in situ* by a gradient exposure to small molecule amines.

4.4 Results and Discussion

4.4.1 Synthesis of PGMA and PVDMA

A PGMA macro-CTA having a number-average molecular weight, $M_n = 5,900$ g mol⁻¹ and dispersity, D , of 1.31 was synthesized by RAFT polymerization. This PGMA macro-CTA was used to create various PGMA-b-PVDMA diblock copolymers by chain extension with VDMA. The diblock copolymers synthesized by RAFT polymerization are listed in Table 4-1. The number-average molecular weight, M_n , and dispersity, D , of the PGMA-b-PVDMA copolymers confirm that the RAFT polymerization of VDMA using the PGMA macro-CTA is well-controlled.

Table 4-1. Polymerization Conditions and Macromolecular Properties of PGMA-b-PVDMA Synthesized by Chain Extension of PGMA macro-CTA ($M_n = 5,900 \text{ g mol}^{-1}$ and $D = 1.31$) via RAFT Polymerization.

Sample ^a	[PGMA macro-CTA] :[VDMA] ^b	M_n (g mol^{-1})	D
PGMA ₄₁ -b-PVDMA ₁₈₀	3:970	31,000	1.13
PGMA ₄₁ -b-PVDMA ₂₆₄	1:431	42,700	1.19
PGMA ₄₁ -b-PVDMA ₃₂₆	1:539	51,300	1.16

^a Subscripts indicate the degree-of-polymerization of each block.

^b Concentration ratio used to achieve the desired molecular weight of the PVDMA block. Each polymerization was prepared using a CPDT:V-70 ratio of 3:1 and a [VDMA] = 0.99 M.

4.4.2 PVDMA brush formation: Surface Attachment and Characterization

A “grafting to” approach is used to attach the premade PGMA-b-PVDMA chains to silicon surfaces. As shown by Lokitz *et al.*, increasing the concentration of the block copolymer in solution, annealing temperature, and reaction time yields a linear increase in the thickness of the brush.⁴¹ In this system, the PGMA block prefers the silicon surface and annealing above T_g provides chain mobility, which allows epoxy groups to migrate to the substrate, where they can react with surface hydroxyl groups to form a covalent linkage. This grafting to process results in PVDMA brushes that are end-tethered to a surface-bound PGMA layer.^{41,99} This strategy parallels reports by Luzinov *et al.*, who developed the use of PGMA to create layers of end-grafted chains.^{34,65} Chloroform is used when spin-coating the PGMA-b-PVDMA copolymers, as it yields

smooth, homogeneous thin films.³⁵ After deposition by spin coating, films are annealed at 110 °C for 24 h, after which time the non-bonded chains are removed by sonication in CHCl₃. The thicknesses of the PGMA-b-PVDMA films were determined by multi-angle ellipsometry and resulted in two different film thicknesses that were measured to be 9.3 and 26.3 nm. The thicker layer, 26.3 nm, is attributed to the PGMA block self-cross-linking and results in additional chains farther from the silicon/polymer interface to be incorporated into the film.⁴¹ Because the assembly process produces either layers having thicknesses of 10 nm (nominal) or having thicknesses of 26 nm, I refer to the former as PVDMA brushes and the latter as PVDMA films. I have chosen to focus on the thinner films that are considered polymer brushes. (Specifically, these are PVDMA brushes.) However, this convention is revisited later in the chapter where ellipsometry measurements are presented and discussed.

4.4.3 Physical Characterization of Functionalized PVDMA-Modified Gradient Surfaces

Grafting density is an important parameter that governs interactions between the polymer chains and affects the penetration of small molecules into the brush system.^{14,99} The dry layer thickness of PVDMA measured by ellipsometry, H , and polymer molecular weight determined by GPC are used to calculate grafting density, σ , using the dimensional expression^{14,35,41}

$$\sigma = \frac{H\rho N_A}{M_n} \quad (4-1)$$

In this equation, the ellipsometric thickness, H , is that of the PVDMA layer, the mass density, ρ , of the PVDMA brush is taken to be 1.05 g/cm³,⁴¹ N_A is Avogadro's number

and M_n is the number-average molecular weight of PVDMA, which is given in Table 4-2. As expected, the layer thickness increases as the molecular weight of the grafted PVDMA chains increases, which according to equation 4-1 results in a decrease in grafting density. Grafting densities are listed in Table 4-2. As the molecular weight of the chains increases, the coil volume expands, which decreases the ability of chains to pack closely on the surface.^{4,67,68} The distance between grafted chains, D , is calculated to compare and assess the degree-of-crowding of chains on the surface.

$$D = 2(\pi\sigma)^{-1/2} \quad (4-2)$$

The radius of gyration is given by

$$R_g = bN^{3/5} \quad (4-3)$$

Table 4-2. Characteristic Properties of PVDMA Brushes Made from Preferential Assembly of PGMA-b-PVDMA Diblock Copolymer Chains.

$M_{n\text{-PVDMA}}^a$ (g mol ⁻¹)	H^b (nm)	σ (chains/nm ²)	R_g (nm)	D (nm)	$D/2R_g$
25,100	9.3 ± 2.2	0.246	3.42	2.34	0.34
	26.8 ± 3.6	0.565	3.42	1.55	0.23
36,800	9.5 ± 3.8	0.171	4.26	2.89	0.34
	27.0 ± 3.2	0.370	4.26	2.00	0.24
45,500	9.8 ± 2.8	0.148	4.83	3.06	0.32
	25.2 ± 2.5	0.290	4.84	2.14	0.22

^a M_n of PVDMA block; See Table 4-1 for M_n of PGMA-b-PVDMA copolymers

^b Brush thickness of PVDMA film

where b is 0.15 nm for PVDMA⁶⁹ and N is the degree of polymerization of the PVDMA block. As the degree of polymerization increases, the R_g of the chain expands and increases the R_g of the PVDMA block, as shown in Table 4-2. When grafted chains overlap, which is defined as $D < 2R_g$, they are considered to be in the brush regime.^{70,71} The patterns of behaviors manifest in the calculated values are not unexpected for polymer brushes created from the “grafting to” process.^{41,99} The results presented in Table 4-2 confirm that the process used to graft the PGMA-b-PVDMA copolymers results in degrees-of-overlap that identify the layers as being in the brush regime. It is also worth noting that the characteristic average values are the result of multiple measurements made on replicate samples. From the measured thickness values, σ , R_g , and D are calculated for each molecular weight of the PVDMA diblock copolymer used. These characteristic values are in good agreement with previously reported values^{16,99} (See Table C-1 for uncertainty values associated with σ and D .)

Because the gradient is created by the immersion of a solution, it is important that the thickness of the parent film is uniform (± 1 nm) across the length of the 3.0 cm surface. This is first examined by ellipsometry. AFM is then used to determine the surface topography along the PGMA-b-PVDMA modified surfaces. AFM images reveal that the copolymer films are smooth and homogeneously cover the substrate, as shown in Figure 4-1. This homogeneity of the film is critical to extract quantitative information of the extent-of-functionalization and to make comparisons between different samples.

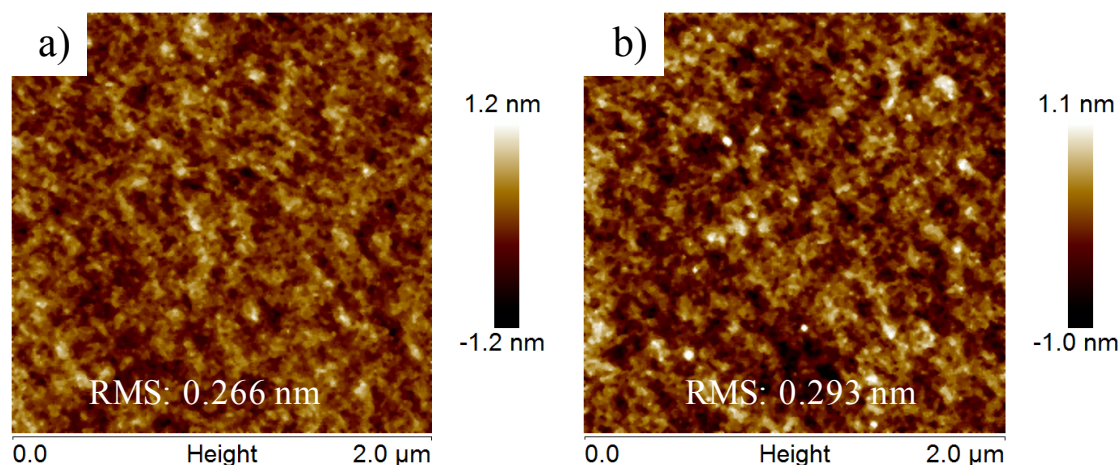


Figure 4-1. AFM height images acquired of $2.0\ \mu\text{m} \times 2.0\ \mu\text{m}$ regions of PVDMA brushes: a) $25,100\ \text{g mol}^{-1}$ PVDMA brush on one end of surface and b) $25,100\ \text{g mol}^{-1}$ PVDMA brush on the opposite end of surface.

4.4.4 Gradient Functionalization of PVDMA Brushes with Primary Amines

After characterization of the assembled layer, brush-modified surfaces were functionalized *in situ* by a constant, controlled injection of chloroform solutions containing either 1-hexylamine (HA), 1-tetradecylamine (TDA), or 1-octadecylamine (ODA) at a concentration of 0.25 wt.%. The injection proceeded over a period of a 0.5, 6, 9, or 12 h, which produces a linear rise in solution level, exposing chains of the PVDMA brush along the substrate to the amine. This range of functionalization (immersion) time was determined based on the original thickness of the parent PVDMA-modified substrate. My preliminary studies showed that the reaction time for nucleophilic addition of the amine to the azlactone ring needed to be increased as the thickness of the parent polymer film increased. These preliminary studies involved

measuring the change in layer thickness upon functionalization because the extent of functionalization is directly related to the change in ellipsometric thickness (before and after the functionalization reaction).^{16,35,99}

The extent of functionalization, f , which describes the fraction of azlactone rings that are modified by ring-opening nucleophilic addition, is calculated using (4-4), which is adapted from Soto-Cantu *et al.*.³⁵

$$f = \frac{[(H_{\text{PVDMA-Amine}} \cdot \rho_{\text{PVDMA-Amine}} \cdot m_{0,\text{PVDMA-Amine}}) - (H_{\text{PVDMA}} \cdot \rho_{\text{PVDMA}} \cdot m_{0,\text{PVDMA}})]}{[H_{\text{PVDMA}} \cdot \rho_{\text{PVDMA}} \cdot (m_{0,\text{PVDMA-Amine}} - m_{0,\text{PVDMA}})]} \quad (4-4)$$

In this expression, the subscripts on brush thickness, H , and mass density, ρ , refer to the parent PVDMA brush or the modified PVDMA-amine conjugate. Also, m_0 is the molar mass of the VDMA repeat unit ($m_{0,\text{PVDMA}} = 139.2 \text{ g mol}^{-1}$) or amine-modified repeat units ($m_{0,\text{PVDMA-Amine}} = 240.4 \text{ g mol}^{-1}$, 352.6 g mol^{-1} , and 408.7 g mol^{-1} for HA, TDA, and ODA, respectively).⁶⁴ When calculating f from changes in ellipsometric thicknesses, it is assumed that the thickness increase is only due to reactive modification of the PVDMA chains; in other words, the PGMA layer thickness does not change.⁹⁹ This assumption seems quite appropriate given that in neutron reflectometry (NR) studies of PVDMA brushes made by attachment of end-functionalized chains to a PGMA primer layer, there was no change in neutron scattering length density or thickness of the PGMA layer after the functionalization reaction.⁹⁹

Because the molecular weights of the monomer and functionalizing agents are known, the main source of uncertainty in applying Equation (4-4) originates from the mass densities of surface-tethered thin films (unfunctionalized or functionalized). Thin film mass densities are generally assumed to be equivalent to the bulk values; however

in thin films confinement to the surface distorts chain conformation and affects chain packing. Recent NR studies, including studies reported in Chapter 2 and 3, have shown that the mass density of the thin polymer brushes do, in fact, deviate from their bulk values.^{35,72,99} Dry layer thicknesses measured by ellipsometry are expected to be accurate within ± 1 nm; however in thin films, thickness and refractive index, η , are coupled.^{72,99} Usually, refractive indices are based on bulk systems or estimated for thin organic films to be $\eta = 1.5$. In order to simplify the situation, the assumption that the refractive index does not changed by functionalization has been used.^{14,35}

While NR studies provide more information on the depth-dependent distribution of the functionalizing agents and loss of chains, as mentioned in Chapter 2, however the measured thickness values (unfunctionalized and functionalized) are comparable with those determined by ellipsometry (± 1 nm). The advantage of the designed gradient system is to gradually change the underlying parent material. NR cannot be used because it requires a large surface area and position-sensitive studies cannot be completed, defeating the purpose of this study. From the NR studies described in Chapter 3, it was concluded that these block copolymers have a low grafting density and only single-layer fits are needed to describe the neutron reflectivity. These single-layer fits have a single extent of functionalization, meaning that there is no depth-dependence to the distribution of amines. Therefore, based on this understanding, it should be appreciated that NR measurements will not enhance the conclusions for this specific work – Ellipsometry is sufficient to assess the brush thickness and determine the average extent of functionalization along the gradient. In order to use Equation 4-4, I assume a constant mass density of the parent and modified films to be $\rho_{\text{PVDMA}} = \rho_{\text{PVDMA-amine}} = 1.05 \text{ g cm}^{-3}$.

The amount of time the sample substrate is exposed to the functionalization solution is a key variable in this study. The exposure time must be long enough so that the small molecules can diffuse into the brush; however, too long of an exposure to the amine solution may cause some of the chains to be cleaved from the surface,⁹⁹ resulting in an ambiguous determination of the extent of functionalization or, in the extreme, a decrease in thickness of the polymer brush. From work presented in Chapter 2, I concluded that polymer chains were cleaved during the functionalization process. Therefore, it is important to conduct parametric studies examining exposure time and position along the substrates to determine highest extent of functionalization. Gradient experiments were first made on 10 nm-thick films of PGMA-b-PVDMA modified surfaces by controlled immersion over 6 h of functionalization time. From my previous work I learned that when the polymer-modified surface is exposed to the amine-containing solution, the most accessible azlactone rings, which are located at the solution/brush interface, are functionalized first. Although Table 4-3 shows that the extent of functionalization increases as the functionalization time increases across the surface, it reveals a low extent of functionalization as determined from the change in ellipsometric thickness (before and after functionalization). This low extent of functionalization led me to the conclusion that the reaction is not complete, and surfaces should be immersed for a longer time to allow more time for the small molecule amines to diffuse and react within the PVDMA brush layer. This differs from Chapter 2, where the PVDMA brushes were 6 nm thick and only required 2 h of functionalization time. The results shown in Table 4-4 and visually represented in Figure 4-2 show that as the

Table 4-3. PVDMA Molecular Weight and the Extent of Functionalization across the Gradient Substrate using 6 Hours of Functionalization Time.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹)	FA	$f(\%)^{\text{a}}_{3\text{h}}^{\text{b}}$	$f(\%)_{4\text{h}}$	$f(\%)_{5\text{h}}$
25,100	TDA	9.0	11.4	16.0
	ODA	12.4	13.4	17.6
36,800	HA	30.7	43.0	54.2
	TDA	12.6	16.9	28.4
	ODA	9.6	16.2	18.6
45,500	HA	33.9	40.7	52.1
	TDA	67.4	73.9	87.9
	ODA	18.4	19.0	22.0

^a Extent of functionalization determined via ellipsometry; $\rho_{\text{PVDMA}} = \rho_{\text{PVDMA-amine}} = 1.05 \text{ g cm}^{-3}$

^b Subscript gives length of functionalization time (position on surface)

Table 4-4. PVDMA Molecular Weight and the Extent of Functionalization across the Gradient Substrate using 9 Hours of Functionalization Time.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹)	FA	$f(\%)^{\text{a}}_{3\text{h}}^{\text{b}}$	$f(\%)_{5\text{h}}$	$f(\%)_{8\text{h}}$
25,100	HA	65.4	77.7	87.0
	TDA	25.6	46.3	83.5
	ODA	24.3	36.5	50.6
36,800	HA	65.3	70.0	82.2
	TDA	20.7	24.6	35.4
	ODA	12.5	32.8	40.4
45,500	HA	39.4	66.3	81.4
	TDA	24.7	61.9	68.8
	ODA	24.9	39.8	41.4

^a Extent of functionalization determined via ellipsometry; $\rho_{\text{PVDMA}} = \rho_{\text{PVDMA-amine}} = 1.05 \text{ g cm}^{-3}$

^b Subscript gives length of functionalization time (position on surface)

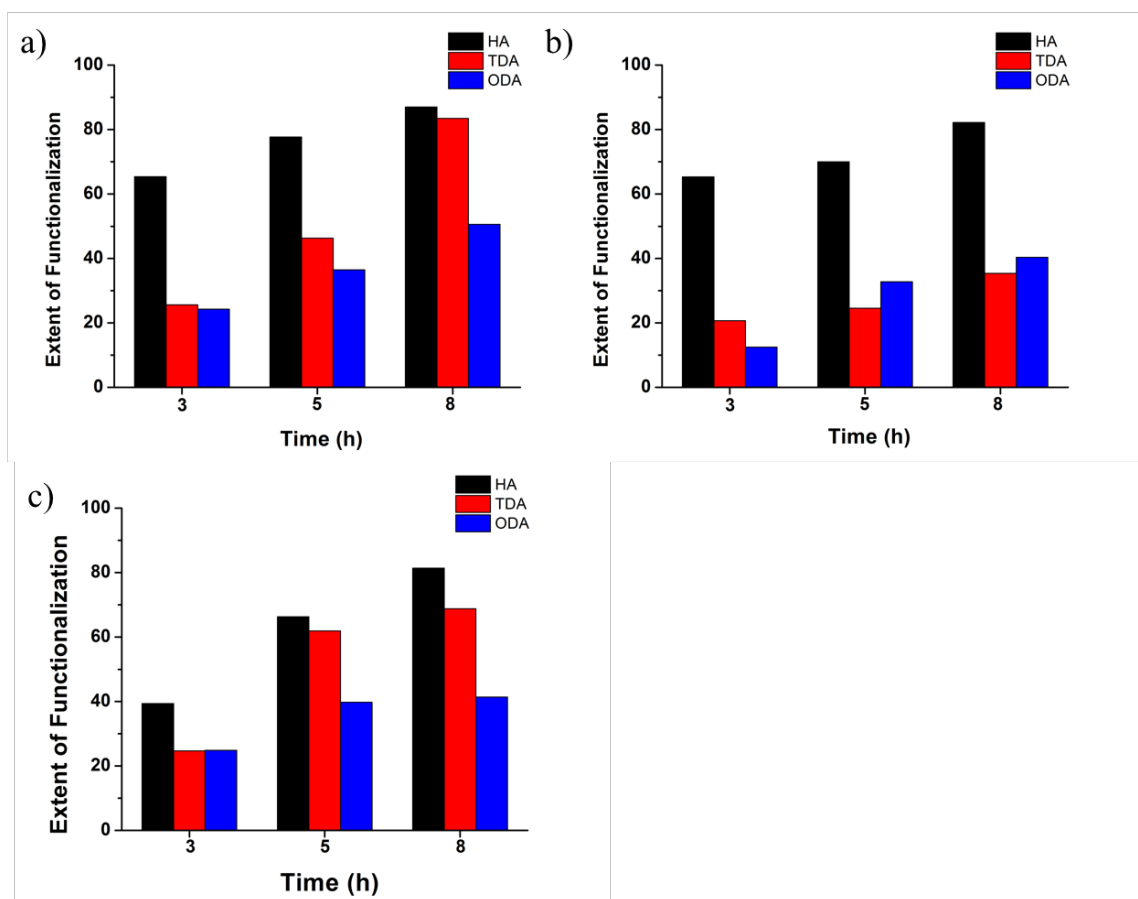


Figure 4-2. The extent of functionalization of a) 25,100 g mol⁻¹, b) 36,800 g mol⁻¹, and c) 45,500 g mol⁻¹ PVDMA brushes (nominally 10 nm thick) based on the functionalization time and size of amine used (HA, TDA, ODA). Time also represents the position along the surface, as it indexes the rise of the fluid level in the flow cell. Short times represents the end of the substrate with the shortest exposure time (top) and long times represents the end with the longest reaction time for functionalization (bottom).

functionalization time increases (over a period of 9 h) across the 10 nm-thick PGMA-b-PVDMA modified films, the extent of functionalization increases. This supports the conclusion that a film (of specific thickness) requires a certain functionalization time for complete reaction. As shown in Table 4-4, film thicknesses of approximately 10 nm require at least 8 h of functionalization time to reach a high extent of functionalization.

The maximum functionalization achieved using the gradient processes of post-polymerization modification of PVDMA surfaces using HA, TDA, and ODA are shown in Table 4-5 and Figure 4-3 for each molecular weight. Ellipsometric measurements for pre- and post-functionalized heights (H_0 and H_M) are reported as the average value taken from multiple measurements on at least 10 replicate samples. Consistent with my prior results, the extent of reaction is affected by the size of the small molecule amine: smaller amines diffuse into the crowded brush and react with more azlactone moieties, resulting in a higher extent of functionalization. This is best observed when grafting densities are similar, e.g. ~ 0.26 chains/nm² for the 25,100 g mol⁻¹ or 0.16 chains/nm² for the 45,000 g mol⁻¹ PVDMA block sizes, as shown in Table 4-5.

When grafting densities are different, interpreting the extent of functionalization is more difficult. The grafting density of the parent film strongly affects the extent of functionalization, and this behavior is clearly observed between brushes having large differences in grafting density, especially when TDA and ODA are used as modifiers. Because ODA is the largest amine used for functionalization, it is expected to result in the lowest extent of functionalization. However, if two brushes having different grafting densities are compared, unusual patterns of behavior can appear. For example, and as may be observed from Table 4-6, a film with a higher grafting density (0.57 chains/nm²

Table 4-5. Maximum Extent of Functionalization Achieved for PVDMA Brushes immersed for 9 Hours.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹) ^a	H_0 (nm) ^b	σ (chains/nm ²)	FA ^c	H_M (nm) ^d	f (%) ^e
25,100	9.2	0.257	HA	16.4	89.0
	11.1	0.277	TDA	17.7	83.5
	9.3	0.249	ODA	14.2	50.6
36,800	8.2	0.140	HA	14.6	82.2
	14.1	0.242	TDA	22.2	53.2
	8.4	0.161	ODA	14.3	40.4
45,500	12.5	0.185	HA	20.7	81.5
	9.6	0.152	TDA	16.8	68.8
	10.6	0.156	ODA	15.5	41.4

^a determined from GPC and are given in Table 4-2

^b Parent PVDMA brush thickness

^c HA = hexylamine; TDA = tetradecylamine; ODA = octadecylamine

^d modified-PVDMA layer thickness after functionalization

^e Calculated according to Equation (4-4); $\rho_{\text{PVDMA}} = \rho_{\text{PVDMA-amine}} = 1.05 \text{ g cm}^{-3}$

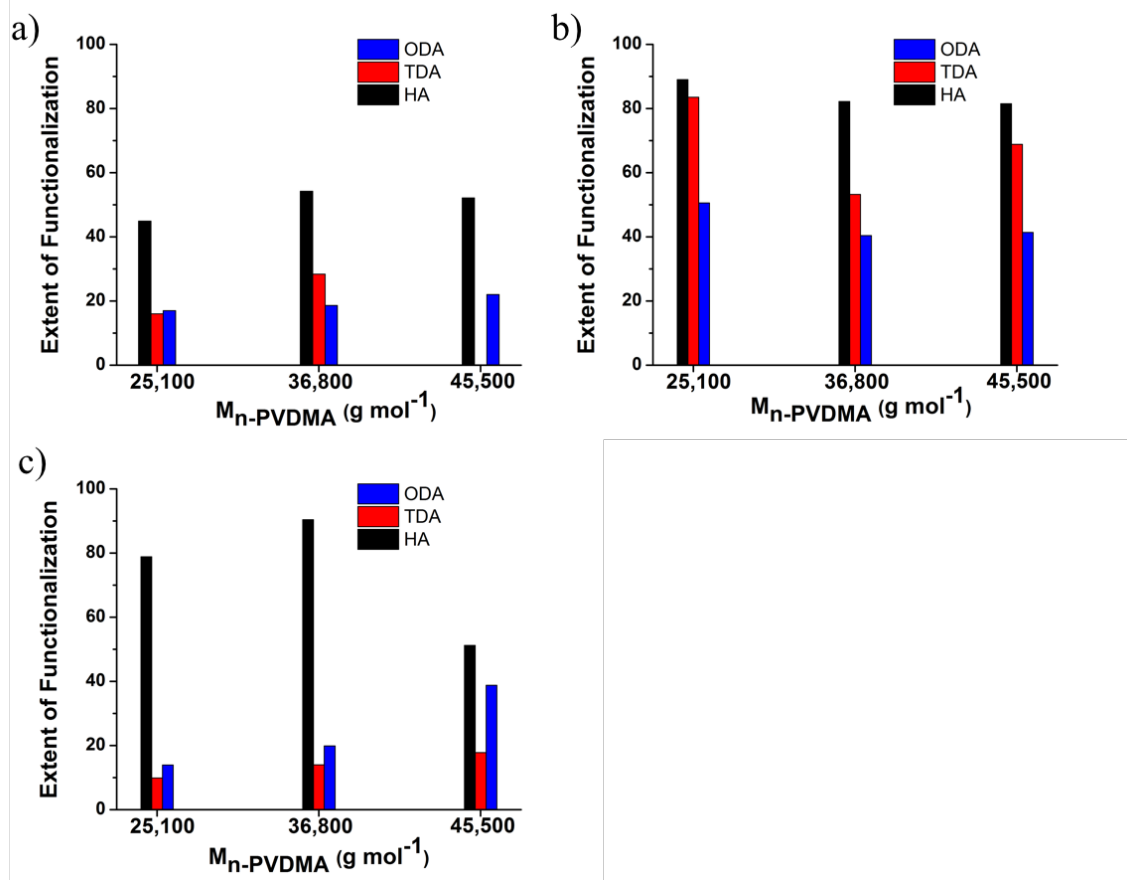


Figure 4-3. The maximum extent of functionalization for the 25,100 g mol⁻¹, 36,800 g mol⁻¹, and 45,500 g mol⁻¹ PVDMA films based on the functionalization time of a) 6 h, b) 9 h, and c) 12 h and size of amine used (HA, TDA, ODA).

Table 4-6. Maximum Extent of Functionalization Achieved for PVDMA Films Immersed for 12 Hours.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹) ^a	H_0 (nm) ^b	σ (chains/nm ²)	FA ^c	H_M (nm) ^d	f (%) ^e
25,100	28.7	0.665	HA	42.2	78.8
	22.9	0.569	TDA	25.4	9.9
	25.9	0.643	ODA	30.0	13.9
36,800	30.5	0.236	HA	41.7	90.4
	32.4	0.567	TDA	37.48	14.0
	25.5	0.437	ODA	33.8	19.9
45,500	17.2	0.239	HA	21.1	51.2
	24.7	0.343	TDA	27.9	17.8
	24.1	0.334	ODA	35.3	38.8

^a determined from GPC and are given in Table 4-2

^b Parent PVDMA layer thickness

^c HA = hexylamine; TDA = tetradecylamine; ODA = octadecylamine

^d modified-PVDMA layer thickness after functionalization

^e Calculated according to Equation (4-4); $\rho_{\text{PVDMA}} = \rho_{\text{PVDMA-amine}} = 1.05 \text{ g cm}^{-3}$

for the 36,800 g mol⁻¹ PVDMA block) functionalized with TDA compared to a film with lower grafting density (0.44 chains/nm² of the 36,800 g mol⁻¹ PVDMA block) functionalized with ODA gives the appearance that ODA gives a higher extent of reaction: $f_{M,ODA} = 19.9$ compared to $f_{M,TDA} = 14.0$. Data in Table 4-7 for two brushes made from the diblock having a 25,100 g mol⁻¹ PVDMA block shows the same behavior – the brush with the higher grafting density and smaller amine (TDA) gives a lower f than the brush with the lower grafting density and larger amine (ODA). Therefore the grafting density of the parent brush plays an important role in the ability of reactive modifiers to diffuse into the brush layer and react.

The impact of grafting density is further examined using the set of thicker layers generated by preferential assembly of PGMA-b-PVDMA diblock copolymers. As seen in Table 4-2, the thicker layers are ~26 nm thick and have higher grafting densities than the PVDMA brushes. For the thicker layers made with the diblocks having PVDMA blocks of 25,100 and 36,800 g mol⁻¹, HA is able to diffuse through the layer and extents of functionalization similar to those for the brushes. (Compare data in Table 4-5 and Table 4-6, which lists results for brushes and films, respectively). For the thicker films, which have high grafting densities (>0.30 chains/nm²), the diffusion of TDA or ODA appears to be significantly hindered, resulting in much lower extents of functionalization. (See Table 4-7.) These groups of results confirm that larger amines are not able to reach high extents of functionalization in a swollen, crowded polymer film. Additionally and as pointed out previously, each amine that reacts creates additional steric hindrance that interferes with further functionalization. Furthermore, conjugation of the alkylamine may decrease the solubility of the tethered chains, which would further

Table 4-7. Maximum Extent of Functionalization Achieved for PVDMA Brushes Immersed for 6 Hours.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹) ^a	H_0 (nm) ^b	σ (chains/nm ²)	FA ^c	H_M (nm) ^d	f (%) ^e
25,100	7.4	0.184	HA	9.8	44.9
	9.8	0.253	TDA	12.2	16.0
	8.6	0.222	ODA	12.8	17.6
36,800	7.1	0.122	HA	9.4	54.2
	10.9	0.196	TDA	12.4	28.4
	7.0	0.119	ODA	12.1	18.6
45,500	8.6	0.103	HA	10.1	52.1
	7.4	0.102	ODA	13.1	22.0

^a determined from GPC and are given in Table 4-2

^b Parent PVDMA layer thickness

^c HA = hexylamine; TDA = tetradecylamine; ODA = octadecylamine

^d modified-PVDMA layer thickness after functionalization

^e Calculated according to Equation (4-4); $\rho_{\text{PVDMA}} = \rho_{\text{PVDMA-amine}} = 1.05 \text{ g cm}^{-3}$

limit access to azlactone rings buried within the layer, resulting in lower extents of functionalization.

In addition to ellipsometry, ATR-FTIR spectroscopy was used to qualitatively examine functionalization along the gradient. As shown in Figure 4-4, there are 2 distinctive modes for PVDMA: the carbonyl peak at 1825 cm^{-1} and the imine stretch at 1660 cm^{-1} . When the azlactone ring is exposed to a nucleophile and participates in a ring-opening reaction, the intensity of the carbonyl peak at 1825 cm^{-1} decreases and the imine stretch decreases while the amide peak shifts to 1650 cm^{-1} , indicating amide formation. Figure 4-4a compares a series of spectra measured along a gradient that was produced using an immersion time of 30 min. (This is the minimum time required to fill the fluid cell.) The extent of functionalization along the gradient, expressed as a time and calculated from ellipsometric thickness, is provided in the legend. The combination of results – a decrease in azlactone modes at 1825 cm^{-1} and 1660 cm^{-1} with a concomitant increase in amide mode I at 1650 cm^{-1} and amide mode II at 1550 cm^{-1} , as shown in the extended spectra of Figure 4-4b, in tandem with an increase in extent of functionalization – support my previous conclusion that longer reaction times lead to higher extents of functionalization. Amide I at 1650 cm^{-1} is present from the stretching of C=O. Amide II at 1550 cm^{-1} is the N-H bending and C-N stretching, and appears once the azlactone is ring-opened, as shown in Figure 4-4b. Amide III is attributed to the C-H stretching, N-H bending, and C-N stretching between $1400 - 1300\text{ cm}^{-1}$ and is present in the PVDMA and amine-modified PVDMA spectra. While it appears that ATR-FTIR spectroscopy and ellipsometry are both useful for tracking the extent of functionalization or changes in surface chemistry along the gradient. Figure 4-4b shows that the azlactone

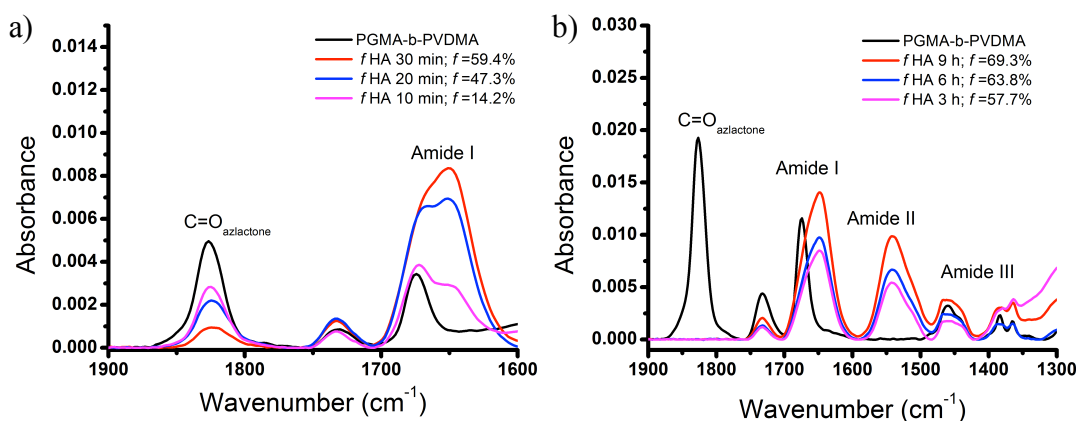


Figure 4-4. Partial ATR-FTIR spectra emphasizing the changes in vibrational modes associated with reactive modification of PVDMA brushes with amines. (a) 25,100 g mol^{-1} PVDMA brush upon exposure to a HA solution over 30 minutes, and (b) 25,100 g mol^{-1} PVDMA brush upon exposure to a HA solution over 9 h. The azlactone ring of the parent PVDMA film is intact, as evidenced by the carbonyl stretch at 1825 cm^{-1} and imine stretch at 1660 cm^{-1} (black lines). The azlactone rings of the brushes are ring-opened by exposure to a 0.25 wt.% hexylamine solution, indicating reactive modification that corresponds to a specific f , as shown by the decrease in intensity of the carbonyl mode (red, blue and magenta lines, respectively).

peak completely disappears after $f \approx 60\%$ (determined by ellipsometry). Thus ATR-FTIR spectroscopy is not very useful when long immersion times (injection periods) are used to produce gradient surfaces. This is due, in part, to the sensitivity of the technique to ultrathin films.

AFM was used to image the surface topography and evaluate the roughness of the PVDMA brushes and the reactively modified brushes. Images presented in Figure 4-5 show that PVDMA brushes are smooth and homogenous before and after functionalization. The RMS (root mean squared) roughnesses of the brushes are < 2 nm before and after functionalization, confirming that the surfaces remain smooth. There is a slight increase in RMS roughness after 1h functionalization and a larger increase in RMS roughness with longer functionalization times (4h, bottom right image), which suggests that longer exposure times, which result in higher extent-of-functionalization, lead to an increase in surface roughness relative to the parent film.

Finally, contact angle measurements were made to qualitatively examine changes in wettability along the gradient. The water contact angle measured for PVDMA brushes was 68° , which agrees with previously reported values.^{41,122} The surface was gradually immersed in a 0.25 wt.% TDA solution over 6 h. Multiple contact angle measurements were made along the gradient. Table 4-8 shows that the water contact angle increases as the functionalization time increases, indicating an increase in hydrophobicity. This is expected as the content of n-alkyl amines in the brush increases as functionalization time increases. (See Appendix C for images of water droplets on the PVDMA-modified surfaces.)

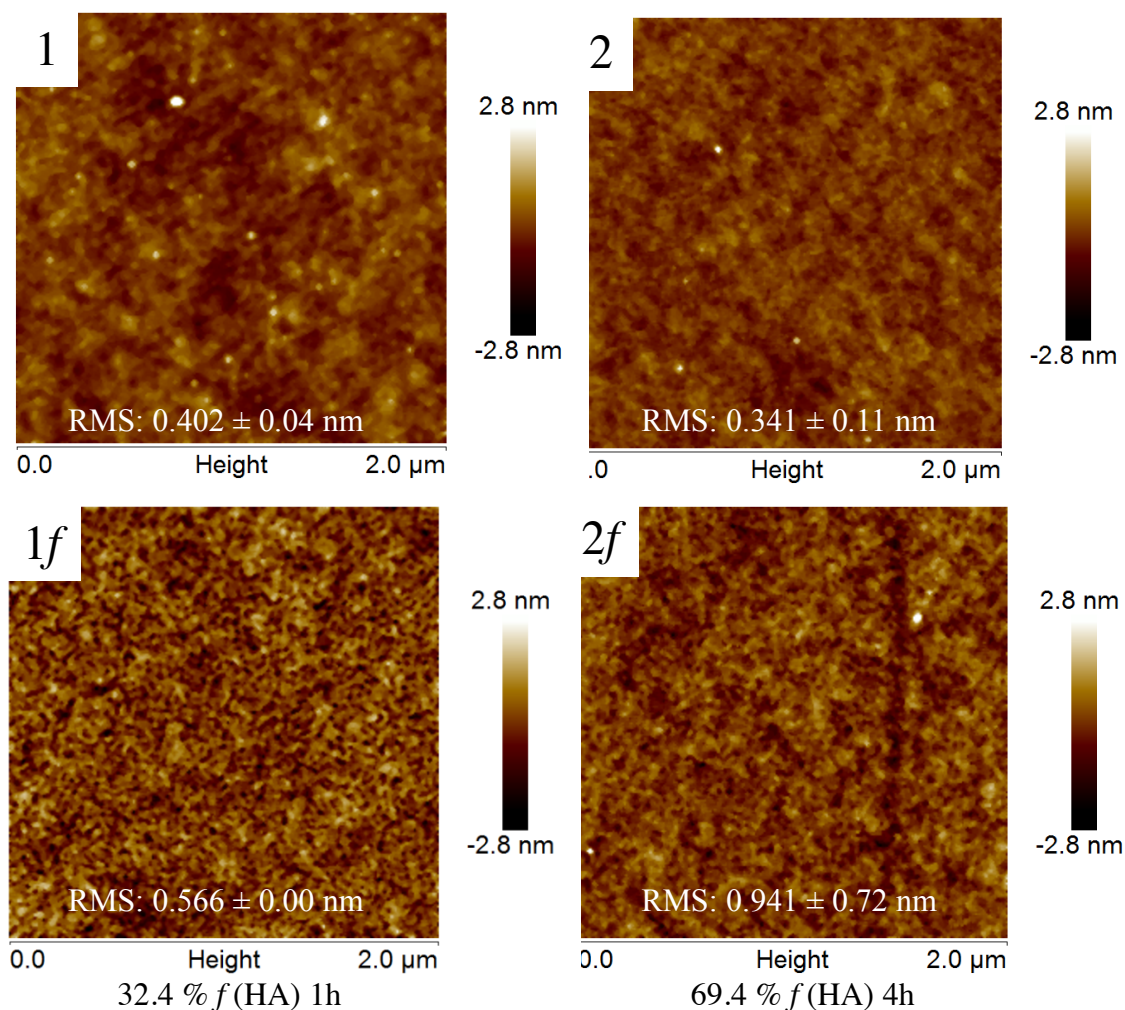


Figure 4-5. AFM height images acquired over $2.0\ \mu\text{m} \times 2.0\ \mu\text{m}$ regions of PVDMA brushes: 1) $25,100\ \text{g mol}^{-1}$ PVDMA brush, and 1f) HA-modified $25,100\ \text{g mol}^{-1}$ PVDMA brush having $f = 32.4\%$ after a 1 h functionalization; 2) $25,100\ \text{g mol}^{-1}$ PVDMA brush, and 2f) HA-modified $25,100\ \text{g mol}^{-1}$ PVDMA brush having $f = 69.4\%$ after 4 h of functionalization.

Table 4-8. Water Contact Angles of TDA-modified PVDMA Brush Surfaces Functionalized by Gradual Immersion in a 0.25 wt.% TDA Solution over 6 Hours.

<i>Sample</i> ^a	<i>CA</i> _{0h} ^b	<i>CA</i> _{2h}	<i>CA</i> _{3h}	<i>CA</i> _{4h}	<i>CA</i> _{5h}
1	69°	81°	82°	89°	94°
2	68°	80°	81°	87°	90°
3	67°	76°	80°	86°	87°
4	68°	80°	84°	86°	94°

^a replicate samples of 10 nm films made from 25,100 g mol⁻¹ PGMA-b-PVDMA brushes

^b subscript indicates the exposure time each specific position was in contact with the TDA solution

4.5 Conclusions

Gradual immersion was used to create a chemical gradient by reactive modification of PVDMA brushes created by preferential assembly of PGMA-b-PVDMA diblock copolymers. *In situ* functionalization along the substrate was examined to determine the extent of functionalization as a function of immersion time (position) and monitor the changes in interfacial chemistry. The highest extents of functionalization were determined for various gradient surfaces and examined in light of key variables, including thickness, grafting density, and the small molecule amine used for modification. Film thickness had an effect of extent of functionalization: thicker substrates required longer immersion times to achieve high extents of reaction. Larger amines give lower degrees of functionalization, implying that their penetration into the brush is hindered or that the modification changes the solubility of the brushes. The

degree of functionalization is inversely correlated to grafting density. This work demonstrates how post-polymerization modification can be used to create gradients in interfacial and surface properties along the substrate in a facile manner. The method of gradual immersion provides a way to examine a wide range of conditions, which should be of use in endeavors to create biomaterial scaffolds, coatings, membranes, or sensors.

Chapter 5

Summary, Conclusions, and Future Work

5.1 Summary and Conclusions

The overarching objective of my dissertation research is to understand how structure and properties of ultrathin films are changed by reactive functionalization. These studies provide deep insights into how soft interfacial layers can be transformed by *in situ* modification and the resulting structural changes. Main variables investigated include size of the reactive species, grafting density of surface-tethered polymer chains and their molecular weight. This effort is expanded by developing an efficient method to produce gradient surfaces. This method will accelerate discovery and optimization of surface properties by allowing a broad parameter space to be investigated in a single sample. Neutron reflectivity, *in situ* ellipsometry and FTIR spectroscopy are key tools used in my research. This work is broadly applicable to any situation where polymer interfaces or thin films are modified *in situ* to alter their properties or structure.

My work focuses on how the design of polymer thin films affects the ability to alter surface properties by *in situ* chemical reactions. This work enables thin, interfacial layers with specific chemical functionality or inter-surface interactions to be created. Using post-assembly chemical modification also allows chemical properties to be varied in ways that cannot be accessed (or cannot be practically accessed) by changing monomer type. I have refined a robust method for creating interfacial thin films that can be easily transformed by chemical modification. This process involves creating a surface-anchored “primer” layer of poly(glycidyl methacrylate) (PGMA) chains (synthesized via free radical polymerization) and then covalently attaching poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) chains by one end to the PGMA layer. The PVDMA chains are end-functional by the specific chain transfer agent (CTA) used in the

reversible addition-fragmentation chain transfer (RAFT) polymerization. Molecular weight of the end-grafted PVDMA chains and areal density of chains were widely varied to access a range of interfacial structures.

To generate design-structure-property relationships, chain molecular weight was characterized via GPC and surface structure examined using neutron reflectivity (NR), ellipsometry, scanning probe microscopy, and FTIR spectroscopy. After characterizing the “parent” polymer thin films, they were reactively modified using a series of primary amines of different size as model compounds: Hexylamine, tetradecylamine, and octadecylamine (HA, TDA, and ODA, respectively) were used because they undergo an atom-efficient reaction (no by-products) with the pendant azlactone rings of PVDMA, enabling a fundamental study of *in situ* functionalization that links chain characteristics and thin film structure with size of the modifying agent, reaction time, and concentration. Moreover, the ring-opening nucleophilic addition of the amine to the azlactone ring induces intra-layer crowding, causing the PVDMA chains to stretch. Neutron reflectivity (NR) and an innovative, highly constrained analysis are used to determine the location and amount of functionalizing agent in the thin film, providing a quantitative measure of the extent of functionalization of VDMA repeat units in the chain. AFM, FTIR spectroscopy and ellipsometry are used as complementary techniques that provide additional insight into changes in height, chemical composition and film topography.

The focus of my first project is to understand from a fundamental point-of-view how *in situ* functionalization of PVDMA thin films (with primary amines) impacts the amount and distribution of the small-molecule modifying agent that penetrates into and

react in the film, and the resulting changes in structure and interfacial properties. My research has revealed new phenomenological understandings as well as new insights. For instance, when a larger amine (TDA or ODA) is used for the functionalization reaction, the change in film thickness (difference between “parent” film and modified film thickness) tends to increase. While this might suggest a greater extent of modification, neutron reflectivity (NR) showed lower extents of functionalization. In addition, analyses of NR data showed the distribution is stratified in two layers and functionalization is incomplete. These and other findings change the conventional understandings of *in situ* modification of ultrathin polymer films. The ability to describe how the thickness of the film and the grafting (areal) density of chains impact the extent of functionalization and distribution (which are impacted by reaction conditions) provides systematic guidance to efforts to produce polymer thin films with tailored properties.

Neutron reflectivity provided unprecedented insight into fundamental behaviors and properties of polymer thin films undergoing reactive modification. Through the grafting to approach, it is learned that thin films do not obtain their bulk mass density. Also, as the mass density (number of chains per area) of the parent film increases, additional stretching due to functionalization results in an increased “entropic death” of chains: chains are lost due to stretch-activated scission. Because of this entropic death of chains as well as because mass is added to the repeat unit upon functionalization, the mass density of a film can no longer be assumed constant, resulting in a functionalization-dependent change in the areal density of the brush. This is insightful and changes the way the community thinks and understands polymer brushes because

most assume a constant mass density and grafting density upon reactive modification. My results are also consistent with previous findings concerning the role of grafting density on the penetration of small molecules into brushes. In addition to all of these findings, I developed broadly applicable framework for analyzing NR data of reactively modified films to determine quantitative relationships that describe the structure of the polymer film and distribution of functionalizing agents. This framework provides a complete accounting of the amount and distribution of additives, the structural change of the brush, and loss of chains. This information results from a highly constrained model and uses only one adjustable parameter, the mass density of the functionalized thin film.

Two challenges arose during the course of this work: First, because the polymer films are so thin (< 10 nm), there are signal-to-noise complications in measurements; Second, because each thin film sample is only one measurement, carrying out parametric studies is laborious. To resolve these problems I used RAFT polymerization to create PGMA-block-PVDMA diblock copolymers, which yielded PVDMA films of higher thickness. In addition, I designed, tested and used a fluid cell system that allows gradients in surface functionality to be created by metering the solution concentration of functionalizing agent (amine) or solution volume. Thus, each gradient sample spans a range of amine concentrations or exposure times, which enables parametric studies of these important variables. I have used this “gradient by immersion system” along with ellipsometry and ATR-FTIR spectroscopy measurements to examine how extent of surface functionalization and, therefore, film structure and properties, are impacted. This is a noteworthy advance because it dramatically increases the amount of information that comes from one surface.

5.2 Future Work

I believe the work for reactive modification of poly(2-vinyl-4,4-dimethyl azlactone) chains should be adapted and is applicable for new materials containing novel polymer architectures such as cylindrical molecular brushes. Cylindrical molecular brushes, which consist of a linear polymer backbone with grafted oligomeric or polymeric side chains, have drawn attention to areas of research in stimuli-responsive materials, rheological modifiers, lubricants, drug delivery, and photonics.^{123–127} The characteristic feature of a molecular brush is that the polymer side chains are attached to each repeat unit of the backbone, resulting in highly grafted brush-like architecture.^{128–}
¹³¹ Bottlebrush polymers have generated special interest because the brush-like architecture generates superior properties to linear polymers because bottlebrush polymers do not chain entangle due to the steric repulsions of side chains. This results in high chain mobility and fast rheological dynamics compared to their linear counterparts.¹³² In addition, the solution assembly of bottlebrushes is marked by a lower critical micelle concentration, the kinetics of assembly are faster, and aggregates of bottlebrush block copolymers are more stable compared to those formed from linear block copolymers.^{133–135} While the overall size of bottlebrushes has been measured, structure-property relationships are under-developed and consequently poorly understood. These relationships are particularly complex because morphological and physical properties of bottlebrushes and their blends or assemblies are dictated by the grafting density of side chains and their length. As a result, there is a need to quantitatively analyze the impact of side chain length and degree-of-polymerization of the bottlebrush backbone to understand how these parameters affect conformational

properties and overall structure.¹³¹ These design parameters also affect rheological response, chain stiffness, and solubility.

To address design-structure-property relationships, I recommend designing a series of novel bottlebrushes with poly(2,2-vinyl,4,4-dimethylazlactone) (PVDMA) side chains and use these systems to provide a better understanding of structure-property relationships. PVDMA can be reactively modified with alcohols or amines to introduce a specific chemical moiety via post-polymerization modification. Reactive modification is a useful method to change properties, yielding multiple pathways to make materials for different applications. Side chain properties such as length, grafting density, and type of monomer used as the pendant side chain have an effect on extent of functionalization. Thus, having the ability to adjust these parameters will accomplish the main research objective of generating fundamental information relating structure and its effect on reactive modification. Specifically, the following research is recommended:

1. Prepare cylindrical molecular bottlebrushes with PVDMA side chains that vary in the degree-of-polymerization of the polymer backbone, grafting density of side chains, and side chain length;
2. Investigate how the design of the bottlebrush (side chain length, backbone length, and grafting density) affects the structure of bottlebrush polymers and their rheological properties; and
3. Modify PVDMA side chains with sulfopropylbetaine (SPB) amine, sulfobutylbetaine (SBB) amine, tetrahydrofurfurylamine (THF-amine), and benzylamine (Bz-amine), and investigate how these modifications

change both the chemistry of the bottlebrush and the rheological properties.

To complete this research, I will synthesize molecular brushes containing PVDMA side chains with varying side chain lengths, backbone lengths, grafting density and composition. Side chains of different molecular weights will be synthesized using reversible addition-fragmentation chain transfer (RAFT) polymerization using a norbornene-chain transfer agent (NB-CTA) to create norbornenyl-macromonomers of PVDMA chains. A “grafting through” technique to polymerize the PVDMA-macromonomers by ring-opening metathesis polymerization (ROMP) will yield bottlebrushes. The degree-of-polymerization, grafting density and composition of the backbone will be systematically investigated to understand the role of the NB-PVDMA side chain length, backbone length, and composition on the molecular conformation. Varying the molecular weight of the side chains will provide insight as to how its length affects solubility, functionalization, and flexibility of the overall structure and rheological response of bottlebrush copolymers. The side chains of the bottlebrush polymer will be functionalized with small molecules that induce stimuli-responsive (thermoresponsive) behavior to the bottlebrush. These functionalized side chains will promote phase separation upon heating above a lower critical solution temperature (LCST) and/or cooling below an upper critical solution temperature (USCT). Although thermoresponsive linear polymer systems are well-known, there is a gap in understanding thermoresponsive behavior of non-linear systems and, more specifically, how to design and tailor non-linear architectures and their properties. Rheological properties of the bottlebrush will be investigated to understand how introducing

chemical modifications that provide thermoresponsive character changes the complex viscosity and modulus of the bottlebrush in aqueous solutions of varying concentration. It is important to complete an extent of functionalization study of the azlactone ring of VDMA to create stimuli-responsive materials that responds to external stimuli, specifically in unique environments and how these stimuli affect the physical properties. Because the series of amines provides the ability to change the solubility of the bottlebrush, I can explore the rheological response of solution and gel phases of the bottlebrushes after reactive modification.

Gel permeation chromatography (GPC), NMR spectroscopy, small-angle neutron scattering (SANS), static light scattering (SLS), rheometry, atomic force microscopy (AFM), and contact angle (CA) measurements will be used to complete this proposed research. GPC and ^1H NMR will be used to determine the molecular weight and composition (grafting density) of the bottlebrush. SANS will be used to determine the size and conformation of the bottlebrush. SANS and SLS will be made in different solvents over a range of temperatures. Combining SANS and SLS will provide quantitative insights into how the structure of the bottlebrush changes as it is functionalized and how the structures respond to temperature changes. Rheology measurements will be used to determine the viscoelastic properties, dynamic response, and chain entanglement of each bottlebrush. AFM imaging will provide information about the structure of these bottlebrushes.

This suggested research will deliver important fundamental knowledge about structural and physical properties of PVDMA bottlebrushes in bulk and solution. Understanding how the bottlebrush structure changes and what properties are generated

after modification will aid in the design of smart materials. More specifically, the suggested research will give insight into properties of hydrogels that can be used in biomedical applications, such as drug delivery, gene delivery, and tissue engineering.

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Appendices

Appendix A-

Supporting Information for Chapter 2: Assessing Chemical Transformation of Reactive, Interfacial Thin Films Made of End- Tethered Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) Chains

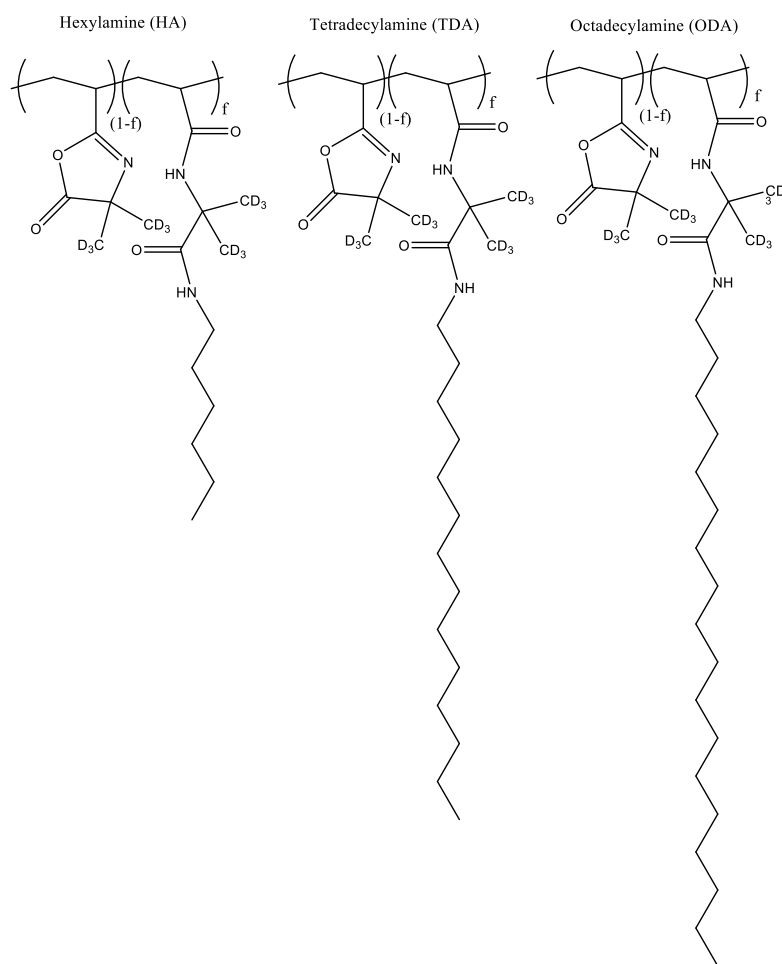


Figure A-1. Chemical structures representing reactively modified PVDMA- d_6 chains by various n-alkyl amines. The specific amine is identified above each structure.

Table A-1. Calculated Scattering Lengths, b_V , and M_V Values for VDMA-d₆ and Various Amines used for *in situ* Modification.

Compound	Formula	b_V (10^{-5} Å)	M_V (g mole ⁻¹)
VDMA-d ₆	C ₇ H ₃ D ₆ NO ₂	96.30	145.029
HA	C ₆ H ₁₅ N	-6.85	101.125
TDA	C ₁₄ H ₃₁ N	-13.51	213.252
ODA	C ₁₈ H ₃₉ N	-16.83	269.315

Table A-2. Experimental Values Determined from the Reflectivity Data used to Fit the Reflectivity Model. All symbols are defined in *Chapter 2*.

Sample ^a - Modification	time	Σ_0 ($10^{-6} \text{ \AA}^{-2}$)	d ($\text{\AA}$)	σ_R^b ($\text{\AA}$)	Σ_{M1} ($10^{-6} \text{ \AA}^{-2}$)	d_{M1} ($\text{\AA}$)	σ_R ($\text{\AA}$)	Σ_{M2} ($10^{-6} \text{ \AA}^{-2}$)	d_{M2} ($\text{\AA}$)	σ_R ($\text{\AA}$)
1. PVDMA-HA	15 m	3.835	45.0	10	2.505	67.0	10	—	—	23
2. PVDMA-HA	15 m	3.170	38.0	1	2.415	47.5	5	—	—	10
3. PVDMA-HA	2 h	3.630	50.0	13	2.680	64.0	13	—	—	17
4. PVDMA-HA	2 h	3.185	50.5	9	2.785	58.5	16	—	—	8
5. PVDMA-TDA	2 h	4.225	50.5	16	2.135	27.5	22	1.590	93.0	23
6. PVDMA-TDA	2 h	3.645	45.0	5	2.610	26.5	16	1.960	33.0	7
7. PVDMA-TDA	15 m	3.750	41.0	5	1.765	16.0	6	1.355	84.5	14
8. PVDMA-ODA	2 h	3.545	47.0	15	2.055	24.5	17	1.660	62.0	15
9. PVDMA-ODA	15 m	3.505	38.5	13	1.580	27.0	11	1.335	52.5	11

^a PVDMA-d₆ had an $M_n = 32,500 \text{ g mol}^{-1}$ and $\bar{D} = 1.14$.

^b Interfacial Roughness, σ_R

Neutron Reflectivity Data: The following series of figures present a) neutron reflectivity data (circles) and best-fits (lines) in R versus Q format (with the corresponding RQ^4 versus Q representation inset) measured for various PVDMA- d_6 brushes before (black) and after functionalization with small molecule amines (red), and b) SLD profiles for the “parent” PVDMA- d_6 brush (black) and amine-modified PVDMA brush (red). In all cases and as described in the Chapter 2, the PVDMA- d_6 chains have an $M_n = 32,500 \text{ g mol}^{-1}$ and D of 1.14.

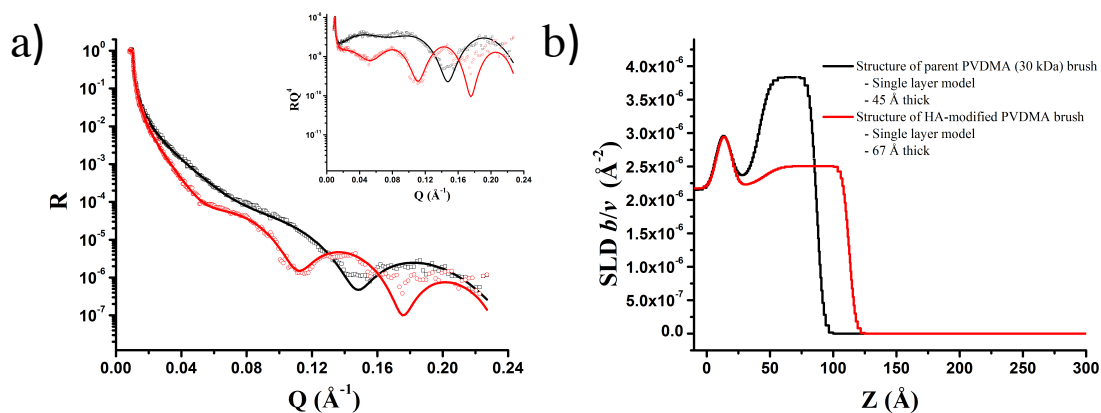


Figure A-2. PVDMA brush (Sample 1) modified with HA for 15 min.

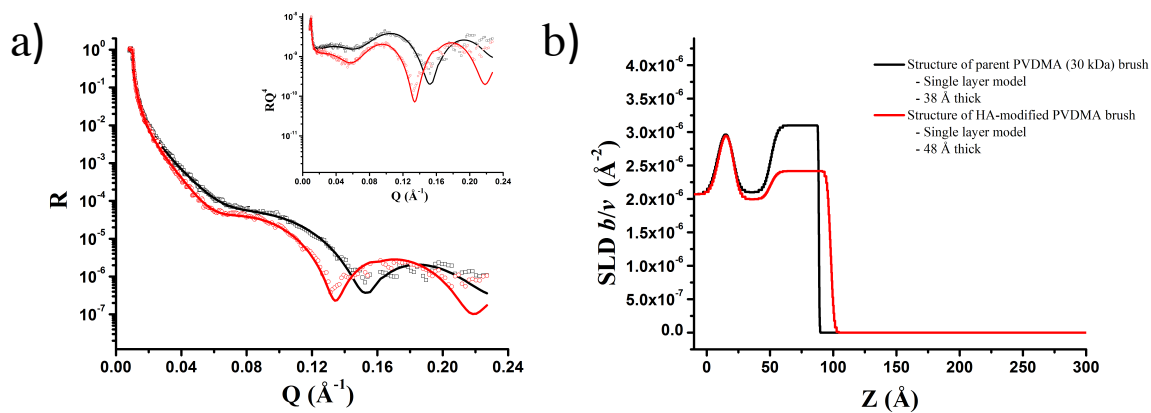


Figure A-3. PVDMA brush (Sample 2) modified with HA for 15 min.

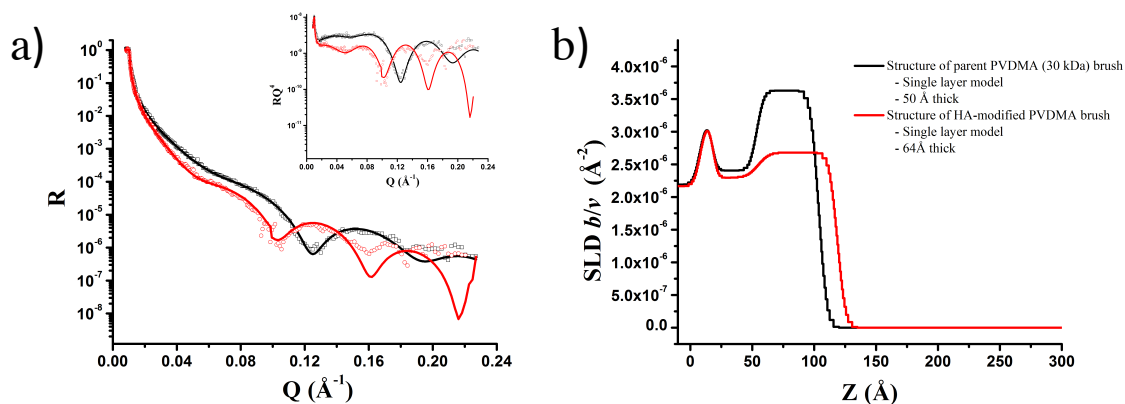


Figure A-4. PVDMA brush (Sample 3) modified with HA for 2h.

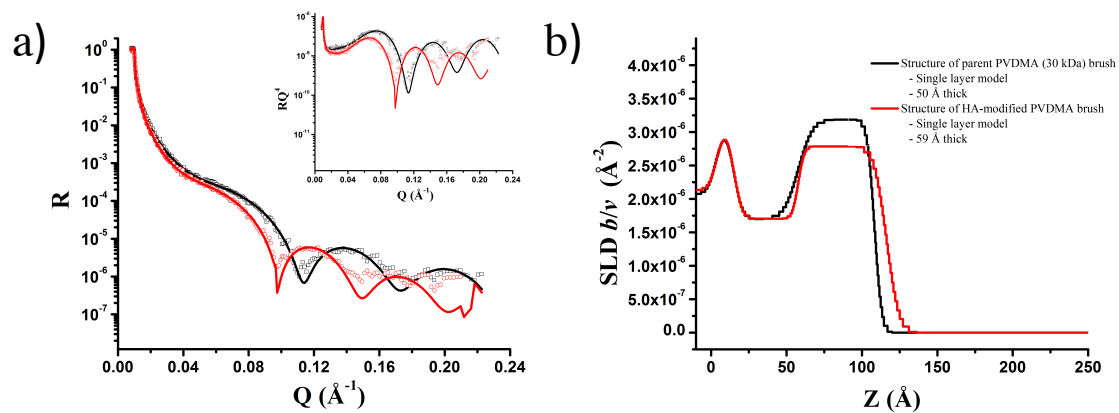


Figure A-5. PVDMA brush (Sample 4) modified with HA for 2h.

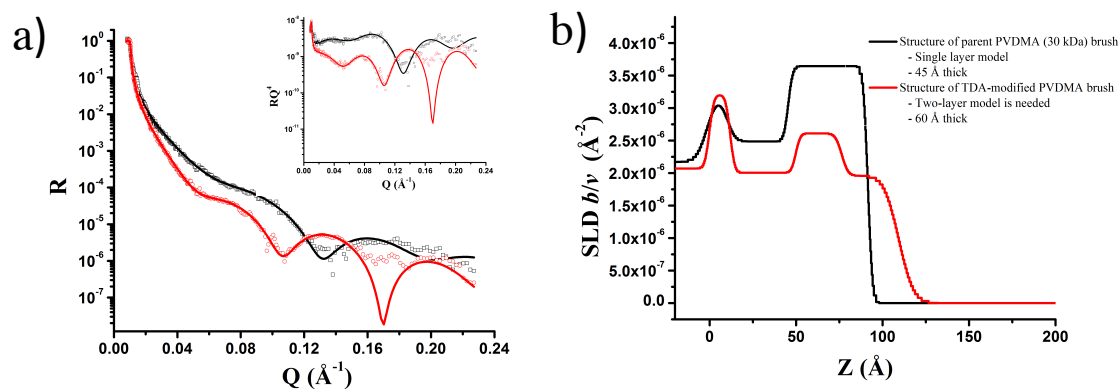


Figure A-6. PVDMA brush (Sample 6) modified with TDA for 2 h.

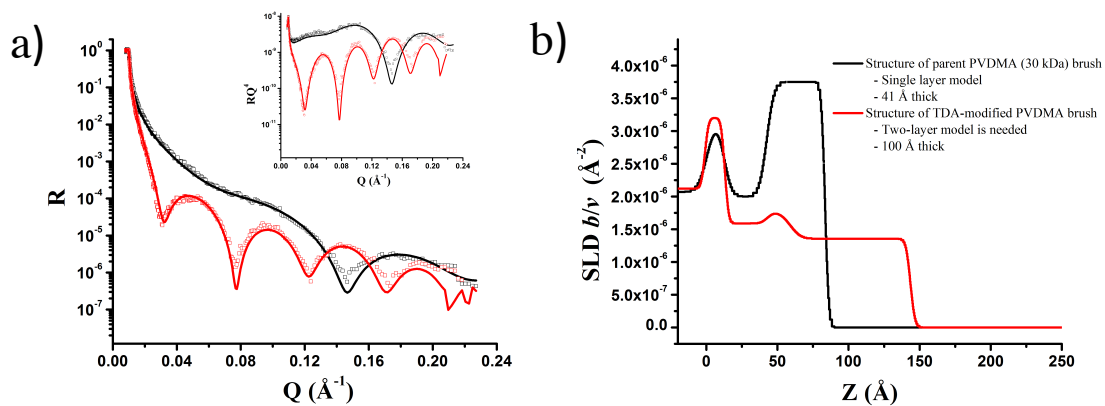


Figure A-7. PVDMA brush (Sample 7) modified with TDA for 15 min.

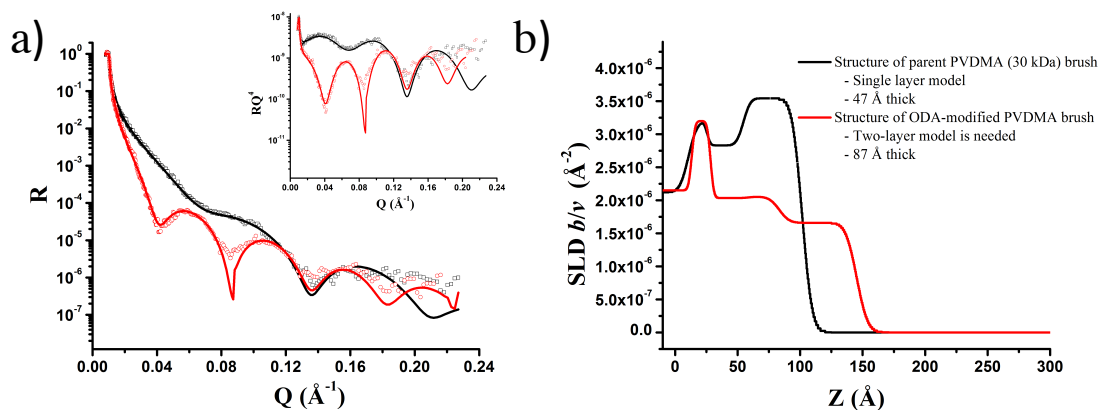


Figure A-8. PVDMA brush (Sample 8) modified with ODA for 2 h.

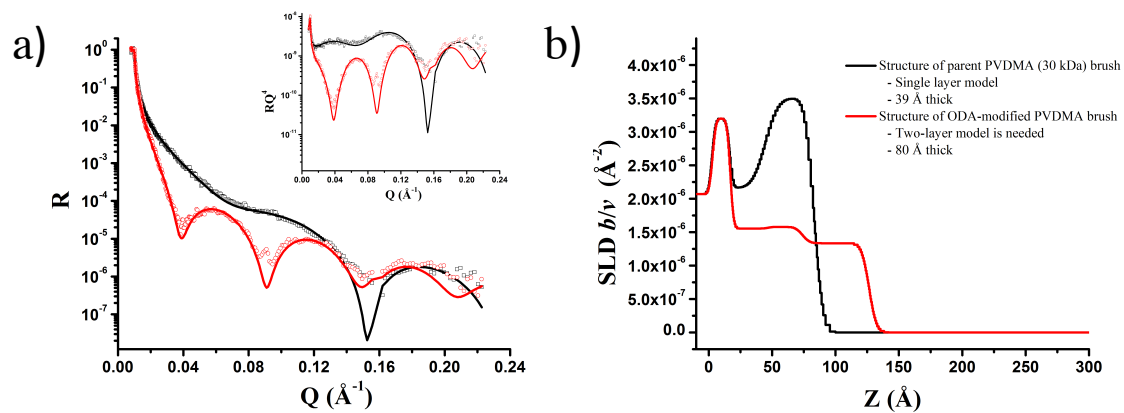


Figure A-9. PVDMA brush (Sample 9) modified with ODA for 15 min.

Table A-3. Estimated Extent of Functionalization, $f_{M,est}$ and Estimated Fraction of PVDMA Chains Lost, $f_{PVDMA-lost}$, in Relation to Smallest and Largest Mass Densities (in units of $g\ cm^{-3}$) Measured for the Parent PVDMA- d_6 Brushes.^a

Sample Modification	$f_{PVDMA-lost}$ ($\rho_{M,est} = 0.79$)	$f_{M,est}$ ($\rho_{M,est} = 0.79$)	$f_{PVDMA-lost}$ ($\rho_{M,est} = 1.06$)	$f_{M,est}$ ($\rho_{M,est} = 1.06$)
1. PVDMA-HA	0.33	0.33	0.31	0.85
2. PVDMA-HA	0.22	0.39	0.18	0.92
3. PVDMA-HA	0.25	0.23	0.22	0.72
4. PVDMA-HA	0.11	0.17	0.08	0.65
5. PVDMA-TDA	0.56	0.49	0.54	0.81
6. PVDMA-TDA	0.36	0.24	0.34	0.51
7. PVDMA-TDA	0.58	0.69	0.56	1.05
8. PVDMA-ODA	0.47	0.36	0.44	0.61
9. PVDMA-ODA	0.55	0.55	0.53	0.84

^a As noted in the *Chapter 2*, $f_{PVDMA-lost}$ is hardly affected by the mass density of the brush layer.

Converted fraction plots based on analyses of reflectivity data: The converted fraction plots presented below provide a complete, depth-dependent accounting of reactive modification of PVDMA brush films, including how much was lost, converted, and did not react, based on the two extremes of mass density measured for the parent films. The amount of PVDMA available to be functionalized is represented by the fraction under the black line. If a mass density $\rho_{M,est} = 0.79$ (blue line) or $\rho_{M,est} = 1.06$ (red line) is assumed, the proportion of the converted film varies between the top of each of the blue and red line. The space between those curves and the black line represents unreacted VDMA monomer.

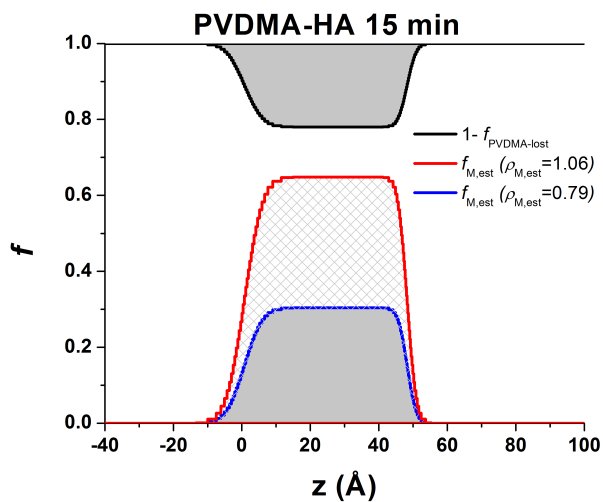


Figure A-10. Converted fraction plot of PVDMA brush (Sample 1) modified with HA for 15 min.

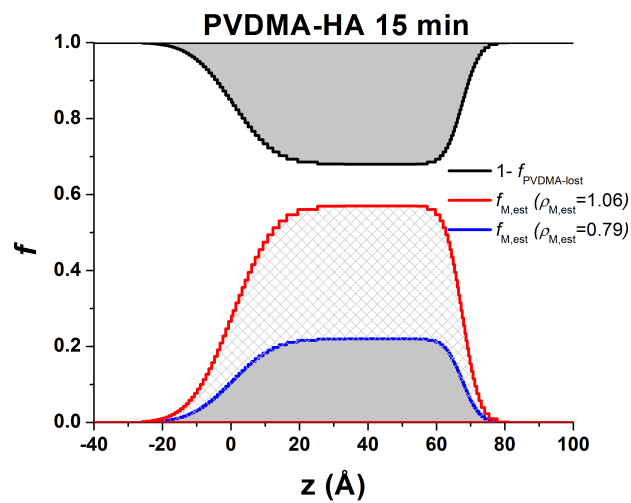


Figure A-11. Converted fraction plot of PVDMA brush (Sample 2) modified with HA for 15 min.

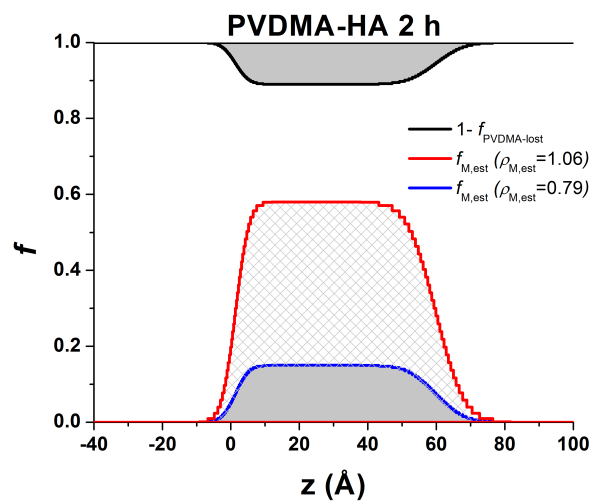


Figure A-12. Converted fraction plot of PVDMA brush (Sample 4) modified with HA for 2 h.

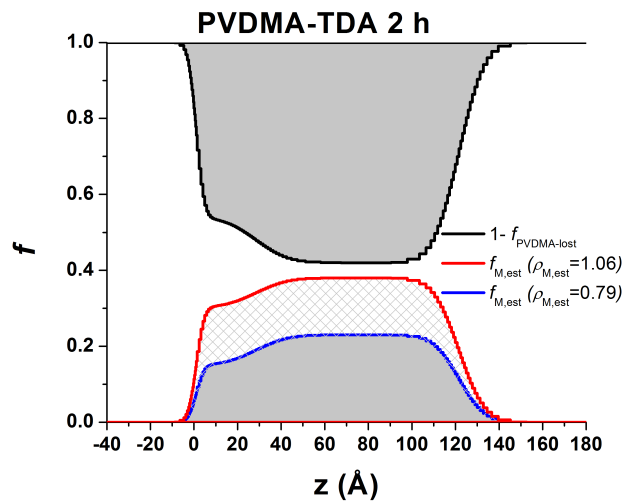


Figure A-13. Converted fraction plot of PVDMA brush (Sample 6) modified with TDA for 2 h.

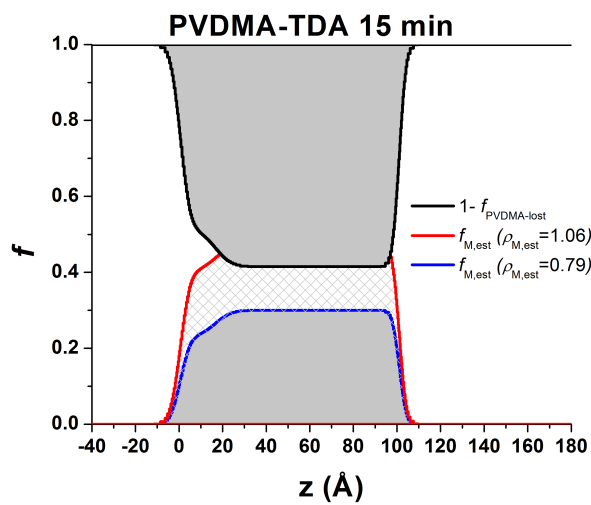


Figure A-14. Converted fraction plot of PVDMA brush (Sample 7) modified with TDA for 15 min.

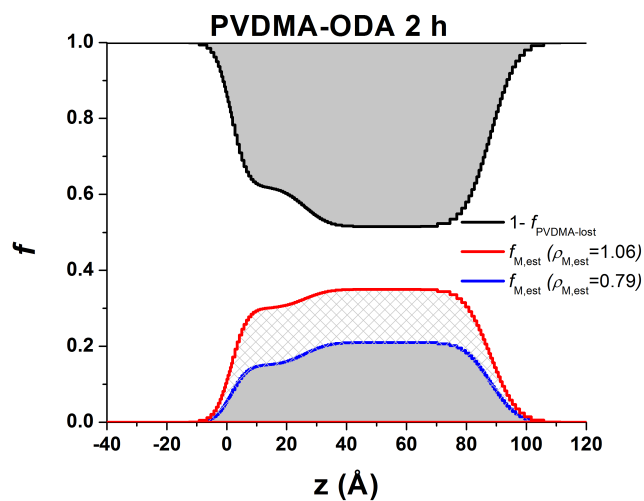


Figure A-15. Converted fraction plot of PVDMA brush (Sample 8) modified with ODA for 2 h.

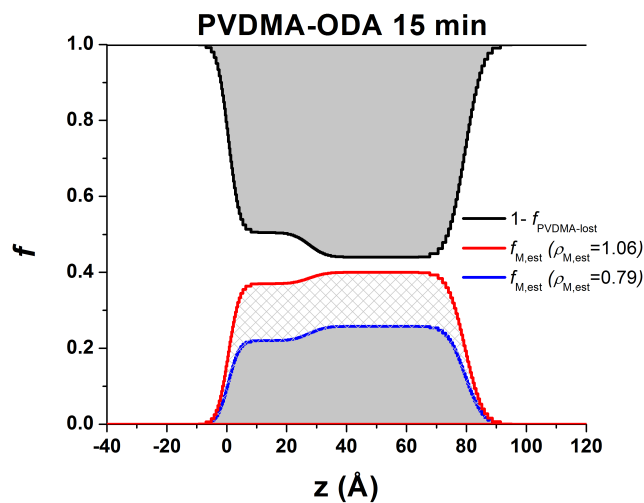


Figure A-16. Converted fraction plot of PVDMA brush (Sample 9) modified with ODA for 15 min.

Table A-4. Ellipsometric Measurements Confirming Functionalization and Refunctionalization of PVDMA brushes.

M_n (g mol ⁻¹)	H_{PVDMA} (nm)	$H_{\text{PVDMA-Amine}}$ (nm) ^a	$H_{\text{PVDMA-Amine}}$ (nm) ^b
4,800	5.2 ± 3.2	6.3 ± 5.3	6.3 ± 2.3
9,300	6.0 ± 1.8	6.9 ± 1.8	7.6 ± 1.7
17,300	6.1 ± 3.0	7.4 ± 3.4	7.9 ± 3.7
29,400	6.6 ± 2.3	8.1 ± 1.9	8.2 ± 1.5

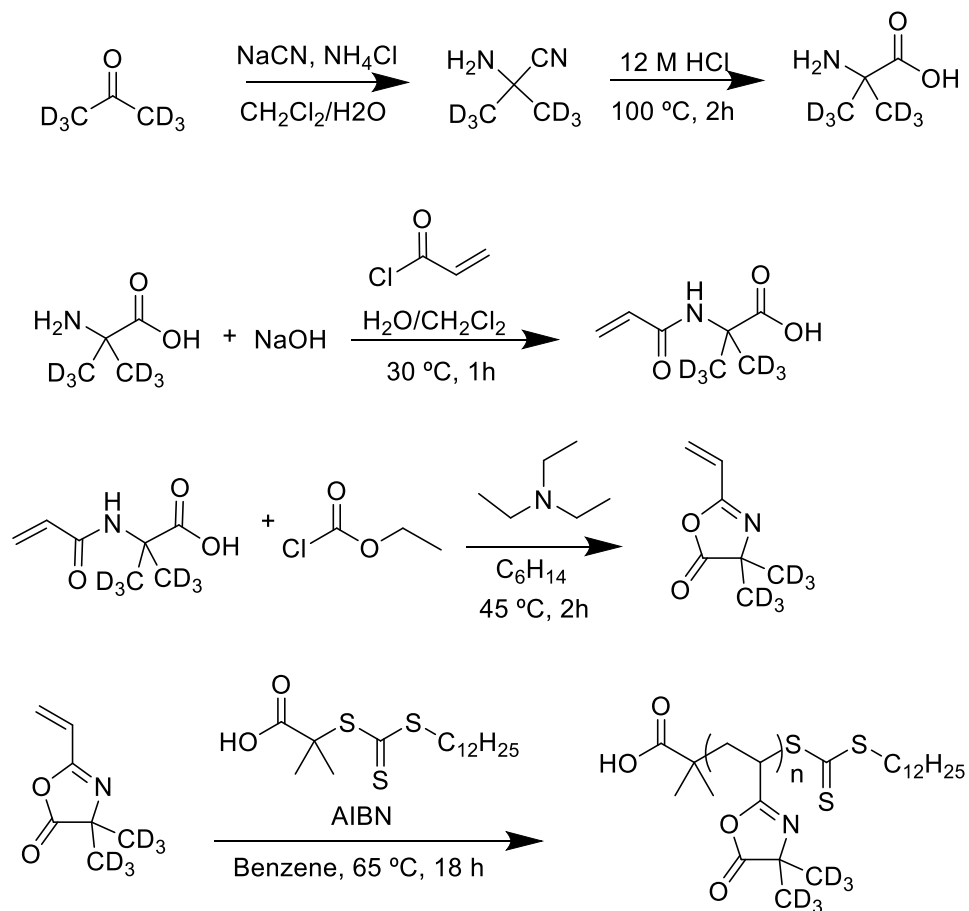
^a PVDMA thickness after functionalization with the small molecule amine.

^b The thickness of the amine-modified PVDMA brush after re-functionalization with 0.25 wt.% hexylamine for 1h.

Appendix B-

Supporting Information for Chapter 3: Neutron Reflectivity Study:

**Entropic Death from Chemical Transformation of End-Tethered
Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) Thin Films via *in situ*
Modification**



Scheme B-1. Synthesis of 4,4-dimethyl-d₆-2-vinyl-oxazolone (VDMA-d₆). VDMA-d₆ is synthesized by RAFT polymerization using DMP as the chain transfer agent.

Table B-1. Experimental Values Determined from the Reflectivity Data used in Model Fits. All symbols are defined in *Chapter 3*.

Sample ^a - Modification	Anneal time	Σ_0 ($10^{-6} \text{ \AA}^{-2}$)	d ($\text{\AA}$)	σ_R^b ($\text{\AA}$)	Σ_{M1} ($10^{-6} \text{ \AA}^{-2}$)	d_{M1} ($\text{\AA}$)	σ_R ($\text{\AA}$)
1. PVDMA-TDA	18 h	2.710	314.9	69	2.240	407.0	100
2. PVDMA-TDA	18 h	2.720	352.4	29	2.300	420.3	35
3. PVDMA-ODA	18 h	2.730	340.0	35	2.150	414.7	29
4. PVDMA-ODA	18 h	3.420	291.5	12	1.390	534.0	87
5. PVDMA-HA	18 h	2.930	337.0	35	2.470	385.8	46
6. PVDMA-HA	18 h	2.640	322.7	55	2.150	410.0	40
1. PVDMA-TDA	24 h	2.890	321.0	24	2.190	398.0	34
2. PVDMA-TDA	24 h	3.410	291.8	25	1.780	515.0	75
3. PVDMA-ODA	24 h	2.800	345.0	22	2.440	388.0	24
4. PVDMA-ODA	24 h	3.550	238.4	13	1.870	452.4	52
5. PVDMA-HA	24 h	2.930	337.0	35	2.470	385.8	46
6. PVDMA-HA	24 h	3.170	254.9	29	2.150	340.0	50
1. PVDMA-TDA	30 h	2.850	363.0	26	2.450	409.0	30
2. PVDMA-TDA	30 h	2.980	346.2	31	2.130	474.0	64
3. PVDMA-ODA	30 h	2.800	359.0	30	2.190	450.0	32
4. PVDMA-ODA	30 h	3.340	340.3	65	1.890	529.3	130
5. PVDMA-HA	30 h	2.730	394.5	43	2.540	425.0	47
6. PVDMA-HA	30 h	3.450	308.3	31	2.100	460.0	60

^a PVDMA-d₆ had an $M_n = 27,000 \text{ g mol}^{-1}$ and $\bar{D} = 1.18$.

^b Interfacial Roughness, σ_R

Neutron Reflectivity Data: The following series of figures present a) neutron reflectivity data (circles) and best-fits (lines) in R versus Q format (with the corresponding RQ^4 versus Q representation inset) measured for various PVDMA- d_6 brushes before (black) and after functionalization with small molecule amines (red), and b) SLD profiles for the “parent” PVDMA- d_6 brush (black) and amine-modified PVDMA brush (red). In all cases and as described in the Article, the PVDMA- d_6 chains have an $M_n = 27,000 \text{ g mol}^{-1}$ and D of 1.18.

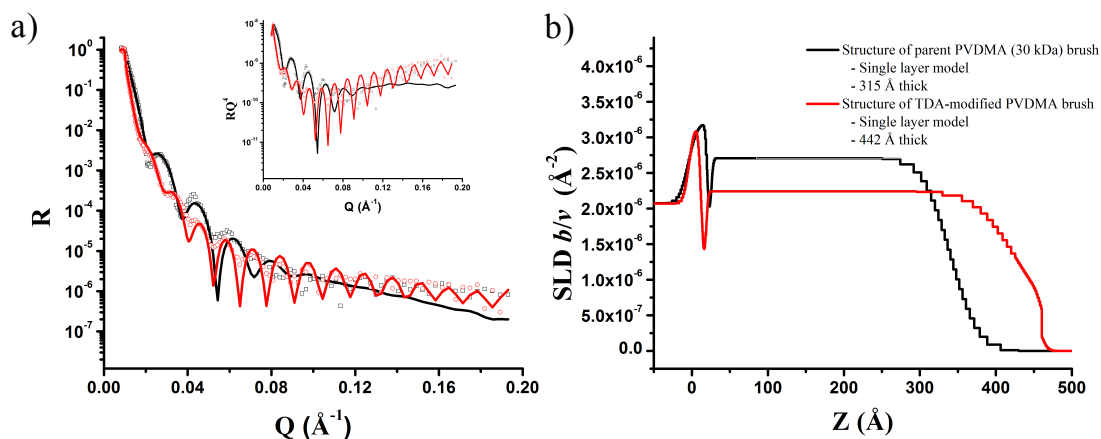


Figure B-1. PVDMA brush (Sample 1) annealed for 18 h and modified with TDA for 12

h.

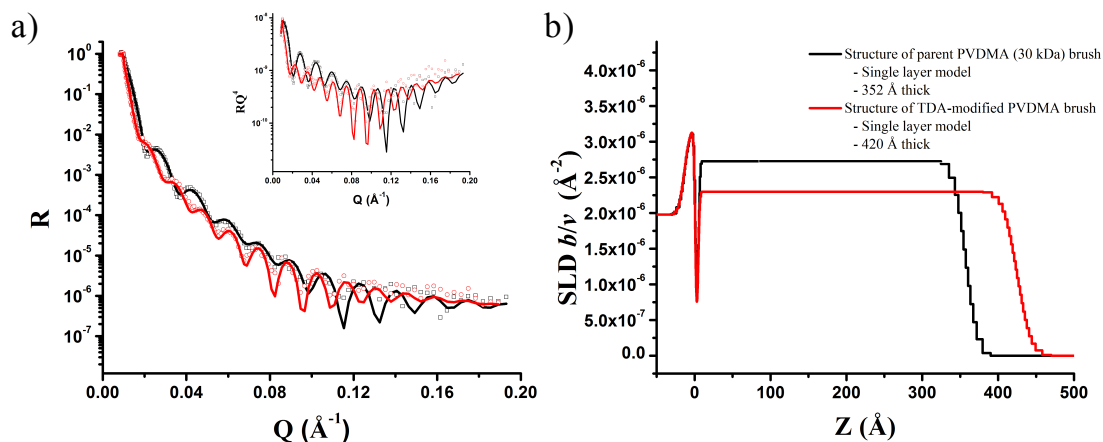


Figure B-2. PVDMA brush (Sample 2) annealed for 18 h and modified with TDA for 12

h.

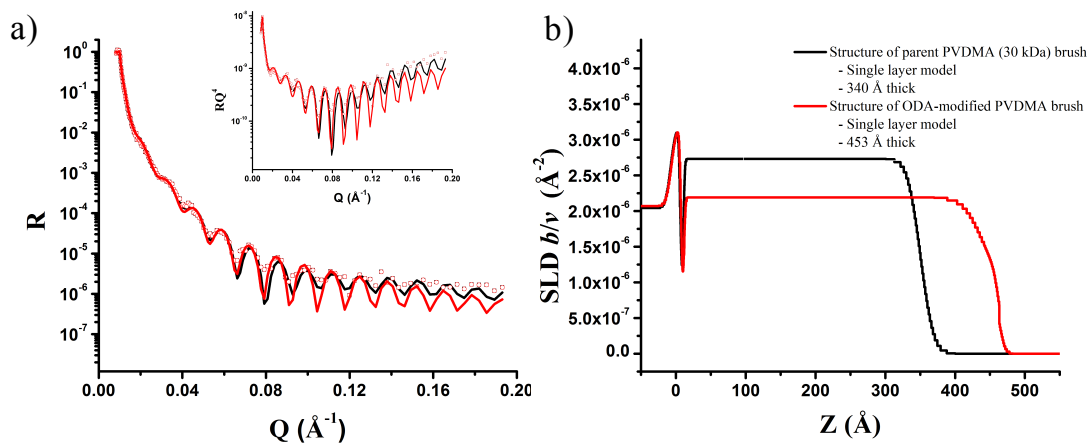


Figure B-3. PVDMA brush (Sample 3) annealed for 18 h and modified with ODA for 12

h.

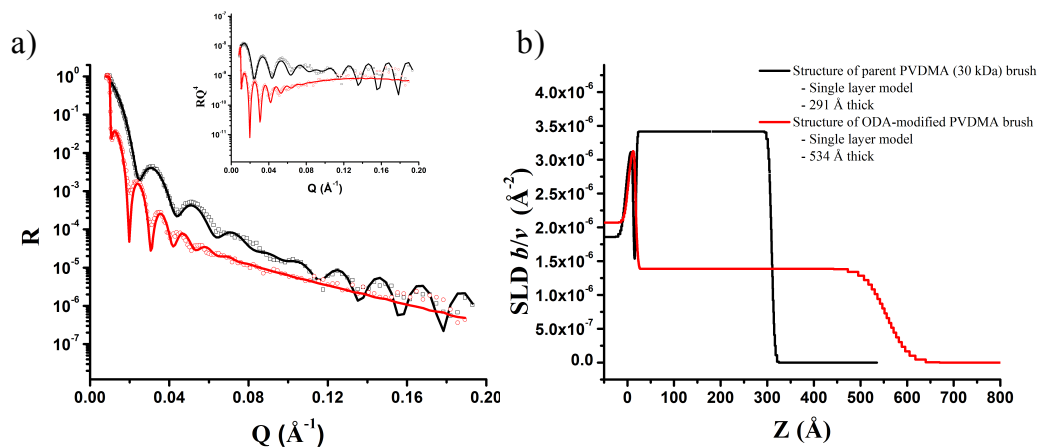


Figure B-4. PVDMA brush (Sample 4) annealed for 18 h and modified with ODA for 12

h.

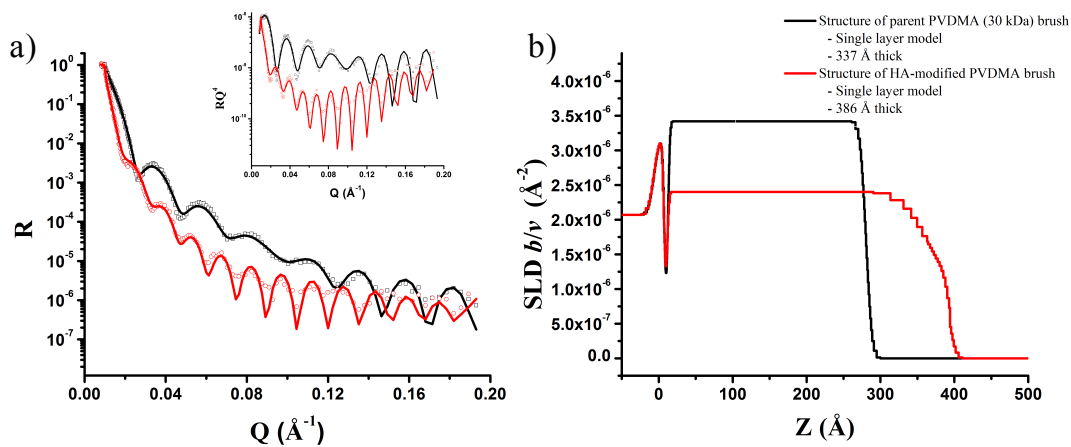


Figure B-5. PVDMA brush (Sample 5) annealed for 18 h and modified with HA for 12

h.

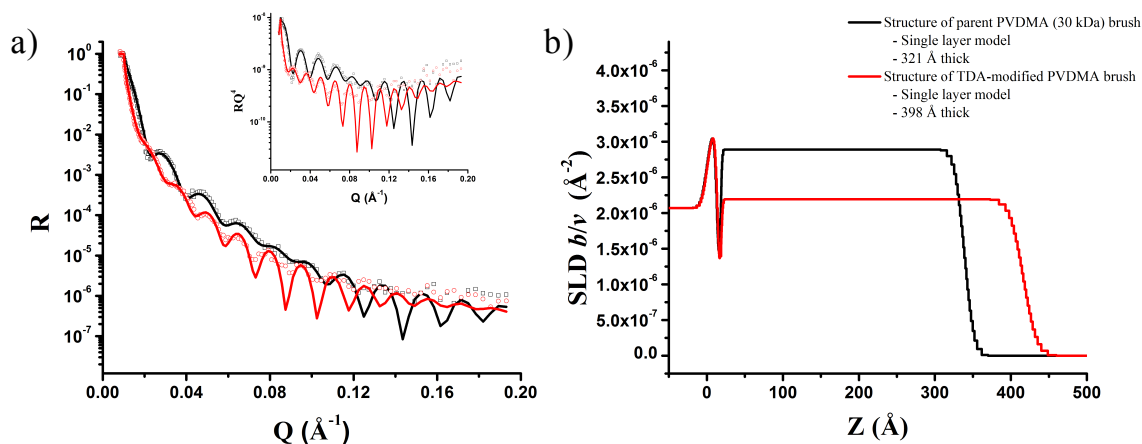


Figure B-6. PVDMA brush (Sample 1) annealed for 24 h and modified with TDA for 12

h.

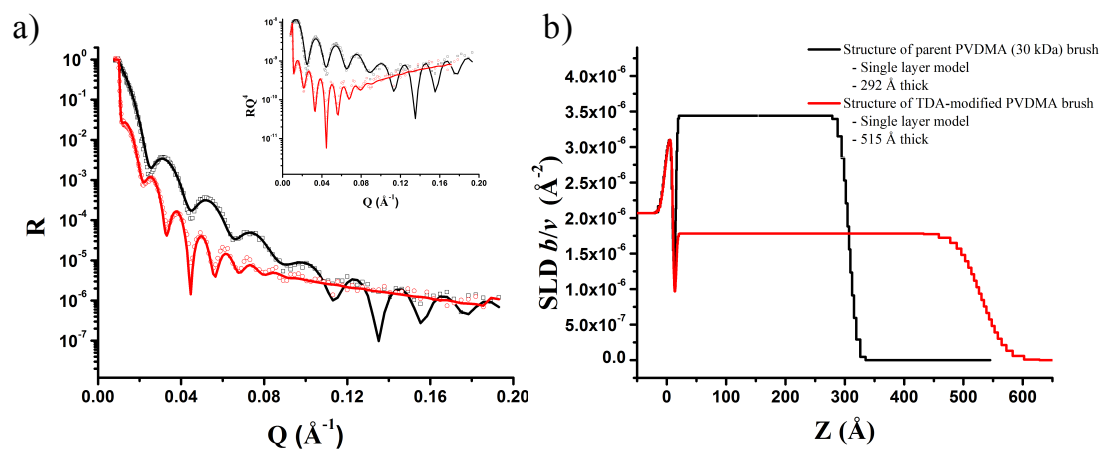


Figure B-7. PVDMA brush (Sample 2) annealed for 24 h and modified with TDA for 12

h.

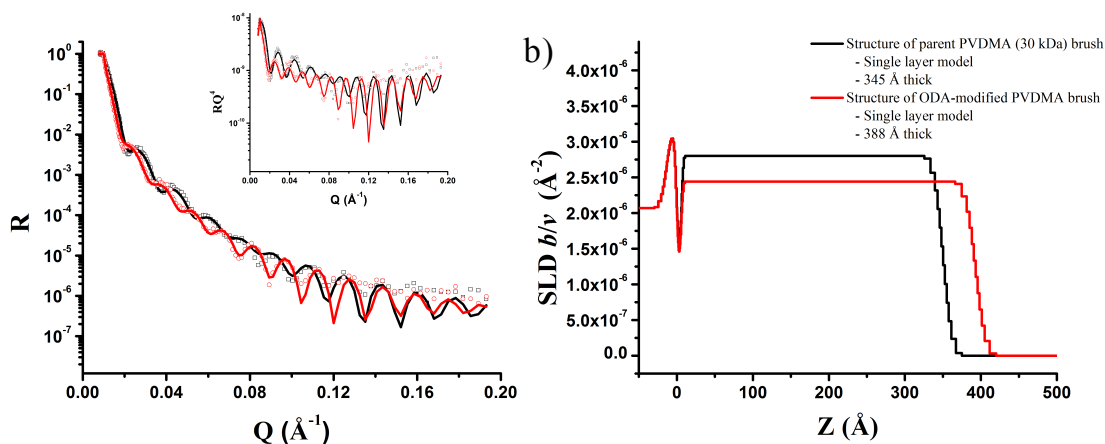


Figure B-8. PVDMA brush (Sample 3) annealed for 24 h and modified with ODA for 12

h.

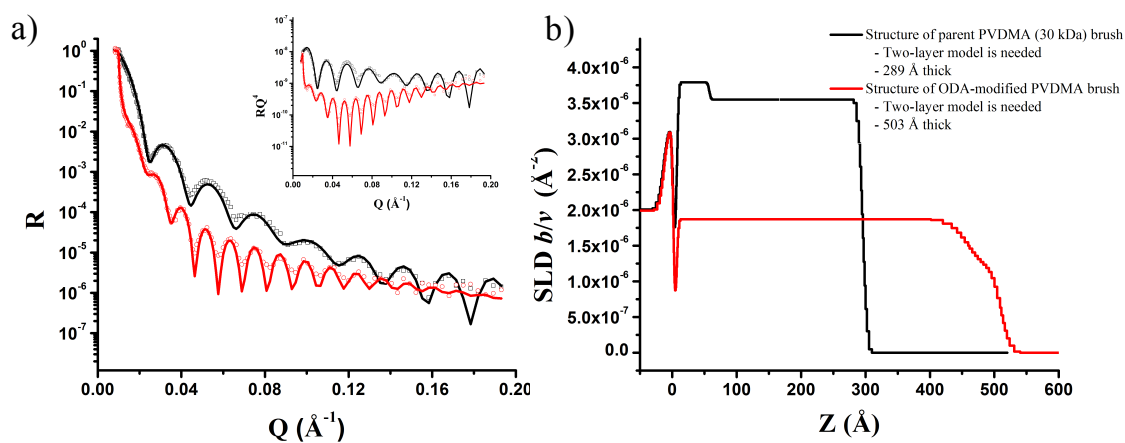


Figure B-9. PVDMA brush (Sample 4) annealed for 24 h and modified with ODA for 12

h.

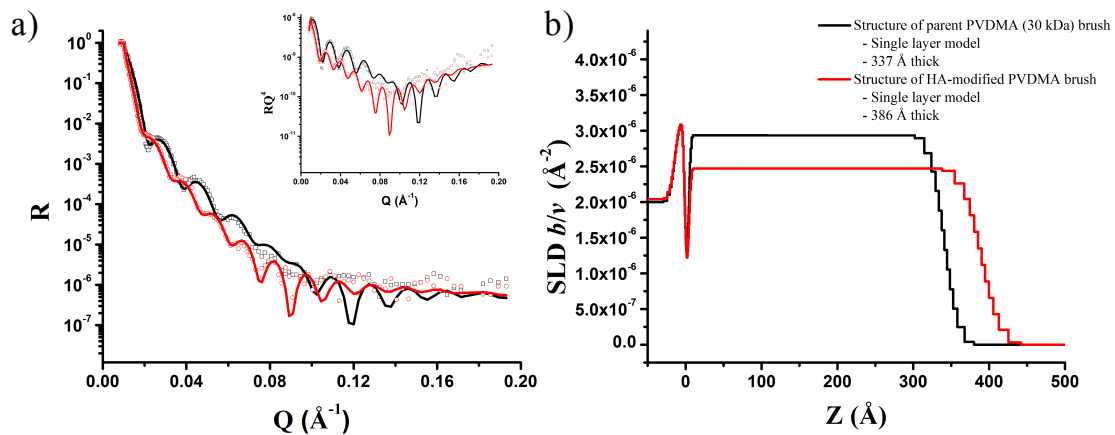


Figure B-10. PVDMA brush (Sample 5) annealed for 24 h and modified with HA for 12

h.

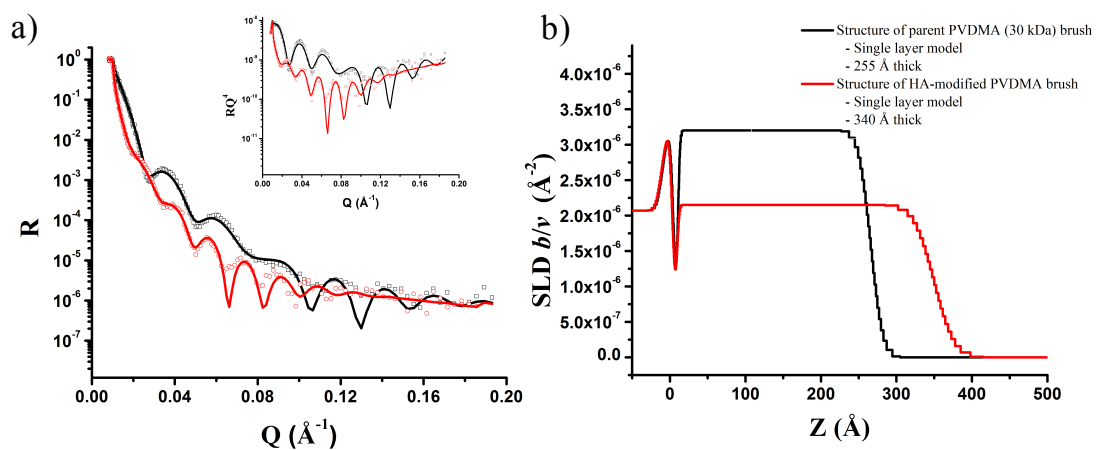


Figure B-11. PVDMA brush (Sample 6) annealed for 24 h and modified with HA for 12

h.

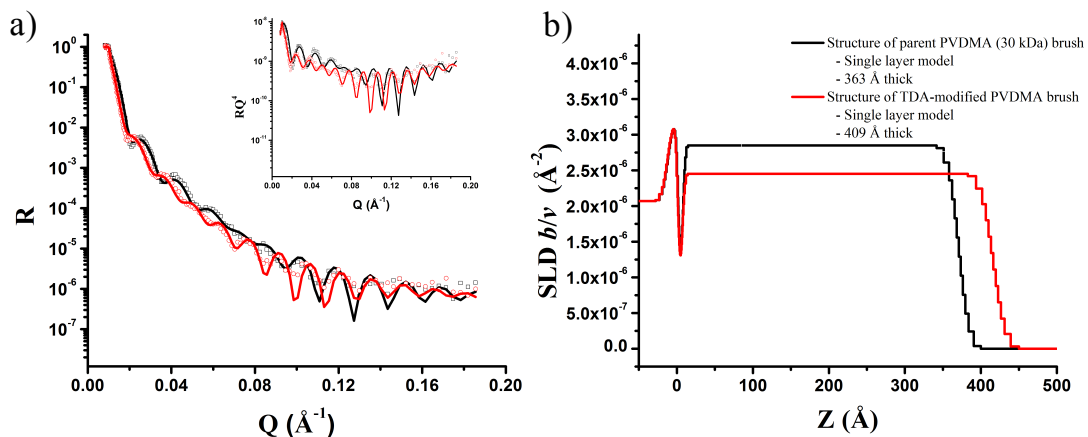


Figure B-12. PVDMA brush (Sample 1) annealed for 30 h and modified with TDA for 12 h.

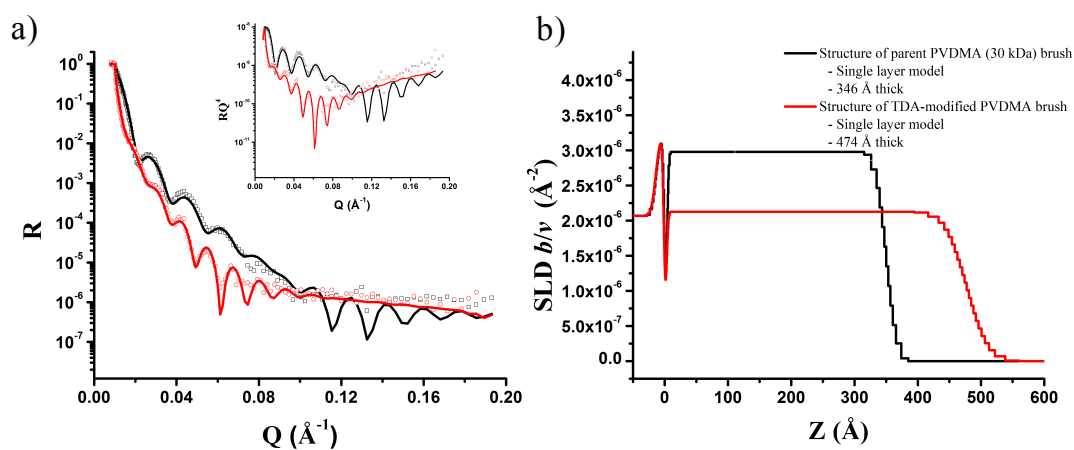


Figure B-13. PVDMA brush (Sample 2) annealed for 30 h and modified with TDA for 12 h.

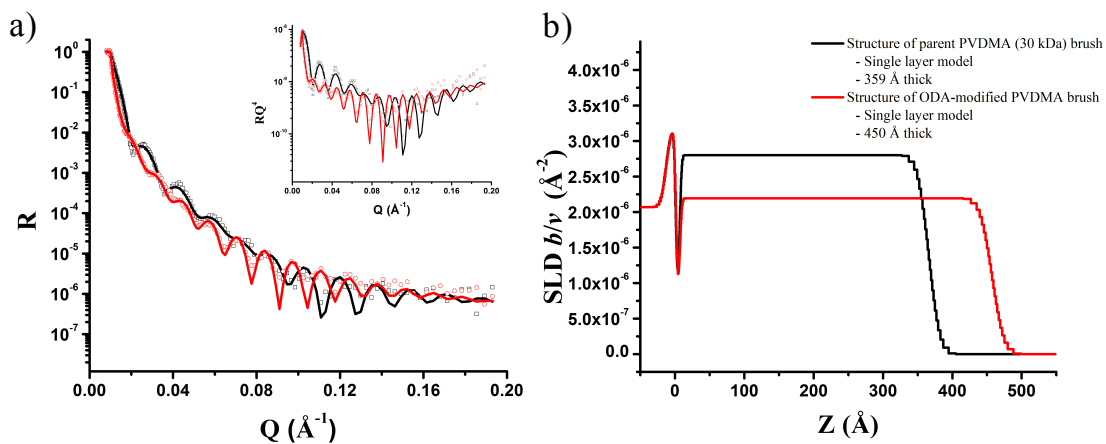


Figure B-14. PVDMA brush (Sample 3) annealed for 30 h and modified with ODA for 12 h.

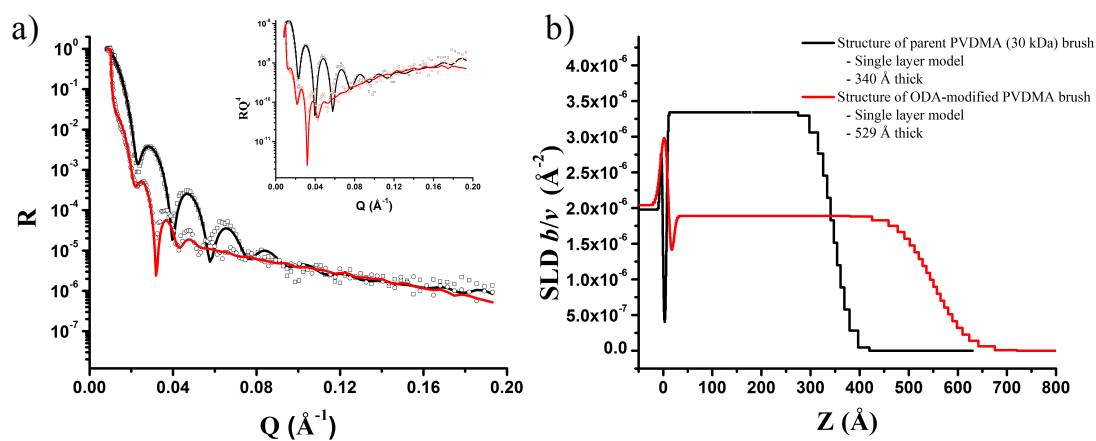


Figure B-15. PVDMA brush (Sample 4) annealed for 30 h and modified with ODA for 12 h.

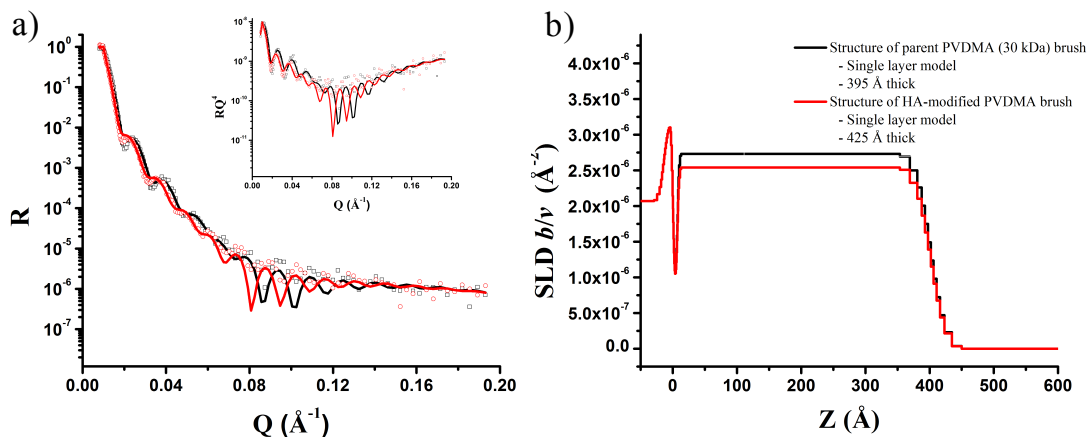


Figure B-16. PVDMA brush (Sample 5) annealed for 30 h and modified with HA for 12

h.

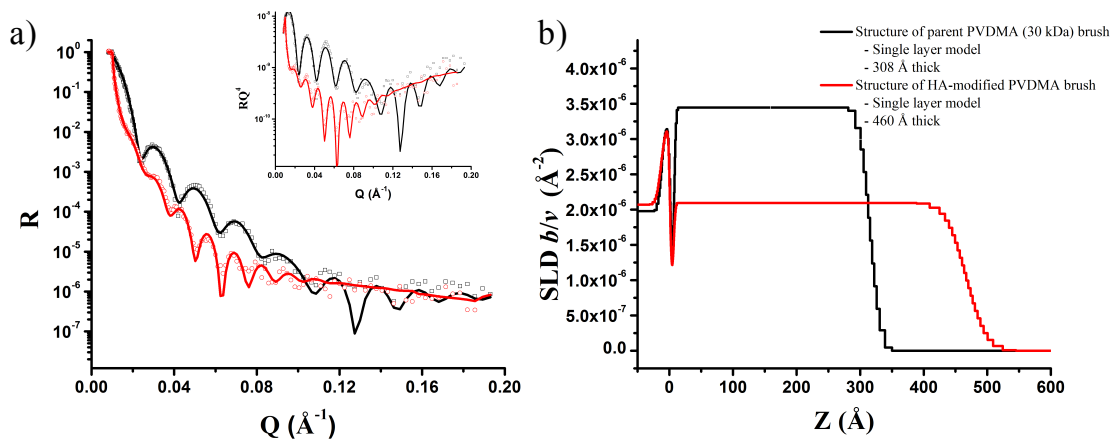


Figure B-17. PVDMA brush (Sample 6) annealed for 30 h and modified with HA for 12

h.

Refunctionalization Study. Select samples that were previously annealed for 24 or 30 h were exposed to a 0.25 wt.% solution containing hexylamine for 1h. Reflectivity data was collected on these refunctionalized samples and additional functionalization was observed. In each of the following figures, the data (points) and best-fit model (line) in black corresponds to the “parent” film, those in red represent after the first functionalization, and those in blue are after refunctionalization with hexylamine.

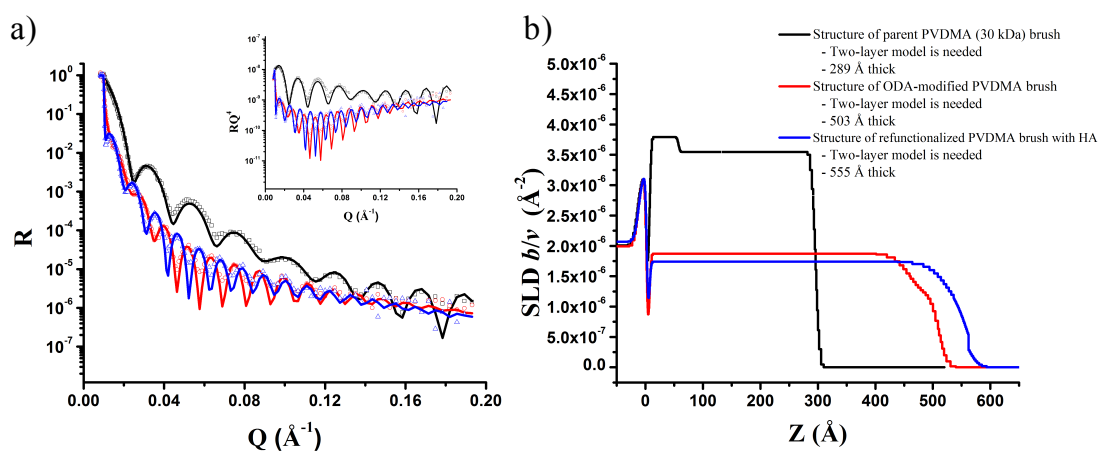


Figure B-18. ODA-modified PVDMA brush (Sample 4) annealed for 24 h and refunctionalized with HA for 1 h.

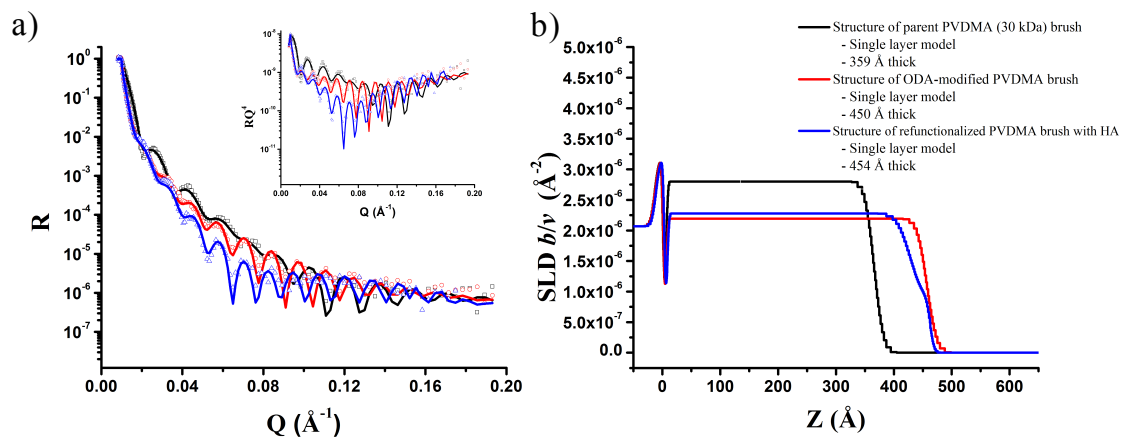


Figure B-19. ODA-modified PVDMA brush (Sample 3) annealed for 30 h and refunctionalized with HA for 1 h.

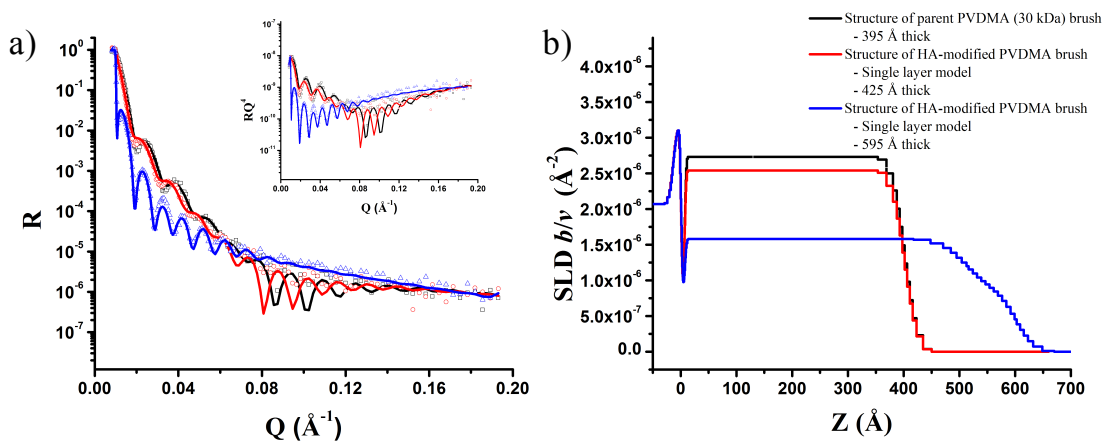


Figure B-20. HA-modified PVDMA brush (Sample 5) annealed for 30 h and refunctionalized with HA for 1 h.

Table B-2. Estimated Extent of Functionalization, $f_{M,est}$, and Estimated Fraction of PVDMA Chains Lost, $f_{PVDMA-lost}$, in Relation to Smallest and Largest Mass Densities (in units of $g\ cm^{-3}$) Measured for the Parent PVDMA- d_6 Brushes.^a

Sample Modification	$f_{PVDMA-lost}$ ($\rho_{M,est} = 0.66$)	$f_{M,est}$ ($\rho_{M,est} = 0.66$)	$f_{PVDMA-lost}$ ($\rho_{M,est} = 0.89$)	$f_{M,est}$ ($\rho_{M,est} = 0.89$)
1. PVDMA-TDA	0.16	0.11	0.13	0.35
2. PVDMA-TDA	0.14	0.09	0.11	0.32
3. PVDMA-ODA	0.20	0.11	0.17	0.31
4. PVDMA-ODA	0.56	0.41	0.54	0.68
5. PVDMA-HA	0.15	0.09	0.12	0.55
6. PVDMA-HA	0.17	0.29	0.14	0.80
1. PVDMA-TDA	0.23	0.12	0.20	0.37
2. PVDMA-TDA	0.46	0.29	0.43	0.57
3. PVDMA-ODA	0.12	0.04	0.09	0.22
4. PVDMA-ODA	0.45	0.20	0.43	0.41
5. PVDMA-HA	0.15	0.09	0.12	0.55
6. PVDMA-HA	0.31	0.29	0.28	0.80
1. PVDMA-TDA	0.13	0.05	0.11	0.27
2. PVDMA-TDA	0.27	0.15	0.24	0.39
3. PVDMA-ODA	0.20	0.10	0.18	0.29
4. PVDMA-ODA	0.41	0.19	0.39	0.40
5. PVDMA-HA	0.07	0.05	0.04	0.50
6. PVDMA-HA	0.38	0.33	0.35	0.85

^a As noted in the *Chapter 3*, $f_{PVDMA-lost}$ is hardly affected by the mass density of the brush layer.

Converted fraction plots based on analyses of reflectivity data: The converted fraction plots presented below provide a complete, depth-dependent accounting of reactive modification of PVDMA brush films made by assembly of PGMA-block-PVDMA copolymers. The plots show how much PVDMA was lost, converted, and did not react, based on the two extremes of mass density measured for the parent films. The amount of PVDMA available to be functionalized is represented by the fraction under the black line. If a mass density $\rho_{M,est} = 0.66$ (blue line) or $\rho_{M,est} = 0.89$ (red line) is assumed, the proportion of the original film converted varies between the top of each of the blue and red line. The space between those curves and the black line represents unreacted VDMA monomer.

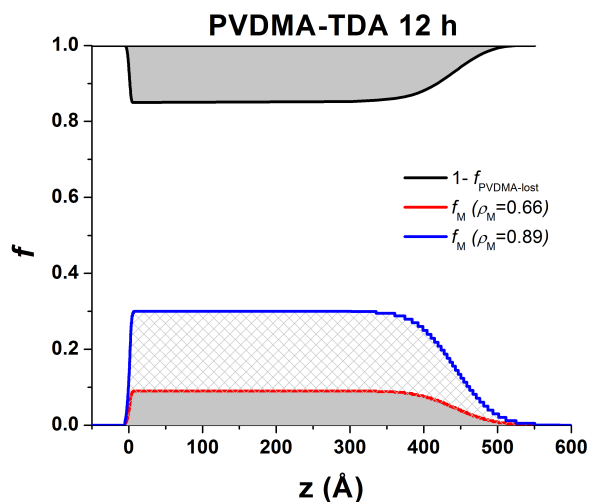


Figure B-21. Converted fraction plot of a PVDMA brush (Sample 1) annealed for 18 h and modified with TDA for 12 h.

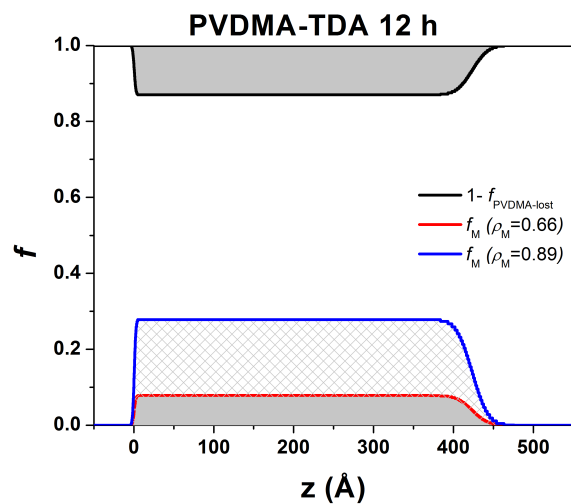


Figure B-22. Converted fraction plot of a PVDMA brush (Sample 2) annealed for 18 h and modified with TDA for 12 h.

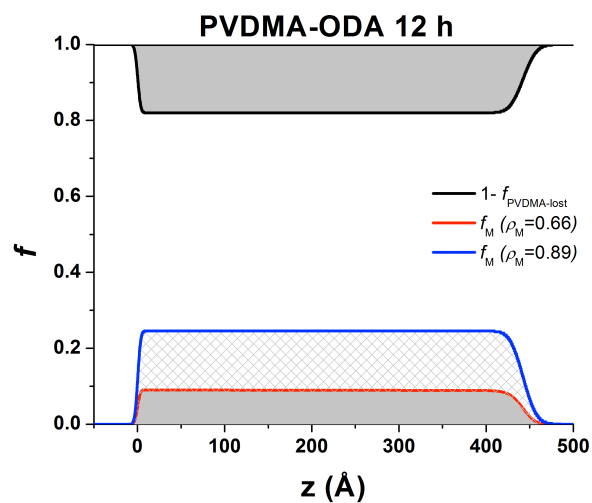


Figure B-23. Converted fraction plot of a PVDMA brush (Sample 3) annealed for 18 h and modified with ODA for 12 h.

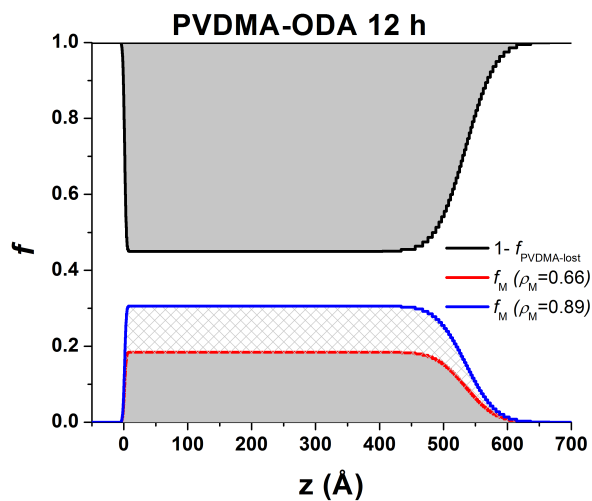


Figure B-24. Converted fraction plot of a PVDMA brush (Sample 4) annealed for 18 h and modified with ODA for 12 h.

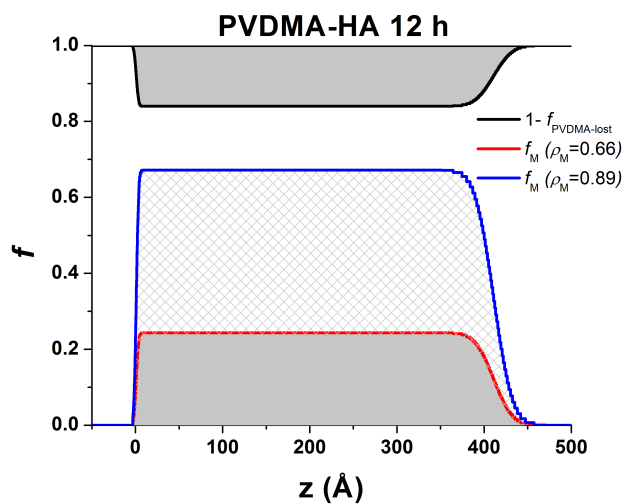


Figure B-25. Converted fraction plot of a PVDMA brush (Sample 6) annealed for 18 h and modified with HA for 12 h.

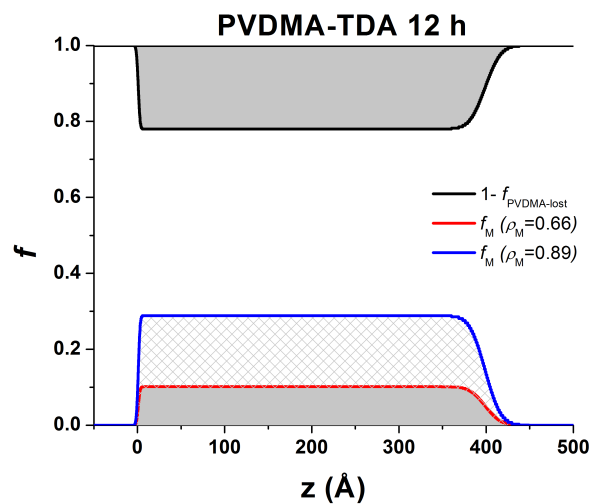


Figure B-26. Converted fraction plot of a PVDMA brush (Sample 1) annealed for 24 h and modified with TDA for 12 h.

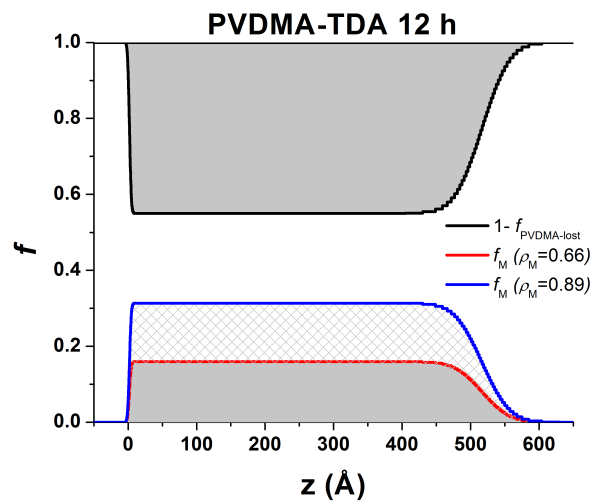


Figure B-27. Converted fraction plot of a PVDMA brush (Sample 2) annealed for 24 h and modified with TDA for 12 h.

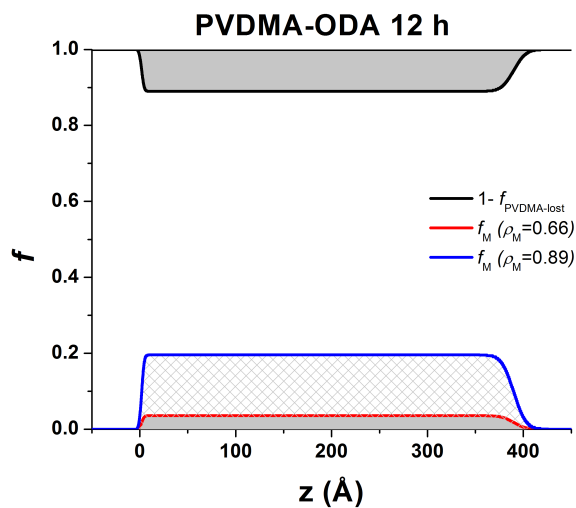


Figure B-28. Converted fraction plot of a PVDMA brush (Sample 3) annealed for 24 h and modified with ODA for 12 h.

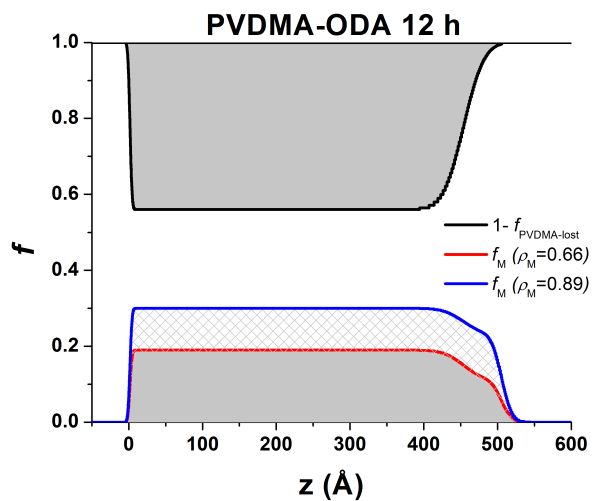


Figure B-29. Converted fraction plot of a PVDMA brush (Sample 4) annealed for 24 h and modified with ODA for 12 h.

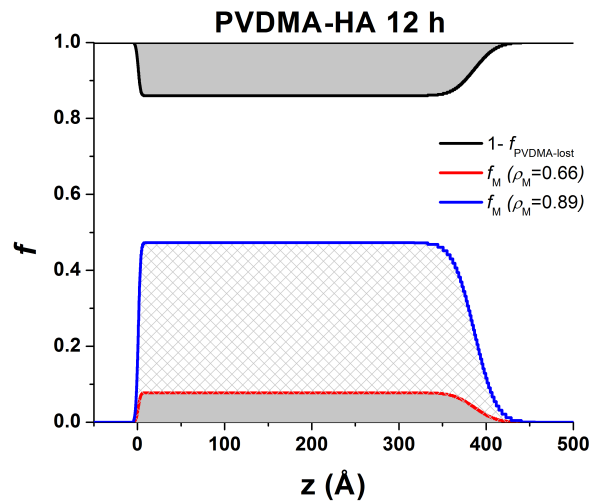


Figure B-30. Converted fraction plot of a PVDMA brush (Sample 5) annealed for 24 h and modified with HA for 12 h.

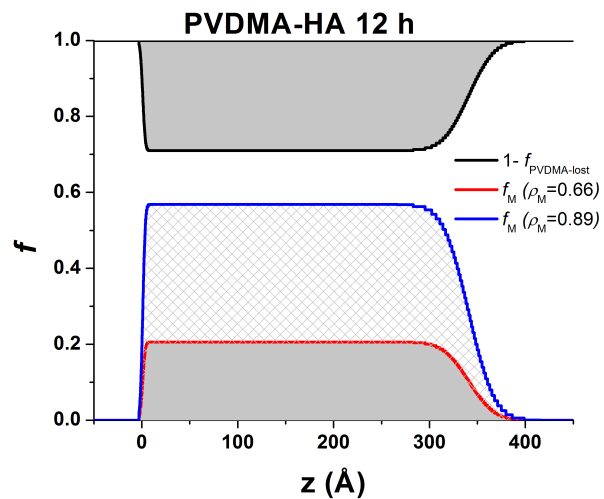


Figure B-31. Converted fraction plot of a PVDMA brush (Sample 6) annealed for 24 h and modified with HA for 12 h.

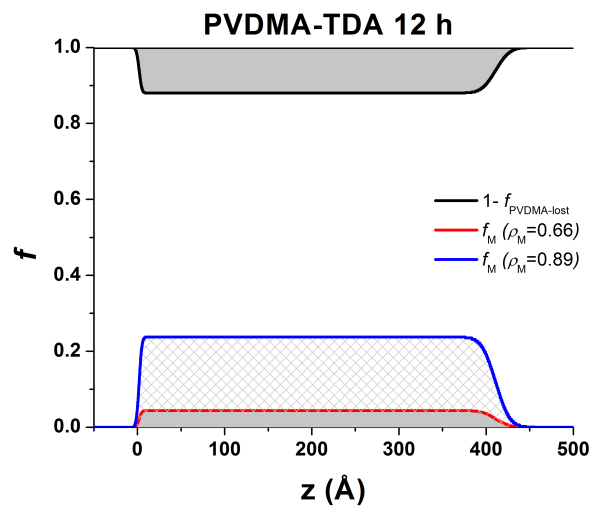


Figure B-32. Converted fraction plot of a PVDMA brush (Sample 1) annealed for 30 h and modified with TDA for 12 h.

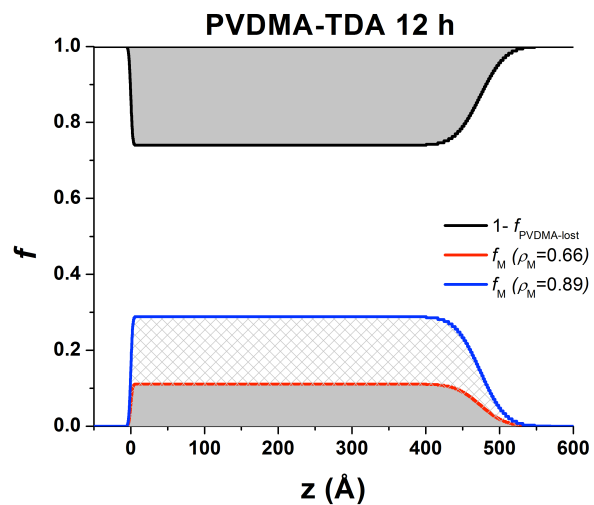


Figure B-33. Converted fraction plot of a PVDMA brush (Sample 2) annealed for 30 h and modified with TDA for 12 h.

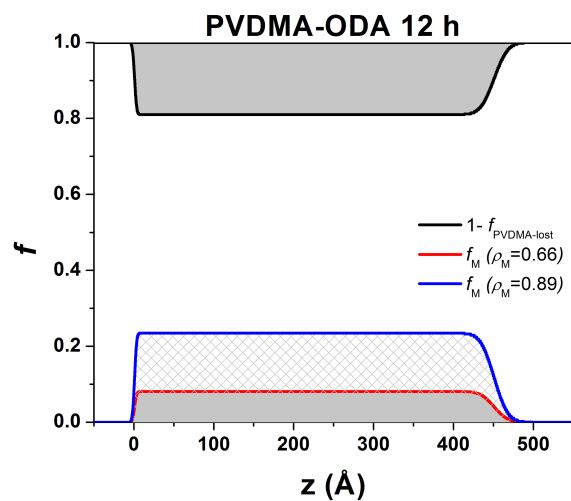


Figure B-34. Converted fraction plot of a PVDMA brush (Sample 3) annealed for 30 h and modified with ODA for 12 h.

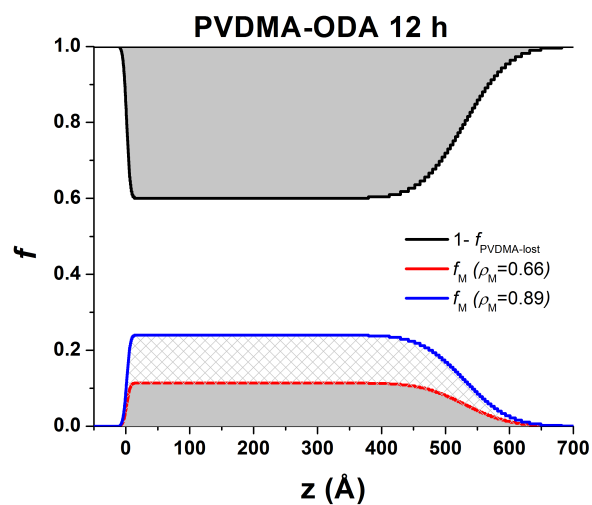


Figure B-35. Converted fraction plot of a PVDMA brush (Sample 4) annealed for 30 h and modified with ODA for 12 h.

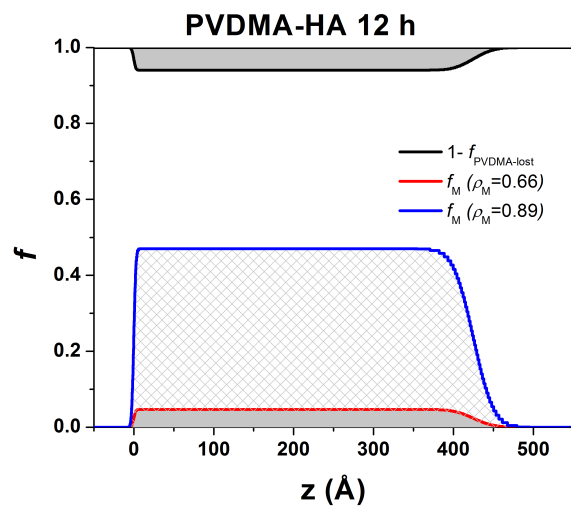


Figure B-36. Converted fraction plot of a PVDMA brush (Sample 5) annealed for 30 h and modified with HA for 12 h.

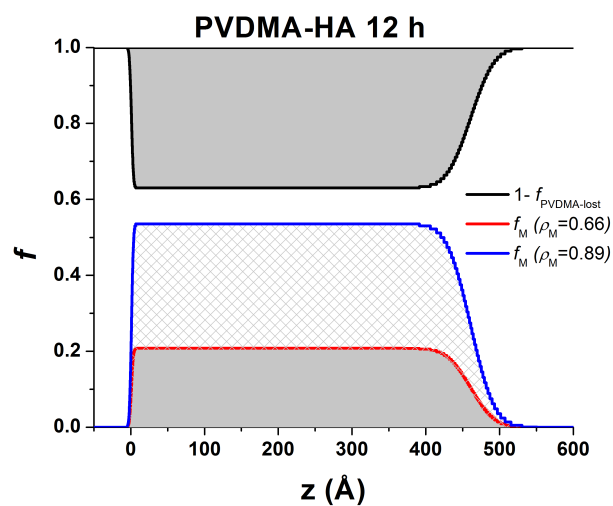
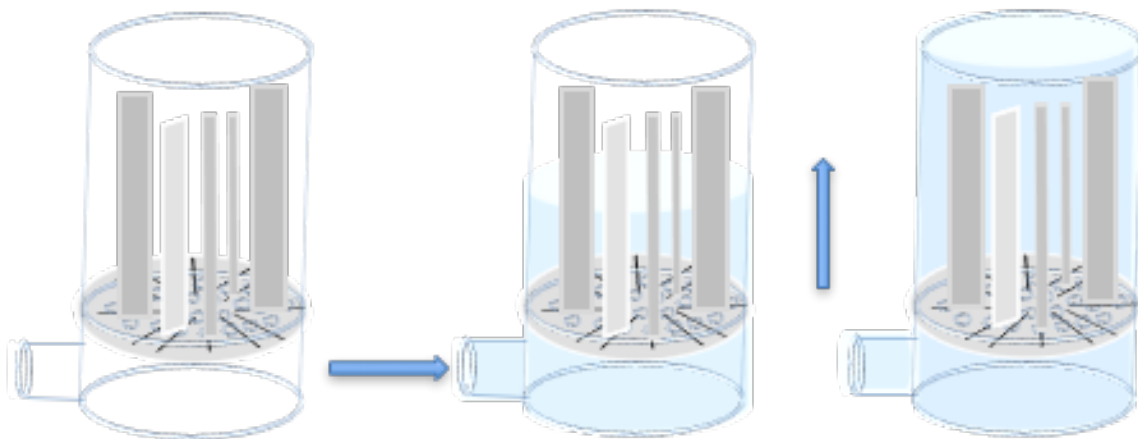


Figure B-37. Converted fraction plot of a PVDMA brush (Sample 6) annealed for 30 h and modified with HA for 12 h.

Appendix C-

Supporting Information for Chapter 4: Functionality Gradients in Poly(2-vinyl-4,4-dimethyl azlactone) (PVDMA) Thin Films Created by *in situ* Modification



Scheme C-1. Schematic of the glass cell apparatus used for gradient preparation process. The surfaces are held vertically with a custom-designed Teflon holder. The rising functionalizing solution gradually immerses the PVDMA-modified surfaces at a controlled rate (mL/h).

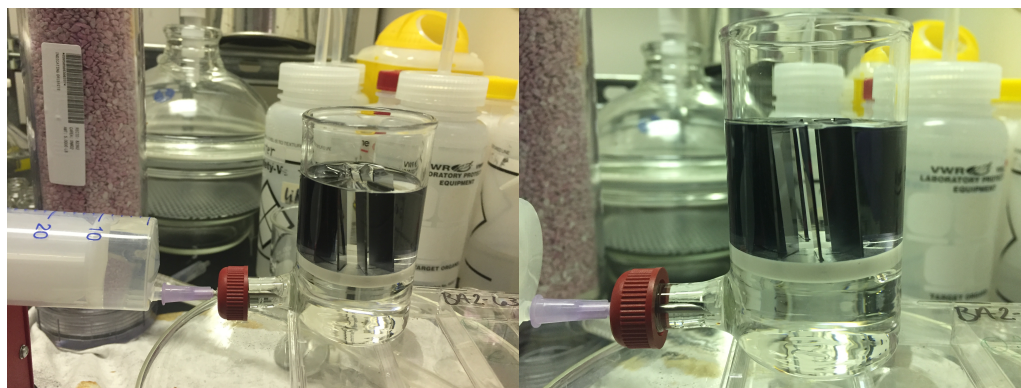


Figure C-1. Images of the fluid cell apparatus with ports for controlled injection.

Table C-1. Characteristic Properties of PVDMA Brushes made by Preferential Assembly of PGMA-b-PVDMA Diblock Copolymer Chains.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹)	H (nm) ^a	σ (chains/nm ²)	R_g (nm)	D (nm)	$D/2R_g$
25,100	9.3 ± 2.2	0.246 ± 0.07	3.42	2.34 ± 0.31	0.34
	26.8 ± 3.6	0.565 ± 0.13	3.42	1.55 ± 0.21	0.23
36,800	9.5 ± 3.8	0.171 ± 0.08	4.26	2.89 ± 0.50	0.34
	27.0 ± 3.2	0.370 ± 0.14	4.26	2.00 ± 0.54	0.24
45,500	9.8 ± 2.8	0.148 ± 0.05	4.83	3.06 ± 0.50	0.32
	25.2 ± 2.5	0.290 ± 0.07	4.84	2.14 ± 0.38	0.22

^a As discussed in Chapter 4, films <10 nm thick are assumed to be brushes, but those that are ~26 nm thick are thin films.

Table C-2. PVDMA Molecular Weight and the Extent of Functionalization across the Gradient Substrate using 12 Hours of Functionalization Time.

$M_{n\text{-PVDMA}}$ (g mol ⁻¹)	FA	$f(\%)^{\text{a}}_{3\text{h}}^{\text{b}}$	$f(\%)_{7\text{h}}$	$f(\%)_{11\text{h}}$
25,100	HA	62.4	68.2	78.0
	ODA	7.5	13.0	13.9
36,800	HA	57.0	71.8	90.4
	TDA	8.3	10.2	14.0
	ODA	5.1	7.8	14.9
	TDA	9.3	15.3	17.8
	ODA	28.9	35.9	38.8

^a Extent of functionalization determined via ellipsometry

^b Subscript gives length of functionalization time (position on surface)

Table C-3. Water contact angles of TDA-modified PVDMA brush surfaces.

<i>Sample</i>	CA_{0h}^a	CA_{2h}	CA_{3h}	CA_{4h}	CA_{5h}
1	67°	-	90°	91°	97°
2	69°	81°	82°	84°	88°
3	69°	84°	85°	87°	96°
4	70°	83°	84°	87°	96°
5	68°	80°	83°	87°	95°

^a subscript indicates the exposure time each specific position was in contact with the TDA solution

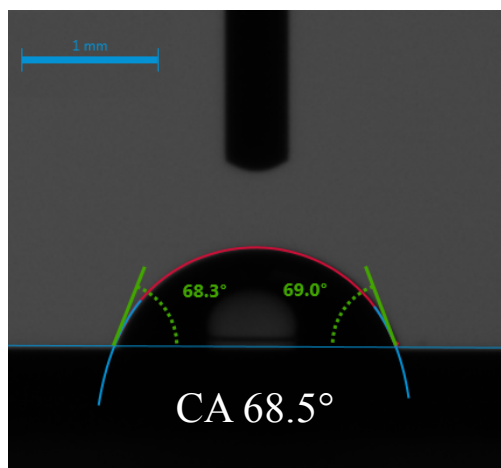


Figure C-2. Sessile drop water contact angle measurements for a PVDMA brush-modified surface.

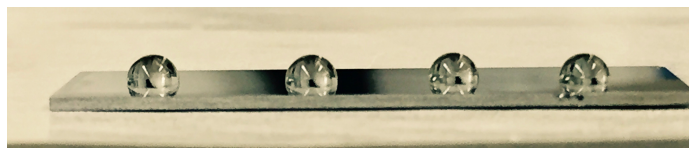


Figure C-3. Image of 5 μ L drops of deionized water along a PVDMA brush-modified surface.

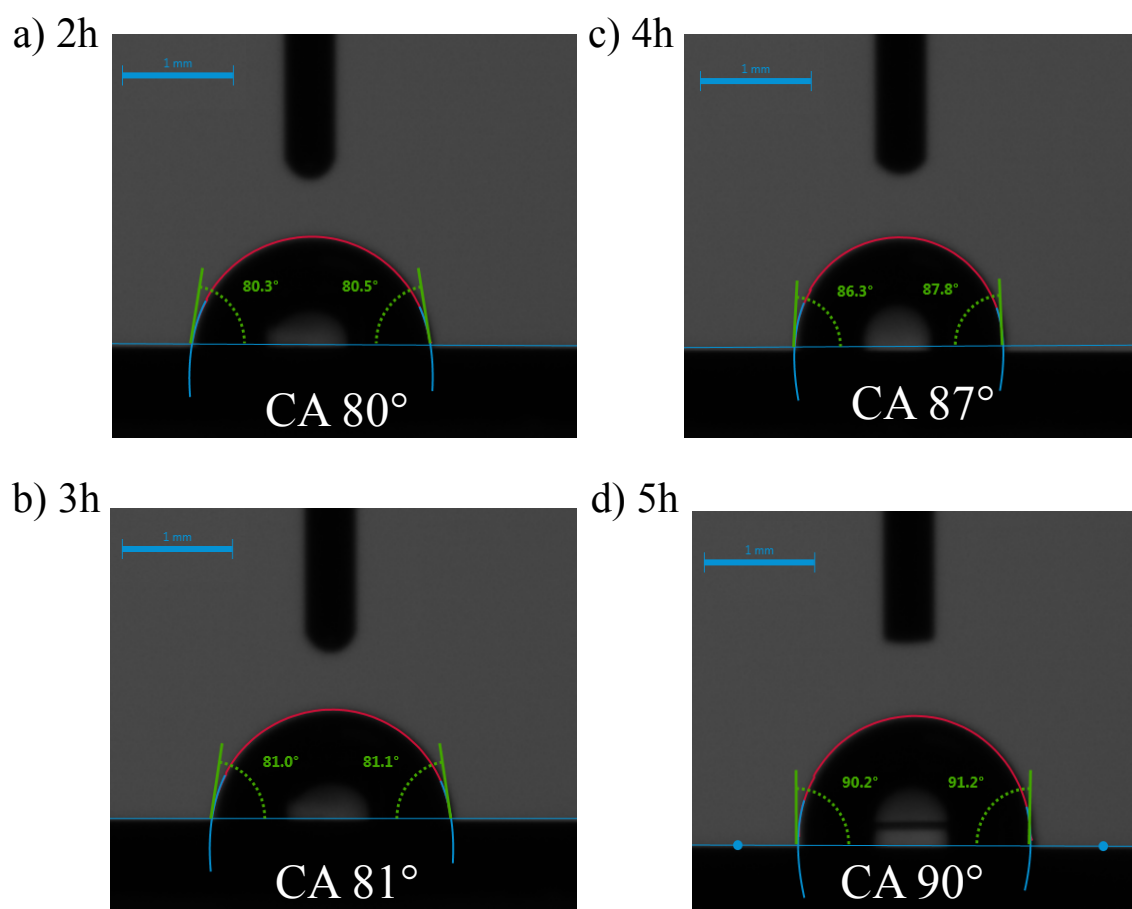


Figure C-4. Water contact angles of TDA-modified PVDMA brush surfaces. Each surface was functionalized by a gradual immersion into a 0.25 wt.% TDA solution over a period of 6 h: a) 2 h amine exposure, b) 3 h, c) 4 h, and d) 5 h.

Vita

Bethany Aden was born and raised in McKenzie, Tennessee. In 2008, she graduated from McKenzie High School. After high school, she enrolled at the University of Tennessee at Martin and graduated Cum Laude in 2012 with a Bachelor of Science degrees in Chemistry and in Cell and Molecular Biology. Bethany served as a Chemistry Teaching Assistant for the Chemistry Department at UT Martin where she taught general chemistry labs. She also conducted research for three years in the TWRA Forensic Lab with Mike Stockdale. In 2011 she was awarded the 2011 Undergraduate ACS Award in Analytical Chemistry. Bethany continued her academic career at the University of Tennessee at Knoxville where she earned her Ph.D. in Polymer Chemistry under the direction of Professor Mike Kilbey. Her research focused on the chemical transformation of reactively modified interfacial thin films. In 2016 she was awarded the Eastman Chemical Summer Fellowship in Polymer Characterization and was awarded the Burchfield Burrige Warner Fellowship in Polymer Chemistry in 2017. Bethany was actively involved with the Commission for Women: STEM Committee, serving as the financial director and she was a co-founder of the student organization, Pipeline: Vols for Women in STEM.