

SYNTHESIS AND CHARACTERIZATION OF NOVEL POLYMERS FOR FUNCTIONAL AND STIMULI RESPONSIVE SILICON SURFACES

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Synthesis and Characterization of Novel Polymers for Functional and Stimuli Responsive Silicon Surfaces

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ABSTRACT

The use of polymers as surface modifiers enables control over many variables such as film thickness, chemical composition and areal density of functional groups. The synthesis of a variety of novel functionalized polymers using living polymerization techniques to achieve functional and stimuli responsive coatings on silica surfaces are described. Since microscopic features on a surface influence the overall wetting properties of the surface, a systematic investigation of the influence of polymer architecture on the microscopic characteristics of the modified surfaces was studied using silane-functionalized linear and novel star-branched polystyrene (PS). Star-branched modifiers provide functional and relatively well-defined model systems for probing surface properties compared to ill-defined highly branched systems and synthetically challenging dendrimers. Using these simple star-shaped macromolecules it was shown that the topographies of the polymer-modified surfaces were influenced by the polymer architecture. A model explaining the observed surface features was proposed.

A living polymerization strategy was also used to synthesize centrally functionalized amphiphilic triblock copolymers, where the central functionalized block covalently anchored the copolymers to silica surfaces. The amphiphilic copolymers exhibited stimuli responsive changes in surface hydrophobicity. In spite of multiple solvent exposures, the copolymer films remained stable on the surface indicating that the observed changes in surface properties were due to selective solvent

induced reversible rearrangement of the copolymer blocks. The chemical composition of the copolymers was tailored in order to tune the response time of the surface anchored polymer chains. Thus, the polymer coatings were used to reversibly change the surface polarities in an on-demand fashion and could find possible applications as smart adhesives, sensors and reusable membrane devices.

In contrast to the afore-mentioned covalent modification approach, which often leads to permanent modification of surfaces, renewable surfaces exhibiting “universal” adhesion properties were also obtained through non-covalent modification. By employing hydrogen bonding interactions between DNA bases, surfaces functionalized with adenine groups were found to reversibly associate with thymine-functionalized polymers. This study describing the solvato-reversible polymer coating was the first demonstration on silica surfaces. A systematic investigation of the influence of surface concentration of the multiple hydrogen bonding groups and their structure on the extent of polymer recognition by the modified surfaces is also presented.

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Table 7-4: Water contact angle and ellipsometric thickness data on thymine-modified silicon/SiO₂ surfaces after treatment with Co-3-19k262

CHAPTER 1: DISSERTATION OVERVIEW

Solid surfaces are often modified with organic thin films in order to improve properties such as wettability, adhesion, and lubricity. The use of polymeric modifiers has become one of the most promising approaches for solid surface modification. With the developments on the synthetic front with respect to achieving polymers with controlled architecture and molecular weights, it is now possible to tailor the properties of the surface through proper choice of the polymeric modifier. Research objectives will focus on the synthesis and characterization of novel linear homopolymers, block copolymers, and star-branched polymers and the subsequent modification of silicon/SiO₂ surfaces with these polymers via covalent as well as non-covalent approaches to design functional and stimuli responsive surfaces.

Chapter two presents a detailed review on solid surface modification with a variety of branched and amphiphilic copolymers. In addition, literature pertaining to surface modification with groups exhibiting non-reversible associations with molecules in solution will be discussed. In the following chapters, the synthesis and surface modification with functionalized polymers will be described.

Chapter three will present results and discussion on the synthesis and characterization of novel star-branched polystyrene (PS) obtained through acid catalyzed hydrolysis and condensation of trimethoxysilane-functionalized linear PS synthesized via *sec*-butyllithium initiated living anionic polymerization of styrene. Silicon/SiO₂ surface modification with the star-branched polymers and the resulting surface properties were characterized using various surface characterization techniques and compared to the results from linear polymers.

Chapter four describes the synthesis and characterization of novel amphiphilic block copolymers used as stimuli responsive coatings on surfaces. The behavior of surfaces covalently modified with these copolymers in response to different solvent treatments was studied using various techniques.

Chapter five describes the utility of non-covalent interactions such as multiple hydrogen bonding between DNA bases adenine and thymine to create stimuli responsive polymer coatings on surfaces. The synthesis and characterization of novel adenine-functionalized surface coupling agent and solvent responsive association between the functionalized surfaces and thymine-functionalized PS will be described. Molecular recognition promoted associations on surfaces as described between the DNA bases in this study is significantly affected by the surface concentration of the molecular recognition groups. Chapter six will discuss a systematic investigation of the influence of surface adenine concentration on polymer recognition of adenine-modified surfaces. The influence of multiple hydrogen bonding groups on the association of adenine-containing copolymers to surfaces functionalized with a novel thymine-functionalized coupling agent will be discussed in chapter seven.

CHAPTER 2: Literature Review

2.1 Introduction to Surface Modification

A thorough knowledge of a material behavior requires a good understanding of the bulk properties of that material. However, this in itself does not give a complete picture of performance. As stated, “pure materials are idealizations of the physicist rather than widely encountered realities.”¹ Most of the materials that we encounter in our day-to-day lives are composed of different phases containing specific interfaces. These interfaces are very important in determining the properties of the bulk; although there usually, are significant differences in properties of the bulk and the interface. Also, the surface structure of a solid material and its chemical composition strongly influences its interfacial properties.¹

Solid surfaces find widespread applications in various fields of materials science. Solid substrates such as metals, metal oxides and inorganic particles are used to make various materials and components for separation substrates for gas and liquid chromatography, substrates for electrophoresis, catalysis, fillers, biosensors, microelectronic devices and pigments.² It is often desirable to modify surfaces in order to tailor properties such as adhesion, wettability, lubricity, biocompatibility, and environmental resistance.³ Surface modification of common organic polymers is also an area that has witnessed widespread interest since the utility of many commercially

¹ Jones, R. A. L.; Richards, R. W., "Polymers at Surfaces and Interfaces." Cambridge University Press: New York, 1999.

² McCarthy, T. J.; Fadeev, A. Y. "Surface Modification Using Hydridosilanes to Prepare Monolayers." US 6331329, **2001**.

³ Claes, M.; Voccia, S.; Detrembleur, C.; Jérôme, C.; Gilbert, B.; Leclère, P.; Geskin, V. M.; Gouttebaron, R.; Hecq, M.; Lazzaroni, R.; Jérôme, R. "Polymer Coating of Steel by a Combination of Electrografting and Atom-Transfer Radical Polymerization." *Macromolecules* **2003**, 36, 5926-5933.

available polymers critically depends on their surface properties to a large extent.^{4,5} The control of surface chemistry as well as topography in the case of polymers, is crucial in many applications including adhesives, coatings and membranes because these influence the wetting, adhesion and optical characteristics of the surface. Thin organic films are often used to control and alter the material properties of a solid surface.

This chapter will discuss the commonly employed techniques for modifying surfaces with polymers, with specific emphasis on a covalent modification approach and on the use of non-covalent but specific associations. The first part will include a discussion on the modification, characterization, and applications of surfaces modified with branched polymers. The second section discuss the covalent modification method to obtaining adaptive surfaces using mixed polymer brushes, which include block copolymers and binary homopolymer mixtures. The last section in this chapter will describe the design of responsive surfaces through molecular recognition promoted association between various molecules and surfaces.

2.2 Surface Modification with Polymers

2.21 Introduction

There are many different ways of chemically modifying surfaces with organic thin films. The most commonly employed surface modification strategies include deposition of self-assembled monolayers/multilayers (SAMs), and Langmuir-Blodgett (LB) films, which typically yield ultrathin films.⁶ LB-techniques in most cases only lead to physical modification of the surface. Covalent modification of surfaces with thin

⁴ Mittal, K. L.; Lee, K.-W., "Polymer Surfaces: Characterization, Modification and Application." VPS: Utrecht, **1997**.

⁵ Garbassi, F.; Morra, M.; Ochiello, E., "Polymer Surfaces: From Physics to Technology." John Wiley & Sons, Ltd. (UK): Chichester, UK, **1998**.

organic films is commonly achieved by the use of SAMs. Well-known examples are thiolates and disulfides on gold, silanes on oxide surfaces, carboxylic acids/phosphates on metal (oxides).⁷

Despite the large number of potential schemes feasible for surface modification, the attachment of polymers to surfaces may be the most promising approach. The commercial availability of a wide variety of polymers and the ability to tune the physical/chemical properties of polymers through suitable synthetic design has given polymer coatings significant advantages over other materials.⁸ Recent studies have shown that polymer films could also serve as effective etching barrier for microlithographic application,⁹ provide excellent mechanical and chemical protection, and alter the chemical and electrical properties of the surface,¹⁰ as well as introduce specific functionalities onto the surface for molecular recognition and sensing applications.¹¹ In addition, polymer films present significantly higher concentration of functional groups compared to those obtained from two-dimensional SAMs.^{12,13} Thus, polymer modified substrates find potential applications in a variety of surface based technologies such as advanced microelectronics, chemical and biosensors, biomimetic

⁶ Ulman, A., "An Introduction to Ultrathin Organic Films." Academic Press: Boston, **1991**.

⁷ Ulman, A. "Formation and Structure of Self-Assembled Monolayers." *Chem. Rev.* **1996**, 96, 1533-1554.

⁸ Yan, M.; Ren, J. "Covalent Immobilization of Ultrathin Polymer Films by Thermal Activation of Perfluorophenyl Azide." *Chem. Mater.* **2004**, 16, 1627-1632.

⁹ Thompson, L. F.; Wilson, C. G.; Bowden, M. J., "Introduction to Microlithography." 2nd ed.; American Chemical Society: Washington DC, **1994**.

¹⁰ Kong, X.; Kawai, T.; Abe, J.; Iyoda, T. "Amphiphilic Polymer Brushes Grown from the Silicon Surface by Atom Transfer Radical Polymerization." *Macromolecules* **2001**, 34, 1837-1844.

¹¹ Yoshizumi, A.; Kanayama, N.; Maehara, Y.; Ide, M. G.; Kitano, H. "Self-Assembled Monolayer of Sugar-Carrying Polymer Chain: Sugar Balls from 2-Methacryloxyethyl D-Glucopyranoside." *Langmuir* **1999**, 15, 482-488.

¹² Yan, M.; Ren, J. "Covalent Immobilization of Ultrathin Polymer Films by Thermal Activation of Perfluorophenyl Azide." *Chem. Mater.* **2004**, 16, 1627-1632.

¹³ Rühle, J., "Polymer Brushes: On the Way to Tailor-Made Surfaces." In *Polymer Brushes*, Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rühle, J., Eds. Wiley-VCH: Weinheim, Germany, **2004**; pp 1-31.

materials and stimuli responsive surfaces/membranes to mention a few.¹⁴ Surface modification with polymers is usually accomplished via physisorption, electrostatic adsorption, or covalent grafting approach.

2.2.2 Physisorption of Polymers onto Surfaces

In physisorption, a polymer is adsorbed onto a surface through preferential physical interactions. For example, the deposition of monomolecular layers of homopolymer and graft/block copolymers occurs through multiple attractive interactions with the underlying substrates. Adsorbed polymers have played determinant role in controlling interparticle interactions and the subsequent properties of colloidal particles, nanocomposites etc. Steric stabilization of colloidal particles through polymer adsorption has been well known in the literature for many decades.¹⁵

Physisorbed systems require some external means of stabilization like crosslinking- otherwise such systems suffer from instability. This is because interaction between the surface and the polymer is too weak since the main attractive forces responsible for such an interaction are the secondary interactions such as van der Waals or hydrogen bonding. Unless desired, such a weak interaction may prompt ready desorption of the polymer in the presence of a good solvent for the anchor or substances, which compete with the anchor for adsorption sites on the surface. The small decrease in the interaction between the polymer and the surface may manifest as a huge change in the physical properties of the surface.¹⁶ The thermal stability of such physically adsorbed

¹⁴ Caster, K. C., "Applications of Polymer Brushes and Other Surface-Attached Polymers." In *Polymer Brushes*, Advincula, R. C.; Brittain, W. J.; Caster, K. C.; R  he, J., Eds. Wiley-VCH: Weinheim, Germany, **2004**; pp 331-371.

¹⁵ Cohen-Stuart, M.; Cosgrove, T.; Vincent, B. "Experimental Aspects of Polymer Adsorption at Solid/Solution Interfaces." *Adv. Colloid Interf. Sci.* **1986**, *24*, 143-239.

¹⁶ Prucker, O.; R  he, J. "Synthesis of Poly(Styrene) Monolayers Attached to High Surface Area Silica Gels through Self-Assembled Monolayers of Azo Initiators." *Macromolecules* **1998**, *31*, 592-601.

systems is usually poor. For example, physisorbed ultrathin polymer films are known to dewet the surfaces on which they are deposited when annealed above their respective glass transition temperatures.^{17, 18} A recent study on a PS-*b*-PI (50:50 w/w) adsorbed onto silica gel showed that dewetting patterns were observed at room temperature after 3 days of storage.¹⁹ The incompatibility between the film thickness and the microdomain dimension was the reason given for observing such patterns. This shows that the adsorbed chains have enough lateral mobility to rearrange on a macroscopic scale thus reflecting the instability such a physisorbed system suffers.

On the other hand, the tethering of polymers to surface through covalent bonding produces a much stronger interaction between the two components. Thus, most of the ongoing research in this direction has concentrated on the grafting of polymers to surfaces. Polymer grafted surfaces is achieved primarily by two techniques, the “grafting to” and the “grafting from” approach, described below.

2.2.3 Polymer Attachment to Surfaces via “Grafting to” Approach

In the “grafting to” approach, preformed end-functionalized polymers or polymers containing functional side chains are reacted with a suitable substrate under appropriate conditions to generate a polymer brush off the surface. The stability of this structure comes from the covalent linkage between the polymer chains and the substrate. Figure 2-1 depicts the formation of end-tethered polymer chains, where the functional groups “A” on the surface react with “B” groups on polymer chain ends.

¹⁷ Yerushalmi-Rozen, R.; Klein, J.; Fetters, L. J. "Suppression of Rupture in Thin, Nonwetting Liquid Films." *Science* **1994**, 263, 793-795.

¹⁸ Reiter, G.; Khanna, R. "Negative Excess Interfacial Entropy between Free and End-Grafted Chemically Identical Polymers." *Phys. Rev. Lett.* **2000**, 85, 5599-5602.

¹⁹ Leonard, D. N.; Russell, D. A.; Smith, S. D.; Spontak, R. J. "Multiscale Dewetting of Low-Molecular-Weight Block Copolymer Ultrathin Films." *Macromol. Rapid Commun.* **2002**, 23, 205-209.

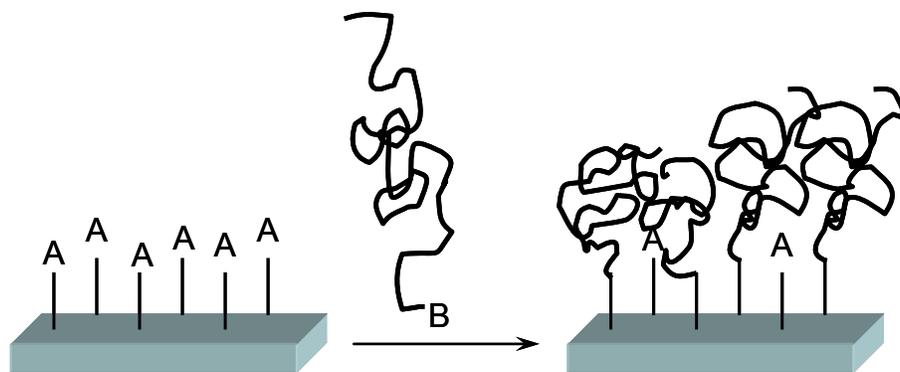


Figure 2-1: “Grafting to” approach depicting the attachment of end-functionalized polymer chains to a surface functionality.

Several different polymerization techniques such as anionic, cationic, conventional/ living free radical, and ring opening/ ring opening metathesis polymerizations were used to obtain a variety of functionalized macromolecules. In addition, the use of living polymerization strategies allow for the synthesis of well-defined polymers with narrow molecular weight distributions leading to polymer films with uniform properties. In addition, it is possible to functionalize the polymer chains with selected functional groups capable of reacting with a surface.²⁰

Although a “grafting to” approach leads to covalently attached polymers it has some drawbacks. The amount of polymer that can be immobilized by this method is typically small due to the steric constraints. The steric hindrance arises because the polymer chains have to diffuse from the solution or the melt through the existing polymer film to reach the reactive sites on the surface. This barrier increases with increasing film thickness. The result is a limiting of the film thickness and grafting density (number of polymer chains grafted per unit area of the surface). In order to circumvent this issue, a “grafting from” approach has been widely used to obtain polymer-modified surfaces.

2.2.4 Polymer Attachment to Surfaces via “Grafting from” Approach

In this method, the polymer chains are directly grown from surface immobilized initiators. The surface attached initiators are obtained by either plasma treatment or covalent immobilization through a self-assembly or LB-technique and followed by in situ surface initiated polymerization as shown in Figure 2-2.²¹

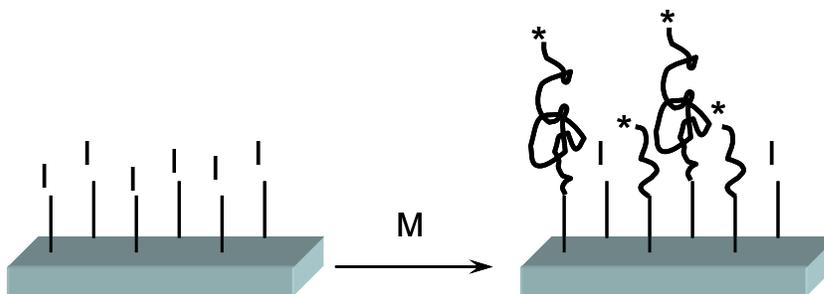


Figure 2-2: “Grafting from” approach depicting the growth of polymer chains from surface attached initiating sites.

Although the generation of initiators by plasma treatment of the surface is simple and convenient,²² it is very difficult to control the initiator type and amount. Thus, very little or no control over the tethered polymer chains usually results. Surface attachment of initiator containing SAMs on the other hand leads to very well defined polymer brush systems. This method of tethering polymer chains has been extensively studied in the past decade. The initiators immobilized on the surface may include those employed for conventional free radical, cationic, anionic, controlled free radical or ring opening polymerizations. Since polymerization proceeds from the surface attached initiators, the growth of polymer chains occurs through monomer diffusion to the active sites, which is

²⁰ Granville, A. M.; Brittain, W. J., "Recent Advances in Polymer Brush Synthesis." In *Polymer Brushes*, Advincula, R. C.; Brittain, W. J.; Caster, K. C.; Rhe, J., Eds. Wiley-VCH: Weinheim, Germany, **2004**; pp 35-50.

²¹ Zhao, B.; Brittain, W. J. "Polymer Brushes: Surface-Immobilized Macromolecules." *Prog. Polym. Sci.* **2000**, *25*, 677-710.

much faster and easier compared to the diffusion of polymer chains through the preformed polymer layer.²³ Thus, the “grafting from” technique gives a very high chain grafting density making it the most popular and well-studied technique for obtaining dense surface tethered polymers. However, there is uncertainty concerning the kinetics of surface initiated polymerizations when compared to corresponding homogeneous solution processes.^{24, 25} Characterization of the molecular weight of surface grafted polymers is not trivial since low chain concentration reduces the accuracy of its calculation. This necessitates the use of spherical particles with high specific surface area followed by grafted chain extraction in order to obtain sufficient material for analysis as well as the use of cleavable junction points with the surface that must also be stable towards the polymerization conditions. Takayuki *et al.* used hydrolyzable ester containing photoiniferters to grow polymer chains on Merrifield resin. Subsequent hydrolysis of the ester groups was used to degraft polymer chains for analysis.²⁶ Brooks and coworkers reported the growth of poly(dimethyl acrylamide) brushes on the surface of PS latex.²⁷ The molecular weight of the grafted chains was determined using SEC following base catalyzed hydrolysis of the polymer chains attached to the particle through an ester linkage. Similarly, Wang *et al.* used atom transfer radical polymerization

²² Ito, Y.; Nishi, S.; Park, Y. S.; Imanishi, Y. "Oxidoreduction-Sensitive Control of Water Permeation through a Polymer Brushes-Grafted Porous Membrane." *J. Am. Chem. Soc.* **1997**, 30, 5856-5859.

²³ Jordan, R.; Ulman, A. "Surface Initiated Living Cationic Polymerization of 2-Oxazolines." *J. Am. Chem. Soc.* **1998**, 120, 243-247.

²⁴ Husemann, M.; Morrison, M.; Benoit, D.; Frommer, J.; Mate, M.; Hinsberg, W. D.; Hedrick, J. L.; Hawker, C. J. "Manipulation of Surface Properties by Patterning of Covalently Bound Polymer Brushes." *J. Am. Chem. Soc.* **2000**, 122, 1844-1845.

²⁵ Wittmer, J. P.; Cates, M. E.; Johnner, A.; Turner, M. S. "Diffusive Growth of a Polymer Layer by in Situ Polymerization." *Europhys. Lett.* **1996**, 33, 397-402.

²⁶ Takayuki, O.; Ogawa, T.; Yamamoto, T. "Solid-Phase Block Copolymer Synthesis by the Iniferter Technique." *Macromolecules* **1986**, 19, 2087-2089.

(ATRP) to grow PMMA and PMMA-*b*-PS on silica surfaces where the silica core was hydrolyzed using HF etch to degraft the polymer chains from the surface.²⁸ In order to obtain controlled polymerization on surfaces, a large excess of free initiators in solution is typically required.²⁹ This leads to large amounts of free polymers in solution leading to considerable wastage of monomers, thereby restricting the use of expensive monomers.

In addition, the polymers formed in this case are not very well defined since surface anchored chains were shown to possess higher polydispersities than the free polymers formed in solution. Matyjaszewski and coworkers used simulations to show that for moderate density of surface attached initiators, the chain distribution gets broader with polymerization time for surface initiated polymerizations that involve one type of reactive chain end (as that encountered in anionic polymerization).³⁰ This effect was found to be more pronounced at higher densities of the initiating sites on the surface. The simulation also showed that the chain end distribution within the polymer films became more diffuse indicating the non-uniform growth of the chains.

2.2.5 Electrostatic Adsorption of Polymers onto Surfaces

Another commonly used approach for obtaining polymer films on the surface is electrostatic adsorption as shown in Figure 2-3. In this technique, surfaces are treated

²⁷ Goodman, D.; Kizakkedathu, J. N.; Brooks, D. E. "Evaluation of an Atomic Force Microscopy Pull-Off Method for Measuring Molecular Weight and Polydispersity of Polymer Brushes: Effect of Grafting Density." *Langmuir* **2004**, *20*, 6238-6245.

²⁸ Wang, Y.-P.; Pei, X.-W.; He, X.-Y.; Yuan, K. "Synthesis of Well-Defined, Polymer-Grafted Silica Nanoparticles via Reverse Atrp." *Eur. Polym. J.* **2005**, *41*, 1326-1332.

²⁹ Blomberg, S.; Ostberg, S.; Harth, E.; Bosman, A. W.; Van Horn, N.; Hawker, C. J. "Production of Crosslinked, Hollow Nanoparticles by Surface-Initiated Living Free-Radical Polymerization." *J. Polym. Sci., Part A: Polym. Chem.* **2002**, *40*, 1309-1320.

³⁰ Matyjaszewski, K.; Miller, P. J.; Shukla, N.; Immaraporn, B.; Gelman, A.; Luokala, B. B.; Siclovan, T. M.; Kickelbick, G.; Vallant, T.; Hoffmann, H.; Pakula, T. "Polymers at Interfaces: Using Atom Transfer Radical Polymerization in the Controlled Growth of Homopolymers and Block Copolymers from Silicon Surfaces in the Absence of Untethered Sacrificial Initiator." *Macromolecules* **1999**, *32*, 8716-8724.

with solutions of oppositely charged polyelectrolytes in a sequential manner.³¹ The deposition of the first layer of polymer film occurs through electrostatic/hydrophobic interactions following which a second oppositely charged polymer layer is deposited. Repetition of this process generates successive layers of oppositely charged polymeric layers and therefore this is known as the layer-by-layer (LBL) technique.

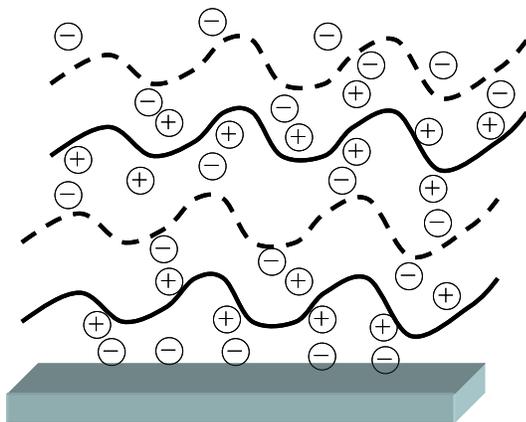


Figure 2-3: LBL deposition of alternating layers of anionic and cationic polyelectrolyte multilayers on charged surfaces.

The ability to construct highly ordered polymer thin films incorporating a variety of functional groups using a very simple solution deposition route has made this approach very promising for obtaining functionalized surfaces for use in many devices.³² The seminal work in this field was published by Decher in 1991. Due to the nature of deposition, it is possible to tune the thickness of the polymer films formed on the surface, which is not possible with adsorbed neutral polymers.³³ Following the original work of Decher *et al.*, several groups have reported the modification of solid substrates as well as

³¹ Hammond, P. T. "Recent Explorations in Electrostatic Multilayer Thin Films." *Curr. Opin. Colloid Interface Sci.* **1999**, 4, 430-442.

³² Gittins, D. I.; Caruso, F. "Tailoring the Polyelectrolyte Coating of Nanoparticles." *J. Phys. Chem. B* **2001**, 105, 6846-6852.

³³ Decher, G. "Fuzzy Nanoassemblies: Toward Layered Polymeric Multicomposites." *Science* **1997**, 277, 277-282.

nanoparticles with polyelectrolyte multilayers.^{34, 35, 36} But stability of the multilayer films depended on many factors such as the ionic strength, solvent, pH of the deposition solution, temperature, concentration of the charged species, etc. Thus, in recent years many studies were aimed at constructing stable multilayer films using covalent crosslinking between the layers to enhance the mechanical strength of the films.³⁷

2.2.6 Conformations of Surface Attached Polymer Chains

Polymers that are end-tethered to surfaces show many different morphologies depending on the solvent and the density of grafting.³⁸ Two commonly encountered polymer chain structures on surfaces include “mushrooms” (Figure 2-4a) and “brushes” (Figure 2-4b).

In the mushroom conformation, the distance between the grafted polymer chains is greater than or equal to the typical chain dimension (R_g). In the brush conformation, however, the distance between the grafted chains is less than R_g and as a result, the chains stretch away from the surface in order to prevent overlapping with the neighboring chains.

³⁴ Fou, A. C.; Rubner, M. F. "Molecular-Level Processing of Conjugated Polymers. 1. Layer-by-Layer Manipulation of Conjugated Polyions." *Macromolecules* **1995**, 28, 7107-7114.

³⁵ Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. "1. Ultrathin Multilayer Polyelectrolyte Films on Gold: Construction and Thickness Determination." *Langmuir* **1997**, 13, 3422-3426, Caruso, F.; Niikura, K.; Furlong, D. N.; Okahata, Y. "2. Assembly of Alternating Polyelectrolyte and Protein Multilayer Films for Immunosensing." *Langmuir* **1997**, 13, 3427-3433.

³⁶ Clark, S. L.; Montague, M. F.; Hammond, P. T. "Ionic Effects of Sodium Chloride on the Templated Deposition of Polyelectrolytes Using Layer-by-Layer Ionic Assembly." *Macromolecules* **1997**, 30, 7237-7244.

³⁷ Sun, J.; Wu, T.; Liu, F.; Wang, Z.; Zhang, X.; Shen, J. "Covalently Attached Multilayer Assemblies by Sequential Adsorption of Polycationic Diazo-Resins and Polyanionic Poly(Acrylic Acid)." *Langmuir* **2000**, 16, 4620-4624.

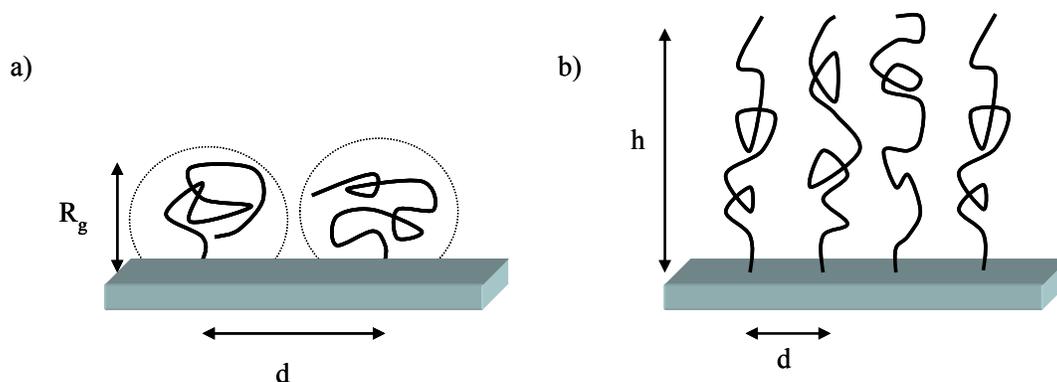


Figure 2-4: Depiction of polymer chains in the mushroom conformation (a), and the brush conformation (b).

The average distance between grafted chains (d) is shown in equation 1.³⁹

$$d = (\sigma)^{-1/2} = (M_n / h * N_A * \rho)^{1/2} \dots\dots\dots (1)$$

where, σ , M_n , h , ρ , and N_A refer to the grafting density (chains/nm²), number average molecular weight of the grafted polymer chains (g/mol), dry thickness of the grafted layer (nm), polymer bulk density (g/cc), and Avogadro number, respectively. The commonly used qualitative criteria for determining conformations of grafted polymer chains are as shown in equations 2a and 2b:

$$\text{Mushroom region: } d \geq 2R_g \dots\dots\dots (2a)$$

$$\text{Brush region: } d \leq 2R_g \dots\dots\dots (2b)$$

The stretching of chains is an entropically unfavorable process. However, this is compensated by the enthalpic change associated with the favorable interaction between the polymer chains and the surface. This behavior of the surface attached polymer chains is in contrast to the random walk configurations adopted by the chains in solution. This deformation of the chain conformation is responsible for the many novel properties

³⁸ Koutsos, V.; Van der Vegte, E. W.; Hadziioannou, G. "Direct View of Structural Regimes of End-Grafted Polymer Monolayers: A Scanning Force Microscopy Study." *Macromolecules* **1999**, 32, 1233-1236.

exhibited by the polymer brushes; thus, in recent years there have been many studies on surface modification with polymer brushes.

2.3 Surface Modification with Branched Polymers

2.3.1 Introduction

In terms of chemical compositions, polymers attached to surfaces include homopolymers (both neutral and charged), mixed homopolymers, block copolymers, random copolymers, and graft copolymers.⁴⁰ Depending on topology, polymer chains attached to surfaces may be classified as linear or branched polymers. Several studies have described the covalent modification of surfaces with a variety of linear polymers both using the “grafting to” and the “grafting from” approaches.⁴¹

In recent years, a number of studies involved the use of branched polymers as surface modifiers. Branched polymers have attracted considerable interest due to their low intrinsic viscosity and high solubility. In addition, the high density of functional groups in branched polymers make them attractive candidates for chemical sensors, drug delivery agents, nanoscale catalysts, and smart adhesives. Branched polymers that were used for surface modification include dendrons/dendrimers, comb polymers, hyperbranched/highly branched polymers and star-branched polymers.

2.3.2 Surface Modification with Dendrimers

Dendrimers, which are highly functionalized monodisperse and three-dimensional macromolecules, have generated widespread attention as catalysts, drug delivery agents,

³⁹ Milner, S. T. "Polymer Brushes." *Science* **1991**, 251, 905-914.

⁴⁰ Zhao, B.; Brittain, W. J. "Polymer Brushes: Surface-Immobilized Macromolecules." *Prog. Polym. Sci.* **2000**, 25, 677-710.

⁴¹ Advincula, R. C.; Brittain, W. J.; Caster, K. C.; R uhe, J., "Polymer Brushes." Wiley-VCH: Weinheim, **2004**; p 483.

and sensors.⁴² Several earlier studies have reported the noncovalent immobilization of dendrimers to surfaces. Watanabe and Regan used the LBL technique to assemble multilayers of amine-terminated dendrimers with Pt²⁺ coated on aminopropylsilane functionalized silicon/SiO₂ surfaces.⁴³ Tsukruk *et al.* constructed multilayers of oppositely charged poly(amidoamine) (PAMAM) dendrimers on silicon surfaces and visualized the surface topography using scanning probe microscopy.⁴⁴ Crooks and coworkers assembled different generation PAMAM dendrimers on gold surfaces and used AFM to study the dendrimer desorption upon exposure to ethanolic solutions of hexadecanethiol.⁴⁵ Prolonged exposure to hexadecanethiol solution was found to remove the dendrimers from the surface. PAMAM dendrimers adsorbed onto mica surfaces were also imaged using AFM. Depending on the dendrimer concentration used in the adsorption solution, individual dendrimers to monolayer films of PAMAM were observed.⁴⁶ PAMAM dendrimers of various generations and terminated with either carboxylate or amino groups were respectively adsorbed onto alumina or silica surfaces.⁴⁷ The amount of dendrimer adsorbed onto the surface increased with the generation number. PAMAM dendrimers were also used to stabilize gold nanoparticles prepared in

⁴² Tully, D. C.; Fréchet, J. M. J. "Dendrimers at Surfaces and Interfaces: Chemistry and Applications." *Chem. Commun.* **2001**, 14, 1229-1239.

⁴³ Watanabe, S.; Regan, S. L. "Dendrimers as Building Blocks for Multilayer Construction." *J. Am. Chem. Soc.* **1994**, 119, 8855-8856.

⁴⁴ Tsukruk, V. V.; Rinderspacher, F.; Bliznyuk, V. N. "Self-Assembled Multilayer Films from Dendrimers." *Langmuir* **1997**, 13, 2171-2176.

⁴⁵ Hierlemann, A.; Campbell, J. K.; Baker, L. A.; Crooks, R. M.; Ricco, A. J. "Structural Distortion of Dendrimers on Gold Surfaces: A Tapping-Mode AFM Investigation." *J. Am. Chem. Soc.* **1998**, 120, 5323-5324.

⁴⁶ Li, J.; Piehler, L. T.; Qin, D.; Baker Jr., J. R.; Tomalia, D. A. "Visualization and Characterization of Poly(Amidoamine) Dendrimers by Atomic Force Microscopy." *Langmuir* **2000**, 16, 5613-5616.

⁴⁷ Esuni, K.; Goino, M. "Adsorption of Poly(Amidoamine) Dendrimers on Alumina/Water and Silica/Water Interfaces." *Langmuir* **1998**, 14, 4466-4470.

solution through the reduction of HAuCl_4 .⁴⁸ The dendrimer/gold nanocomposite solutions were stable for extended periods and were isolated as solids.

PAMAM dendrimers terminated with amine and hydroxyl groups were assembled onto gold surfaces through polydentate interactions. Using electrochemical impedance measurements it was shown that dendrimers of lower generations formed highly porous structures while at higher generations, the dendrimer layer became impervious to electroactive species, $\text{Fe}(\text{CN})_6^{3-}$.⁴⁹ The availability of the non-bonded functional groups of the dendrimers for coordination with external reactants was demonstrated using amidation reaction between the amine groups and an acid chloride in solution. The rearrangement of the surface bound dendrimers upon immersion in a thiol solution was also examined. Using the LBL technique, a covalently linked Gantrez[®] (a copolymer of maleic anhydride and methyl vinyl ether) and PAMAM composite film was constructed on a PAMAM coated gold surface to form a pH switchable anionic and cationic redox-active film.⁵⁰

Use of PAMAM dendrimers as adhesion promoters between SiO_2 /glass surfaces and vapor deposited gold films was also investigated.⁵¹ Peel analysis showed that the stability of the gold films deposited on dendrimer coated SiO_2 /glass surface increased with dendrimer generation number. Earlier, Zawodzinski and coworkers had employed

⁴⁸ Garcia, M. E.; Baker, L. A.; Crooks, R. M. "Preparation and Characterization of Dendrimer-Gold Colloid Nanocomposites." *Anal. Chem.* **1999**, 71, 256-258.

⁴⁹ Tokuhisa, H.; Zhao, M.; Baker, L. A.; Phan, V. T.; Dermody, D. L.; Garcia, M. E.; Peez, R. F.; Crooks, R. M.; Mayer, T. M. "Preparation and Characterization of Dendrimer Monolayers and Dendrimer-Alkanethiol Mixed Monolayers Adsorbed to Gold." *J. Am. Chem. Soc.* **1998**, 120, 4492-4501.

⁵⁰ Liu, Y.; Zhao, M.; Bergbreiter, D. E.; Crooks, R. M. "pH-Switchable, Ultrathin Permselective Membranes Prepared from Multilayer Polymer Composites." *J. Am. Chem. Soc.* **1997**, 119, 8720-8721.

⁵¹ Baker, L. A.; Zamborini, F. P.; Sun, L.; Crooks, R. M. "Dendrimer-Mediated Adhesion between Vapor-Deposited Au and Glass or Si Wafers." *Anal. Chem.* **1999**, 71, 4403-4406.

amine terminated starburst dendrimers as adhesion promoters for gold to silicon/glass/tin oxide surfaces.⁵²

Polyether-based dendrons were adsorbed onto iron sulfide clusters and the electroactivity of the dendrons-modified clusters was analyzed as a function of the dendron generation number.⁵³ Terminal ferrocene functionalized silicon dendrimers assembled on Pt and indium tin oxide electrodes gave reproducible and stable electrochemical signal without any detectable loss of the surface bound dendrimer molecules over time.⁵⁴ This indicated strong interaction between the dendrimer and the electrode surfaces. Similarly Takada *et al.* modified Pt electrode surfaces with ferrocene functionalized diaminobutane-*dend*-(NHCOFc)_n and observed that the dendrimer monolayer was firmly attached to the surface while multilayers were easily removed upon reduction. AFM analysis indicated that upon adsorption onto the electrode surfaces the dendrimers flattened out.⁵⁵ Fréchet and coworkers ionically assembled carboxylic acid functionalized poly(benzylether) dendrimers onto aminopropylsilane-modified silicon/SiO₂ surfaces for use as either positive or negative tone photoresists.⁵⁶

⁵² Godínez, L. A.; Lin, J.; Muñoz, M.; Coleman, A. W.; Rubin, R.; Parikh, A.; Zawodzinski Jr., T.; Loveday, D.; Ferraris, J. P.; Kaifer, A. E. "Multilayer Self-Assembly of Amphiphilic Cyclodextrin Hosts on Bare and Modified Gold Substrates: Controlling Aggregation Via Surface Modification." *Langmuir* **1998**, *14*, 137-144.

⁵³ Gorman, C. B.; Parkhurst, B. L.; Su, W. Y.; Chen, K.-Y. "Encapsulated Electroactive Molecules Based Upon an Inorganic Cluster Surrounded by Dendron Ligands." *J. Am. Chem. Soc.* **1997**, *119*, 1141-1142.

⁵⁴ Alonso, B.; Morán, M.; Casado, C. M.; Lobete, F.; Losada, J.; Cuadrado, I. "Electrodes Modified with Electroactive Films of Organometallic Dendrimers." *Chem. Mater.* **1995**, *7*, 1440-1442.

⁵⁵ Takada, K.; Díaz, D. J.; Abruña, H. D.; Cuadrado, I.; Casado, C.; Alonso, B.; Morán, M.; Losada, J. "Redox-Active Ferrocenyl Dendrimers: Thermodynamics and Kinetics of Adsorption, in-Situ Electrochemical Quartz Crystal Microbalance Study of the Redox Process and Tapping Mode Afm Imaging." *J. Am. Chem. Soc.* **1997**, *119*, 10763-10773.

⁵⁶ Tully, D. C.; Trimble, A. R.; Fréchet, J. M. J.; Wilder, K.; Quate, C., F. "Synthesis and Preparation of Ionically Bound Dendrimer Monolayers and Application toward Scanning Probe Lithography." *Chem. Mater.* **1999**, *11*, 2892-2898.

Assembly of carbosilane dendrimers containing mesogenic (Frey *et al.*)⁵⁷ and hydroxyl groups (Sheiko *et al.*)⁵⁸ onto mica surfaces were reported. Sheiko and coworkers studied the wetting behavior of carbosilane dendrimers terminated with hydroxyl groups and adsorbed onto native and semifluorinated mica surfaces using contact angle microscopy. Cai and coworkers imaged mica surfaces modified with physisorbed carbosilane dendrimers containing a large number of SiCl₃ groups, which upon annealing formed robust crosslinked films.

Many studies have also described the covalent immobilization of dendrimers to solid surfaces. Combining the attractive properties of dendrimers with the stability of covalent linkages leads to robust multifunctional organic thin films. Wells and Crooks were the first to report the covalent attachment of PAMAM dendrimers to mercaptoundecanoic acid (MUA) SAM functionalized gold surfaces through the formation of amide bonds.⁵⁹ FTIR was used to confirm the covalent immobilization of the dendrimers to the surfaces and the functionalization of the free amino groups with methyl acrylate to form methyl ester terminated dendrimers. The surface anchored dendrimers exhibited rapid and reversible response to volatile organic compounds (VOCs), with acid vapors showing maximum binding affinity. Likewise, Tokuhisa and Crooks reported the attachment of poly(iminopropane-1,3-diyl) dendrimer containing 64 terminal amino groups to gold surfaces modified with a mixture of MUA and

⁵⁷ Coen, M. C.; Lorenz, K.; Kressler, J.; Frey, H.; Mülhaupt, R. "Mono- and Multilayers of Mesogen-Substituted Carbosilane Dendrimers on Mica." *Macromolecules* **1996**, *29*, 8069-8076.

⁵⁸ Sheiko, S. S.; Muzafarov, A. M.; Winkler, R. G.; Getmanova, E. V.; Eckert, G.; Reineker, P. "Contact Angle Microscopy on a Carbosilane Dendrimer with Hydroxyl End Groups: Method for Mesoscopic Characterization of the Surface Structure." *Langmuir* **1997**, *13*, 4172-4181.

⁵⁹ Wells, M.; Crooks, R. M. "Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 10. Preparation and Properties of Chemically Sensitive Dendrimer Surfaces." *J. Am. Chem. Soc.* **1996**, *118*, 3988-3989.

mercaptopentane.⁶⁰ The reactivity of the surface bound dendrimers to benzoyl chloride was studied using FTIR and VOC dosing experiments were carried out to evaluate the performance of the dendrimer coated surfaces as sensors. The dendrimers either were prefunctionalized before immobilization on gold or were functionalized following immobilization. The prefunctionalized dendrimer coated surfaces were better sensors for planar analytes such as benzene compared to dendrimer coated surfaces that were functionalized following surface attachment.

Gorman *et al.* immobilized focally functionalized organothiol containing generations 1-3 (G1-G3) poly(benzyl ether) dendrons on gold surfaces. The porosity of the films evaluated using cyclic voltammetry, capacitance measurements, and small molecule trapping experiments indicated that the G3 dendron grafted surfaces were the most permeable.⁶¹ Fréchet and coworkers modified silicon/SiO₂ surfaces with monochlorosilane functionalized poly(benzyl ether) dendrons.⁶² Scanning probe lithography was used to generate patterns on the dendrimer-modified surfaces. A positive voltage applied to the surface led to degradation of the monolayer along with the electrochemical oxidation of the underlying silicon substrate that resulted in oxide relief features in the patterned region. The surfaces were subsequently immersed in HF, where the surface attached dendrimers resisted the HF attack, while the oxide relief features were easily removed generating positive patterns on the surface.

⁶⁰ Tokuhisa, H.; Crooks, R. M. "Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 12. Two New Methods for Surface-Immobilization and Functionalization of Chemically Sensitive Dendrimer Surfaces." *Langmuir* **1997**, 13, 5608-5612.

⁶¹ Gorman, C. B.; Miller, R. L.; Chen, K.-Y.; Bishop, A. R.; Haasch, R. T.; Nuzzo, R. G. "Semipermeable, Chemisorbed Adlayers of Focally-Substituted Organothiol Dendrons on Gold." *Langmuir* **1998**, 14, 3312-3319.

Covalent modification of silicon/SiO₂ surfaces with composite films of Gantrez[®] and hydroxylamine terminated PAMAM dendrimer was achieved through the LBL technique.⁶³ First, an aminosilylated silica surface was reacted with Gantrez[®] to give a surface immobilized copolymer film, which was crosslinked by reaction with PAMAM dendrimer and the process was repeated to obtain a composite film. Thermal annealing of the composite film resulted in further crosslinking through imidization and retro-Michael/Michael reactions making them impervious to ion passage. Therefore, following hydrophobic modification, these films served as effective corrosion resistant coatings for aluminum coated silicon surfaces in alkaline and neutral media. Fujiki and coworkers reported the growth of PAMAM dendrimer from amino-modified silica surface.⁶⁴ Reaction of the surface amino groups with methyl acrylate and subsequent amidation of the methyl ester groups using ethylenediamine/hexamethylenediamine resulted in the growth and propagation of the surface bound dendrimers. Light scattering measurements indicated that the size of the silica particles increased with the generation number of the grafted dendrimer. However, the grafted dendrimers were not effective in preventing aggregation of the silica nanoparticles.

Badyal and coworkers described a universal approach for the immobilization of PAMAM dendrimers onto solid surfaces such as glass and polypropylene (PP).⁶⁵ The amine groups of the dendrimer was reacted with the anhydride groups of a maleic

⁶² Tully, D. C.; Wilder, K.; Freché, J. M. J.; Trimble, A. R.; Quate, C., F. "Dendrimer-Based Self-Assembled Monolayers as Resists for Scanning Probe Lithography." *Adv. Mater.* **1999**, 11, 314-318.

⁶³ Zhao, M.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. "Preparation of Highly Impermeable Hyperbranched Polymer Thin-Film Coatings Using Dendrimers First as Building Blocks and Then as in Situ Thermosetting Agents." *J. Am. Chem. Soc.* **1999**, 121, 923-930.

⁶⁴ Fujiki, K.; Sakamoto, M.; Sato, T.; Tsubokawa, N. "Postgrafting of Hyperbranched Dendritic Polymer from Terminal Amino Groups of Polymer Chains Grafted onto Silica Surface." *J. Macromol. Sci., Pure Appl. Chem.* **2000**, A37, 357-377.

anhydride coating that was plasma polymerized onto glass/PP. The adhesion between two maleic anhydride plasma polymer coated PP surfaces, which were further modified with the PAMAM dendrimer, was evaluated using lap shear measurements. Dendrimer sandwiched PP surfaces showed enhanced adhesion following annealing which promoted crosslinking between the dendrimer amino groups and the polymer anhydride groups. Negligible adhesion was observed between PP surfaces without any dendrimer coating. Surface bound dendrimers sandwiched between maleic anhydride plasma polymer coated PP sheets also showed enhanced gas barrier properties compared to untreated PP.

PAMAM dendrimers were also used to construct thickness “tunable” enzyme/dendrimer multilayer thin films on gold surfaces for use as biosensors. The LBL technique was used to construct multilayers of G4 PAMAM dendrimer and glucose oxidase (GOx).⁶⁶ First, the enzyme was covalently immobilized onto cystamine functionalized gold surfaces through imine formation between the surface amino groups and aldehyde groups on the enzyme surface. Further reaction of the enzyme aldehyde groups with the dendrimer amino groups resulted in the formation of a layer of enzyme/dendrimer composite. Repetition of this process yielded the biocomposite film. The sensitivity of the enzyme/dendrimer composite film towards glucose was measured using voltammetry and was found to increase with increasing number of layers.

Functionalized dendrons containing surface reactive functionalities were also used to control the density of functional groups deposited on various surfaces. The surface

⁶⁵ Fail, C. A.; Evenson, S. A.; Ward, L. J.; Schofield, W. C. E.; Badyal, J. P. S. "Controlled Attachment of PAMAM Dendrimers to Solid Surfaces." *Langmuir* **2002**, 18, 264-268.

⁶⁶ Yoon, H. C.; Kim, H.-S. "Multilayered Assembly of Dendrimers with Enzymes on Gold: Thickness-Controlled Biosensing Interface." *Anal. Chem.* **2000**, 72, 922-926.

density of the functional groups was tuned by varying the dendron generation number.⁶⁷ Chechik and Crooks assembled G4 PAMAM dendrimer where either part or all of the peripheral amino groups were replaced with thiol groups. Following deposition on gold surfaces, XPS revealed that dendrimers partially functionalized with the thiol groups interacted with the surface through all the available thiol groups.⁶⁸ This indicated that the surface adsorbed dendrimer molecules were flexible towards rearrangement. Similarly, formation of stable water soluble gold nanoparticles in the presence of the multidentate G4 dendrimer was described. Reinhoudt and coworkers used cyclic voltammetry to study the assembly of ferrocene-modified poly(propyleneimine) dendritic multidisulfides onto gold surfaces.⁶⁹ Direct self-assembly of G0-G4 dendrons resulted in a flattened orientation of the molecules, while when transferred as an LB-film, a dense, close packed structure was observed.

Cai and coworkers reported the deposition of terminal bromomethylated carbosilane dendrons containing multiple thiol groups onto gold⁷⁰ and multiple allylic⁷¹/chlorosilane⁷² groups respectively onto oxidized/hydrogen passivated silicon surfaces. Following deposition, palladium catalyzed Heck reaction between the terminal

⁶⁷ Xiao, Z.; Cai, C.; Mayeux, A.; Milenkovic, A. "The First Organosiloxane Thin Films Derived from SiCl₃-Terminated Dendrons. Thickness-Dependent Nano and Mesoscopic Structures of the Films Deposited on Mica by Spin-Coating." *Langmuir* **2002**, 18, 7728-7739.

⁶⁸ Chechik, C.; Crooks, R. M. "Monolayers of Thiol-Terminated Dendrimers on the Surface of Planar and Colloidal Gold." *Langmuir* **1999**, 15, 6364-6369.

⁶⁹ Liebau, M.; Janssen, H. M.; Inoue, H.; Shinkai, S.; Huskens, J.; Sijbesma, R. P.; Meijer, E. W.; Reinhoudt, D. N. "Preparation of Dendritic Multisulfides and Their Assembly on Air/Water Interfaces and Gold Surfaces." *Langmuir* **2002**, 18, 674-682.

⁷⁰ Yam, C. M.; Cho, J.; Cai, C. "Preparation, Characterization, and Heck Reaction of Multidentate Thiolate Films on Gold Surfaces." *Langmuir* **2003**, 19, 6862-6868.

⁷¹ Yam, C. M.; Cho, J.; Cai, C. "Preparation and Heck Reaction of Multidentate Carbosilane Films Derived from Focally Functionalized and Allyl-Terminated Dendrons on Hydrogen-Terminated Silicon(111) Surfaces." *Langmuir* **2004**, 20, 1228-1233.

⁷² Deluge, M.; Cai, C. "Preparation, Characterization, and Heck Reaction of Siloxane Films Derived from Carbosilane Dendrons with a Bromophenyl Group at the Focal Point and up to 27 SiCl₃ Groups at the Periphery." *Langmuir* **2005**, 21, 1917-1922.

bromine groups and 4-fluorostyrene was investigated using XPS. With increasing generation number, the Heck reaction yield decreased, which indicated that the percentage of Br atoms in an unfavorable orientation increased with generation number.

Dendrimer modification of surfaces was also used to construct bioreactive surfaces. Beier *et al.* reported the anchoring and synthesis of pre-fabricated nucleic acids such as oligonucleotides on glass/PP surfaces using dendrimers as flexible linkers.⁷³ The amine terminated dendrimer was generated on aminopropylsilane-modified surfaces using an iterative approach that involved stepwise acylation of the amino groups and subsequent reaction with multifunctional amines. The concentration of the amino groups controlled the surface loading of the nucleic acids; however, the surface concentration of the bound DNA did not effect its subsequent hybridization with a complementary strand. Wöhrle *et al.* assembled PAMAM starburst dendrimers containing 64 primary amino groups onto activated glass surfaces.⁷⁴ DNA microarrays were constructed on the dendrimer-modified surfaces through covalent attachment of amine-modified oligonucleotides. The hybridization efficiency of the surface immobilized DNA with a fluorescently labeled complementary strand was twice as much as that observed with a conventional linear spacer and the covalently attached dendrimer layer was stable over multiple hybridization and regeneration cycles. The use of PAMAM-modified surfaces for streptavidin immobilization was also investigated. PAMAM dendrimers covalently coupled to (N-hydroxysuccinimide) functionalized gold surfaces were patterned using microcontact printing and dip pen nanolithography to yield stable micro and nanopatterns

⁷³ Beier, M.; Hoheisel, J. D. "Versatile Derivatization of Solid Support Media for Covalent Bonding on DNA-Microchips." *Nucleic Acid Res.* **1999**, *27*, 1970-1977.

⁷⁴ Benters, R.; Niemeyer, C. M.; Wöhrle, D. "Dendrimer-Activated Solid Supports for Nucleic Acid and Protein Microarrays." *Chembiochem* **2001**, *2*, 686-694.

for possible applications in the construction of DNA and protein chips.⁷⁵ Pathak and coworkers used G1-G5 poly(propyleneimine) dendrimers coated glass surfaces as building blocks for the immobilization of various proteins.⁷⁶ Surfaces modified with G4 and G5 dendrimers showed higher surface density of attached proteins with enhanced catalytic activity compared to a PEG ($M_n = 10,000$ g/mol) modified surface. In 2005, Yu and coworkers reported the covalent immobilization of amine terminated poly(ethyleneimine) dendrimer onto gold surfaces that were modified with three hydroxyl-terminated dendron thiol and activated using N,N-succinimidyl carbonate.⁷⁷ Excess peripheral amino groups were used to immobilize biotin and subsequent non-covalent binding of streptavidin to the surface bound biotin groups. Mitchell and coworkers reported the immobilization of carboxyl functionalized chiral L-glutamic acid-based dendrimers on aminopropylsilane-modified silica surfaces for potential use in high performance liquid chromatography (HPLC) as chiral stationary phases.⁷⁸

Some groups have also described the functionalization of fullerenes and carbon nanotubes with dendrimers. Fréchet and coworkers reacted phenol functionalized C_{60} fullerenes with the focal benzylic bromide functionality of a G4 poly(benzylether) dendrimer to form stable, soluble carbon clusters.⁷⁹ Sano and coworkers observed star-

⁷⁵ Degenhart, G. H.; Dordi, B.; Schönherr, H.; Vansco, G. J. "Micro- and Nanofabrication of Robust Reactive Arrays Based on the Covalent Coupling of Dendrimers to Activated Monolayers." *Langmuir* **2004**, *20*, 6216-6224.

⁷⁶ Pathak, S.; Singh, A. K.; McElhanon, J. R.; Dentinger, P. M. "Dendrimer-Activated Surfaces for High Density and High Activity Protein Chip Applications." *Langmuir* **2004**, *20*, 6075-6079.

⁷⁷ Yang, M.; Tsang, E. M. W.; Wang, Y. A.; Peng, X.; Yu, H. S. "Bioreactive Surfaces Prepared via the Self-Assembly of Dendron Thiols and Subsequent Dendrimer Bridging Reactions." *Langmuir* **2005**, *21*, 1858-1865.

⁷⁸ Mathews, B. T.; Beezer, A. E.; Snowden, M. J.; Hardy, M. J.; Mitchell, J. C. "The Synthesis of Immobilised Chiral Dendrimers." *New J. Chem.* **2001**, *25*, 807-818.

⁷⁹ Wooley, K. L.; Hawker, C. J.; Fréchet, J. M. J.; Wudl, F.; Srdanov, G.; Shi, S.; Li, C.; Kao, M. "Fullerene-Bound Dendrimers: Soluble, Isolated Carbon Clusters." *J. Am. Chem. Soc.* **1993**, *115*, 9836-9837.

shaped nanostructures upon modification of acylated single-walled carbon nanotubes with G10 PAMAM dendrimers.⁸⁰

Although dendrimers offer attractive properties, traditional dendrimer synthesis is tedious. Hyperbranched/highly branched polymers, which exhibit many of the same advantageous properties as dendrimers, are easier to synthesize. Thus, surface modification with hyperbranched polymers was examined as an alternative to dendrimer modification.

2.3.3 Surfaces Modification with Hyperbranched Polymers

Fujiki and coworkers grafted PS and poly(ϵ -caprolactone) using cationic polymerization from pendant acylium perchlorate groups of random copolymer chains previously grafted onto ultrafine silica surfaces to form highly branched comb-shaped copolymers. The random copolymer of styrene and acryloyl chloride was obtained using free radical polymerization from surface grafted azo initiators.⁸¹ High amounts of grafted polymer were obtained; however, the polymers had a randomly branched structure rather than that of a hyperbranched polymer. Matsuda and coworkers used surface immobilized RAFT agent to prepare well-defined comb polymers using photopolymerization. Homopolymers of chloromethylstyrene (CMS) or its copolymers with N,N-dimethyl acrylamide (DMAAm) were used to graft parent polymer chains onto glass surfaces. Subsequent replacement of the Cl atoms with the RAFT agent (benzyl N,N-diethyldithiocarbamate) and polymerization of sodium acrylate yielded polyacrylate

⁸⁰ Sano, M.; Kamino, A.; Shinkai, S. "Construction of Carbon Nanotube "Stars" with Dendrimers." *Angew. Chem. Int. Ed. Eng.* **2001**, 40, 4661-4663.

⁸¹ Fujiki, K.; Motoji, N.; Tsuchida, H.; Tsubokawa, N. "Branched Polymer-Grafted Silica. Cationic Postgrafting from Pendant Acylium Perchlorate Groups of Grafted Polymer Chains on Ultrafine Silica Surface." *Polymer J.* **1994**, 26, 271-278.

daughter chains from the grafted parent polymer chains.⁸² Successive functionalization with RAFT agent followed by copolymerizations of CMS with DMAAm resulted in multigeneration hyperbranched graft copolymers on surfaces.⁸³

Bergbreiter and coworkers reported the formation of hyperbranched poly(acrylic acid) (PAA) films on MUA coated gold surfaces.⁸⁴ The acid group was activated using mixed anhydride and subsequently reacted with diamine-terminated poly(*tert*-butyl acrylate) (PTBA-diamine). Acid hydrolysis of the *tert*-butyl groups in PTBA produced PAA. Repetition of the acid activation and subsequent amidation steps with PTBA-diamine led to the growth of thick and tightly packed layers of hyperbranched PAA. Ellipsometric thickness of the PAA films increased non-linearly with number of grafted polymer layers. The PAA films were able to complex high levels of Fe³⁺ in solution. Similarly, Bergbreiter *et al.* constructed fluorinated PAA films on MUA treated gold surfaces or aminopropylsilane treated silicon/SiO₂ surfaces.⁸⁵ In the first approach, the fluorination was performed as a final step through fluoramidation of the grafted PAA film to give hydrophobic surface with a water contact angle of ~ 107° compared to 30° observed for the neat PAA film. In the second approach, fluorinated film with hydrophilic exterior (water contact angle ~41°-56°) was achieved through simultaneous grafting of PTBA-diamine and aminofluorocarbons on MUA treated gold surfaces followed by iterative grafting of PAA multilayers.

⁸² Lee, H.-J.; Nakayama, Y.; Matsuda, T. "Spatio-Resolved, Macromolecular Architectural Surface: Highly Branched Graft Polymer Via Photochemically Driven Quasiliving Polymerization Technique." *Macromolecules* **1999**, 32, 6689-6995.

⁸³ Nakayama, Y.; Sudo, M.; Uchida, K.; Matsuda, T. "Spatio-Resolved Hyperbranched Graft Polymerized Surfaces by Iniferter-Based Photograft Copolymerization." *Langmuir* **2002**, 18.

⁸⁴ Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. "Preparation of Hyperbranched Polymer Films Grafted on Self-Assembled Monolayers." *J. Am. Chem. Soc.* **1996**, 118, 3773-3774.

⁸⁵ Zhou, Y.; Bruening, M. L.; Liu, Y.; Crooks, R. M.; Bergbreiter, D. E. "Synthesis of Hyperbranched, Hydrophilic Fluorinated Surface Grafts." *Langmuir* **1996**, 12, 5519-5521.

Functionalization of the PAA films with a variety of amine and alcohol containing molecules have also been studied.⁸⁶ Fluorescence measurements of pyrene-modified PAA films showed excimer emission indicating the presence of a large number of pyrene groups in close proximity. Likewise, modification of the PAA films with ferrocene groups resulted in electrochemically active films. These films also exhibited pH induced reversible changes in film thickness. In addition, modification with fluorocarbons reduced the hydrogen bonding between the amide groups and improved the sensitivity of the films to VOCs because of enhanced permeability. Crooks *et al.* studied the pH swellability of surface grafted hyperbranched PAA films.⁸⁷ The thin films swelled reversibly up to 300% in acidic solution and up to 500% in basic medium. A significant decrease in swelling was observed upon partial fluoramidation of the films. The pH modulated reversible cation exchange capacity of poly(sodium acrylate) films was also investigated using polyvalent cations such as poly-L-lysine, and poly(allylamine). The poly(sodium acrylate) films were found to reversibly trap amine functionalized GOx and horse radish peroxidase enzymes.⁸⁸ Crooks *et al.* also demonstrated the formation of micrometer scale patterns of PAA⁸⁹ or dye functionalized PAA film⁹⁰ using microcontact printing and photoacid-based lithography.

⁸⁶ Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. "Synthesis and Characterization of Surface-Grafted, Hyperbranched Polymer Films Containing Fluorescent, Hydrophobic, Ion-Binding, Biocompatible, and Electroactive Groups." *Langmuir* **1997**, 13, 770-778.

⁸⁷ Peez, R. F.; Dermody, D. L.; Franchina, J. G.; Jones, S. J.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. "Aqueous Solvation and Functionalization of Weak-Acid Polyelectrolyte Thin Films." *Langmuir* **1998**, 14, 4232-4237.

⁸⁸ Franchina, J. G.; Lackowski, W. M.; Dermody, D. L.; Crooks, R. M.; Bergbreiter, D. E. "Electrostatic Immobilization of Glucose Oxidase in a Weak Acid, Polyelectrolyte Hyperbranched Ultrathin Film on Gold: Fabrication, Characterization, and Enzymatic Activity." *Anal. Chem.* **1999**, 71, 3133-3139.

⁸⁹ Lackowski, W. M.; Ghosh, P.; Crooks, R. M. "Micron-Scale Patterning of Hyperbranched Polymer Films by Micro-Contact Printing." *J. Am. Chem. Soc.* **1999**, 121, 1419-1420.

⁹⁰ Aoki, A.; Ghosh, P.; Crooks, R. M. "Micrometer-Scale Patterning of Multiple Dyes on Hyperbranched Polymer Thin Films Using Photoacid-Based Lithography." *Langmuir* **1999**, 15, 7418-7421.

Modification of hydrophobic polyethylene (PE) surfaces with hyperbranched PAA was also reported.⁹¹ The PE surfaces were oxidized with CrO₃-H₂SO₄ mixture and acylated before reaction with PTBA-diamine. Ionic modification of the PAA films with G4 PAMAM dendrimer was found to construct robust ionic nanocomposites with PE. The growth of PAA films on PE was also achieved via multistep grafting using Ce(IV) and acrylic acid.^{92, 93} In the first step, the oxidized PE surface was activated with chloroformate in order to graft a layer of PTBA-diamine. Reduction of the acid groups obtained by the hydrolysis of PTBA yielded poly(allyl alcohol), which was used as the initiator layer for the growth of PAA hyperbranched grafts. In a recent publication, Bergbreiter and coworkers employed a “grafting from” route to obtain hyperbranched polyamine grafts through Pd-catalyzed ring opening polymerization (ROP) of 5-vinyl-2-oxazolidone initiated from amine-modified silicon/SiO₂ surfaces.⁹⁴ The surface mechanical properties, which were probed using a nanoindenter, improved upon polymer modification.

Park *et al.* polymerized aziridine from surface hydroxyl groups of silica/silicon/glass surfaces to form a highly branched poly(ethyleneimine) presenting very high density of primary amino groups.⁹⁵ Further, the pH and thermal stability of the polymer films was evaluated. The grafted films showed good pH stability; however, they

⁹¹ Bergbreiter, D. E.; Franchina, J. G.; Kabza, K. "Hyperbranched Grafting on Oxidized Polyethylene Surfaces." *Macromolecules* **1999**, *32*, 4993-3998.

⁹² Bergbreiter, D. E.; Tao, G. "Chemical Modification of Hyperbranched Ultrathin Films on Gold and Polyethylene." *J. Polym. Sci., Part A: Polym. Chem.* **2000**, *38*, 3944-3953.

⁹³ Bergbreiter, D. E.; Boren, D.; Kippenberger, A. M. "New Routes to Hyperbranched Poly(Acrylic Acid) Surface Grafts on Polyethylene Films and Powders." *Macromolecules* **2004**, *37*, 8686-8691.

⁹⁴ Bergbreiter, D. E.; Kippenberger, A. M.; Lackowski, W. M. "New Syntheses of Hyperbranched Polyamine Grafts." *Macromolecules* **2005**, *38*, 47-52.

⁹⁵ Kim, C. O.; Cho, S. J.; Park, J. W. "Hyperbranching Polymerization of Aziridine on Silica Solid Substrates Leading to a Surface of Highly Dense Reactive Amine Groups." *J. Colloid Interf. Sci.* **2003**, *260*, 374-378.

were thermally stable only up to 70 °C. Khan and Huck employed anionic ROP of glycidol to prepare hyperbranched polyglycidol brushes on silicon/SiO₂ surfaces.⁹⁶ The structure and degree of branching of the hyperbranched polymer was determined using ¹³C NMR spectroscopic analysis of the degrafted polymer. Müller and coworkers employed self-condensing vinyl polymerization (SCVP) of (meth)acrylate inimers, such as 2-(2-bromopropionyloxy)ethyl acrylate (BPEA) from surface attached ATRP initiator.⁹⁷ AFM analysis of the surfaces modified with these highly branched polymer brushes showed several nanoscale protrusions, the number and density of which depended on the feed ratio of the inimer and the catalyst. Similarly, SCVP of mixtures of BPEA and *tert*-butyl acrylate from surface attached ATRP initiator resulted in branched PAA brushes on silica nanoparticles.⁹⁸

Recently, Gao and coworkers reported a “grafting from” strategy for growing multihydroxyl dendrimer like hyperbranched macromolecules from acylated multi-walled carbon nanotube (MWNT) surfaces using ring-opening polymerization of 3-ethyl-3-(hydroxymethyl)oxetane as shown in Figure 2-5.⁹⁹ The polymer was cleaved off the nanotube surface using base hydrolysis for subsequent SEC analysis, which revealed that the molecular weight and the degree of branching of the polymer increased with increasing feed ratios of the monomer to macroinitiator functionalized MWNTs.

⁹⁶ Khan, A.; Huck, W. T. S. "Hyperbranched Polyglycidol on Si/SiO₂ Surfaces via Surface-Initiated Polymerization." *Macromolecules* **2003**, 36, 5088-5093.

⁹⁷ Mori, H.; Boker, A.; Krausch, G.; Müller, A. H. E. "Surface Grafted Hyperbranched Polymers via Self-Condensing Atom Transfer Radical Polymerization from Silicon Wafers." *Macromolecules* **2001**, 34, 6871-6882.

⁹⁸ Mori, H.; Seng, D. C.; Zhang, M.; Müller, A. H. E. "Hybrid Nanoparticles with Hyperbranched Polymer Shells via Self-Condensing Atom Transfer Radical Polymerization from Silica Surfaces." *Langmuir* **2002**, 18, 3682-3693.

⁹⁹ Xu, Y.; Gao, C.; Kong, H.; Yan, D.; Jin, Y. Z.; Watts, P. C. P. "Growing Multihydroxyl Hyperbranched Polymers on the Surfaces of Carbon Nanotubes by in Situ Ring-Opening Polymerization." *Macromolecules* **2004**, 37, 8846-8853.

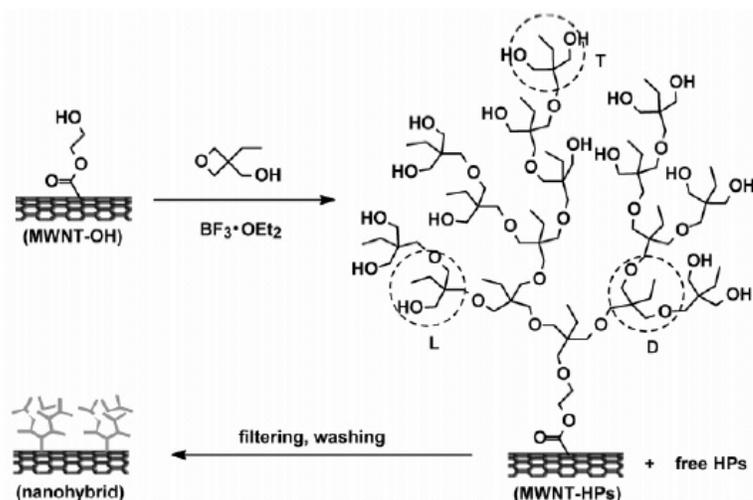


Figure 2-5: Synthesis of multihydroxyl-functionalized dendritic hyperbranched polymers on carbon nanotube surfaces by the “grafting from” approach. Reprinted with permission from ref. 99. Copyright (2004) American Chemical Society.

Due to the presence of a high density of functional groups, hyperbranched polymer films are good candidates for a number of technological applications such as sensors, catalysts, and protective coatings. However, a major limitation with the hyperbranched systems is the absence of good control over the polymer molecular weight and the molecular weight distribution.¹⁰⁰

2.3.4 Surface Modification with Star-branched Polymers

Star-branched polymers, which consist of several linear polymer chains emanating from a single branch point, are the simplest form of branched structures. While star-branched polymers are not as highly functional as dendritic or highly branched/hyperbranched polymers, it is possible to obtain star-branched polymers with a large number of functional groups using suitable polymerization techniques. In addition, star-branched polymers are well-defined macromolecules and often exhibit narrow

¹⁰⁰ Mori, H.; Müller, A. H. E. "Hyperbranched (Meth)Acrylates in Solution, Melt, and Grafted from Surfaces." *Top. Curr. Chem.* **2003**, 228, 1-37.

polydispersity compared to highly branched polymers. However, there are not many studies on star-branched macromolecules as surface modifiers.

Most studies on surface attached star-branched polymers have concentrated on the use of PEG-based systems to impart enhanced biocompatibility to silicon surfaces. Sofia *et al.* reported the modification of aminosilylated silicon/SiO₂ surface with tresyl chloride-functionalized linear and star-PEG in order to determine the influence of polymer topology on the protein resistance of the modified surfaces.¹⁰¹ Sufficiently dense tethering of linear PEG on surfaces was required to impart complete resistance to proteins. The star-PEG-modified surfaces, on the other hand, could resist protein adsorption even at moderate grafting densities because of their hard sphere nature. In a related study Mayes and coworkers correlated the chain segment density profile of surface tethered linear and star-PEG with their protein resistance characteristics.¹⁰² Although the segment density of 70 arm star-PEG was higher than the linear polymers, star-PEG showed a lower protein resistance compared to the linear polymers. The lower protein resistance of the star-PEG modified surfaces was attributed to the presence of void spaces between the anchored star-PEG molecules due to the absence of chain overlapping. However, star-PEG presented a far higher concentration of functional groups on the surface compared to linear PEG. It thus could provide better surfaces for ligand immobilization compared to linear polymers.

Moeller *et al.* used a crosslinking strategy to improve the protein resistance of PEG modified surfaces. Crosslinking of isocyanate terminated star-PEG with amino-

¹⁰¹ Sofia, S. J.; Premnath, V.; Merrill, E. W. "Poly(Ethylene Oxide) Grafted to Silicon Surfaces: Grafting Density and Protein Adsorption." *Macromolecules* **1998**, 31, 5059-5070.

functionalized glass surfaces was achieved through urea formation.^{103, 104} Fluorescence measurements showed negligible adsorption of the protein, fluorophore modified RNA H on star-PEG modified surfaces compared to linear PEGs. The crosslinked star-PEG modified surfaces also provided a non-interacting platform for the attachment of proteins. Reversible conformational changes on protein attachment occurred without their irreversible denaturation. In addition, the construction of films between 3 and 500 nm thick was achieved using crosslinking of isocyanate terminated 6 arm star-shaped PEG on aminosilylated surfaces.¹⁰⁵ For film thickness between 3 and 50 nm, no avidin adsorption was observed. Furthermore, the reaction of free amino groups with 4-chloro-7-nitrobenzofurazan was confirmed using fluorescence microscopy.

Moeller *et al.* investigated the use of cross-linked star-PEG modified surfaces for cell growth and differentiation.¹⁰⁶ Following functionalization of the unreacted isocyanate groups with amino groups of RGD peptides, the star-PEG modified surfaces were found to support cell growth. The concentration of the RGD peptides on the surfaces influenced the number of cells adhering to the surface. Minko and coworkers reported the grafting of heteroarm star-branched copolymer of PS and PVP emanating from divinylbenzene (DVB) core onto bromoalkylsilane functionalized silicon/SiO₂

¹⁰² Irvine, D. J.; Mayes, A. M.; Satija, S. K.; Barker, J. G.; Sofia-Allgor, S. J.; Griffith, L. G. "Comparison of Tethered Star and Linear Poly(Ethylene Oxide) for Control of Biomaterials Surface Properties." *J. Biomed. Mater. Res.* **1998**, 40, 498-509.

¹⁰³ Groll, J.; Amirgoulova, E. V.; Ameringer, T.; Heyes, C. D.; Røcker, C.; Nienhaus, G. U.; Moller, M. "Biofunctionalized, Ultrathin Coatings of Cross-Linked Star-Shaped Poly(Ethylene Oxide) Allow Reversible Folding of Immobilized Proteins." *J. Am. Chem. Soc.* **2004**, 126, 4234-4239.

¹⁰⁴ Amirgoulova, E. V.; Groll, J.; Heyes, C. D.; Ameringer, T.; Røcker, C.; Möller, M.; Nienhaus, G. U. "Biofunctionalized Polymer Surfaces Exhibiting Minimal Interaction Towards Immobilized Proteins." *Chem. Phys. Chem.* **2004**, 5, 552-555.

¹⁰⁵ Groll, J.; Ameringer, T.; Spatz, J. P.; Moeller, M. "Ultrathin Coatings from Isocyanate-Terminated Star PEG Prepolymers: Layer Formation and Characterization." *Langmuir* **2005**, 21, 1991-1999.

¹⁰⁶ Groll, J.; Fiedler, J.; Engelhard, M. H.; Ameringer, T.; Tugulu, S.; Klok, H.-A.; Brenner, R. E.; Moeller, M. "A Novel Star PEG-Derived Surface Coating for Specific Cell Adhesion." *J. Biomed. Mater. Res., A* **2005**, 74A, 607-617.

surfaces.¹⁰⁷ The star-branched copolymer modified surfaces exhibited switchable surface characteristics upon exposure to block selective solvents.

Penn and coworkers investigated the rates of tethering of amine-functionalized linear and star-PEG onto epoxide-derivatized silica from solution.¹⁰⁸ The star-PEG exhibiting multidentate attachment to the surface showed higher areal density compared to the linear polymer. The higher attachment observed for the amine-functionalized star-PEG was attributed to the contraction of star-PEG following surface attachment, which allowed the diffusion, and anchoring of further chains leading to higher amounts of polymer.

2.4 Surface Modification with Mixed Polymer Brushes

2.4.1 Introduction

Diverse surface modification techniques have been used to temporarily and permanently alter the wettability of a surface. Introduction of organic functionalities through SAM deposition is the most commonly used approach for permanently tuning surface polarities.¹⁰⁹ Surface treatments with plasma, UV/ozone, or corona discharge lead to temporary increases in hydrophilicity of the surface. However, the limitation with this approach is that the surface has a propensity to rearrange over time in order to decrease the net surface energy and thus loses its hydrophilicity. Thus, it is necessary to create surfaces that can respond to an external stimulus and render the surface hydrophilic under appropriate conditions.

¹⁰⁷ Lupitsky, R.; Roiter, Y.; Tsitsilianis, C.; Minko, S. "From Smart Polymer Molecules to Responsive Nanostructured Surfaces." *Langmuir* **2005**, 21, 8591-8593.

¹⁰⁸ Huang, H.; Fulchiero, E. C.; Penn, L. S. "Comparison of Tethering of Linear and Four-Arm Star Poly(Ethylene Oxide)." *Macromolecules* **2005**, 38, 1028-1030.

Stimuli responsive surfaces reversibly alter their properties in response to various external stimuli such as solvent, temperature, mechanical perturbation, electrical potential, or light. For example, mechanically responsive surface energies were obtained through grafting of perfluoroalkanes onto a stretched PDMS elastomer.¹¹⁰ Upon relaxation, the elastomeric surface became extremely hydrophobic due to an increase in the areal density of the hydrophobic fluorocarbons due to a decrease in the surface area of the elastomer. Reversible changes in surface hydrophobicity were observed upon repeated expansion and contraction of the elastomer. Mechanical perturbation was also used to reversibly switch the wetting properties of a multilayer thin film formed from alternating layers of poly(allylamine)-Nafion and poly(allylamine)-acrylic acid.¹¹¹

Thermally induced phase transitions in poly(N-isopropylacrylamide) gels resulted in surfaces exhibiting reversible hydrophilicity/hydrophobicity below and above the critical solution temperature, respectively.¹¹² Temperature dependent surface rearrangement of polar functional groups such as carboxylic acids introduced through oxidation of uncrosslinked and crosslinked poly(1,4-butadiene) was reported to reversibly tune the hydrophilicity of the elastomeric surface^{113, 114} and also their adhesion to

¹⁰⁹ Whitesides, G. M.; Laibinis, P. E. "Wet Chemical Approaches to the Characterization of Organic Surfaces: Self-Assembled Monolayers, Wetting, and the Physical-Organic Chemistry of the Solid-Liquid Interface." *Langmuir* **1990**, *6*, 87-96.

¹¹⁰ Genzer, J.; Efimenko, K. "Creating Long-Lived Superhydrophobic Polymer Surfaces through Mechanically Assembled Monolayers." *Science* **2000**, *290*, 2130-2133.

¹¹¹ Hemmerlé, J.; Roucoules, V.; Fleith, G.; Nardin, M.; Ball, V.; Lavalle, P.; Marie, P.; Voegel, J.-C.; Schaff, P. "Mechanically Responsive Films of Variable Hydrophobicity Made of Polyelectrolyte Multilayers." *Langmuir* **2005**, *21*, 10328-10331.

¹¹² Zhang, J.; Pelton, R.; Deng, Y. "Temperature-Dependent Contact Angles of Water on Poly(N-Isopropylacrylamide) Gels." *Langmuir* **1995**, *11*, 2301-2302.

¹¹³ Carey, D. H.; Ferguson, G. S. "A Smart Surface: Entropic Control of Composition at a Polymer/ Water Interface." *J. Am. Chem. Soc.* **1996**, *118*, 9780-9781.

¹¹⁴ Khongtong, S.; Ferguson, G. S. "Integration of Bulk and Interfacial Properties in a Polymeric System: Rubber Elasticity at a Polybutadiene/Water Interface." *J. Am. Chem. Soc.* **2001**, *123*, 3588-3594.

aluminum.¹¹⁵ Polymer surfaces exhibiting thermally switchable tack and wetting properties were constructed from side chain liquid-crystalline polymers comprised of perfluoroalkylated acrylate and a methacrylate monomer containing long alkyl chains.¹¹⁶ The reversible wettability and tackiness of the polymer arises due to thermally induced transition between a highly ordered smectic phase to an isotropic phase.

UV induced dimerization and cleavage led to reversible changes in wetting characteristics of gold surfaces modified with a thin coating of thymine SAM.¹¹⁷ This change in wettability was attributed to an enhanced acidity constant of the dimer compared to the monomer. Electrochemical reduction aided physical removal of alkanethiolates from surfaces and their reattachment was used to reversibly tune the wettability of gold surfaces modified with alkanethiolate SAM.¹¹⁸

In an alternative approach for dynamically controlling the surface properties, Langer and coworkers took advantage of electrochemically induced conformational transitions to reverse the wettability of a surface modified with carboxylate functionalized SAM.¹¹⁹ Upon application of a negative potential, the molecules adopt an all trans conformation because of repulsion between the surface and the carboxylate group, making the surface hydrophilic. However, upon application of a positive potential, the attraction between carboxylate and the positively charged surface causes the

¹¹⁵ Khongtong, S.; Ferguson, G. S. "A Smart Adhesive Joint: Entropic Control of Adhesion at a Polymer/Metal Interface." *J. Am. Chem. Soc.* **2002**, 124, 7254-7255.

¹¹⁶ Crevoisier, G. d.; Fabre, P.; Corpart, J.-M.; Leibler, L. "Switchable Tackiness and Wettability of a Liquid Crystalline Polymer." *Science* **1999**, 285, 1246-1249.

¹¹⁷ Abbott, S.; Ralston, J.; Reynolds, G.; Hayes, R. "Reversible Wettability of Photoresponsive Pyrimidine-Coated Surfaces." *Langmuir* **1999**, 15, 8923-8928.

¹¹⁸ Abbott, N. L.; Gorman, C. B.; Whitesides, G. M. "Active Control of Wetting Using Applied Electrical Potentials and Self-Assembled Monolayers." *Langmuir* **1995**, 11, 16-18.

¹¹⁹ Lahann, J.; Mitragotri, S.; Tran, T.-N.; Kaido, H.; Sundaram, J.; Choi, I. S.; Hoffer, S.; Somorjai, G. A.; Langer, R. "A Reversibly Switching Surface." *Science* **2003**, 297, 371-374.

molecules to adopt a gauche conformation, thereby exposing the hydrophobic alkyl chains to the surface.

Hadjichristidis and coworkers demonstrated an elegant way of switching the surface properties of a PS-*b*-PI film by using a hydrophilic group at the end of the surface active PI block.¹²⁰ Upon exposure to water vapor, the hydrophilic group that was initially buried in the film when in contact with dry air migrated to the surface thus significantly decreasing the water contact angle. Successive exposure to dry and wet environments led to surfaces exhibiting hydrophobic and hydrophilic properties, respectively. Crowe and Genzer created responsive surfaces of poly(vinylmethylsiloxane) networks that were modified with mercaptoalkanols of various alkyl chain lengths following surface oxidation with ozone.¹²¹ The extent and kinetics of surface reorganization of the hydroxyl-modified surfaces in the presence of water depended on the alkyl chain length. Dynamic water contact angle measurements demonstrated that the reorganization of shorter alkyl chain modifiers was highly reversible and rapid. On the other hand, longer alkyl chain modifiers, due to their semicrystalline nature did not show significant reorganization.

Modification of surfaces with grafted polymers of various chemical compositions and topology is a well-known approach to obtain stable and robust organic thin films on surfaces for achieving controlled properties such as wettability, adhesion, friction etc. There are some reports that describe the grafting of poly(N-isopropyl acrylamide) to

¹²⁰ Anastasiadis, S. H.; Retsos, H.; Pispas, S.; Hadjichristidis, N.; Neophytides, S. "Smart Polymer Surfaces." *Macromolecules* **2003**, 36, 1994-1999.

¹²¹ Crowe, J. A.; Genzer, J. "Creating Responsive Surfaces with Tailored Wettability Switching Kinetics and Reconstruction Reversibility." *J. Am. Chem. Soc.* **2005**, 127.

create thermally responsive surfaces with reversible wetting properties.^{122, 123} In recent years, the use of mixed polymer brushes to generate surfaces, which can respond to external stimulus has received significant attention. Mixed polymer brushes are polymer films composed of polymer chains of different chemical compositions randomly grafted onto a surface. Such polymer films are obtained either through grafting of block copolymers, random copolymers, or two different homopolymers in a sequential manner. Such mixed polymer brush modified surfaces comprising polymer chains of sufficiently different polarities switch their surface energetics upon exposure to different solvents because of chain reorganization leading to different surface wettabilities, and nanomorphologies.¹²⁴

2.4.2 Surface Modification with Amphiphilic Block Copolymers

Amphiphilic diblock and triblock copolymers have found application as colloidal stabilizers. As such one block can anchor to the surface of the colloid particles while the other blocks can extend into the surrounding medium and bring about the required stabilization. Amphiphilic block copolymers were also used as effective compatibilizers, where they were found to improve the strength and toughness of interfaces formed between homopolymer blends.¹²⁵ In addition, due to the self-organizing properties of block copolymers into ordered nanodomains, block copolymers are useful materials for

¹²² Takei, Y. G.; Aoki, T.; Sanui, K.; Ogata, N.; Sakurai, Y.; Okano, T. "Dynamic Contact Angle Measurement of Temperature-Responsive Surface Properties for Poly(N-Isopropylacrylamide) Grafted surfaces." *Macromolecules* **1994**, *27*, 6163-6166.

¹²³ Balamurugan, S.; Mendez, S.; Balamurugan, S. S.; O'Brien II, M. J.; López, G. P. "Thermal Response of Poly(N-Isopropylacrylamide) Brushes Probed by Surface Plasmon Resonance." *Langmuir* **2003**, *19*, 2545-2549.

¹²⁴ Julthongpipit, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Amphiphilic Brushes with Switchable Micellar Surface Structures." *J. Am. Chem. Soc.* **2003**, *125*, 15912-15921.

¹²⁵ Bernard, B.; Brown, H. R.; Hawker, C. J.; Kellock, A. J.; Russell, T. P. "Adhesion of Polymer Interfaces Reinforced with Random and Diblock Copolymers as a Function of Geometry." *Macromolecules* **1999**, *32*, 6257-6260.

separation mediums, as scaffolds for growing patterned structures, as nanoreactors, or as templates.¹²⁶

In recent years, research efforts have focused on demonstrating the use of amphiphilic block copolymers for generating stimuli responsive surfaces. Surfaces modified with the block copolymers are obtained either through the “grafting from” or the “grafting to” approach. Zhao and Brittain grafted PS-*b*-PMMA on silicon/SiO₂ through surface initiated sequential carbocationic polymerization of styrene and radical polymerization of MMA.¹²⁷ The tethered polymers showed reversible changes in water contact angles between ~100° and ~75° following exposure to methylcyclohexane and CH₂Cl₂, respectively. In methylcyclohexane, PS segregates to the surface and thus, water contact angle increased to ~98°, while CH₂Cl₂ (a good solvent for both PS and PMMA), reverses this change because of chain reorganization. Thus, the attached chains had sufficient free volume because of the low grafting density of the initial PS layer which enabled their rearrangement upon solvent treatments. Changes in surface topography following solvent induced rearrangement of the PS and PMMA blocks of the tethered diblock copolymer were also investigated using AFM and XPS.¹²⁸ Well-defined nanopatterns of swollen, collapsed, or micellar chains were observed depending on the solvent treatment.

Similarly, a combination of reverse ATRP, where the polymerization was initiated from azo initiator in the presence of suitable transition metal complexes, and ATRP was

¹²⁶ Kim, H.-C.; Jia, X.; Stafford, C. M.; Kim, D. H.; McCarthy, T. J.; Tuominen, M.; Hawker, C. J.; Russell, T. P. "A Route to Nanoscopic SiO₂ Posts Via Block Copolymer Templates." *Adv. Mater.* **2001**, 13, 795-797.

¹²⁷ Zhao, B.; Brittain, W. J. "Synthesis of Tethered Polystyrene-Block-Poly(Methyl Methacrylate) Monolayer on a Silicate Substrate by Sequential Carbocationic Polymerization and Atom Transfer Radical Polymerization." *J. Am. Chem. Soc.* **1999**, 121, 3557-3558.

used to graft PS-*b*-PMMA on silicon/SiO₂ surfaces.¹²⁹ The behavior of the surface tethered diblock copolymer and a homopolymer brush to selective solvent treatments confirmed that the changes in surface wettabilities were due to solvent induced rearrangement of the blocks. Iyoda *et al.* used ATRP from surface grafted α -bromoester functionalized trichlorosilanes to tether PMMA-*b*-PAAm to silicon/SiO₂ surfaces.¹³⁰ Selective solvent treatments of the surfaces did not produce appreciable changes in water contact angle, which was attributed to quick reorganization of the chains under water. However, block selective solvent treatments resulted in different surface topographies due to selective solvent induced swelling of the blocks and their relative position within the polymer brush.

Quirk and coworkers used *n*-butyllithium initiated anionic polymerization from a surface attached diphenylethylene monolayer to tether hydroxyl-terminated polyisoprene (PI), which was subsequently chain extended with PEO.¹³¹ The hydroxyl-terminated PI block showed an advancing water contact angle of 47°, while upon immersion in benzene the water contact angle increased to ~67°, close to that of neat PI, indicating solvent promoted rearrangement of the terminal groups. Following extension with EO, the contact angle decreased further to ~40°; however, after cyclohexane treatment, the water contact angle increased to ~55°. XPS analysis also showed a similar trend with preferential segregation of the PI block to the air interface following cyclohexane treatment while the surface was enriched in PEO after CH₂Cl₂ exposure.

¹²⁸ Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. "Nanopattern Formation from Tethered PS-*b*-PMMA Brushes Upon Treatment with Selective Solvents." *J. Am. Chem. Soc.* **2000**, 122, 2407-2408.

¹²⁹ Sedjo, R. A.; Mirous, B., K.; Brittain, W. J. "Synthesis of Polystyrene-Block-Poly(Methyl Methacrylate) Brushes by Reverse Atom Transfer Radical Polymerization." *Macromolecules* **2000**, 33, 1492-1493.

¹³⁰ Kong, X.; Kawai, T.; Abe, J.; Iyoda, T. "Amphiphilic Polymer Brushes Grown from the Silicon Surface by Atom Transfer Radical Polymerization." *Macromolecules* **2001**, 34, 1837-1844.

Brittain *et al.* also investigated switchable properties of ABA-type triblock copolymers grafted on silicon/SiO₂ surfaces.¹³² The triblock copolymers comprising PS-*b*-PMA-*b*-PS and PMA-*b*-PS-*b*-PMA, where PMA refers to poly(methyl acrylate), were obtained from surface tethered ATRP initiators through sequential monomer addition. In the case of PMA-*b*-PS-*b*-PMA, a switch from CH₂Cl₂ (a non-selective solvent) to cyclohexane (good solvent for PS) changed the water contact angle from ~70° to ~90°. The surface topography also changed from a very smooth to a highly textured surface upon block selective solvent treatment. Similarly, the contact angle changed between ~90° and ~70° for PS-*b*-PMA-*b*-PS following CH₂Cl₂ and acetone treatments, respectively. However, the surfaces showed segregated structures even in CH₂Cl₂ that was attributed to chain length effect.

Brittain and coworkers used ATRP to grow semifluorinated block copolymers on silicon/SiO₂ surfaces.¹³³ The block copolymers composed of PS or PMA as the hydrocarbon inner block and a fluoropolymer outer block. Diblock copolymers containing PMA as the inner block showed greater difference in water contact angles following selective solvent treatments compared to the copolymers composed of inner PS block. In addition, XPS showed that following rearrangement in hydrocarbon solvents, the surfaces showed photoelectron peaks from residual F. This indicated that the rearrangement of the block copolymer films of ~15 nm thickness was confined to the

¹³¹ Quirk, R. P.; Mathers, R. T.; Cregger, T.; Foster, M. D. "Anionic Synthesis of Block Copolymer Brushes Grafted from a 1,1-Diphenylethylene Monolayer." *Macromolecules* **2002**, 35, 9964-9974.

¹³² Boyes, S. G.; Brittain, W. J.; weng, X.; Cheng, S. Z. D. "Synthesis, Characterization and Properties of ABA Type Triblock Copolymer Brushes of Styrene and Methyl Acrylate Prepared by Atom Transfer Radical Polymerization." *Macromolecules* **2002**, 35, 4960-4967.

¹³³ Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. "Synthesis and Characterization of Stimuli-Responsive Semifluorinated Polymer Brushes Prepared by Atom Transfer Radical Polymerization." *Macromolecules* **2004**, 37, 2790-2796.

near-surface region. In a subsequent study, the authors used a combination of solvent and temperature to rearrange the blocks.¹³⁴ Surface segregation of the hydrocarbon block was achieved using a hydrocarbon solvent while thermal annealing promoted the rearrangement of the fluorocarbon blocks to the surface. In this work the annealing temperature was greater than 100 °C for PS containing copolymers and ~60 °C PMA containing block copolymers. The rate of rearrangement of the fluorinated block depended on the T_g of the fluorinated block, with lower T_g block rearranging faster than blocks with higher T_g s.

Ward and coworkers reported the first example of surfaces modified with stimuli responsive block copolymers by the “grafting to” approach.¹³⁵ The block copolymers composed of poly(styrene-*b*-triethoxysilylated styrene-*b*-methyl methacrylate) was synthesized using living anionic polymerization followed by a post polymer modification strategy. The triethoxysilane functionalized central block anchored the copolymer to the hydrophilic silicon/SiO₂ surface. The modified surfaces showed reversible changes in hydrophobicity/hydrophilicity after successive treatments with either toluene (a good solvent for PS) or CH₂Cl₂ (a good solvent for PMMA), respectively.¹³⁶

In recent years, Tsukruk and coworkers have reported surface modification with Y-shaped polymer brushes, where two incompatible homopolymer chains attached to a single focal point reactive group were grafted to the surface. The homopolymers

¹³⁴ Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. "Thermoresponsive Behavior of Semifluorinated Polymer Brushes." *Macromolecules* **2005**, 38, 3263-3270.

¹³⁵ Wang, J. L.; Kara, S.; Long, T. E.; Ward, T. C. "Synthesis of Central Functionalized Asymmetric Triblock Copolymers for Surface Modification and Switchable Surface Properties." *J. Polym. Sci., Polym. Chem.* **2000**, 38, 3742-3750.

¹³⁶ Wang, J. "Design and Characterization of Central Functionalized Asymmetric Tri-Block Copolymer Modified Surfaces." Electronic, Virginia Polytechnic Institute & State University, Blacksburg, 2001.

constituted PS and poly(*t*BA) that was partially hydrolyzed to PAA following surface attachment. Y-shaped polymer brushes modified surfaces exhibited reversible changes in water contact angle and novel surface topographies consisting of pinned micelles following selective solvent treatment.^{137, 138} Ultrathin mixed homopolymer films of PS and PAA showed reversible wetting properties following successive treatments with toluene and water. Variation in the tribological properties such as the friction coefficient and wear resistance of the surfaces following selective solvent treatments were investigated.¹³⁹ Surfaces treated with water showed a bimodal distribution of elastic modulus due to the presence of both polymers on the surface. In contrast, the surface properties were dominated by PS after toluene treatment. Although, PAA rich surfaces exhibited higher adhesion and heterogeneous surface composition, they showed better tribological properties compared to PS rich surfaces.¹⁴⁰

Recently, Zhao and coworkers demonstrated the growth of Y-shaped brushes of PMMA and PS using a combination of ATRP and NMP from surface tethered Y-shaped binary ATRP/NMP initiator.¹⁴¹ The wetting properties of the surfaces was primarily dominated by the length of the PS and PMMA blocks. Even upon treatment with CHCl₃, high PS-like water contact angles were observed only when the PS chain length was

¹³⁷ Julthongpiput, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Polymer Brushes: Nanoscale Switchable Surfaces." *Langmuir* **2003**, 19, 7832-7836.

¹³⁸ Julthongpiput, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Amphiphilic Brushes with Switchable Micellar Surface Structures." *J. Am. Chem. Soc.* **2003**, 125, 15912-15921.

¹³⁹ Lemieux, M.; Julthongpiput, D.; Bergman, K. N.; Cuong, P. D.; Ahn, H.-S.; Lin, Y.-H.; Tsukruk, V. V. "Ultrathin Binary Grafted Polymer Layers with Switchable Morphology." *Langmuir* **2003**, 20, 10046-10054.

¹⁴⁰ Lemieux, M.; Lin, Y.-H.; Cuong, P. D.; Ahn, H.-S.; Zubarev, E. R.; Tsukruk, V. V. "Microtribological and Nanomechanical Properties of Switchable Y-Shaped Amphiphilic Polymer Brushes." *Adv. Funct. Mater.* **2005**, 15, 1529-1540.

¹⁴¹ Zhao, B.; He, T. "Synthesis of Well-Defined Mixed Poly(Methyl Methacrylate)/Polystyrene Brushes from an Asymmetric Difunctional Initiator-Terminated Self-Assembled Monolayer." *Macromolecules* **2003**, 36, 8599-8602.

equal or longer than the PMMA chain.¹⁴² While PMMA rearranged in acetic acid, PS rearrangement was induced chemically using cyclohexane as the solvent or promoted thermally.¹⁴³ Grafting of PS and PMMA mixed brushes from a silica surface tethered binary initiator was used to obtain responsive silica particles.¹⁴⁴ The binary homopolymer grafted silica nanoparticles exhibited stable suspensions in both CHCl₃ and methanol due to chain reorganization, which was not observed with homopolymer grafted nanoparticles.

The above-mentioned studies have clearly demonstrated that appropriate variation in the block copolymer and binary homopolymer composition in grafted polymer films can lead to surfaces exhibiting vastly different wetting, adhesion, tribological, or aggregation properties and surface topographies. Recent investigations have shown that sequential grafting of two immiscible polymer chains in the same polymer film could also confer responsive properties to surfaces. Such statistically distributed chains chemically grafted at one end to a surface do not macrophase separate. However, they would show a change in surface properties upon exposure to a selective solvent. It was predicted that collective response of the chains occurred when they were grafted at sufficiently high grafting densities.¹⁴⁵

¹⁴² Zhao, B.; Haasch, R. T.; MacLaren, S. "Solvent-Induced Self-Assembly of Mixed Poly(Methyl Methacrylate)/Polystyrene Brushes on Planar Silica Substrates: Molecular Weight Effect." *J. Am. Chem. Soc.* **2004**, 126, 6124-6134.

¹⁴³ Zhao, B.; Haasch, R. T.; MacLaren, S. "Self-Reorganization of Mixed Poly(Methyl Methacrylate)/Polystyrene Brushes on Planar Silica Substrates in Response to Combined Selective Solvent Treatments and Thermal Annealing." *Polymer* **2004**, 45, 7979-7988.

¹⁴⁴ Li, D.; Sheng, X.; Zhao, B. "Environmentally Responsive "Hairy" Nanoparticles: Mixed Homopolymer Brushes on Silica Nanoparticles Synthesized by Living Radical Polymerization Techniques." *J. Am. Chem. Soc.* **2005**, 127, 6248-6256.

¹⁴⁵ Halperin, A.; Tirrell, M.; Lodge, T. P. "Polymer Brushes." *Adv. Polym. Sci.* **1992**, 100, 31-71.

2.4.3 Surface Modification with Mixed Polymer Brushes

Stamm and coworkers first demonstrated the grafting of mixed homopolymer brushes comprising PS and PVP from silicon/SiO₂ surfaces using surface tethered azo initiators.¹⁴⁶ Using the “grafting from” approach, polymer films of thicknesses between 10 and 100 nm were obtained. Exposure to selective solvents promoted the swelling of one component of the mixed polymer brushes rendering the surface either hydrophobic or hydrophilic. Binary brushes of PS and PVP were also constructed on silicon/SiO₂ using the “grafting to” approach through sequential grafting of carboxyl-terminated polymers to epoxidized surfaces.¹⁴⁷ The composition of the binary brushes was changed by varying the annealing temperature and time of grafting of each component. Such polymer modified surfaces exhibited reversible changes in surface energetics and surface morphologies following selective solvent treatment. Treatment with toluene made the surface hydrophobic while an acidic water treatment made the surfaces hydrophilic. Exposure to toluene (a good solvent for PS) led to the formation of dimples due to segregation of PS to the air interface. In a non-selective solvent like ethanol, a ripple-like morphology was observed consistent with lateral phase segregation of the polymer chains.¹⁴⁸

The adhesion of PS and PVP mixed polymer brush grafted surfaces to a hydrophobic elastomeric adhesive following selective solvent treatments was

¹⁴⁶ Sidorenko, A.; Minko, S.; Schenk-Meuser, K.; Duschner, H.; Stamm, M. "Switching of Polymer Brushes." *Langmuir* **1999**, 15, 8349-8355.

¹⁴⁷ Minko, S.; Patil, S.; Datsyuk, V.; Simon, F.; Eichhorn, K.-J.; Motornov, M.; Usov, D.; Tokarev, I.; Stamm, M. "Synthesis of Adaptive Polymer Brushes via “Grafting to” Approach from Melt." *Langmuir* **2002**, 18, 289-296.

¹⁴⁸ Zhulina, E.; Balazs, A. C. "Designing Patterned Surfaces by Grafting Y-Shaped Copolymers." *Macromolecules* **1996**, 29, 2667-2673.

investigated.¹⁴⁹ Mixed polymer brushes of PS and PVP were also grafted from azo initiators attached to nylon plates and nylon fabric.¹⁵⁰ Water's contact angle switched between 90° and 60° following exposure to toluene and ethanol, respectively. Upon exposure to acidic water, PVP chains were protonated and as a result, the contact angle dropped even further to 35°. On the other hand, water's contact angle on polymer coated nylon fabric changed from 150° to 50° following toluene and ethanol exposure, respectively, while complete wetting was observed after exposure to acidic water. This indicated the influence of surface roughness on the surface wetting characteristics.

In order to investigate the influence of brush composition on the solvent selectivity of mixed brush modified surfaces, a one-dimensional gradient surface with increasing density of one component was obtained through the "grafting to" approach.¹⁵¹ The composition of PS in the near-surface region following exposures to different solvents was estimated using the Cassie equation, which is given in equation 3:

$$\cos\theta = f \cos\theta_A + (1-f) \cos\theta_B \quad \dots\dots\dots (3)$$

where, θ , θ_A , and θ_B are the respective water contact angles on a mixed brush, PS homopolymer, and PVP homopolymer modified surfaces, and "f" refers to the mol fraction of PS on the surface. In the case of toluene surface treatment, the surface was always enriched in PS irrespective of the brush composition. Following ethanol, the PS segregation occurred only when the PS fraction in the mixed brush was greater than 85%.

¹⁴⁹ Retsos, H.; Gorodyska, G.; Kiriya, A.; Stamm, M.; Creton, C. "Adhesion between Chemically Heterogeneous Switchable Polymeric Brushes and an Elastomeric Adhesive." *Langmuir* **2005**, 21, 7722-7725.

¹⁵⁰ Motornov, M.; Minko, S.; Eichhorn, K.-J.; Nitschke, M.; Simon, F.; Stamm, M. "Reversible Tuning of Wetting Behavior of Polymer Surface with Responsive Polymer Brushes." *Langmuir* **2003**, 19, 8077-8085.

¹⁵¹ Ionov, L.; Sidorenko, A.; Stamm, M. "Gradient Mixed Brushes: "Grafting to" Approach." *Macromolecules* **2004**, 37, 7421-7423.

This study therefore demonstrated that by appropriate choice of the surface grafted mixed polymer brush composition it is possible to obtain surfaces with vastly different wetting characteristics. However, such gradient surfaces were not capable of reversing their wettability gradient. Hence, Stamm and coworkers constructed responsive gradient thin films of mixed polyelectrolytes brushes which were covalently grafted onto silicon/SiO₂ surfaces. The gradient films composed of PAA and PVP showed pH responsive changes in wettability.¹⁵² Zhao *et al.* grafted PS and PMMA by sequential polymerization of PS and PMMA from a mixed ATRP/NMP initiator SAM modified surfaces.¹⁵³ The surfaces showed solvent switchable water contact angles and surface topographies that were dependent on homopolymer chain lengths.¹⁵⁴

2.5 Surface Modification with Molecular Recognition Groups Exhibiting Non-covalent Associations

2.5.1 Introduction

Molecular recognition, which is defined as the specific interaction between two molecules without the involvement of covalent bonding forms the basis of supramolecular organization in biological systems.¹⁵⁵ Non-covalent interactions such as electrostatic, hydrogen bonding, host-guest, and π - π stacking are all of central importance in molecular recognition.^{156, 157} Although relatively weak, these directional, multivalent

¹⁵² Ionov, L.; Houbenov, N.; Sidorenko, A.; Stamm, M.; Luzinov, I.; Minko, S. "Inverse and Reversible Switching Gradient Surfaces from Mixed Polyelectrolyte Brushes." *Langmuir* **2004**, 20, 9916-9919.

¹⁵³ Zhao, B. "Synthesis of Binary Mixed Homopolymer Brushes by Combining Atom Transfer Radical Polymerization and Nitroxide-Mediated Radical Polymerization." *Polymer* **2003**, 44, 4079-4083.

¹⁵⁴ Zhao, B. "A Combinatorial Approach to Study Solvent-Induced Self-Assembly of Mixed Poly(Methyl Methacrylate)/ Polystyrene Brushes on Planar Silica Substrates: Effect of Relative Grafting Density." *Langmuir* **2004**, 20, 11748-11755.

¹⁵⁵ Lindoy, I. F.; Atkinson, M. F., " Self-Assembly in Supramolecular Systems." RSC: Cambridge, 2000.

¹⁵⁶ Whitesides, G. M.; Grzybowski, B. " Self-Assembly at All Scales." *Science* **2002**, 295, 2418-2421.

¹⁵⁷ Stupp, S. I.; LeBonheur, V.; Walker, K.; Li, L. S.; Huggins, K. E.; Keser, M.; Amstutz, A. "Supramolecular Materials: Self-Organized Nanostructures." *Science* **1997**, 276, 384-389.

interactions lead to self-assembly of molecules into complex hierarchies with well-defined functional superstructures.

Surface modification with non-covalently interacting molecular recognition groups provides a versatile tool for the control of the physical and chemical properties of a surface. The use of weak, yet directional multivalent interactions not only paves the way for some fundamental studies on the influence of the surface on such processes,¹⁵⁸ but also allows the construction of functional surfaces for a myriad of applications ranging from sensors to nanoscale catalysts. Surface modification with the desired functional groups may be achieved through either physisorption or covalent attachment. While covalent attachment lends stability to the assembled structures, it does not allow for self-correction, necessary for the construction of sophisticated devices. Physisorption, on the other hand, does allow self-correction; however, there is no control over the assembly process and stability of the assembled structures. Supramolecular interactions through molecular recognition on surfaces that are covalently modified with the molecular recognition groups combine the advantages of both the physisorption and covalent modification routes and thus, allows for tuning the stability and reversibility of the surface assembled structures. Therefore suitable methods for obtaining functional surfaces with controlled concentration and orientation of the molecular recognition groups is desirable and often times are achieved using SAM of functional thiols/disulfides or silanes.¹⁵⁹

¹⁵⁸ Schönherr, H.; Paraschiv, V.; Zapotoczny, S.; Crego-Calama, M.; Timmerman, P.; Frank, C. W.; Vansco, G. J.; Reinhoudt, D. N. "Unraveling the Nanostructure of Supramolecular Assemblies of Hydrogen-Bonded Rosettes on Graphite: An Atomic Force Microscopy Study." *Proc. Natl. Acad. Sci. USA* **2002**, 99, 5024-5027.

¹⁵⁹ Ulman, A. "Formation and Structure of Self-Assembled Monolayers." *Chem. Rev.* **1996**, 96, 1533-1554.

Several studies describing receptor-ligand interactions such as biotin-avidin,^{160, 161} antibody-antigen,¹⁶² carbohydrate-lectin¹⁶³ on surfaces for use in biosensing and affinity chromatography were reported. Likewise surface tethered nucleic acids employed as biosensors for forming microarrays and for the reversible assembly of nanoparticles have been extensively explored.^{164, 165}

Functional group complementarity is essential for molecular-recognition-aided design of receptive surfaces. In recent years, many studies have attempted to use groups involving inclusional complexation through host-guest interactions and ionic/ hydrogen bonding interactions on surfaces for reversible adsorption studies. Such specific yet reversible interactions on surfaces allows for the regeneration of a surface after use and may find applications in reusable chemical sensors, separation devices and surfaces with switchable adhesive and wetting properties. This review will primarily focus on surface modification with organic groups that reversibly bind to analytes through specific non-covalent interactions such as those mentioned above for the formation of novel thin films for potential use as sensors, catalysts, and responsive surfaces.

¹⁶⁰ Häussling, L.; Ringsdorf, H.; Schmitt, F.-J.; Knoll, W. "Biotin-Functionalized Self-Assembled Monolayers on Gold: Surface Plasmon Optical Studies of Specific Recognition Reactions." *Langmuir* **1991**, *17*, 1837-1840.

¹⁶¹ Salem, A. K.; Chao, J.; Leong, K. W.; Searson, P. C. "Receptor-Mediated Self-Assembly of Magnetic Nanoparticles." *Adv. Mater.* **2004**, *16*, 268-271.

¹⁶² Jung, S.-H.; Son, H.-Y.; Yuk, J. S.; Jung, J.-W.; Kim, K. H.; Lee, C.-H.; Hwang, H.; Ha, K.-S. "Oriented Immobilization of Antibodies by a Self-Assembled Monolayer of 2-(Biotinamido)Ethanethiol for Immunoarray Preparation." *Colloids Surf., B* **2006**, *47*, 107-111.

¹⁶³ Anilyte, J.; Liesiene, J.; Niemeyer, B. "Evaluation of Cellulose-Based Biospecific Adsorbents as a Stationary Phase for Lectin Affinity Chromatography." *J. Chromatogr. B* **2006**, *831*, 24-30.

¹⁶⁴ Rogers, P. H.; Michel, E.; Bauer, C. A.; Vanderet, S.; Hansen, D.; Roberts, B. K.; Calvez, A.; Crews, J. B.; Lau, K. O.; Wood, A.; Pine, D. J.; Schwartz, P. V. "Selective, Controllable, and Reversible Aggregation of Polystyrene Latex Microspheres via DNA Hybridization." *Langmuir* **2005**, *21*, 5562-5569.

2.5.2 Host-guest Interactions on Surfaces

Host-guest complexes are formed through non-covalent interactions between inner guest molecules that fit into the cavity of the outer host molecules. Host-guest interactions on surfaces were initially used in field effect transistors for the detection of heavy metal ions.¹⁶⁶ Employing host-guest interactions in the design of stable molecular sensors requires the immobilization of one of the species to a surface, which is commonly accomplished through SAM formation.

Some of the commonly studied host molecules are cyclodextrins (CD),¹⁶⁷ which are naturally occurring glucoamylose receptors consisting of 6 (α), 7 (β), 8 (γ), or 9 (δ) 1,4-linked glucose units. CDs consists of a hydrophobic core and a hydrophilic exterior. Because of their amphiphilic character, CDs are capable of forming inclusion complexes with a variety of guest molecules ranging from hydrophobic to ionic molecules. Supramolecular assembly of CDs with a variety of guest species for the construction of molecular machines, motors and switches was recently reviewed by Harada.¹⁶⁸

In 1994, Kaifer and coworkers reported the formation of a SAM of thiolated β -CD on gold surfaces.¹⁶⁹ Due to the large size of the CD head group, the SAM formed was imperfect. Thus, the surfaces were back-filled with pentanethiol prior to studying

¹⁶⁵ Peelen, D.; Smith, L. M. "Immobilization of Amine-Modified Oligonucleotides on Aldehyde-Terminated Alkanethiol Monolayers on Gold." *Langmuir* **2005**, 21, 266-271.

¹⁶⁶ Cobben, P. L. H. M.; Egberink, R. J. M.; Bommer, J. G.; Bergveld, P.; Verboom, W.; Reinhoudt, D. N. "Transduction of Selective Recognition of Heavy Metal Ions by Chemically Modified Field Effect Transistors (Chemfets)." *J. Am. Chem. Soc.* **1992**, 114, 10573-10582.

¹⁶⁷ Noltemeyer, M.; Saenger, W. "Topography of Cyclodextrin Inclusion Complexes. 12. Structural Chemistry of Linear α -Cyclodextrin-Polyiodide Complexes. X-Ray Crystal Structures of ((α -Cyclodextrin)₂.LiI₃).I₂.8H₂O and ((α -Cyclodextrin)₂.Cd_{0.5}).I₅.27H₂O. Models for the Blue Amylose-Iodine Complex." *J. Am. Chem. Soc.* **1980**, 102, 2710-2722.

¹⁶⁸ Harada, A. "Cyclodextrin-Based Molecular Machines." *Acc. Chem. Res.* **2001**, 34, 456-464.

¹⁶⁹ Rojas, M. T.; Koniger, A.; Stoddart, J. F.; Kaifer, A. E. "Supported Monolayers Containing Preformed Binding Sites. Synthesis and Interfacial Binding Properties of a Thiolated β -Cyclodextrin Derivative." *J. Am. Chem. Soc.* **1995**, 117, 336-343.

the molecular recognition capability of the surface attached CDs. The sensing of ferrocene molecules from solution was evaluated using cyclic voltammetry. Upon addition of *m*-toluic acid, which competes with ferrocene for the binding sites on CD and shows higher affinity for the CD cavity, partial removal of the adsorbed ferrocene was observed indicating the reversible nature of the association. Maeda and Kitano used surface-enhanced resonance Raman spectroscopy to study the recognition of azo dyes into the cavities of thiolated β -CDs that were assembled onto Ag colloids.¹⁷⁰ Mittler-Neher and coworkers synthesized several different mono- and multithiolated derivatives of β -CD with different molecular spacers in order to determine the influence of these parameters on the SAM packing density.¹⁷¹ However, no recognition studies with guest molecules were investigated.

Functionalization of amino functionalized β -CD with SAM of MUA-disulfide on gold surfaces produced a densely packed β -CD SAM.¹⁷² The specific recognition of 2-(*p*-toluidinyl)naphthalene-6-sulfonic acid in the presence of a structurally similar 1-anilino-naphthalene-2-sulfonic acid was studied using impedance spectroscopy, which measures the charge transfer to a surface. For a SAM modified surface in the absence of a host, electroactive marker ions $[\text{Fe}(\text{CN})_6]^{3-}/[\text{Fe}(\text{CN})_6]^{4-}$ diffused to the gold electrode through the defects. However, upon adsorption of the guest molecules, the defects were sealed and as a result the charge transfer decreased. On the other hand, non-specific

¹⁷⁰ Maeda, Y.; Kitano, H. "Inclusional Complexation by Cyclodextrins at the Surface of Silver as Evidenced by Surface-Enhanced Resonance Raman Spectroscopy." *J. Phys. Chem.* **1995**, 99, 487-488.

¹⁷¹ Nelles, G.; Weisser, M.; Black, R.; Wolhart, P.; Wenz, G.; Mittler-Neher, S. "Controlled Orientation of Cyclodextrin Derivatives Immobilized on Gold Surfaces." *J. Am. Chem. Soc.* **1996**, 118, 5039-5046.

¹⁷² Henke, C.; Steinem, C.; Janshoff, A.; Steffan, A.; Luftmann, H.; Sieber, M.; Galla, H.-J. "Self-Assembled Monolayers of Monofunctionalized Cyclodextrins onto Gold: A Mass Spectrometric Characterization and Impedance Analysis of Host-Guest Interaction." *Anal. Chem.* **1996**, 68, 3158-3165.

guest molecules did not effectively seal the defects and, as a result, did not block the transfer of the anions as effectively as the specific guests.

Kitano and coworkers investigated chiral recognition characteristics of gold surface confined α -CDs using hydroquinone as a probe.¹⁷³ The extent of reduction in the CD-complexed hydroquinone redox peak currents due to its displacement by the chiral azo dyes of *o*- and *p*-methyl red and their complexes with (*R*)- and (*S*)-1-phenylethylamine was probed using cyclic voltammetry. The *o*-isomer exhibited stronger association with the CD than the *p*-isomer consistent with the solution results; however, the association constant (K_{asn}) between the surface confined CD and the dye molecules in solution was greater than that observed in a homogeneous solution.¹⁷⁴ In addition, stereoselectivity was observed only with the *ortho*-isomer- the (*R*)-enantiomer showed greater association compared to the (*S*)-enantiomer. The enantioselective complexation between gold electrode confined α -CDs and electrochemically active α -amino acid 3,4-dihydroxyphenylalanine (DOPA) and its derivative was investigated.¹⁷⁵ While K_{asn} for the DOPA derivatives with CD SAMs was lower than that observed in solution, surface confined CDs showed better stereoselectivity for the *D*-enantiomer compared to the *L*-enantiomer.

In a similar vein, K_{asn} for interaction between α -CD attached to gold electrodes and various phthalate ester (PAE) derivatives was investigated using hydroquinone as an

¹⁷³ Maeda, Y.; Fukuda, T.; Yamamoto, H.; Kitano, H. "Regio- and Stereoselective Complexation by a Self-Assembled Monolayer of Thiolated Cyclodextrin on a Gold Electrode." *Langmuir* **1997**, 13, 4187-4189.

¹⁷⁴ Yamamoto, H.; Maeda, Y.; Kitano, H. "Molecular Recognition by Self-Assembled Monolayers of Cyclodextrin on Ag." *J. Phys. Chem. B* **1997**, 101, 6855-6860.

¹⁷⁵ Fukuda, T.; Maeda, Y.; Kitano, H. "Stereoselective Inclusion of DOPA Derivatives by a Self-Assembled Monolayer of Thiolated Cyclodextrin on a Gold Electrode." *Langmuir* **1999**, 15, 1887-1890.

indirect electrochemical probe.¹⁷⁶ The K_{asn} values for PAE with CD SAM were higher than that observed with free CDs. The length of the aliphatic alcohols of PAE also influenced the K_{asn} values, with longer alcohols showing better association. However, a similar study with bisphenols (BPA and BPS) showed that the K_{asn} with α -CD SAM was lower than that observed with free CD in solution. The strength of the complexation between BPA and CD SAM was enhanced by the addition of free BPS in solution prior to CD assembly on surfaces possibly due a templating effect where complexed BPS caused a favorable reorganization of the CD cavity before surface deposition. No enhancement for either BPS or BPA association with CD SAMs was observed when BPA was used as the directing agent in solution. Recently Kitano and coworkers showed that the orientation of β -CD in a SAM influenced their complexation with BP derivatives.¹⁷⁷ Surface confined CDs always showed lower K_{asn} than free CDs with the BP derivatives. The adsorption and desorption behavior of random copolymers of BP functionalized methacrylate and acrylamide was investigated using SPR measurements on a modified glass slide coated with CD SAM functionalized colloidal gold.

The assembly of cationic ferrocene functionalized disulfides onto gold surfaces and their interaction with α - and β -CDs in solution was investigated using cyclic voltammetry.¹⁷⁸ In addition to the primary inclusional complexation between the surface confined ferrocene and CDs in solution, a concerted secondary interaction between the

¹⁷⁶ Kitano, H.; Taira, Y.; Yamamoto, H. "Inclusion of Phthalate Esters by a Self-Assembled Monolayer of Thiolated Cyclodextrin on a Gold Electrode." *Anal. Chem.* **2000**, *72*, 2976-2980.

¹⁷⁷ Endo, H.; Hirabayashi, T. D.; Morokoshi, S.; Ide, M. G.; Kitano, H. "Orientational Effect of Surface-Confined Cyclodextrin on the Inclusion of Bisphenols." *Langmuir* **2005**, *21*, 1314-1321.

¹⁷⁸ Sabapathy, R. C.; Bhattacharya, S.; Cleland, W. E.; Hussey, C. L. "Host-Guest Complexation in Self-Assembled Monolayers: Inclusion of a Monolayer-Anchored Cationic Ferrocene-Based Guest by Cyclodextrin Hosts." *Langmuir* **1998**, *14*, 3797-3807.

counter anions attached to the cationic ferrocene and the hydrophilic groups of CDs led to a very strong irreversible association between the host and the guest.

In 2004, Matsui and coworkers reported electrochemically induced specific and reversible attachment/detachment of ferrocene functionalized peptide nanotubes on β -CD SAM modified patterned gold substrates.¹⁷⁹ In a related work, they also reported the assembly of azobenzene containing peptide nanotubes on α -CD SAM functionalized gold surfaces.¹⁸⁰ Photoisomerization of the azobenzene moieties to the cis conformation was used to detach the immobilized nanotubes from the surface. This photoisomerization induced attachment/detachment of the nanotubes to CDs was completely reversible. Such reversibly associating nanotubes could find potential applications as electrical switches or photochemical sensors.

Another well-known interaction is that between CDs and adamantane. CD capped adamantyl-functionalized PPI dendimer (PPI-Ad) was assembled onto β -CD SAM modified gold surfaces.¹⁸¹ Due to multiple interactions with the substrate, the adsorbed PPI-Ad was very stable to water washes; however, it was removed upon rinsing with aqueous CD solutions because of competitive interactions. Similarly, microcontact printing was used to assemble a variety of molecules such as calixarenes, rhodamine dye, and PPI dendrimers functionalized with multiple adamantyl groups in specific locations

¹⁷⁹ Chen, Y.; Banerjee, I. A.; Yu, L.; Djalali, R.; Matsui, H. "Attachment of Ferrocene Nanotubes on α -Cyclodextrin Self-Assembled Monolayers with Molecular Recognitions." *Langmuir* **2004**, 20, 8409-8413.

¹⁸⁰ Banerjee, I. A.; Yu, L.; Matsui, H. "Application of Host-Guest Chemistry in Nanotube-Based Device Fabrication: Photochemically Controlled Immobilization of Azobenzene Nanotubes on Patterned α -CD Monolayer/Au Substrates Via Molecular Recognition." *J. Am. Chem. Soc.* **2003**, 125, 9542-9543.

¹⁸¹ Huskens, J.; Deij, M. A.; Reinhoudt, D. N. "Attachment of Molecules at a Molecular Printboard by Multiple Host-Guest Interactions." *Angew. Chem. Int. Ed. Eng.* **2002**, 41, 4467-4471.

on β -CD SAM modified gold surfaces.¹⁸² Binding strengths for multiple β -CD/adamantane interactions on surfaces ($\sim 10^9$ - 10^{10} M⁻¹) was significantly higher than that observed for such a binding event in solution ($\sim 10^7$ M⁻¹). This enhanced binding on surfaces was attributed to high localized concentrations of CD on the surface. Similar cooperative β -CD/adamantane interactions were used for forming complex structures such as molecular capsules of calixarenes on gold surfaces.^{183, 184} A positively charged adamantyl-calixarene was assembled on β -CD SAM through multiple host-guest interactions. Then a second layer of anionic calixarene was electrostatically assembled on top of the previously immobilized cationic calixarene. Thus, molecular recognition through cooperative non-covalent associations has enabled the construction of complex architectures, which display tunable stability and reversibility on surfaces.

Metal and semiconductor nanoparticles have unique optical, electronic, and material properties that could find a wide range of applications such as sensors, quantum dots, and nanoscale devices to name a few. Thus, the assembly of nanoparticles into controlled aggregates with tunable properties for use in devices has gained importance in recent years. Mirkin and coworkers have used DNA to assemble gold nanoparticles into

¹⁸² Auletta, T.; Dordi, B.; Mulder, A.; Sartori, A.; Onclin, S.; Bruinink, C. M.; Péter, M.; Nijhuis, C. A.; Beijleveld, H.; Schönherr, H.; Vancso, G. J.; Casnati, A.; Ungaro, R.; Ravoo, B. J.; Huskens, J.; Reinhoudt, D. N. "Writing Patterns of Molecules on Molecular Printboards." *Angew. Chem. Int. Ed. Eng.* **2004**, *43*, 369-373.

¹⁸³ Corbellini, F.; Mulder, A.; Sartori, A.; Ludden, M. J. W.; Casnati, A.; Ungaro, R.; Huskens, J.; Crego-Calama, M.; Reinhoudt, D. N. "Assembly of a Supramolecular Capsule on a Molecular Printboard." *J. Am. Chem. Soc.* **2004**, *126*, 17050-17058.

¹⁸⁴ Mulder, A.; Auletta, T.; Sartori, A.; Ciotto, S. D.; Casnati, A.; Ungaro, R.; Huskens, J.; Reinhoudt, D. N. "Divalent Binding of a Bis(Adamantyl)-Functionalized Calix[4]Arene to α -Cyclodextrin-Based Hosts: An Experimental and Theoretical Study on Multivalent Binding in Solution and at Self-Assembled Monolayers." *J. Am. Chem. Soc.* **2004**, *126*, 6627-6636.

large assemblies with controlled and variable material properties for use in detectors, and nanodevices.^{185, 186}

Kaifer and coworkers were the first to demonstrate the use of host-guest interactions between ferrocene and β -CD to associate gold nanoparticles into reversible macroscopic aggregates.¹⁸⁷ The gold nanoparticle surfaces modified with thiolated β -CD were complexed with ferrocene dimer, which resulted in the flocculation of the particles.¹⁸⁸ The addition of monofunctional ferrocene in solution at higher temperature led to partial redispersion of the flocculated colloidal particles. Earlier the preparation of water soluble Au, Pt, and Pd nanoparticles and their complexation with guests such as ferrocenemethanol and 1-adamantol was reported.^{189, 190}

Calix[n]arenes, which are bucket-shaped molecules consisting of $n = 4-11$ phenyl units, are capable of sensing a variety of organic molecules and ions in solution through a combination of weak van der Waals, π - π and induced dipole interactions.¹⁹¹ Modification of solid surfaces with calixarenes has therefore been explored to develop highly sensitive organic molecule sensors. Reinhoudt *et al.* were the first to covalently

¹⁸⁵ Mirkin, C. A.; Letsinger, R. L.; Mucic, R. C.; Storhoff, J. J. "A DNA-Based Method for Rationally Assembling Nanoparticles into Macroscopic Materials." *Nature* **1996**, 382, 607-609.

¹⁸⁶ Elghanian, R.; Storhoff, J. J.; Mucic, R. C.; Letsinger, R. L.; Mirkin, C. A. "Selective Colorimetric Detection of Polynucleotides Based on the Distance-Dependent Optical Properties of Gold Nanoparticles." *Science* **1997**, 277, 1078-1081.

¹⁸⁷ Liu, J.; Mendoza, S.; Roman, E.; Lynn, M. J.; Xu, R.; Kaifer, A. E. "Cyclodextrin-Modified Gold Nanospheres. Host-Guest Interactions at Work to Control Colloidal Properties." *J. Am. Chem. Soc.* **1999**, 121, 4304-4305.

¹⁸⁸ Liu, J.; Alvarez, J.; Kaifer, A. E. "Metal Nanoparticles with a Knack for Molecular Recognition." *Adv. Mater.* **2000**, 12, 1381-1383.

¹⁸⁹ Liu, J.; Ong, W.; Román, E.; Lynn, M. J.; Kaifer, A. E. "Cyclodextrin-Modified Gold Nanospheres." *Langmuir* **2000**, 16, 3000-3002.

¹⁹⁰ Liu, J.; Alvarez, J.; Ong, W.; Román, E.; Kaifer, A. E. "Tuning the Catalytic Activity of Cyclodextrin-Modified Palladium Nanoparticles through Host-Guest Binding Interactions." *Langmuir* **2001**, 17, 6762-6764.

¹⁹¹ Gutsche, C. D., "Calixarenes." The Royal Society of Chemistry: London, 1989.

modify gold surfaces with calix[4]arene for use as sensors.¹⁹² Following this study Crooks *et al.* modified gold surfaces with self-assembled bilayers of polydiacetylene and various calixarenes and studied the sensing of various VOCs by the surface confined calixarenes.¹⁹³ Allara *et al.* modified quartz crystals with thiolated calixarenes and studied the influence of monolayer order on the sensing of various aromatic and aliphatic analytes from solution.¹⁹⁴ Silica/quartz/gold surfaces functionalized with calixarene SAMs were used for selective and reversible sensing of aromatic molecules in solution¹⁹⁵,¹⁹⁶ Kitano and coworkers described the use of surface immobilized calix[6]arenes as highly sensitive sensors for the detection of various bisphenol derivatives, which are potential endocrine disrupters.¹⁹⁷ The K_{asn} values for the surface bound complex was lower than the complex formed in solution, which was attributed to steric and orientation issues associated with the calixarene molecules in the SAM. As a result, the obtained sensors displayed reversible association with the bisphenol molecules. Kaifer and

¹⁹² Huisman, B.-H.; Van Velzen, E. U. T.; Van Veggel, F. C. J. M.; Engbersen, J. F. J.; Reinhoudt, D. N. "Self-Assembled Monolayers of Calix[4]Arene Derivatives on Gold." *Tetrahedron Lett.* **1995**, 36, 3273-3276.

¹⁹³ Dermody, D. L.; Crooks, R. M.; Kim, T. "Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 11. Synthesis, Characterization, and Chemical Sensitivity of Self-Assembled Polydiacetylene/Calix[n]Arene Bilayers." *J. Am. Chem. Soc.* **1996**, 118, 11912-11917.

¹⁹⁴ Cygan, M. T.; Collins, G. E.; Dunbar, T. D.; Allara, D. L.; Gibbs, C. G.; Gutsche, C. D. "Calixarene Monolayers as Quartz Crystal Microbalance Sensing Elements in Aqueous Solution." *Anal. Chem.* **1999**, 71, 142-148.

¹⁹⁵ Marengo, C.; Stirling, C. J. M.; Yarwood, J. "Thiacalixarene Self-Assembled Monolayers on Roughened Gold Surfaces and Their Potential as SERS-Based Chemical Sensors." *J. Raman. Spectrosc.* **2001**, 32, 183-194.

¹⁹⁶ Leyton, P.; Domingo, C.; Sanchez-Cortes, S.; Campos-Vallette, M.; Garcia-Ramos, J. V. "Surface Enhanced Vibrational (IR and Raman) Spectroscopy in the Design of Chemosensors Based on Ester Functionalized p-Tert-Butylcalix[4]Arene Hosts." *Langmuir* **2005**, 21, 11814-11820.

¹⁹⁷ Nakaji-Hirabayashi, T.; Endo, H.; Kawasaki, H.; Gemmei-Ide, M.; Kitano, H. "Inclusion of Bisphenols by a Self-Assembled Monolayer of Thiolated Calix[6]Arene on a Gold Surface." *Environ. Sci. Technol.* **2005**, 39, 5414-5420.

coworkers investigated the interaction between free calix[4]arene and ferrocene molecules immobilized on gold surfaces.¹⁹⁸

C₆₀, which shows many interesting properties such as superconductivity, non-linear optical properties, and biological activity have been assembled on surfaces using SAMs and the LB-technique to form well-defined fullerene arrays. The immobilization however, partially destroys their π -delocalization, which, in turn, affects their electronic properties. In addition, fullerenes exhibit high tendency for aggregation in solution that also affects their electronic properties. Thus, non-covalent host-guest associations between C₆₀ and a variety of host molecules such as calix[n]arenes, cyclohexatrylene (CTV) and crown ethers were investigated in order to obtain stable C₆₀ complexes.^{199, 200} Recently, Echegoyen *et al.* described the use of surface immobilized cyclohexatrylene for the non-covalent assembly of C₆₀ on gold surfaces.²⁰¹ The structure of the cyclohexatrylene derivatives influenced their complexation with the underivatized C₆₀. Despite immobilization, the C₆₀ molecules showed a well-defined redox behavior very similar to that observed in solution. Thus, the host-guest interaction mediated surface immobilization of C₆₀ did not affect the properties of the surface-confined fullerene molecules. In a related study, the same group reported the host-guest complexation

¹⁹⁸ Zhang, L.; Godínez, L. A.; Lu, T.; Gokel, G. W.; Kaifer, A. E. "Molecular Recognition at an Interface: Binding of Monolayer-Anchored Ferrocenyl Groups by an Amphiphilic Calixarene Host." *Angew. Chem. Int. Ed. Eng.* **1995**, 34, 235-237.

¹⁹⁹ Atwood, J. L.; Kousantonis, G. A.; Raston, C. L. "Purification of C₆₀ and C₇₀ by Selective Complexation with Calixarenes." *Nature* **1994**, 368, 229-231.

²⁰⁰ Steed, J. W.; Junk, P. C.; Atwood, J. L. "Ball and Socket Nanostructures: New Supramolecular Chemistry Based on Cyclohexatrylene." *J. Am. Chem. Soc.* **1994**, 116, 10346-10347.

²⁰¹ Zhang, S.; Palkar, A.; Fragoso, A.; Prados, P.; de Mendoza, J.; Echegoyen, L. "Noncovalent Immobilization of C₆₀ on Gold Surfaces by SAMs of Cyclohexatrylene Derivatives." *Chem. Mater.* **2005**, 17, 2063-2068.

between calix[n]arene SAMs on gold electrodes and C₆₀ in solution.²⁰² Only calix[8]arene was found to bind the C₆₀ molecules while calixarenes with smaller cavity sizes could not bind the fullerenes. Recently, Gasparrini *et al.* described a variable temperature chromatographic procedure for the determination of *p-tert*-butylcalixarenes and silica surface immobilized C₆₀, C₇₀ complex stabilities.²⁰³

The assembly of polymers containing host molecules as described above allows the formation of robust thin films of varying thickness and concentration of functional groups, which could enhance the sensitivity of the sensors. Yang *et al.* designed polymeric thin films on silicon/silica surfaces using a stepwise approach.²⁰⁴ Surfaces functionalized with vinyl terminated SAM were reacted with poly(dimethylhydrosilane)s, which were subsequently functionalized with β -CD. In an alternate approach, the direct immobilization of β -CD containing copolymers was attempted. Surface acoustic wave measurements were used to study the organic vapor sensing of the modified surfaces. Very good sensitivity was observed for *o*-nitrotoluene vapors at parts per billion levels and the coatings were stable for extended periods without any detectable loss in their sensing response.

2.5.3 Electrostatic Interactions on Surfaces

Apart from host-guest interactions, electrostatic or ion-ion binding interactions were also used to assemble molecules on surfaces. Electrostatic interactions between oppositely charged molecules are strong enough to obtain stable assemblies; however,

²⁰² Zhang, S.; Echegoyen, L. "Supramolecular Incorporation of Fullerenes on Gold Surfaces: Comparison of C₆₀ Incorporation by Self-Assembled Monolayers of Different Calix[n]Arene (n = 4, 6, 8) Derivatives." *J. Org. Chem.* **2005**, *70*, 9874-9881.

²⁰³ Gasparrini, F.; Misiti, D.; Della Negra, F.; Maggini, M.; Scorrano, G.; Villani, C. "Molecular Recognition of *p*-Tert-Butylcalixarenes by Surface-Linked Fullerenes C₆₀ and C₇₀." *Tetrahedron* **2001**, *57*, 6997-7002.

they are also highly reversible upon the application of a suitable stimulus such as pH or ionic strength. Crooks and coworkers investigated electrostatic interactions between carboxylic- and sulfonic acid functionalized SAMs and vapors of n-alkylamine.²⁰⁵ The interaction was purely electrostatic when the SAM was disordered while hydrogen bonding was prevalent with ordered SAMs. Bilayers formed between the acid SAMs and base molecules through electrostatic interactions were stable over extended periods of time compared to those that involved just hydrogen bonding interactions. Using electrostatic assembly between a carboxylate SAM on gold and Cu^{2+} , Crooks *et al.* constructed a chemical sensor, which exhibited selective and reversible binding to a nerve agent stimulant diisopropylphosphonate.²⁰⁶

Interfacial force microscopy was used to study the strengths of electrostatic interactions in comparison to other non-covalent interactions typically encountered at interfaces such as van der Waals and hydrogen bonding.²⁰⁷ The adhesion energies between two gold surfaces modified with thiolated SAMs terminated with -methyl, $-\text{NH}_2$ and $-\text{COOH}$ groups were determined using the adhesive pull-off forces. Maximum adhesion energy was observed for surfaces interacting electrostatically through acid-base interactions compared to those that involved only hydrogen bonding interactions.

The preparation of electrode surfaces presenting preformed binding sites that are capable of molecular recognition for possible use as sensors requires multistep assembly

²⁰⁴ Yang, X.; Shi, J.; Johnson, S.; Swanson, B. "Growth of Ultrathin Covalently Attached Polymer Films: Uniform Thin Films for Chemical Microsensors." *Langmuir* **1998**, *14*, 1505-1507.

²⁰⁵ Sun, L.; Crooks, R. M.; Ricco, A. J. "Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 5. Acid-Base Interactions." *Langmuir* **1993**, *9*, 1775-1780.

²⁰⁶ Kepley, L. J.; Crooks, R. M.; Ricco, A. J. "Selective Surface Acoustic Wave-Based Organophosphonate Chemical Sensor Employing a Self-Assembled Composite Monolayer: A New Paradigm for Sensor Design." *Anal. Chem.* **1992**, *64*, 3191-3193.

²⁰⁷ Thomas, R. C.; Houston, J. E.; Crooks, R. M.; Kim, T.; Michalske, T. A. "Probing Adhesion Forces at the Molecular Scale." *J. Am. Chem. Soc.* **1995**, *117*, 3830-3834.

and often times leads to disorganized monolayers. Kaifer and coworkers demonstrated a convenient approach for the assembly of well-organized multilayers of amphiphilic amine terminated α -, β -, and γ -CD derivatives on gold through electrostatic interactions with acid terminated SAM.²⁰⁸ Spontaneous adsorption of the derivatized CDs from neutral solutions onto bare gold surfaces, on the other hand, led to disorganized monolayers.

Similarly, other studies have also described the assembly of host-guest complexes through electrostatic interactions onto surfaces. Shinkai and coworkers electrostatically deposited 2:1 cationic complexes of homooxalix[3]arene and C₆₀ fullerenes onto indium tin oxide (ITO) electrodes functionalized with sulfonate SAMs.²⁰⁹ The immobilized C₆₀ showed reversible redox behavior characteristic of free C₆₀. In addition, the immobilized C₆₀ showed very good photoresponsive behavior under visible light irradiation. Amplification of the photocurrent was achieved using electrostatic assembly of a copolymer functionalized with photoactive metallo-porphyrin groups on the cationic homooxalix[3]arene/C₆₀ complex.²¹⁰

Other researchers revealed pH responsive bilayers constructed between mercaptopyrindine SAM formed on gold surfaces and anthraquinone sulfonic acids.²¹¹

²⁰⁸ Godínez, L. A.; Lin, J.; Muñoz, M.; Coleman, A. W.; Rubin, R.; Parikh, A.; Zawodzinski Jr., T.; Loveday, D.; Ferraris, J. P.; Kaifer, A. E. "Multilayer Self-Assembly of Amphiphilic Cyclodextrin Hosts on Bare and Modified Gold Substrates: Controlling Aggregation Via Surface Modification." *Langmuir* **1998**, *14*, 137-144.

²⁰⁹ Hatano, T.; Ikeda, A.; Akiyama, T.; Yamada, S.; Sano, M.; Kanekiyo, Y.; Shinkai, S. "Facile Construction of an Ultrathin [60]Fullerene Layer from [60]Fullerene-Homooxalix[3]Arene Complexes on a Gold Surface." *J. Chem. Soc., Perkin Trans. 2* **2000**, 909-912.

²¹⁰ Ikeda, A.; Hatano, T.; Shinkai, S.; Akiyama, T.; Yamada, S. "Efficient Photocurrent Generation in Novel Self-Assembled Multilayers Comprised of [60]Fullerene-Cationic Homooxalix[3]Arene Inclusion Complex and Anionic Porphyrin Polymer." *J. Am. Chem. Soc.* **2001**, *123*, 4855-4856.

²¹¹ Jones, T. A.; Perez, G. P.; Johnson, B. J.; Crooks, R. M. "Interactions between Organized, Surface-Confined Monolayers and Liquid-Phase Probe Molecules. 3. Fundamental Aspects of the Binding Interaction between Charged Probe Molecules and Organomeraptan Monolayers." *Langmuir* **1995**, *11*, 1318-1328.

Electrostatic adsorption between acid SAMs and bolamphiphiles, which are molecules containing two hydrophilic groups separated by a hydrophobic spacer, were used to form surfaces exhibiting reversible electrical and adhesion properties.²¹² A pH reversible chemically selective coating was obtained through electrostatic adsorption between an acid terminated SAM on gold and a pentamidine amphiphile.²¹³ Complete disassembly/reassembly of this coating was observed when the pH was changed between 8.7 and 3. The positively charged amidinium surface was capable of reversibly sensing phosphate biomolecules and DNA-oligonucleotides.²¹⁴ Reversible assembly of positively charged surfactants and proteins to acid SAMs, and negatively charged proteins to the amidinium coated SAM surface was also demonstrated.²¹⁵

Using a similar concept, Ulman *et al.* constructed a tunable metal nanocomposite assembly. Acid SAM terminated gold nanoparticles were assembled on mercaptohexanoic acid SAM functionalized gold surface through electrostatic interactions with a bisamidine crosslinker.²¹⁶ The length of the alkyl chain of the bisamidine crosslinker influenced the packing density and stability of the surface assembled nanoparticles. The immobilized nanoparticles exhibited optical properties that were similar to bulk gold indicating the uniformity of this modification approach.

²¹² Mao, G.; Tsao, Y.-H.; Tirrell, M.; Davis, H. T. "Monolayers of Bolaform Amphiphiles: Influence of Alkyl Chain Length and Counterions." *Langmuir* **1994**, 10, 4174-4184.

²¹³ Sellergren, B.; Swietlow, A.; Arnebrant, T.; Unger, K. "Consecutive Selective Adsorption of Pentamidine and Phosphate Biomolecules on a Self-Assembled Layer: Reversible Formation of a Chemically Selective Coating." *Anal. Chem.* **1996**, 68, 402-407.

²¹⁴ Sellergren, B.; Auer, F.; Arnebrant, T. "Selective Adsorption of Oligonucleotides on Switchable Self-Assembled Monolayers." *Chem. Commun.* **1999**, 2001-2002.

²¹⁵ Auer, F.; Schubert, D. W.; Stamm, M.; Arnebrant, T.; Swietlow, A.; Zizlsperger, M.; Sellergren, B. "Switchable Assembly of Stable, Ordered Molecular Layers." *Chem. Eur. J.* **1999**, 5, 1150-1159.

²¹⁶ Auer, F.; Scotti, M.; Ulman, A.; Jorden, R.; Sellergren, B.; Garno, J.; Liu, G.-Y. "Nanocomposites by Electrostatic Interactions: 1. Impact of Sublayer Quality on the Organization of Functionalized Nanoparticles on Charged Self-Assembled Layers." *Langmuir* **2000**, 16, 7554-7557.

The electrostatic assembly of mixed nanoparticles for the formation of tunable macroscopic aggregates was demonstrated by Rotello and coworkers.²¹⁷ Silica and gold nanoparticles were functionalized with amine and carboxylic acid SAMs, respectively. Acid-base interactions between the nanoparticles led to the spontaneous formation of gold/SiO₂ mixed-colloid aggregates. The size and shape of the assembled constructs were controlled by varying the particle size of the two components and their stoichiometry in the initial mixture. Similarly, porous gold, silica, and mixed gold/silica aggregates were constructed using acid SAM functionalized nanoparticles and amine functionalized random copolymers of styrene and chloromethylstyrene.²¹⁸ In order to vary the density of amine groups in the polymer, the chloromethyl groups were converted to unreactive ether groups and the remaining chlorine sites were converted to amino groups. The size of the binary nanoparticle/polymer aggregates created depended on the ratio of the two components: increasing the ratio of the nanoparticle relative to the polymer led to aggregates as large as tens of micrometers. In the case of ternary mixtures, the aggregate size was strongly dependent on the relative ratios of the nanoparticles. The order of component addition also affected the ensemble structure; premixing led to homogeneous nanocomposites, while stepwise addition of nanoparticles and polymer resulted in segregated structures.

Murphy and coworkers used electrostatic assembly to immobilize positively charged cetyltrimethylammonium bromide stabilized gold nanorods onto 16-

²¹⁷ Galow, T. H.; Boal, A. K.; Rotello, V. M. "A "Building Block" Approach to Mixed-Colloid Systems through Electrostatic Self-Organization." *Adv. Mater.* **2000**, 12, 576-579.

²¹⁸ Boal, A. K.; Galow, T. H.; Ilhan, F.; Rotello, V. M. "Binary and Ternary Polymer-Mediated "Bricks and Mortar" Self-Assembly of Gold and Silica Nanoparticles." *Adv. Funct. Mater.* **2001**, 11, 461-465.

mercaptohexadecanoic acid (MHA) SAM modified gold coated glass slides.²¹⁹ Variation of the solution pH used for nanorod immobilization controlled the density of the surface immobilized nanorods as visualized using scanning electron microscopy (SEM). Sastry *et al.* demonstrated pH tunable electrostatic adsorption of carboxylic acid functionalized silver nanoparticles onto 4-aminothiophenol SAM modified gold substrates.²²⁰ Mass changes studied using quartz crystal microbalance showed significant increase only on surfaces coated with the phenolic SAM following immersion in carboxylate functionalized silver colloidal solution. Negligible changes were observed on octadecylthiolated SAM modified surfaces. Thus, silver particles assembled onto the gold surfaces through electrostatic interactions. In addition, ionization of either of the two species to a significant extent resulted in negligible nanoparticle immobilization on the surface as electrostatic repulsive interactions overcame the electrostatic attractions. Recently, formation of mixed organic/inorganic mixed nanocomposites comprising fullerene/cadmium telluride nanoparticles²²¹ or fullerene/gold nanoparticles²²² was reported. The mixed nanocomposites formed through electrostatic interaction between ammonium and carboxylate groups formed stable ensembles in solution.

²¹⁹ Gole, A.; Orendorff, J.; Murphy, J. " Immobilization of Gold Nanorods onto Acid-Terminated Self-Assembled Monolayers via Electrostatic Interactions." *Langmuir* **2004**, 20, 7117-7122.

²²⁰ Gole, A.; Sainkar, S. R.; Sastry, M. " Controlled Organization of Carboxylic Acid Derivatized Colloidal Silver Particles on Amine-Terminated Self-Assembled Monolayers." *Chem. Mater.* **2000**, 12, 1234-1239.

²²¹ Guldi, D. M.; Zilberman, I.; Anderson, G.; Kotov, N. A.; Tagmatarchis, N.; Prato, M. "Versatile Organic (Fullerene)-Inorganic (CdTe Nanoparticle) Nanoensembles." *J. Am. Chem. Soc.* **2004**, 123, 14340-14341.

²²² Lim, I.-I. S.; Ouyang, J.; Luo, J.; Wang, L.; Zhou, S.; Zhong, C.-J. "Multifunctional Fullerene-Mediated Assembly of Gold Nanoparticles." *Chem. Mater.* **2005**, 17, 6528-6531.

Electrostatic adsorption has also found widespread use in the construction of multilayer thin films of synthetic polymers,²²³ DNA,²²⁴ proteins,²²⁵ and nanoparticles²²⁶ for use as biosensors, membranes, and biocompatible coatings. Also, the trapping of several different functional biomolecules such as proteins, polysaccharides and enzymes in the LBL films without significant loss in their activity was possible.^{227, 228, 229} Multilayer thin films comprising strong polyelectrolytes of appreciable molecular weights are typically stable when immersed in salt solutions. Thus, the design of stimuli responsive assembly and disassembly of electrostatically assembled thin films in sensing and drug delivery applications requires the use of low molecular weight species.²³⁰

Schüler and Caruso designed a hollow biodegradable microcapsule using electrostatic LBL assembly of DNA and a low molecular weight naturally occurring polyamine, spermidine (SP) on crosslinked melamine-formaldehyde particles.²³¹ Following acid hydrolysis of the polymer particle, hollow microcapsules of DNA/SP hybrids were obtained. Multilayer assembly consisting of high molecular weight

²²³ Hammond, P. T. "Recent Explorations in Electrostatic Multilayer Thin Films." *Curr. Opin. Colloid Interface Sci.* **1999**, 4, 430-442.

²²⁴ Chen, X.; Lang, J.; Liu, M. "Layer-by-Layer Assembly of DNA-Dye Complex Films." *Thin Solid Films* **2002**, 409, 227-232.

²²⁵ Disawal, S.; Qiu, J.; Elmore, B. B.; Lvov, Y. M. "Two-Step Sequential Reaction Catalyzed by Layer-by-Layer Assembled Urease and Arginase Multilayers." *Colloids Surf., B* **2003**, 32, 145-156.

²²⁶ Mamedov, A. A.; Belov, A.; Giersig, M.; Mamedova, N. N.; Kotov, N. A. "Nanorainbows: Graded Semiconductor Films from Quantum Dots." *J. Am. Chem. Soc.* **2001**, 128, 7738-7739.

²²⁷ Lvov, Y. M.; Ariga, K.; Ichinose, I.; Kunitake, T. "Assembly of Multicomponent Protein Films by Means of Electrostatic Layer-by-Layer Adsorption." *J. Am. Chem. Soc.* **1995**, 117, 6117-6123.

²²⁸ Onda, M.; Lvov, Y. M.; Ariga, K.; Kunitake, T. "Sequential Actions of Glucose Oxidase and Peroxidase in Molecular Films Assembled by Layer-by-Layer Alternate Adsorption." *Biotechnol. Bioeng.* **1996**, 51, 163-167.

²²⁹ Thierry, B.; Winnik, F. M.; Merhi, Y.; Tabrizian, M. "Nanocoatings onto Arteries via Layer-by-Layer Deposition: Toward the in Vivo Repair of Damaged Blood Vessels." *J. Am. Chem. Soc.* **2003**, 125, 7494-7495.

²³⁰ Caruso, F.; Lichtenfeld, H.; Donath, E.; Möhwald, H. "Investigation of Electrostatic Interactions in Polyelectrolyte Multilayer Films: Binding of Anionic Fluorescent Probes to Layers Assembled onto Colloids." *Macromolecules* **1999**, 32, 2317-2328.

²³¹ Schüler, C.; Caruso, F. "Decomposable Hollow Biopolymer-Based Capsules." *Biomacromolecules* **2001**, 2, 921-926.

poly(alginate) and poly(lysine) were stable to immersion in salt solution, while the DNA/SP capsules readily decomposed upon exposure to NaCl solution making them attractive as delivery vehicles for dyes, drugs etc. Chung and Rubner studied the loading and pH induced release of methylene blue dye molecules from PAA/poly(allylamine hydrochloride) (PAH) multilayer thin films assembled at a pH of 2.5.²³² The dye was found to bind at a pH of 7, however; upon decreasing the pH of the solution, the dye molecules were released due to electrostatically induced swelling of the film and the loss of free carboxylate groups.

Hiller and Rubner constructed multilayer thin films of PAH/poly(styrene sulfonic acid) that showed reversible swelling-deswelling behavior at low and high pH, respectively.²³³ This behavior was therefore used in pH induced reversible loading and release of anionic dye molecules. Hydrolytically degradable LBL thin films were obtained from poly(β -amino ester) and model therapeutic polysaccharides.²³⁴ These films were assembled on a non-degradable base layer of PEI/poly(sodium 4-styrenesulfonate) that was deposited on silicon/SiO₂ surfaces. pH dependent degradation and release of the therapeutic agents was evaluated. The films were stable at pH 5 but showed increasing extents of degradation as pH increased from 6.2 to 7.4.

2.5.4 Hydrogen Bonding Interactions on Surfaces

Hydrogen bonding, which is crucial to many basic processes of life such as DNA replication, protein syntheses, and specific molecular recognition, is a directional

²³² Chung, A. J.; Rubner, M. F. "Methods of Loading and Releasing Low Molecular Weight Cationic Molecules in Weak Polyelectrolyte Multilayer Films." *Langmuir* **2002**, 18, 1176-1184.

²³³ Hiller, J.; Rubner, M. F. "Reversible Molecular Memory and pH-Switchable Swelling Transitions in Polyelectrolyte Multilayers." *Macromolecules* **2003**, 36, 4078-4083.

²³⁴ Wood, K. C.; Boedicker, J. Q.; Lynn, D. M.; Hammond, P. T. "Tunable Drug Release from Hydrolytically Degradable Layer-by-Layer Thin Films." *Langmuir* **2005**, 21, 1603-1609.

interaction between a proton donor (A) and a proton acceptor (D). Donors are typically hydrogen atoms bonded to an electronegative atom, while the acceptor is the electronegative atom itself. Due to the electronegativity difference between the hydrogen atom and the electronegative atom, the bond is polarized and this charge separation results in a moderately acidic proton which is attracted to the electronegative donor (D) forming a hydrogen bond. Although hydrogen bonds between neutral organic molecules are not one of the strongest possible interactions, they are widely used in the formation of supramolecular ensembles because of their versatility and directionality.²³⁵ The strength of hydrogen bonds between two molecules depends on many factors such as the acidity of the donor and basicity/nucleophilicity of the acceptor, number of hydrogen bonds between A and D, solvent and temperature. Hydrogen bonds have dissociation energies typically in the range of 1-10 kcal/mol compared to 70-110 kcal/mol observed for covalent bonds. Therefore cooperative multiple hydrogen bonding associations are often desired in order to design supramolecular systems with properties comparable to covalently bonded systems.²³⁶ Supramolecular materials constructed using hydrogen bonds range from systems comprising single hydrogen bonds to those involving up to six hydrogen bonds per molecule. Multiple hydrogen bonding groups are typically classified into two families. Self-complementary multiple hydrogen bonding (SCMHB), involves identical hydrogen bonding units and complementary multiple hydrogen bonding (CMHB) involves dissimilar acceptor and donor units. Some common examples of groups exhibiting multiple hydrogen bond interactions include DNA bases such as

²³⁵ Brunsveld, L.; Folmer, B. J. B.; Meijer, E. W.; Sijbesma, R. P. "Supramolecular Polymers." *Chem. Rev.* **2001**, 101, 4071-4097.

²³⁶ Sherrington, D. C.; Taskinen, K. A. "Self-Assembly in Synthetic Macromolecular Systems via Multiple Hydrogen Bonding Interactions." *Chem. Soc. Rev.* **2001**, 30, 83-93.

adenine-thymine (double), melamine-barbituric acid (triple), diaminotriazine/thymine (triple), and ureidopyrimidinones (quadruple). The structures and the hydrogen bonding between some of these molecules are represented in Figure 2-6.

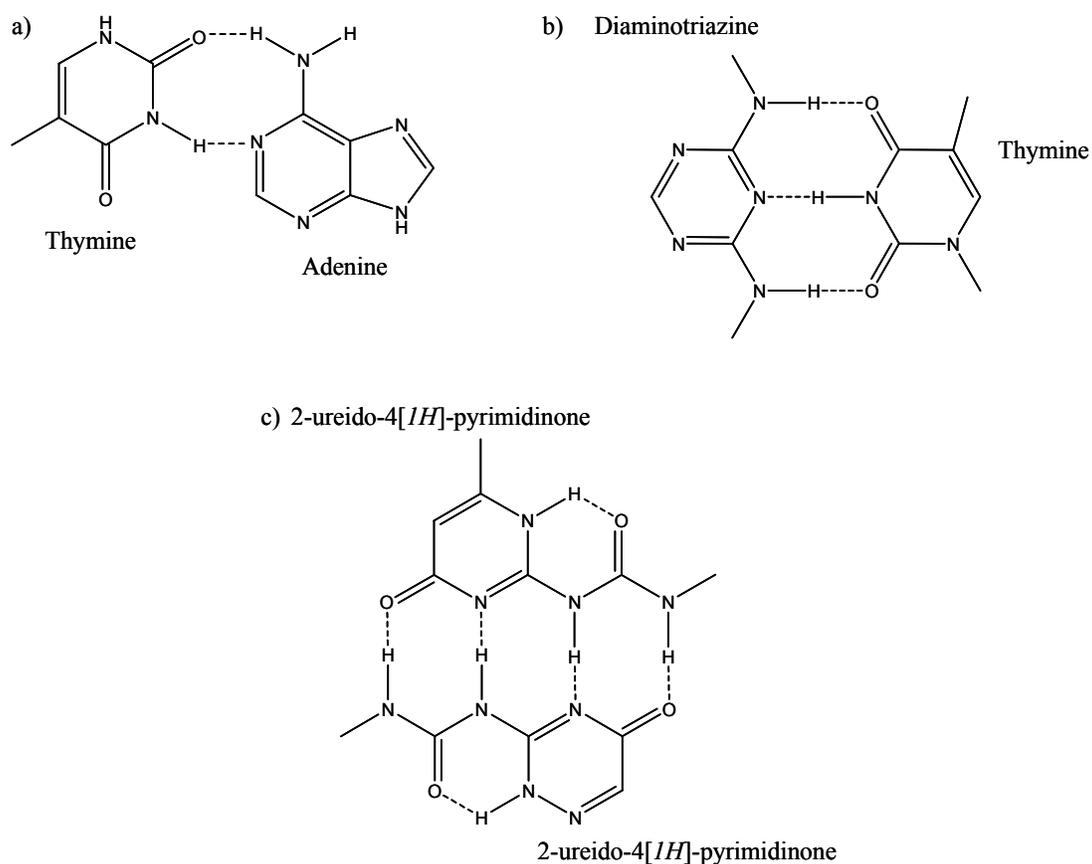


Figure 2-6: Multiple hydrogen bond interactions between a) adenine/thymine (double), b) diaminotriazine/thymine (triple), c) ureidopyrimidinones (quadruple).

Supramolecular organization of small molecules in solution into discrete molecular constructs or organized polymeric arrays as well as organization of functionalized macromolecules into superstructures utilizing hydrogen bonds is well established in the literature.²³⁷ The utilization of hydrogen bonds to self-assemble

²³⁷ Lehn, J.-M., "Supramolecular Chemistry-Concepts and Perspectives." Weinheim, VCH: New York, 1995; p 271.

organic molecules on surfaces in a controlled manner is an emerging discipline. Such hydrogen bond mediated assembly of molecules on surfaces could lead to tunable or reversible surfaces with controlled surface properties for use in nanoscale devices and patterned surfaces for a variety of applications.

In recent years, there has been enormous interest in the construction of nanodevices and, due to limitations with the conventional *top-down* approach such as lithography, a *bottom-up* approach through molecular self-assembly is gaining importance in nanotechnology. The self-assembly of small building block units into supramolecular entities is an elegant way of constructing large-scale ensembles of nanodimensions. For use in device applications, it is often necessary to affix the aggregates on surfaces. Therefore some current research efforts have focused on the construction and characterization of supramolecular aggregates on surfaces. Hydrogen bonding interactions have played a decisive role in self-assembly processes and supramolecular chemistry.²³⁸

Supramolecular hydrogen bonded aggregates of organic molecules have been adsorbed onto solid surfaces in order to control the orientation and microstructure of the resulting films, which subsequently influence many properties of the organic thin films deposited on surfaces.²³⁹ Commonly employed techniques for constructing organic thin films on surfaces such as LB films and SAM involve assembly processes in solution, where the molecules diffuse through the solution to the surface. Because of competing intermolecular interactions in solution it is often difficult to obtain well-ordered films.

²³⁸ Lehn, J.-M. "Toward Self-Organization and Complex Matter." *Science* **2002**, 295, 2400-2403.

²³⁹ Cai, C.; Müller, B.; Weckesser, J.; Barth, J. V.; Tao, Y.; Bösch, M. M.; Kündig, A.; Bosshard, C.; Biaggio, I.; Günter, P. "Model for in-Plane Directional Ordering of Organic Thin Films by Oblique Incidence Organic Molecular Beam Deposition." *Adv. Mater.* **1999**, 11, 750-755.

However, many studies have reported the assembly of monocomponent and multicomponent supramolecular structures onto various substrates from solution.²⁴⁰

Recently, De Feyter and coworkers reported STM investigations on multicomponent hydrogen-bonded nanostructures self-assembled on highly oriented pyrolytic graphite surface.²⁴¹ The various components were perylene bisimide derivatives (PBI), diaminotriazine derivatives (DAT) and merocyanine barbituric acid (MBA). MBA interacts with either PBI or DAT through six hydrogen bonds. The structure of the heterocomplexes formed on the surface depended on the orientation of the hydrogen bonding units within the complex.

Reinhoudt and coworkers studied the assembly of hydrogen bonded rosettes of calixarenemelamine/calixarenedicyanurates on surfaces.²⁴² While polar and ionic mica substrate prevented the association of the functionalized calixarenes, hydrophobic graphite served as a good substrate for the self-assembly of the molecules into linear rod like structures in a suitable solvent. In a recent study, self-assembled hydrogen bonded rosettes of calixarenedimelamine/diethylbarbiturate containing gold nanoparticles were assembled onto amorphous graphite as individual clusters, or onto highly oriented pyrolytic graphite, to form highly oriented nanorod structures.²⁴³ The complexed

²⁴⁰ De Feyter, S.; De Schryver, F. C. "Two-Dimensional Supramolecular Self-Assembly Probed by Scanning Tunneling Microscopy." *Chem. Soc. Rev.* **2003**, 32, 139-150.

²⁴¹ De Feyter, S.; Miura, A.; Yao, S.; Chen, Z.; Würthner, F.; Jonkheijm, P.; Schenning, A. P. H. J.; Meijer, E. W.; De Schryver, F. C. "Two-Dimensional Self-Assembly into Multicomponent Hydrogen-Bonded Nanostructures." *Nano Lett.* **2005**, 5, 77-81.

²⁴² Klok, H.-A.; Jolliffe, K. A.; Schauer, C. L.; Prins, L. J.; Spatz, J. P.; Möller, M.; Timmerman, P.; Reinhoudt, D. N. "Self-Assembly of Rodlike Hydrogen-Bonded Nanostructures." *J. Am. Chem. Soc.* **1999**, 121, 7154-7155.

²⁴³ van Manen, H.-J.; Paraschiv, V.; García-López, J. J.; Schonherr, H.; Zapotoczny, S.; Vansco, G. J.; Crego-Calama, M.; Reinhoudt, D. N. "Hydrogen-Bonded Assemblies as a Scaffold for Metal-Containing Nanostructures: From Zero to Two Dimensions." *Nano Lett.* **2004**, 4, 441-446.

structures were extremely stable in solution and retained their structure and order on surfaces even in the presence of gold nanoparticles.

Some studies have used ultra high vacuum techniques such as organic molecular beam deposition to assemble molecules directly onto surfaces without any solution induced aggregation. Supramolecular aggregation of a variety of organic molecules such as 4-(pyridin-4-ylethynyl)benzoic acid and 4-[*trans*-(4-pyridin-4-ylvinyl)]benzoic acid,²⁴⁴ and 1,3,5-benzenetricarboxylic acid²⁴⁵ deposited under ultra high vacuum conditions were reported. Recently, Beton *et al.* studied the adsorption of diimide derivatives (NTCDI) of naphthalene dianhydride (NTCDA), which forms extended aggregates in the solid state through two hydrogen bonds, under ultra high vacuum conditions onto silver coated silicon surfaces using scanning tunneling microscopy (STM).²⁴⁶ The dianhydride, which had no hydrogen bonding groups, deposited as clusters that were readily displaced by the STM tip. However, the double hydrogen bonding in the diimide derivative controlled the supramolecular ordering and stability of the self-assembled structures. The non-covalent nature of this self-assembly process made it possible to manipulate the assembled structures (either remove or add or move the units) using the STM tip. Thus, as demonstrated in this study, a controlled assembly with the ability to correct any defective alignment is possible with such non-covalent associations on surfaces. However, the displaced units retained their integrity, which indicated that such hydrogen-bonded assemblies were also stable towards disruption.

²⁴⁴ Cai, C.; Bösch, M. M.; Müller, B.; Tao, Y.; Kündig, A.; Bosshard, C.; Gan, Z.; Biaggio, I.; Liakatas, I.; Jäger, M.; Schwer, H.; Günter, P. "Oblique Incidence Organic Molecular Beam Deposition and Nonlinear Optical Properties of Organic Thin Films with a Stable in-Plane Directional Order." *Adv. Mater.* **1999**, 11, 745-749.

²⁴⁵ Dmitriev, A.; Lin, N.; Weckesser, J.; Barth, J. V.; Kern, K. "Supramolecular Assemblies of Trimesic Acid on a Cu(100) Surface." *J. Phys. Chem. B* **2002**, 106, 6907-6912.

Beton and coworkers also reported the formation of well-defined open honeycomb network structure through sextet hydrogen bonding between perylene-tetracarboxylic diimide (PTDI) and melamine.²⁴⁷ The heterocomplex was generated in vacuum by adsorption onto silver coated silicon surfaces. The two-dimensional array of pores served as nanovessels capable of accommodating large guest molecules such as C₆₀ fullerenes, and, the network served as a template for the growth of a fullerene layer atop the hydrogen bonded network.

The above-mentioned studies discussed hydrogen-bonded supramolecular aggregates that were physically adsorbed onto solid substrates. Using hydrogen bonding groups with various chemical structures and orientation it was possible to obtain different kinds of aggregates that varied in strength and assembly patterns. All these studies were primarily aimed at gaining fundamental understanding of the hydrogen-bonded self-assembly of molecules on surfaces and their potential use in device fabrication. Several groups have also reported such interactions at liquid-solid interfaces in the construction of hydrogen bonded polymeric multilayer thin films on surfaces.

LBL technique, introduced by Decher and coworkers is commonly used to construct well-defined polymeric multilayer thin films on surfaces.²⁴⁸ In many of the studies describing LBL technique for multilayer deposition, electrostatic interactions between a polycation and polyanion were used as the assembly driving force. It is also possible to use hydrogen bonding interactions between complementary groups to obtain

²⁴⁶ Keeling, D. L.; Oxtoby, N. S.; Wilson, C.; Humphrey, M. J.; Champness, N. R.; Beton, P. H. "Assembly and Processing of Hydrogen Bond Induced Supramolecular Nanostructures." *Nano Lett.* **2003**, 3, 9-12.

²⁴⁷ Theobald, J. A.; Oxtoby, N. S.; Phillips, M. A.; Champness, N. R.; Beton, P. H. "Controlling Molecular Deposition and Layer Structure with Supramolecular Surface Assemblies." *Nature* **2003**, 424, 1029-1031.

²⁴⁸ Decher, G.; Hong, J.-D. "Buildup of Ultrathin Multilayer Films by a Self-Assembly Process: II. Consecutive Adsorption of Anionic and Cationic Bipolar Amphiphiles and Polyelectrolytes on Charged Surfaces." *Phys. Chem.* **1991**, 1991, 1430-1434.

multilayered films. The pioneering work of Rubner *et al.* demonstrated that LBL films could also be constructed through hydrogen bonding promoted spontaneous adsorption. They demonstrated the formation of thick multilayer films comprising polyaniline and a variety of other non-ionic polymers such as poly(N-vinyl pyrrolidone) (PVPON), PEO, and poly(acrylamide) (PAAm).²⁴⁹ The hydrogen-bonded multilayer films exhibited higher conductivity than typically observed with electrostatically assembled thin films as a result of higher incorporation of polyaniline in the films. This is in contrast to the electrostatic assembly process, where charge repulsions between the layers prevented a higher incorporation of polyaniline. Likewise Zhang and coworkers formed multilayer films containing alternating hydrogen-bonded layers of PVP and poly(acrylic acid) (PAA) via hydrogen bonding as shown in Figure 2-7.²⁵⁰

²⁴⁹ Stockton, W. B.; Rubner, M. F. "Molecular-Level Processing of Conjugated Polymers. 4. Layer-by-Layer Manipulation of Polyaniline via Hydrogen-Bonding Interactions." *Macromolecules* **1997**, 30, 2717-2725.

²⁵⁰ Wang, L.; Fu, Y.; Wang, Z.; Fan, Y.; Zhang, X. "Investigation into an Alternating Multilayer Film of Poly(4-Vinylpyridine) and Poly(Acrylic Acid) Based on Hydrogen Bonding." *Langmuir* **1999**, 15, 1360-1363.

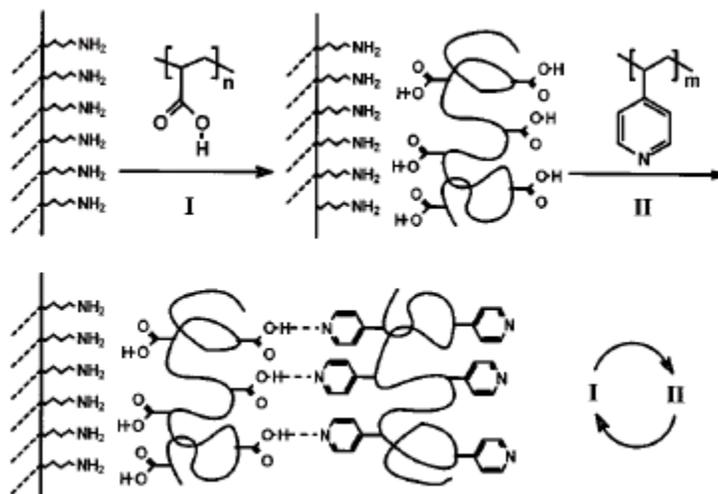


Figure 2-7: Formation of hydrogen-bonded multilayer thin films of PVP and PAA. Reprinted with permission from ref. 250. Copyright (1999) American Chemical Society.

Sukhishvili and Granick reported the formation of labile hydrogen-bonded multilayers of PAA and poly(methacrylic acid) with weak polybases such as PVPON and PEO.²⁵¹ The assembled layers collapsed upon alteration in the solution pH or salt concentration, because of destabilizing electrical charges in the film causing their disruption. pH values at which the films degraded could be tuned depending on the strength of the hydrogen bonds and the degree of ionization of the groups. pH induced release of dye molecules from these perishable multilayers was therefore investigated for potential use in controlled drug delivery applications. Thermal and photochemical imidization induced crosslinking of hydrogen-bonded multilayers of PAA and PAAm was used to generate novel water-based patterned surfaces.²⁵²

²⁵¹ Sukhishvili, S. A.; Granick, S. "Layered, Erasable Polymer Multilayers Formed by Hydrogen-Bonded Sequential Self-Assembly." *Macromolecules* **2002**, 35, 301-310.

²⁵² Yang, S. Y.; Rubner, M. F. "Micropatterning of Polymer Thin Films with pH-Sensitive and Cross-Linkable Hydrogen-Bonded Polyelectrolyte Multilayers." *J. Am. Chem. Soc.* **2002**, 124, 2100-2101.

All the approaches described above featured hydrogen bonded aggregates physisorbed on surfaces. Several studies were reported where one of the groups was covalently anchored to the surface. Covalently bound thin films are robust and are particularly desirable for applications that involve constant exposure to fluids as well as for constructing stable sensors. The use of SAM incorporating hydrogen bonding groups on surfaces provides a platform for tuning the chemical as well as physical properties of a surface in a reversible and “on-demand” fashion without compromising on the stability of the organic thin films.

Surface studies involving hydrogen bonding association have mostly involved small molecules. Crooks *et al.* investigated carboxylic acid SAMs on gold as sensors for vapors of organic acids.²⁵³ Gold surfaces functionalized with 3-mercaptopropionic acid were exposed to vapors of various 1-alkanoic acids. The extent of vapor adsorption was dependent on the alkyl length of the organic acid since the adsorption energy was dependent on both the energy of the hydrogen bond and van der Waals energy between the chains. The acid-acid dimeric interactions were calculated to have a bonding energy of ~ 7.5 kcalmol⁻¹, which was in good agreement with that predicted earlier. Similarly, carboxylic acid SAMs on gold were also used as sensors for vapors of organic bases.²⁵⁴ The extent of vapor adsorption in this case was dependent on the pH of the organic base, and the chemical structure of the acid SAM. For the case of interactions between the acid SAMs and organic base vapors, the vapor phase molecules readily desorbed upon

²⁵³ Sun, L.; Kepley, L. J.; Crooks, R. M. "Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules: Hydrogen-Bonding Interactions." *Langmuir* **1992**, 8, 2101-2103.

²⁵⁴ Yang, H. C.; Dermody, D. L.; Xu, C.; Ricco, A. J.; Crooks, R. M. "Molecular Interactions between Organized Surface-Confined Monolayers and Vapor-Phase Probe Molecules.8. Reactions between Acid-Terminated Self-Assembled Monolayers and Vapor-Phase Bases." *Langmuir* **1996**, 12, 726-735.

nitrogen purging indicating a relatively weak interaction between the sensor and probe molecules.

Kaifer *et al.* reported the assembly of crown-ether fullerenes to gold surfaces through specific hydrogen bonding interactions with ammonium terminated SAMs, while unfunctionalized or phenoxide functionalized fullerenes showed negligible association with the surface bound ammonium groups.²⁵⁵ Upon immersion in nonpolar CH₂Cl₂, the fullerenes slowly desorbed indicating the reversible yet weak association between crown ether and ammonium groups, a result of single hydrogen bonded association.

In recent years, several groups have reported the use of groups exhibiting specific multiple hydrogen bonding interactions with analytes in solution in order to enhance the stability of the surface bound complexes. Motesharei and Myles constructed model membrane surfaces comprising mixed monolayers of octanethiol and bis(2,6-diaminopyridine)amide (DAP amide) of isophthalic acid-functionalized dodecanethiol. The influence of solvent polarity on hydrogen bonding between barbiturate and DAP containing SAM was investigated using fluorescence measurements.²⁵⁶ N-methylated barbiturate did not complex with the surface bound DAP groups confirming that hydrogen bonding was indeed responsible for the formation of barbiturate-DAP complex. These complexes were stable in CH₂Cl₂ and acetonitrile but were disrupted in the more polar ethanol. Thus, the functionalized SAMs could serve as model membranes for probing the effect of various parameters that affect ligand-receptor interactions in

²⁵⁵ Arias, F.; Godínez, L. A.; Wilson, S. R.; Kaifer, A. E.; Echegoyen, L. "Interfacial Hydrogen Bonding. Self-Assembly of a Monolayer of a Fullerene-Crown Ether Derivative on Gold Surfaces Derivatized with an Ammonium-Terminated Alkanethiolate." *J. Am. Chem. Soc.* **1996**, 118, 6086-6087.

²⁵⁶ Motesharei, K.; Myles, D. C. "Molecular Recognition in Membrane Mimics: A Fluorescence Probe." *J. Am. Chem. Soc.* **1994**, 116, 7413-7414.

biological membranes, which are inaccessible due to the complexities associated with biological systems.

In a related study, the aforementioned group conducted competitive adsorption experiments in the presence of non-barbiturate ligand and showed that the surface attached DAP moieties showed preferential affinity for the barbiturate groups.²⁵⁷ In addition, the association on the surface was stable to prolonged CH₂Cl₂ rinsing indicating the enhanced stability of such multiply associating groups. The authors also calculated the association constant (K_b) for barbiturate-DAP interactions as given in equation 4:

$$K_b = \frac{[\text{capped}]}{[\text{free}] [\text{ligand}]} \dots\dots\dots (4)$$

where [capped], [free], and [ligand] refer to the concentrations of associated surface bound DAP, free surface bound DAP, and ligand in solution. K_b for the surface bound DAP-barbiturate determined using a series of fluorescence measurements at varying ligand concentrations in solution was ~10⁴ M⁻¹, which was in good agreement with reported values for the same receptor-ligand pair in CHCl₃ solution. Similar reversible interactions were observed between surface anchored barbiturate groups and DAP ligand in solution confirming that the observed trends were solely attributable to hydrogen bonding promoted molecular recognition process.

Rogers *et al.* studied the reversible assembly of free base porphyrin and metallated porphyrin derivatives on gold surfaces through multiple hydrogen bonding

²⁵⁷ Motesharei, K.; Myles, D. C. "Molecular Recognition on Functionalized Self-Assembled Monolayers of Alkanethiols on Gold." *J. Am. Chem. Soc.* **1998**, 120, 7328-7336.

interactions with acid SAMs.²⁵⁸ Specific hydrogen bonding association between the porphyrin derivatives in solution and acid SAM on gold surfaces was confirmed using control studies. Porphyrin derivatives did not adsorb onto either methyl-terminated SAMs or onto acid SAMs when the free NH groups were derivatized with phenyl groups. The use of free base porphyrins non-covalently associated to surfaces has potential in reusable metal ion sensors.

Garcia-Lopez described an innovative way of assembling nanostructures using the *bottom-up* approach by making use of multiple hydrogen bonding associations between calixarene melamine SAM and barbituric/cyanuric acid.²⁵⁹ Reversible exchange of hydrogen bonding between surface confined calixarene melamines and the calixarene melamine/diethylbarbiturate hydrogen bonded rosettes that were formed in solution led to formation of individual nanometer sized mixed assemblies on surfaces. The surface concentration depended on the number of immobilized calixarenes.

Metal- molecule-metal junctions are useful to gain understanding of the electronic properties of organic thin films on metal surfaces finding application in molecular electronics. Reversible assembly of electroactive species could therefore lead to tunable surface electronic properties. Rotello *et al.* demonstrated the use of hydrogen bonding to introduce and remove electroactive ferrocene-terminated uracil from surfaces that were patterned with diacyl-2,6-diaminopyridine (DAP) in solution using STM.²⁶⁰ Competitive

²⁵⁸ Krishnamohan Sharma, C. V.; Broker, G. A.; Szulczewski, G. J.; Rogers, R. D. "Self-Assembly of Freebase- and Metallated-Tetrapyridylporphyrins to Modified Gold Surfaces." *Chem. Commun.* **2000**, 1023-1024.

²⁵⁹ Garcia-Lopez, J. J.; Zapotoczny, S.; Timmerman, P.; van Veggel, F. C. J. M.; Vansco, G. J.; Crego-Calama, M.; Reinhoudt, D. N. "Growth of Individual Hydrogen-Bonded Nanostructures on Gold Monolayers." *Chem. Commun.* **2003**, 352-353.

²⁶⁰ Credo, G. M.; Boal, A. K.; Das, K.; Galow, T. H.; Rotello, V. M.; Feldheim, D. L.; Gorman, C. B. "Supramolecular Assembly on Surfaces: Manipulating Conductance in Noncovalently Modified Mesoscale Structures." *J. Am. Chem. Soc.* **2002**, 124, 9036-9037.

adsorption between ferrocene and alkyl uracil led to the reversible tuning of the electroactivity of the surface.

The construction of multilayers of helical peptides on gold surfaces through triple hydrogen-bonded thymine-diaminotriazine interactions was also reported.²⁶¹ The helical peptides containing thymine and diaminotriazine functionalities at their C- and N-terminals, respectively, were self-assembled on thymine SAM modified gold surfaces. The use of double hydrogen bonding between DNA bases adenine and thymine was used to assemble ordered arrays of thymine functionalized zeolite particles on adenine functionalized glass surfaces.²⁶² The rearrangement of the surface immobilized zeolites through disruption and reformation of hydrogen bonds was observed when the zeolite-modified surfaces were heated above 50 °C- close to the adenine-thymine hydrogen bond dissociation temperature.

Very recently, Binder and coworkers reported the deposition of ligand functionalized gold nanoparticles onto planar gold surfaces functionalized with receptor molecules.²⁶³ The ligand-receptor pair used in this study was barbituric acid and multivalent Hamilton-type cleft receptor, which displays $K_{asn} \sim 10^4$ - 10^6 M⁻¹. The gold nanoparticles assembled on the receptor coated surfaces were very stable as determined by multiple imaging over time using AFM.

Most of the above studies that had used hydrogen bonding interactions on surfaces were based on complementary hydrogen bonding groups such as acids/bases,

²⁶¹ Miura, Y.; Xu, G.-C.; Kimura, S.; Kobayashi, S.; Iwamoto, M.; Imanshi, Y.; Umemura, J. "Multilayer Formation of Oriented Helical Peptides Glued by Hydrogen Bonding." *Thin Solid Films* **2001**, 393, 59-65.

²⁶² Park, J. S.; Lee, G. S.; Lee, Y.-J.; Park, Y. S.; Yoon, K. B. "Organization of Microcrystals on Glass by Adenine-Thymine Hydrogen Bonding." *J. Am. Chem. Soc.* **2002**, 124, 13366-13367.

²⁶³ Zirbs, R.; Kienberger, F.; Hinterdorfer, P.; Binder, W. H. "Directed Assembly of Au Nanoparticles onto Planar Surfaces via Multiple Hydrogen Bonds." *Langmuir* **2005**, 21, 8414-8421.

diaminotriazine/thymine, diaminotriazine/barbituric acid etc. However, self-complementarity is often desired in certain applications. While the use of complementary groups on surfaces has been abundant, there are only a few reports describing the use of self-complementary hydrogen bonding interactions on surfaces.²⁶⁴

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Vansco and coworkers used quadruple hydrogen bonding associations between 2-ureido-4[1H]-pyrimidinone (UPy) units to reversibly bind ferrocene molecules to gold surfaces.²⁶⁶ In CHCl₃ solution, UPy dimerizes with a very high association constant ($K_{\text{asn}} > 10^7 \text{ M}^{-1}$).²⁶⁷ However, polar solvents and elevated temperatures are shown to reverse the dimeric association. K_{asn} decreased to 50 M^{-1} with the addition of 15 vol% DMSO to CDCl₃ and decreased ~10 fold upon increasing the temperature from 298K to 333K. Because of altered environment around the hydrogen-bonded complex on the surface, it was found that the ferrocene molecules self-assembled through hydrogen bonding interactions displayed extended stability in CHCl₃ when compared to that typically observed for the UPy dimers in solution. However, the interaction on the surface was destroyed upon washing with DMSO and hot CHCl₃.

²⁶⁴ Shenhar, R.; Sanyal, A.; Uzun, O.; Nakade, H.; Rotello, V. M. "Integration of Recognition Elements with Macromolecular Scaffolds: Effects on Polymer Self-Assembly in the Solid State." *Macromolecules* **2004**, *37*, 4931-4939.

²⁶⁵ Folmer, B. J. B.; Sijbesma, R. P.; Versteegen, R. M.; van der Rijt, J. A. J.; Meijer, E. W. "Supramolecular Polymeric Materials: Chain Extension of Telechelic Polymers Using a Reactive Hydrogen-Bonding Synthone." *Adv. Mater.* **2000**, *12*, 874-878.

²⁶⁶ Zou, S.; Zhang, Z.; Forch, R.; Knoll, W.; Schönherr, H.; Vansco, G. J. "Tunable Complex Stability in Surface Molecular Recognition Mediated by Self-Complementary Quadruple Hydrogen Bonds." *Langmuir* **2003**, *19*, 8618-8621.

²⁶⁷ Beijer, F. H.; Sijbesma, R. P.; Kooijman, H.; Spek, A. L.; Meijer, E. W. "Strong Dimerization of Ureidopyrimidones via Quadruple Hydrogen Bonding." *J. Am. Chem. Soc.* **1998**, *120*, 6761-6769.

There are many investigations that have employed polymers functionalized with double,^{268, 269} triple,²⁷⁰ and quadruple^{271, 272} hydrogen bonding groups. The multiple hydrogen bonding groups were found to lead to enhanced mechanical and rheological properties of the polymers. Polymers functionalized with hydrogen bonding groups were also used for the directed assembly of nanoparticles into structural ensembles. Rotello and coworkers studied the aggregation of gold nanoparticles functionalized with thymine containing SAM into spherical aggregates in the presence of PS random copolymers functionalized with the complementary diaminotriazine groups.²⁷³ Since self-assembly is governed by a balance of the enthalpic and entropic energetics, temperature plays a significant role in the assembly process. Lower temperature favored greater recognition between the polymer and the nanoparticles yielding larger aggregates while higher temperatures resulted in much smaller aggregates. However, the polymer-nanoparticle aggregates were stable towards polar solvents, this enhanced stability arising from multivalent polymer-colloid interactions. The observation is consistent with behavior reported for other systems exhibiting multivalent associations. The same group reported a systematic investigation on the influence of the nature of recognition elements as well as the presence of other interactions (such as π - π stacking) on the structure of the

²⁶⁸ Peng, C.-C.; Abetz, V. "A Simple Pathway toward Quantitative Modification of Polybutadiene: A New Approach to Thermoreversible Cross-Linking Rubber Comprising Supramolecular Hydrogen-Bonding Networks." *Macromolecules* **2005**, 38, 5575-5580.

²⁶⁹ Mather, B. D.; Lizotte, J. R.; Long, T. E. "Synthesis of Chain End Functionalized Multiple Hydrogen Bonded Polystyrenes and Poly(Alkyl Acrylates) Using Controlled Radical Polymerization." *Macromolecules* **2004**, 37, 9331-9337.

²⁷⁰ Burd, C.; Weck, M. "Self-Sorting Polymers." *Macromolecules* **2005**, 38, 7225-7230.

²⁷¹ Hofmeier, H.; Hoogenboom, R.; Wouters, M. E. L.; Schubert, U. S. "High Molecular Weight Supramolecular Polymers Containing Both Terpyridine Metal Complexes and Ureidopyrimidinone Quadruple Hydrogen-Bonding Units in the Main Chain." *J. Am. Chem. Soc.* **2005**, 127, 2913-2921.

²⁷² McKee, M. G.; Elkins, C. L.; Park, T.; Long, T. E. "Influence of Random Branching on Multiple Hydrogen Bonding in Poly(Alkyl Methacrylate)S." *Macromolecules* **2005**, 38, 6015-6023.

²⁷³ Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; -Albrecht, T. T.; Russell, T. P.; Rotello, V. M. "Self-Assembly of Nanoparticles into Structured Spherical and Network Aggregates." *Nature* **2000**, 404, 746-748.

nanoparticle assembly.²⁷⁴ Steric hindrance around the binding elements led to a very open structure for the nanoparticle ensemble indicating constrained hydrogen bonding interactions while π - π stacking complemented the hydrogen bonding effect promoting the formation of larger aggregates.

The use of block copolymers, where one of the blocks was partially functionalized with diaminotriazine was also used to control the aggregation of thymine SAM modified gold nanoparticles.²⁷⁵ The size of the core/corona of the micellar nanoparticle-polymer aggregates, which was formed because of copolymer phase separation, depended on the molecular weight of the block.

Rotello and coworkers also used hydrogen bonding interactions to reversibly assemble polymers on solid substrates. Polymers that exhibit reversible interactions with a solid surface hold considerable potential as releasable coatings and smart adhesives. In addition, the capability to reversibly attach polymers to solid surfaces enables tunable surface energetics. Using diaminopyridine-thymine three point hydrogen bonded associations, Rotello and coworkers assembled polyhedral oligomeric silsesquioxanes on gold surfaces.²⁷⁶ Similarly, the adsorption/ desorption profiles of DAP functionalized diblock copolymers of PS-*b*-poly(styrene-*co*-sty-DAP) assembled on thymine functionalized surfaces were studied using a variety of techniques.²⁷⁷ By adjusting the functionalized block length it was possible to control the amount of polymer adsorbed on

²⁷⁴ Boal, A. K.; Gray, M.; Ilhan, F.; Clavier, G. M.; Kapitzky, L.; Rotello, V. M. "Bricks and Mortar Self-Assembly of Nanoparticles." *Tetrahedron* **2002**, 58, 765-770.

²⁷⁵ Frankamp, B. L.; Uzun, O.; Ilhan, F.; Boal, A. K.; Rotello, V. M. "Recognition-Mediated Assembly of Nanoparticles into Micellar Structures with Diblock Copolymers." *J. Am. Chem. Soc.* **2002**, 124, 892-893.

²⁷⁶ Jeoung, E.; Carroll, J. B.; Rotello, V. M. "Surface Modification via a 'Lock and Key' Specific Self-Assembly of Polyhedral Silsesquioxane (POSS) Derivatives to Modified Gold Surfaces." *Chem. Commun.* **2002**, 1510-1511.

²⁷⁷ Sanyal, A.; Norsten, T. B.; Oktay, U.; Rotello, V. M. "Adsorption/Desorption of Mono- and Diblock Copolymers on Surfaces Using Specific Hydrogen Bonding Interactions." *Langmuir* **2004**, 20, 5958-5964.

the surface, while the chemical composition of the unfunctionalized block dictated the properties of the modified surfaces. The surfaces regenerated following polymer desorption were subsequently used for adsorption of other kinds of polymer. Thus, the use of non-covalent recognition elements for surface modification leads to surface properties that could be changed as desired and in a reversible fashion.

Chapter 3: Silicon/SiO₂ Surface Modification with Novel Star-branched Polymers Obtained through Hydrolysis and Condensation of Trimethoxysilane-functionalized Polystyrene

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3.1 Abstract

The synthesis of trimethoxysilane end-capped linear polystyrene (PS), star-branched PS and subsequent silicon/SiO₂ surface modification with the linear and star-branched polymers are described. Trimethoxysilane-functionalized PS was synthesized using *sec*-butyllithium (*sec*-BuLi) initiated anionic polymerization of styrene and subsequent end-capping of the living anions with *p*-chloromethylphenyl trimethoxysilane (CMPTMS). ¹H and ²⁹Si NMR spectroscopy confirmed the successful end-capping of polystyryllithium with the trimethoxysilane functional group. The effect of molar excess of end-capper on the efficiency of functionalization was also investigated and the required excess increased for higher molar mass oligomers. Acid catalyzed hydrolysis and condensation of the trimethoxysilane end-groups resulted in star-branched PS, and NMR spectroscopy and SEC analysis were used to characterize the star-branched polymers. This study is the first report of core-functionalized star-branched polymers as surface modifiers and the first comparative study showing differences in surface topography between star-branched and linear polymer modified surfaces. Surface-sensitive techniques such as ellipsometry, contact angle goniometry, and AFM were used to confirm the attachment of star-branched PS as well as to compare the characteristics of the star-branched and linear PS modified silicon/SiO₂ surfaces. The polymer film

properties were referenced to polymer dimensions in dilute solution, which revealed that linear PS chains were in the intermediate brush regime and the star-branched PS produced a surface with covalently attached chains in the mushroom regime.

3.2 Introduction

Solid surfaces are often chemically modified to improve properties such as adhesion, lubricity, wettability, biocompatibility, and environmental resistance.²⁷⁸ Self-assembled polymeric films offer significant advantages compared to other conventional modification techniques and thus are widely used as surface modifiers. While a polymeric surface modifier dictates the chemical composition of a modified surface, the chain length of the polymer also determines the film thickness. In addition, the density of polymer chains and the concentration of functional groups on a modified surface may be further controlled using branched and dendritic polymer films.

Although there are many approaches for modifying solid surfaces with polymers, covalent grafting of polymer chains is preferred as it generates stable polymer films.²⁷⁹ In recent years, many studies involved the use of branched polymers as surface modifiers, which is partly driven by the high density of functional groups in branched polymers, making them attractive candidates for chemical sensors, drug delivery agents, nanoscale catalysts, and smart adhesives.⁸ Most earlier surface modification investigations with branched polymers have employed covalently bound dendrimers for use as sensors,^{280, 281,}

²⁷⁸ Claes, M.; Voccia, S.; Detrembleur, C.; Jérôme, C.; Gilbert, B.; Leclère, P.; Geskin, V. M.; Gouttebaron, R.; Hecq, M.; Lazzaroni, R.; Jérôme, R. "Polymer Coating of Steel by a Combination of Electrografting and Atom-Transfer Radical Polymerization." *Macromolecules* **2003**, *36*, 5926-5933.

²⁷⁹ Zhao, B.; Brittain, W. J. "Synthesis of Polystyrene Brushes on Silicate Substrates via Carbocationic Polymerization from Self-Assembled Monolayers." *Macromolecules* **2000**, *33*, 342-348.

²⁸⁰ Wells, M.; Crooks, R. M. "Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 10. Preparation and Properties of Chemically Sensitive Dendrimer Surfaces." *J. Am. Chem. Soc.* **1996**, *118*, 3988-3989.

²⁸² photoresists,²⁸³ or bioreactive surfaces.^{284, 285} Although dendrimers offer attractive properties, traditional dendrimer synthesis is tedious. Hyperbranched polymers, which exhibit many of the same advantageous properties as dendrimers, are easier to synthesize and thus were investigated as an alternative to dendrimers as surface modifiers. The hyperbranched polymer films were amenable to further modification due to the presence of a high concentration of accessible functional groups.^{286, 287, 288} Studies on surface attached star-branched polymers has mainly concentrated on the use of PEG-based star polymers to impart enhanced biocompatibility to silicon surfaces compared to linear polymers.^{289, 290}

This chapter will describe the modification of silicon/SiO₂ surfaces with star-branched PS. The star-branched polymers contained surface reactive silanol functionalities in the core. Synthesis of the star-branched PS was achieved using the sol-gel process resulting from acid catalyzed condensation of trimethoxysilane-functionalized

²⁸¹ Tokuhisa, H.; Crooks, R. M. "Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules. 12. Two New Methods for Surface-Immobilization and Functionalization of Chemically Sensitive Dendrimer Surfaces." *Langmuir* **1997**, 13, 5608-5612.

²⁸² Yoon, H. C.; Kim, H.-S. "Multilayered Assembly of Dendrimers with Enzymes on Gold: Thickness-Controlled Biosensing Interface." *Anal. Chem.* **2000**, 72, 922-926.

²⁸³ Tully, D. C.; Wilder, K.; Freché, J. M. J.; Trimble, A. R.; Quate, C., F. "Dendrimer-Based Self-Assembled Monolayers as Resists for Scanning Probe Lithography." *Adv. Mater.* **1999**, 11, 314-318.

²⁸⁴ Beier, M.; Hoheisel, J. D. "Versatile Derivatization of Solid Support Media for Covalent Bonding on DNA-Microchips." *Nucleic Acid Res.* **1999**, 27, 1970-1977.

²⁸⁵ Benters, R.; Niemeyer, C. M.; Wöhrle, D. "Dendrimer-Activated Solid Supports for Nucleic Acid and Protein Microarrays." *Chembiochem* **2001**, 2, 686-694.

²⁸⁶ Zhou, Y.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M.; Wells, M. "Preparation of Hyperbranched Polymer Films Grafted on Self-Assembled Monolayers." *J. Am. Chem. Soc.* **1996**, 118, 3773-3774.

²⁸⁷ Bruening, M. L.; Zhou, Y.; Aguilar, G.; Agee, R.; Bergbreiter, D. E.; Crooks, R. M. "Synthesis and Characterization of Surface-Grafted, Hyperbranched Polymer Films Containing Fluorescent, Hydrophobic, Ion-Binding, Biocompatible, and Electroactive Groups." *Langmuir* **1997**, 13, 770-778.

²⁸⁸ Peez, R. F.; Dermody, D. L.; Franchina, J. G.; Jones, S. J.; Bruening, M. L.; Bergbreiter, D. E.; Crooks, R. M. "Aqueous Solvation and Functionalization of Weak-Acid Polyelectrolyte Thin Films." *Langmuir* **1998**, 14, 4232-4237.

²⁸⁹ Sofia, S. J.; Premnath, V.; Merrill, E. W. "Poly(Ethylene Oxide) Grafted to Silicon Surfaces: Grafting Density and Protein Adsorption." *Macromolecules* **1998**, 31, 5059-5070.

²⁹⁰ Groll, J.; Ameringer, T.; Spatz, J. P.; Moeller, M. "Ultrathin Coatings from Isocyanate-Terminated Star PEG Prepolymers: Layer Formation and Characterization." *Langmuir* **2005**, 21, 1991-1999.

linear PS obtained using living anionic polymerization.²⁹¹ Although rigorous, living anionic polymerization permits the synthesis of well-defined polymers with controlled molecular weights and narrow molecular weight distributions. In addition, it allows for the functionalization of polymers with a variety of electrophilic reagents.²⁹² Particularly, stable, anionic chain ends of polymers formed via alkyllithium initiation were end-capped with a variety of electrophilic reagents to generate a diverse array of functional groups such as hydroxyl,^{293, 294} amine,²⁹⁵ carboxylic acids²⁹⁶ etc. Functionalization of living polymers with alkoxy silanes (-SiOR)₃^{297, 298} generated polymeric surface coupling agents.^{299, 300, 301} In addition, alkoxy silane-functionalized polymers were also used as precursors for obtaining star-branched polymers primarily through sol-gel condensation.^{291, 297}

²⁹¹ Long, T. E.; Kelts, L. W.; Turner, R. S.; Wesson, J. A.; Mourey, T. A. "Synthesis and Characterization of Well-Defined Star Polymers via a Controlled Sol-Gel Process." *Macromolecules* **1991**, 24, 1431-1434.

²⁹² Hsieh, H. L.; Quirk, R. P., "Anionic Polymerization: Principles and Practical Applications." Marcel Dekker, Inc.: New York, **1996**.

²⁹³ Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. "Investigation of Ethylene Oxide Oligomerization During Functionalization of Poly(Styryl)Lithium Using Maldi-TOF MS and NMR." *Macromolecules* **2002**, 35, 2912-2918.

²⁹⁴ Quirk, R. P.; Pickel, D. A.; Hasegawa, H. "Anionic Polymerization Chemistries of Epoxides: Electron-Transfer Processes." *Macromol. Symp.* **2005**, 226, 69-77.

²⁹⁵ Quirk, R. P.; Lee, Y. "Anionic Synthesis of Well-Defined Polymers with Amine End Groups." *Macromol. Symp.* **2000**, 157, 161-169.

²⁹⁶ Quirk, R. P.; Yin, J. "Carbonation of Polymeric Organolithium Compounds: Effects of Chain End Structure." *J. Polym. Sci., Part A: Polym. Chem.* **1992**, 30, 2349-2355.

²⁹⁷ Quirk, R. P.; Huimin, Y. "Anionic Synthesis of Well-Defined trimethoxysilyl-Functionalized Polystyrene." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **1996**, 37, 645-646.

²⁹⁸ Lee, J. S.; Quirk, R. P.; Foster, M. D.; Wollyung, K. M.; Wesdemiotis, C. "A New Methodology for the Synthesis of Star Polymers Utilizing Reaction of Living Polymers with Alkoxy silyl-Functionalized Polymers." *Macromolecules* **2004**, 37, 6385-6394.

²⁹⁹ Dreyfuss, P.; Fetters, L., J.; Gent, A. N. "Coupling of Silane Reactions 2. Reaction of Dimethylmethoxysilanated Poly(Butadiene) with Triethylsilanol." *Macromolecules* **1978**, 11, 1036-1038.

³⁰⁰ Ohata, M.; Yamamoto, M.; Isono, Y. "Preparation and Characterization of End-Alkoxy silylated Polystyrene and the Grafting Behaviors onto Inorganic Pigments. I. Utilization of 4-Isopropoxydimethylsilyl- α -Methylstyrene." *J. Appl. Polym. Sci.* **1995**, 55, 517-525.

³⁰¹ Ohata, M.; Yamamoto, M.; Takano, A.; Isono, Y. "Preparation and Characterization of End-Alkoxy silylated Polystyrene and the Grafting Behaviors onto Inorganic Pigments. 11. Utilization of 4-Triethoxysilyl- α -Methylstyrene." *J. Appl. Polym. Sci.* **1996**, 59, 399-406.

The sol-gel condensation reported herein uniquely results in a core- functionalized star-branched polymer. Despite the steric hindrance associated with the accessibility of the core silanols, core-functionalized polymers were attached to silicon/SiO₂ wafers and presented a significantly different surface topography compared to linear PS analogues. The differences in the surface characteristics of linear and sta-branched PS modified surfaces are discussed below.

3.3 Experimental

3.3.1 Materials

Styrene (99%, Aldrich) was stirred over CaH₂ for 3-4 days, distilled under reduced pressure (0.1 mm Hg, 10 °C) after repeated degassing and freeze-thaw cycles, and stored at -25 °C until further use. Styrene was distilled from dibutylmagnesium (DBM) under similar conditions immediately prior to polymerization. DBM (FMC Corporation Lithium Division, 25% solution in heptane) and *sec*-butyllithium (*sec*-BuLi, Aldrich, 1.4 M in cyclohexane) were used without further purification. *p*-chloromethylphenyl trimethoxysilane (CMPTMS, 95%, Gelest, Inc.) was stirred over CaH₂ for a day and vacuum-distilled (0.1 mm Hg, 50 °C) immediately prior to use. THF (EMD Chemicals), which was the polymerization solvent, was distilled from sodium in the presence of benzophenone immediately prior to use. Methanol (EMD Chemicals) was stored over 5 Å molecular sieves. Conc. H₂SO₄ (VWR International), NH₄OH (30%, VWR International), H₂O₂, (30%, Aldrich), methanol (EMD Chemicals), and dichloromethane (EMD Chemicals) were used as received. Millipore milli-Q water was used for surface cleaning. Silicon wafers used as substrates were a generous gift from Hewlett Packard Company.

3.3.2 Polymer Characterization

Size exclusion chromatography (SEC) data was obtained using a 717 Autosampler system equipped with 3 in-line 5 μm PLgel MIXED-C columns, a Waters 2410 refractive index detector operating at 880 nm, a Wyatt Technology miniDawn[®] multiple angle laser light scattering (MALLS) detector operating at 690 nm and calibrated with polystyrene standards, and a Viscotek Model 270 differential/light scattering dual detector. The refractive index increment (dn/dc) was calculated online. The data from the viscosity detector was also used to calculate the branching coefficient (g') for the star-branched polymers. SEC measurements were performed at 40 °C in THF at a flow rate of 1 mL/min. ¹H NMR and ²⁹Si NMR spectra were obtained on a Varian UNITY spectrometer at 400 MHz and 79.5 MHz respectively, using CDCl₃ as the solvent.

3.3.3 Surface Characterization

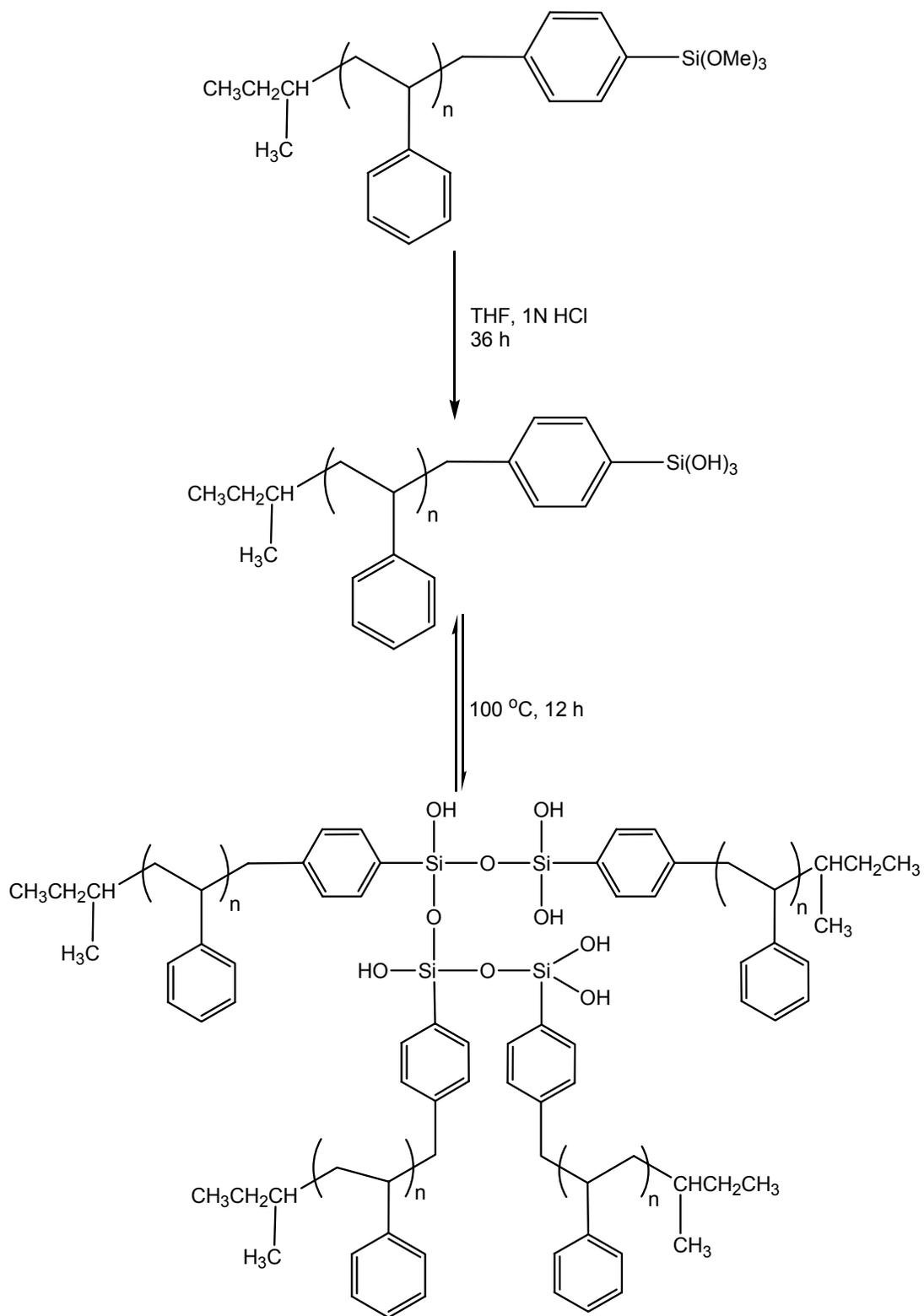
Topographic information on the polymer-modified silicon wafers was obtained using a Digital Instruments Nanoscope III atomic force microscope and software. TAP 300 Si₃N₄ tips with a spring constant of 40 N/m were used and set point ratios of 0.5 to 0.6 were used in the experiments. Static water contact angles on the surfaces were measured in the sessile drop mode on a FTA-125 contact angle goniometer with a syringe-driven droplet. Ellipsometric data at 4-5 different spots on the surface were obtained on a Beaglehole ellipsometer with a He-Ne laser ($\lambda=632.8$ nm) and an angle of incidence of 70°. Refractive indices of 1.46 and 1.59 were used based on previous literature for SiO₂ and PS respectively, in the calculation of polymer layer thickness.⁴⁶

3.3.4 Synthesis of Trimethoxysilane End-capped Polystyrene

The synthesis of trimethoxysilane end-capped PS (PS-Si(OMe)₃), shown in Scheme 3-1, was achieved using anionic polymerization of styrene, which was initiated with *sec*-BuLi in THF at -78 °C and subsequently end-capped with a molar excess of CMPTMS as described by Long *et al.*²⁹¹ The functionalized polymers were isolated by precipitation into 10-fold excess dry methanol. The polymers were then dried at 100 °C overnight.

3.3.5 Hydrolysis and Condensation of Trimethoxysilane-Functionalized Polystyrene

Hydrolysis was performed in THF at 20 wt% solids and 1 N HCl solution was added as the catalyst. The reaction mixture was stirred for 40 h at 25 °C and precipitated into 10-fold excess methanol. The polymer was then dried at 100 °C for 12 h. The synthetic scheme for the hydrolysis, and condensation is summarized in Scheme 3-2.



Scheme 3-2: Synthesis of star-branched PS by hydrolysis and condensation of linear PS- $\text{Si}(\text{OMe})_3$.

3.3.6 Substrate Treatment

Silicon wafers were cut into 1cm^2 pieces and sequentially sonicated for 5 min in dichloromethane and methanol. After blow drying with nitrogen, the wafers were cleaned with 30% NH_3 :30% H_2O_2 : H_2O (v/v/v: 1/1/5) at 60 °C for 15 minutes. After copiously rinsing with milli-Q water, the wafers were cleaned in a freshly prepared Piranha solution (conc. H_2SO_4 :30% H_2O_2 ; v/v: 70/30) at 90 °C for 30 minutes. The wafers were then rinsed with milli-Q water several times, blown dry with nitrogen, and immediately spin coated with the polymer solutions. (**Caution:** *Piranha solution reacts violently with many organic materials and should be handled with care.*)

3.3.7 Polymer Thin Film Preparation

PS-Si(OMe)₃ and the star-branched PS were dissolved in toluene (1 wt% solution). These polymer solutions were filtered through a 0.2 μm PTFE syringe filter and spun cast at 2500 rpm onto silicon wafers that were cleaned as described above. The wafers were then heated at 145 °C for 24 h to enable the polymer end-groups to react with surface hydroxyls. The wafers were then exhaustively sonicated in toluene to remove any physically adsorbed polymer prior to characterization.

3.4 Results and Discussion

3.4.1 Influence of Polymer M_n on the Efficiency of Trimethoxysilane End-capping of PS

A series of trimethoxysilane end-capped polystyrene (PS) homopolymers was synthesized using *sec*-BuLi initiated living anionic polymerization followed by end-capping with molar excess CMPTMS as was described in the literature. Upon the addition of *sec*-butyllithium to the monomer solution in THF, a bright orange colored solution was formed. However, after the addition of CMPTMS following

polymerization, the solution became colorless indicating successful end-capping of the living poly(styryllithium) chains with the electrophilic reagent (CMPTMS). ^1H NMR spectroscopic analysis was performed on the polymers to confirm the successful end-capping with CMPTMS. Figure 3-1 shows a representative ^1H NMR spectrum of oligomeric PS-Si(OMe)₃.

The level of end-capping was determined based on the ratio of the integral for the methoxy protons adjacent to Si (b) at 3.6 ppm to the initiator methyl protons (a) observed between 0.5 and 0.8 ppm. A ratio of 3:2 for b/a agreed well with the expected ratio from end group chemical composition, confirming quantitative end-capping of the polymer with CMPTMS. The number average molecular weights (M_n) were also determined using ^1H NMR analysis by integrating well-defined aromatic proton resonances of PS observed between 6.3 and 7.3 ppm with respect to the initiator methyl proton resonances.

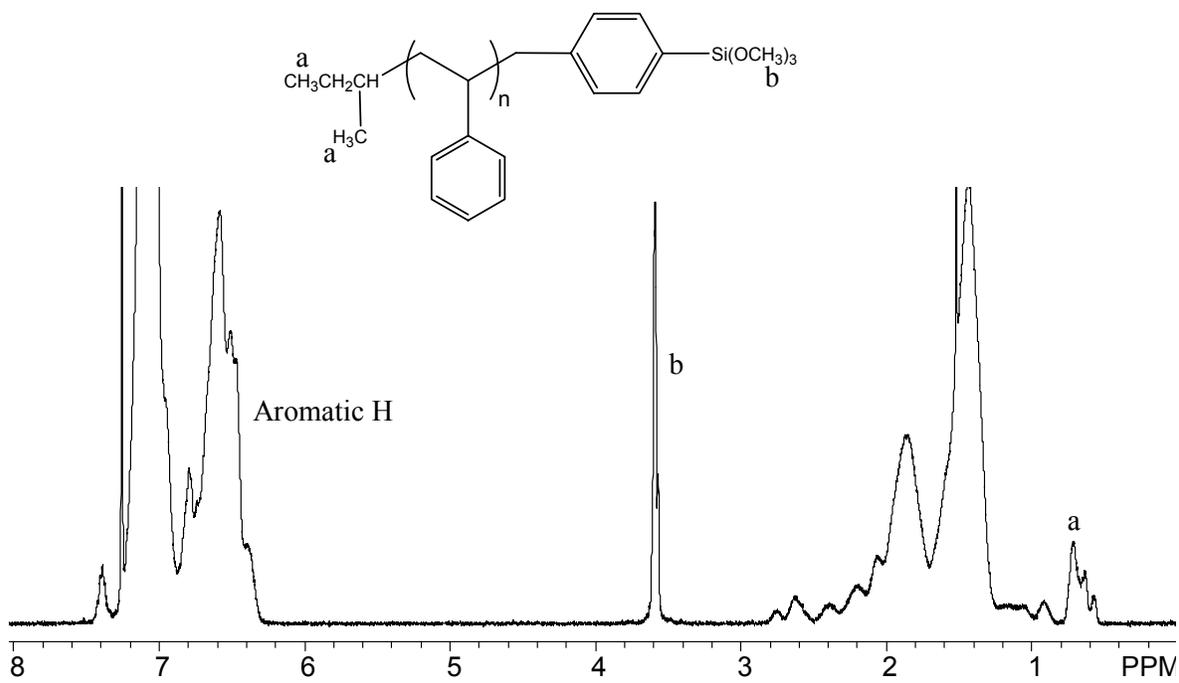


Figure 3-1: ¹H NMR spectrum of oligomeric PS-Si(OMe)₃.

It was previously shown that methoxysilyl groups are susceptible to nucleophilic displacement by carbanions.^{302, 303} Although carbanions are known to displace alkoxysilyl groups, ²⁹Si NMR spectroscopy confirmed the absence of any side reactions in our study, since pronounced shifts in Si resonances to a lower field are expected with increasing alkyl substitution.³⁰⁴ This is attributed to the decrease in the effective dπ-pπ back bonding between Si and O, and progressive substitution with alkyl groups leads to a net deshielding of the Si nucleus. Derouet and coworkers showed that for an alkoxysilane of general formula R_nSi(OR')_{4-n}, the ²⁹Si NMR shifts are distributed in four zones (Table 3-1) depending on the extent of alkyl substituents around the Si nucleus.³⁰⁵ The ²⁹Si NMR spectrum of PS-Si(OMe)₃ shown in Figure 3-2 reveals only one well-defined peak at approximately -53.5 ppm, which is close to the ²⁹Si NMR resonance of the neat end-capper (CMPTMS) observed at -54.8 ppm and is consistent with a RSi(OR')₃ structure. Therefore under the reaction conditions employed displacement of the methoxy group did not occur.

³⁰² Hirao, A.; Hatayama, T.; Nagawa, T.; Yamaguchi, M.; Yamaguchi, K.; Seiichi, N. "Polymerization of Monomers Containing Functional Silyl Groups. 2. Anionic Living Polymerization of (4-Alkoxysilyl)Styrenes." *Macromolecules* **1987**, *20*, 242-247.

³⁰³ Quirk, R. P.; Kevin, J. "Anionic Synthesis of Trialkoxysilyl-Functionalized Polystyrenes and Polybutadienes and Their Hydrolysis to Hybrid-Star Branched Structures." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42*, 27-28.

³⁰⁴ Derouet, D.; Sylvie, F.; Jean-Claude, B. "Synthesis of Alkoxysilyl-Terminated Polyisoprenes by Means of "Living" Anionic Polymerization, 1 Modeling of the Termination Step by Studying the Reaction of Butyllithium with Various Alkoxysilane Reagents." *Macromol. Chem. Phys.* **1998**, *199*, 1835-1842.

³⁰⁵ Derouet, D.; Sylvie, F.; Claude-Jean, B. "Synthesis of Alkoxysilyl-Terminated Polyisoprenes by Means of "Living" Anionic Polymerization, 2 Synthesis of Trialkoxysilyl-Terminated 1,4-Polyisoprenes by Reaction of Polyisoprenyllithium with Various Functional Trialkoxysilanes Selected as End-Capping Agents." *Macromol. Chem. Phys.* **1999**, *200*, 10-24.

Table 3-1: Influence of alkyl group substitution on ^{29}Si resonance

Substituents	δ_{Si} (ppm)
$\text{Si}(\text{OR})_4$	-75 - -85
$\text{RSi}(\text{OR}')_3$	-40 - -52
$\text{R}_2\text{Si}(\text{OR}')_2$	-10 - +10
$\text{R}_3\text{Si}(\text{OR}')$	10 - 25

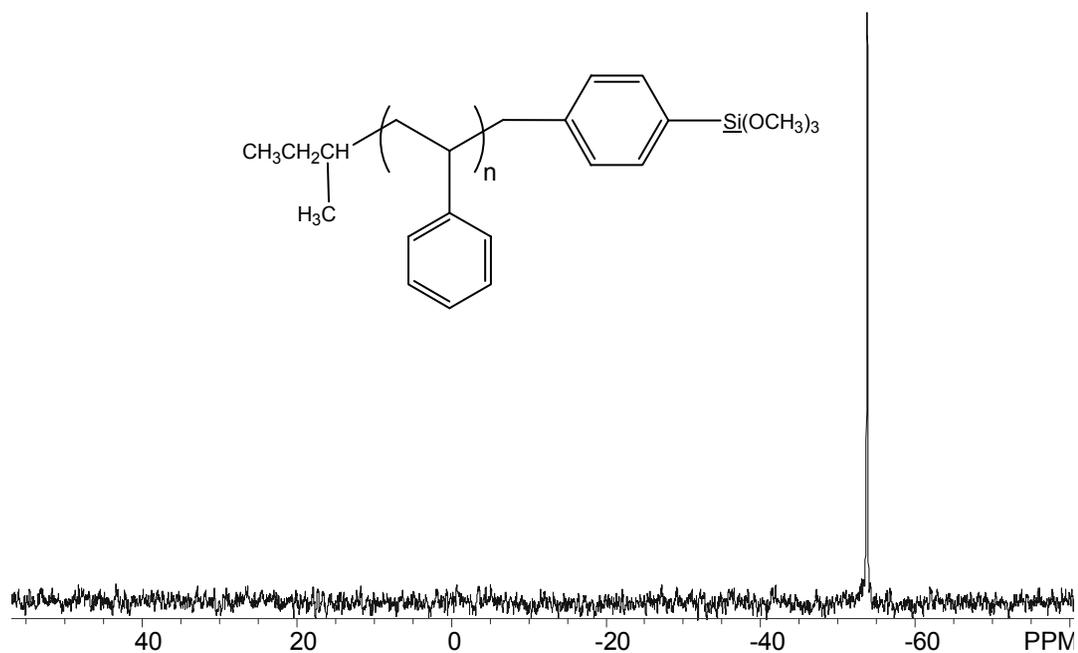


Figure 3-2: ^{29}Si NMR analysis of PS- $\text{Si}(\text{OMe})_3$ in 16 wt% CDCl_3 containing 0.06 M $\text{Cr}(\text{acac})_3$.

After confirming the success of this functionalization approach, a series of molecular weights were targeted as shown in Table 3-2. Good agreement was observed between number-average molecular weights that were determined from ^1H NMR spectroscopy and SEC. The polydispersities of the low molecular weight oligomers were, however, broader than typically expected from living anionic polymerization due to rapid rates of initiation and propagation in THF. But as expected, the polydispersity decreased as the molecular weight increased.³⁰⁶ ^1H NMR spectroscopy also confirmed quantitative end-capping of the living chain ends with CMPTMS. It was, however, necessary to add an excess of CMPTMS to quantitatively end-cap the living chain ends and the molar excess of CMPTMS required for the quantitative end-capping of living chain ends was found to increase with increasing molecular weights.

³⁰⁶ Chanda, M., "Advanced Polymer Chemistry." Marcel Dekker, Inc.: New York, **2000**.

Table 3-2: Molecular weight and % end-capping data for a series of PS-Si(OMe)₃

[CMPTMS]: [<i>sec</i> -BuLi] ^a	M _n (NMR) ^b (g/mol)	M _n (SEC) ^c (g/mol)	M _w /M _n ^c	% end-capping ^d
1.5:1	3,200	3,590	1.22	99
1.5:1	3,900	3,100	1.27	97
1.5:1	2,900	3,600	1.20	98
10:1	11,000	11,000	1.05	95
10:1	9,200	9,200	1.10	100

^aReaction conditions: THF at -78 °C with varying ratios of CMPTMS to *sec*-BuLi. ^bRatio of repeat unit aromatic proton resonance to initiator methyl proton resonance. ^cSEC conditions: THF, 40 °C, RI detector. ^dRatio Si(OCH₃)₃ resonance to initiator methyl resonance.

Earlier studies on the end-capping of living anions with alkoxysilanes were focused on low molecular weight oligomers for use in subsequent hydrolysis and condensation; however, the effect of molecular weights on the efficiency of end-capping with alkoxysilane was not discussed.^{307, 308} During our attempt to obtain a series of PS-Si(OMe)₃ of various M_n, it was found that as M_n of the polymer precursor increased, an increase in the molar excess of end-capper was necessary for quantitative end-capping. In order to gain a better insight into this effect, a systematic study on the extent of functionalization with increasing amounts of end-capper was conducted for polymers of M_n approximately equal to 10,000 g/mol. As shown in Table 3-3, the end-capping efficiency increased as end-capper concentration increased.

3.4.2 Hydrolysis and Condensation of Trimethoxysilane End-capped PS

Based on earlier studies, the hydrolysis was conducted in the presence of 1N HCl and the reaction time was limited to 40 h. ¹H NMR spectroscopic analysis of the condensed product indicated that 40 h was sufficient to obtain quantitative hydrolysis as determined by the absence of the endgroup methoxy protons at 3.6 ppm following hydrolysis and condensation (Figure 3-3).

³⁰⁷ Long, T. E.; Kelts, L. W.; Turner, R. S.; Wesson, J. A.; Mourey, T. A. "Synthesis and Characterization of Well-Defined Star Polymers via a Controlled Sol-Gel Process." *Macromolecules* **1991**, *24*, 1431-1434.

³⁰⁸ Quirk, R. P.; Kevin, J. "Anionic Synthesis of Trialkoxysilyl-Functionalized Polystyrenes and Polybutadienes and Their Hydrolysis to Hybrid-Star Branched Structures." *Polym. Prepr. (Am. Chem. Soc., Div. Polym. Chem.)* **2001**, *42*, 27-28.

Table 3-3: Effect of mol% CMPTMS charged on the % end-capping

[CMPTMS]: [<i>sec</i> -BuLi] ^a	M _n (NMR) ^b (g/mol)	M _n (SEC) ^c (g/mol)	M _w /M _n ^c	% end- capping ^d
2:1	12,400	12,000	1.13	84
2:1	9,300	9,700	1.15	87
3:1	8,300	9,400	1.09	88
10:1	11,000	11,000	1.05	95
10:1	9,200	9,200	1.10	100

^aReaction conditions: THF at -78 °C with varying ratios of CMPTMS to *sec*-BuLi. ^bRatio of repeat unit aromatic proton resonance to initiator methyl proton resonance. ^cSEC conditions: THF, 40 °C, RI detector. ^dRatio Si(OCH₃)₃ resonance to initiator methyl resonance.

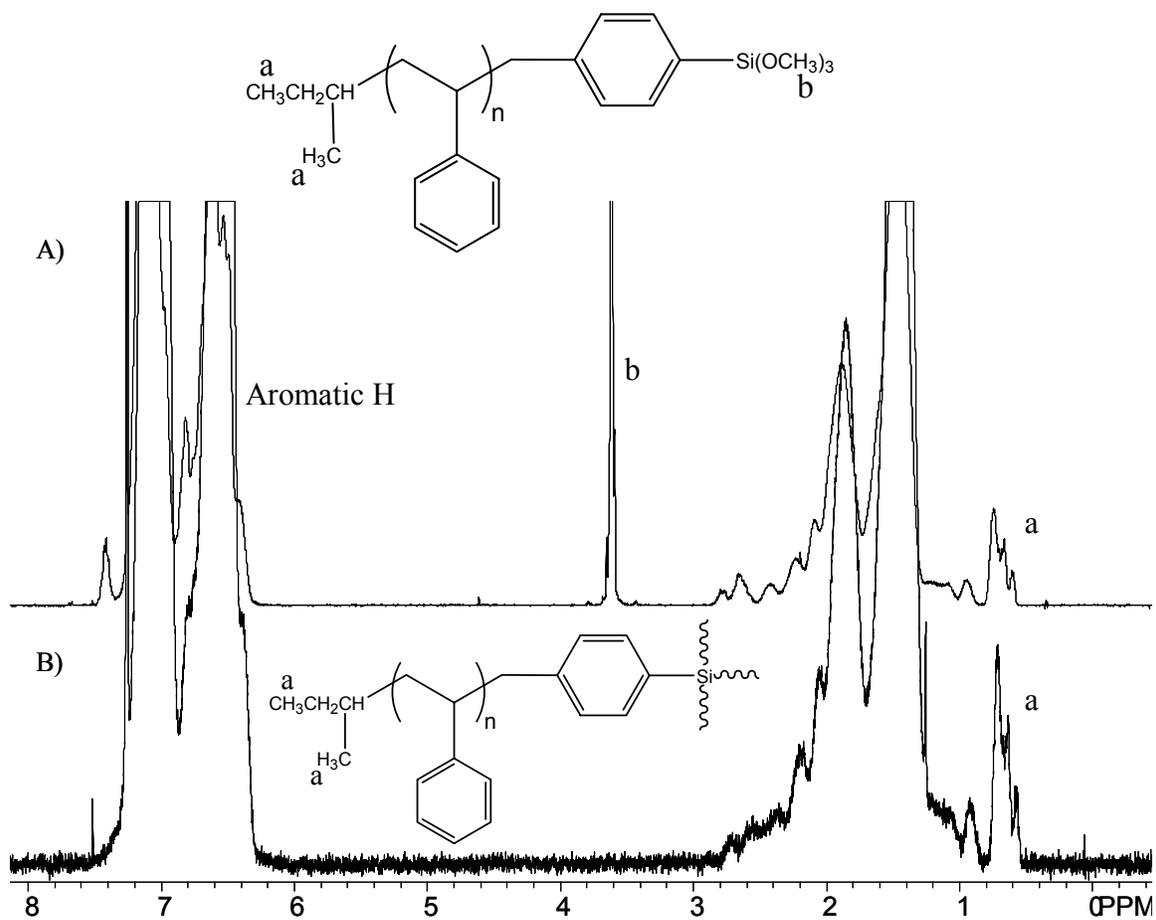


Figure 3-3: ^1H NMR spectra of PS-Si(OMe) $_3$ A) before, and B) after acid-catalyzed hydrolysis and condensation.

As shown in Scheme 1, hydrolysis of the silylmethyl ether results in silanol functionality, which undergoes condensation when heated to form the branched polymer. Condensation of trialkoxysilyl-substituted compounds can lead to a mixture of four different products depending on the extent of hydrolysis and condensation.³⁰⁹ They include uncondensed monomer designated as (T⁰), condensate containing one (T¹), two (T²), or three (T³) siloxane linkages as shown Figure 3-4 and Table 3-4.

Following hydrolysis, the oligomeric PS was not isolated in order to avoid premature condensation during work-up. Comparison of the ²⁹Si NMR spectra of the precursor oligomer and the condensed product indicated the extent of condensation. A representative ²⁹Si NMR spectrum for a precursor oligomer and product that was obtained after hydrolysis and condensation is shown in Figure 3-5. In addition to the disappearance of the single peak at -53.5 ppm, which confirmed hydrolysis of the methoxysilyl groups, two small resonances that were shifted to higher fields were observed. These peaks, designated as T¹ and T², corresponded to Si atoms containing one and two silicon-oxygen-silicon bonds respectively and are indicative of condensation.⁵³ The presence of both T¹ and T² signals in the ²⁹Si NMR suggested the presence of both linear and cyclic products in the condensate. Since the T² peak was broad, it was not possible to separate out contributions from the linear and cyclic T².

³⁰⁹ Kelts, L. W.; Armstrong, N. J. "A Silicon-29 NMR Study of the Structural Intermediates in Low pH Sol-Gel Reactions." *J. Mater. Res.* **1989**, 4, 423-430.

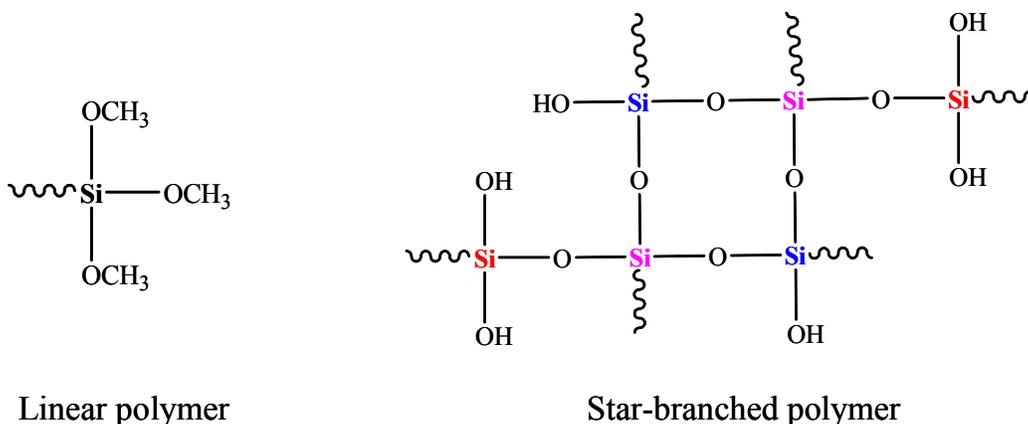


Figure 3-4: Depiction of different environments around Si nucleus in condensates obtained following hydrolysis and condensation of trialkoxysilane-containing linear polymer.

Table 3-4: ^{29}Si NMR designations for Si nucleus in uncondensed linear polymers and polymers containing multiple siloxane linkages

	Number of condensation bonds	^{29}Si NMR designation
Si	0	T^0
Si	1	T^1
Si	2	T^2
Si	3	T^3

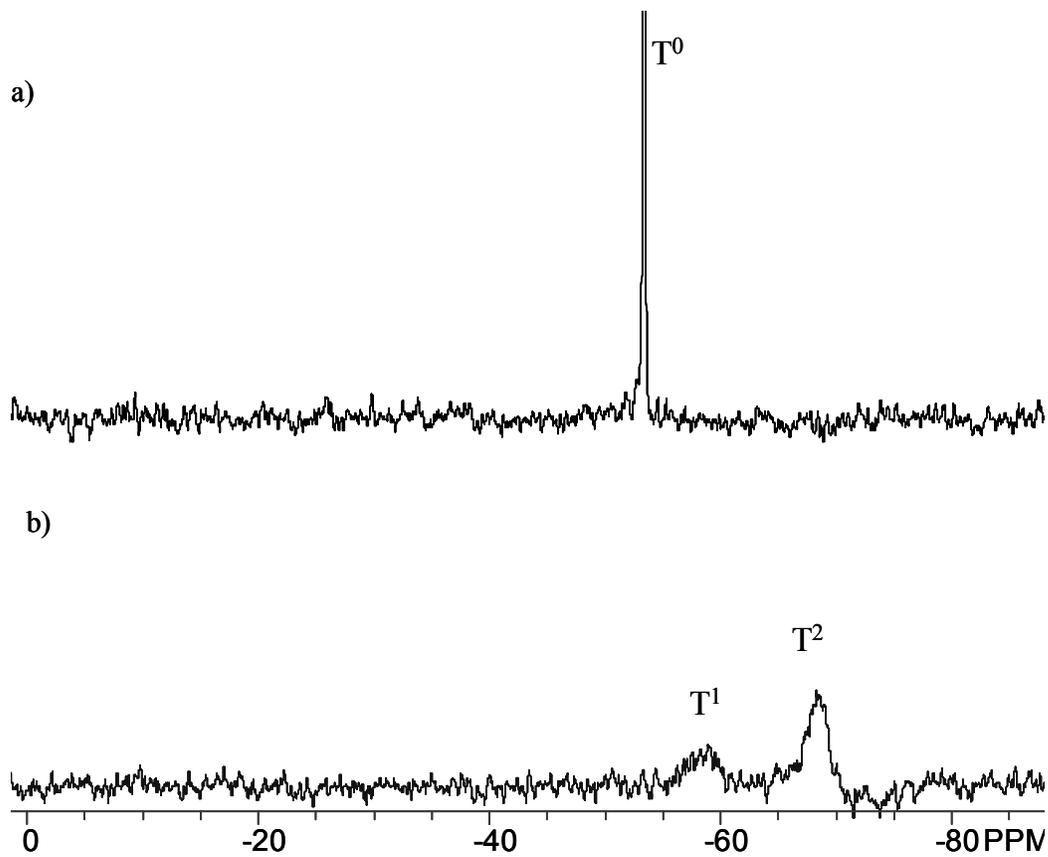


Figure 3-5: ^{29}Si NMR analysis in 16 wt% CDCl_3 containing 0.06 M $\text{Cr}(\text{acac})_3$ of a) precursor linear PS oligomer, and b) star-branched PS.

After confirming the structure of the condensate, the number of arms in the star-branched polymer was determined using SEC. A representative differential refractive index (DRI) trace for the precursor polymer and the branched polymer is shown in Figure 3-6. Only a very small peak associated with uncondensed precursor oligomer is observed in the DRI trace, which suggested that most of the chains had condensed to form branched PS. In order to confirm a branched topology, the branching coefficient g' was calculated for these polymers from the intrinsic viscosity values obtained from the SEC viscosity detector. The data that were obtained for the linear and the star-branched PS are summarized in Table 3-5.

The polymers that are described in Table 3-5 were synthesized from the same precursor PS ($M_w = 3,200$ g/mol). Both intrinsic viscosity and light scattering measurements gave similar molecular weights for the star-branched polymers. The low g' values of ~ 0.7 confirmed the presence of branching in these polymers, which agrees reasonably well with both theory and earlier experimental data for star-branched polymers.³¹⁰ It is known that the determination of branching coefficients based on hydrodynamic properties such as intrinsic viscosity are not accurate for star-branched macromolecules due to complications with ternary excluded-volume interactions and draining effect.³¹¹ However, these effects are pronounced only for densely branched structures. The good agreement between g' values determined in this study and literature indicated that the inconsistencies associated with the calculation of intrinsic viscosities for the branched macromolecules did not affect our measurements to a significant extent.

³¹⁰ Roovers, J. E. L.; Bywater, S. "Preparation and Characterization of Four-Branched Star Polystyrenes." *Macromolecules* **1972**, *5*, 384-388.

³¹¹ Douglas, J. F.; Roovers, J. E. L.; Freed, K. F. "Characterization of Branching Architecture through "Universal" Ratios of Polymer Solution Properties." *Macromolecules* **1990**, *23*, 4168-4180.

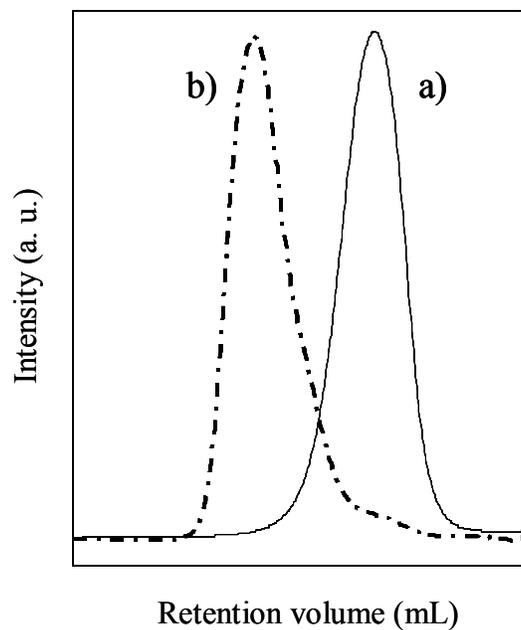


Figure 3-6: SEC DRI traces of a) precursor oligomer ($M_w = 4,790$ g/mol), and b) star-branched PS obtained by hydrolysis and condensation ($M_w = 38,000$ g/mol). Hydrolysis and condensation conditions: 20 wt% solids in THF with $[H_2O]: [Si]$ ratio of 4 added as 1N HCl solution, 40 h stirring and heated at 100 °C for 12 hours.

Table 3-5: Molecular weight data, degree of branching and the calculated number of arms for star-branched PS synthesized by hydrolysis and condensation of PS-Si(OMe)₃ of $M_n = 3,200$ g/mol

Sample designation (<i>topology</i>)	M_w (SEC) ^a (g/mol)	Number of arms ^b	$[\eta]$ _b (dl/g)	$g' = ([\eta]_{br}/[\eta]_i)_M$ ^c
PS-3k (<i>l</i>)	3,200*	n/a	-	n/a
PS-22k (<i>b</i>)	21,800	6.8	0.121	0.73
PS-19k (<i>b</i>)	18,500	5.8	0.101	0.68
PS-18k (<i>b</i>)	17,600	5.5	0.097	0.67

^aSEC conditions: THF, 40°C, viscosity detector. ^bNumber of arms per star were determined by dividing M_w of the branched polymer by M_w of the PS precursor. ^c $[\eta]$ for a given molecular weight was calculated using the Mark-Houwink equation by using values of 0.00021 for “K” and 0.67 for “a” as determined using the viscosity detector.

The average number of arms in the branched polymers were determined using the ratio of the weight average molecular weights (M_w) of the branched polymers obtained from SEC to the linear precursor. All the polymers obtained had an average of 6-7 arms. M_w reported for the linear PS sample in Table 3-5 was obtained using a DRI detector since M_n from DRI measurements was in excellent agreement with the M_n determined from ^1H NMR spectroscopy. M_w for the star-branched polystyrenes was derived from the MALLS absolute molecular weight detector. The g' values for the star-branched macromolecules obtained in this study are slightly higher than that observed in the literature for star-branched PS of similar number of arms.³¹² However, they are in good agreement with the theoretical value of 0.64 for a 6-7 arm star-branched polymers predicted by the Zimm and Kilb equation:- $g' = g^{1/2}$, where g refers to the ratio of the mean-square radius of gyration of the branched polymer to that of the linear polymer of the same molecular weight.³¹³ The value of g was determined using Zimm and Stockmayer equation:- $g = (3f-2)/f^2$, where f is the number of branches in the molecule.³¹⁴

3.4.3 Synthesis of Star-branched PS with Higher Arm Molecular weights.

Synthesis of branched macromolecules from longer alkoxy silane-functionalized precursor polymers was also attempted. Thus, acid catalyzed hydrolysis and condensation of PS-Si(OMe)₃ of higher M_n was performed under similar conditions to that used for lower M_n oligomers. Figure 3-7 shows a representative ^1H NMR spectrum of PS-Si(OMe)₃ of $M_n = 10,000$ g/mol. The complete disappearance of the methoxysilyl

³¹² Douglas, J. F.; Roovers, J. E. L.; Freed, K. F. "Characterization of Branching Architecture through "Universal" Ratios of Polymer Solution Properties." *Macromolecules* **1990**, 23, 4168-4180.

³¹³ Zimm, B. H.; Kilb, R. W. "Dynamics of Branched Polymer Molecules in Dilute Solution." *J. Polym. Sci.* **1959**, 37, 19-42.

³¹⁴ Zimm, B. H.; Stockmayer, W. H. "The Dimensions of Chain Molecules Containing Branches and Rings." *J. Chem. Phys.* **1949**, 17, 1301-1314.

protons at 3.6 ppm indicated quantitative hydrolysis. However, SEC analysis of the condensate showed incomplete condensation (Table 3-6), possibly due to steric hindrance near the Si center as a result of longer polymer chains. Figure 3-8 shows a comparison between the DRI traces for PS-Si(OMe)₃ before and after hydrolysis and condensation. Thus, surface modification studies were attempted only with branched polymers obtained from PS-Si(OMe)₃ of M_n ~3,000 g/mol.

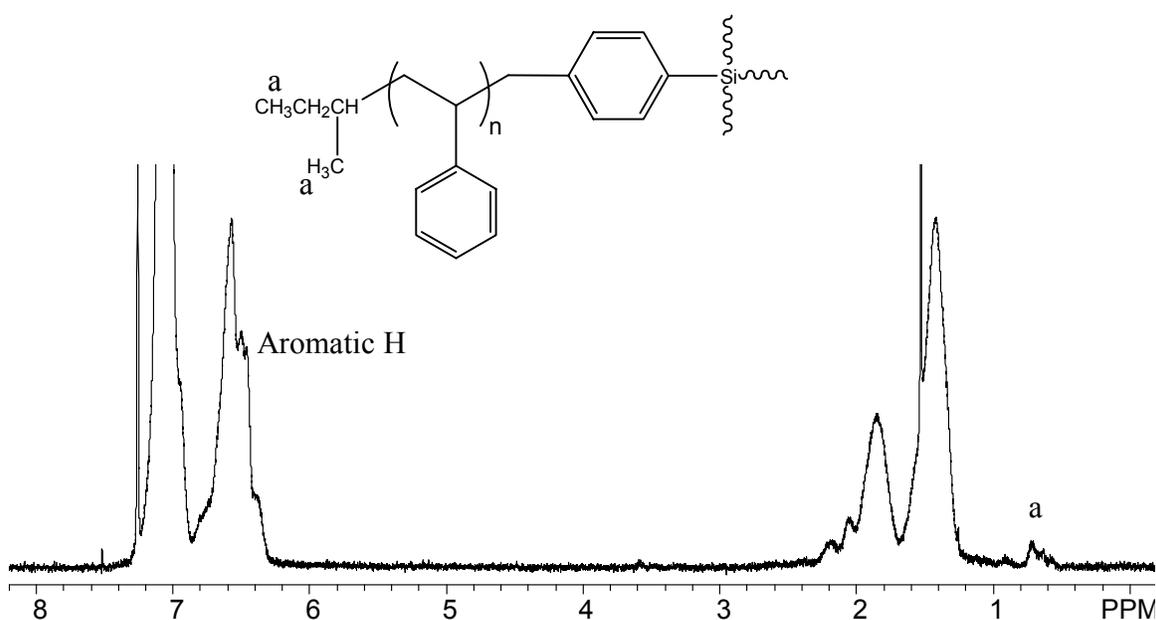


Figure 3-7: ¹H NMR spectra of PS-Si(OMe)₃ of M_n = 10,000 g/mol following hydrolysis and condensation.

Table 3-6: Molecular weight data, degree of branching and the calculated number of arms for branched PS synthesized by hydrolysis and condensation of PS-Si(OMe)₃

Sample designation (<i>topography</i>)	M _w (SEC) ^a (g/mol)	Number of arms (SEC) ^b	SEC trace
PS-10k (<i>l</i>)	10,000	-	monomodal
PS-48k (<i>b</i>)	48,300	4.8	trimodal
PS-17k (<i>l</i>)	17,000	-	monomodal
PS-110k (<i>b</i>)	110,000	6.5	trimodal

^aSEC conditions: THF, 40°C, MALLS detector. ^bNumber of arms per star were determined by dividing M_w of the branched polymer by M_w of the PS precursor.

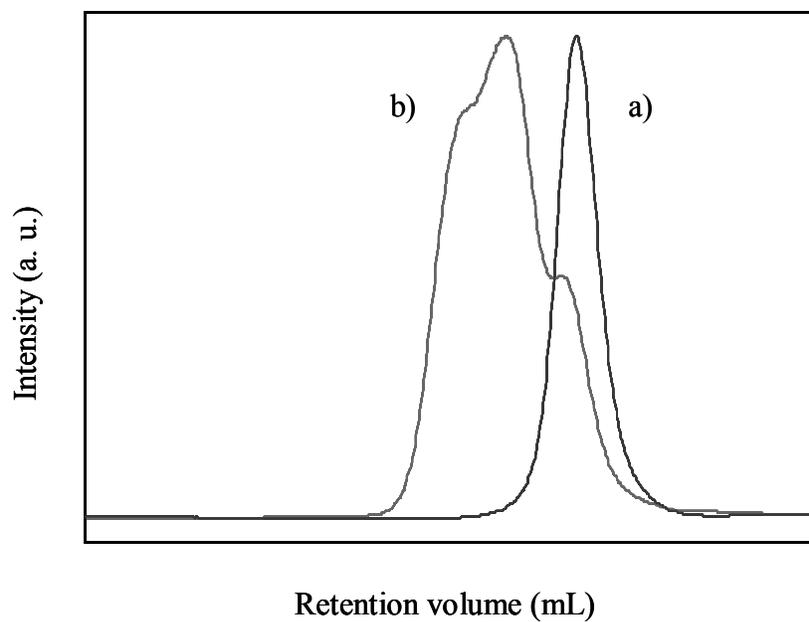


Figure 3-8: SEC DRI traces of a) precursor oligomer ($M_w = 10,000$ g/mol), and b) branched PS obtained by hydrolysis and condensation ($M_w = 48,300$ g/mol). Hydrolysis and condensation conditions: 20 wt% solids in THF with $[H_2O]: [Si]$ ratio of 4 added as 1N HCl solution, 40 h stirring and heated at 100 °C for 12 hours.

3.4.4 Silicon/SiO₂ Surface Modification with Linear and Star-branched PS

Silicon/SiO₂ surfaces were modified with linear PS-Si(OMe)₃ of various M_n to study the influence of polymer M_n on polymer film properties and the modified surfaces were characterized using various surface sensitive techniques. Ellipsometry in air was used to determine the thicknesses of the polymer films based on PS-Si(OMe)₃ oligomers. The ellipsometric thickness of the native SiO₂ layer on the unmodified silicon wafer, which was cleaned as described earlier was 2.0 nm.^{315, 316} The molecular weights of the PS-Si(OMe)₃ oligomers, the measured ellipsometric thickness of the polymer films, and the calculated grafting densities are summarized in Table 3-7.

Grafting densities of 0.36 to 0.6 chains/nm² were obtained for the end-functional PS with M_n values ranging between 3,800 g/mol and 17,000 g/mol that were grafted onto silicon/SiO₂ surfaces from the melt. The grafting density values obtained in our study compare well with those reported in the earlier literature for similar molecular weights. Mansky and coworkers showed that a hydroxyl end-functional PS of M_n = 8,800 g/mol upon grafting, gave a thickness of ~6 nm corresponding to a grafting density of 0.43 chains/nm².³¹⁷ Similarly, Kramer showed that the experimental grafting density values obtained for end-functional PS that were grafted onto silicon/SiO₂ surfaces from the melt were very close to the values predicted theoretically. Extrapolation of their data gave a grafting density of 0.33 chains/nm² for a PS of M_n 17,000 g/mol, which compared well

³¹⁵ Wieringa, R. H.; Siesling, E. A.; Geurts, P. F. M.; Werkman, P. J.; Vorenkamp, E. J.; Erb, V.; Stamm, M.; Schouten, A. J. "Surface Grafting of Poly(L-Glutamates). 1. Synthesis and Characterization." *Langmuir* **2001**, 17, 6477-6484.

³¹⁶ Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. "Controlling Polymer-Surface Interactions with Random Copolymer Brushes." *Science* **1997**, 275, 1458-1460.

³¹⁷ Kramer, E. J. "Grafting Kinetics of End-Functional Polymers at Melt Interfaces." *Isr. J. Chem.* **1995**, 35, 49-54.

with our value (entry 5, Table 3-7).³¹⁸ In addition, the thickness of the grafted layer of linear polymers showed a linear dependence on polymer M_n consistent with the formation of polymer “brushes”.³¹⁹ As shown in Figure 3-9, the grafting density of surface grafted polymer chains decreased with M_n of the grafted chains as expected for the “grafting to” approach. The decrease in grafting density with increasing M_n , illustrates the disadvantage of the “grafting to” approach, where polymer film thickness is limited to approximately 20 nm. However, “grafting to” allows more facile modification of surfaces with well-characterized preformed polymers with various topologies.

³¹⁸ Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. "Controlling Polymer-Surface Interactions with Random Copolymer Brushes." *Science* **1997**, 275, 1458-1460.

³¹⁹ de Gennes, P. G. "Conformations of Polymers Attached to an Interface." *Macromolecules* **1980**, 13, 1069-1075.

Table 3-7: Effect of M_n of PS-S(iOMe)₃ on polymer film characteristics

M_n of PS-Si(OMe) ₃ ^a (g/mol)	Water contact angle (deg)	Ellipsometric thickness ^b (nm)	Grafting density (σ) ^c (chains/nm ²)
3,800	90 ± 2	3.7 ± 0.1	0.59 ± 0.1
6,200	90 ± 2	5.2 ± 0.2	0.51 ± 0.2
8,900	92 ± 2	6.4 ± 0.3	0.44 ± 0.3
9,800	88 ± 2	6.9 ± 0.3	0.43 ± 0.3
17,000	88 ± 2	10 ± 0.1	0.36 ± 0.1

^aSEC conditions: THF, 40 °C, DRI detector. ^bRefractive indices of 1.46 and 1.59 were assumed for SiO₂ and PS respectively. ^cgrafting density (σ) = $h\rho N_a/M_n$; where h is the ellipsometric thickness in nm, ρ is the bulk density of PS in g/cc, N_a is the Avogadro number, M_n is the number average molecular weight of PS-(SiOMe)₃ in g/mole.

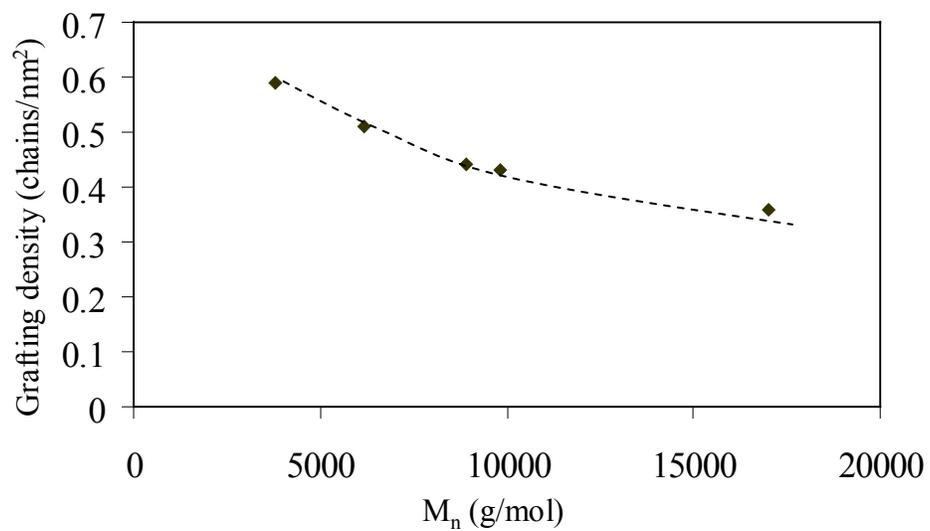


Figure 3-9: Variation of chain grafting density with M_n of PS-Si(OMe)₃.

Many earlier studies have described the attachment of hyperbranched polymers, dendrimers, and surface modification with PEO star polymers. AFM analyses of the dendrimer-coated surfaces in most cases has shown the presence of individual dendrimer molecules dispersed randomly on the surface.^{320, 321, 322} On the other hand, modification of surfaces with hyperbranched polymers leads to more uniformly covered surfaces. However, there are only a few investigations of surface topography of hyperbranched polymer modified surfaces. Müller *et al.* attempted the characterization of silicon/SiO₂ surfaces modified with hyperbranched poly(alkyl methacrylates) to determine the effect of polymer topology on surface topography.³²³ Star-PEO modified surfaces were also recently reported for their protein resistance. Many surface-sensitive techniques such as ellipsometry, contact angle goniometry, and fluorescence microscopy were used to characterize such surfaces; however, information on the surface topography after modification with the star-branched polymers was not reported.^{324, 325}

Synthesis of star-branched polymers using the hydrolysis and condensation of trialkoxysilane end-capped polymers is well known in the literature.^{35,51,52} However, earlier reports do not describe the utility of core-functionalized star-branched polymers in surface modification. The hydrolysis and condensation of the trialkoxysilane-

³²⁰ Hierlemann, A.; Campbell, J. K.; Baker, L. A.; Crooks, R. M.; Ricco, A. J. "Structural Distortion of Dendrimers on Gold Surfaces: A Tapping-Mode AFM Investigation." *J. Am. Chem. Soc.* **1998**, 120, 5323-5324.

³²¹ Li, J.; Piehler, L. T.; Qin, D.; Baker Jr., J. R.; Tomalia, D. A. "Visualization and Characterization of Poly(Amidoamine) Dendrimers by Atomic Force Microscopy." *Langmuir* **2000**, 16, 5613-5616.

³²² Fail, C. A.; Evenson, S. A.; Ward, L. J.; Schofield, W. C. E.; Badyal, J. P. S. "Controlled Attachment of PAMAM Dendrimers to Solid Surfaces." *Langmuir* **2002**, 18, 264-268.

³²³ Mori, H.; Boker, A.; Krausch, G.; Muller, A. H. E. "Surface Grafted Hyperbranched Polymers via Self-Condensing Atom Transfer Radical Polymerization from Silicon Wafers." *Macromolecules* **2001**, 34, 6871-6882.

³²⁴ Sofia, S. J.; Premnath, V.; Merrill, E. W. "Poly(Ethylene Oxide) Grafted to Silicon Surfaces: Grafting Density and Protein Adsorption." *Macromolecules* **1998**, 31, 5059-5070.

functionalized polymers leads to a star-branched polymer with excess unreacted silanol groups in the core that are capable of reacting with silica surfaces. The synthesis of these star-branched polymers is relatively facile and does not require additional functionalization steps to introduce surface reactive functionality. Thus, it was of interest to evaluate these silanol-containing star-branched polymers as surface modifiers and observe differences in the star-branched and linear PS modified surfaces in terms of the surface properties.

In order to confirm the successful modification of surfaces with the star-branched PS, water contact angles on the surfaces were measured. Water contact angle on clean silicon wafers were approximately 10° while silicon wafers that were modified with PS showed a water contact angle greater than 90° irrespective of the PS topology which suggested that the modified surfaces were hydrophobic. However, contact angle measurements did not differentiate the linear and star-branched polymer modified surfaces. Thus, AFM analysis was used to examine the surface topography.

AFM images of the silicon/SiO₂ surface modified with a linear PS ($M_w = 17,000$) and a star-branched PS ($M_n = 18,500$) are shown in Figure 3-10. Although polymer topology did not influence surface roughness, star-branched polymer modified surfaces exhibited distinct and deeper features than linear polymer modified surfaces. The crevices in the topographic image of the star-branched polymer modified surfaces were also observed as distinct mounds in the phase images.

³²⁵ Groll, J.; Amirgoulova, E. V.; Ameringer, T.; Heyes, C. D.; Rocker, C.; Nienhaus, G. U.; Moller, M. "Biofunctionalized, Ultrathin Coatings of Cross-Linked Star-Shaped Poly(Ethylene Oxide) Allow

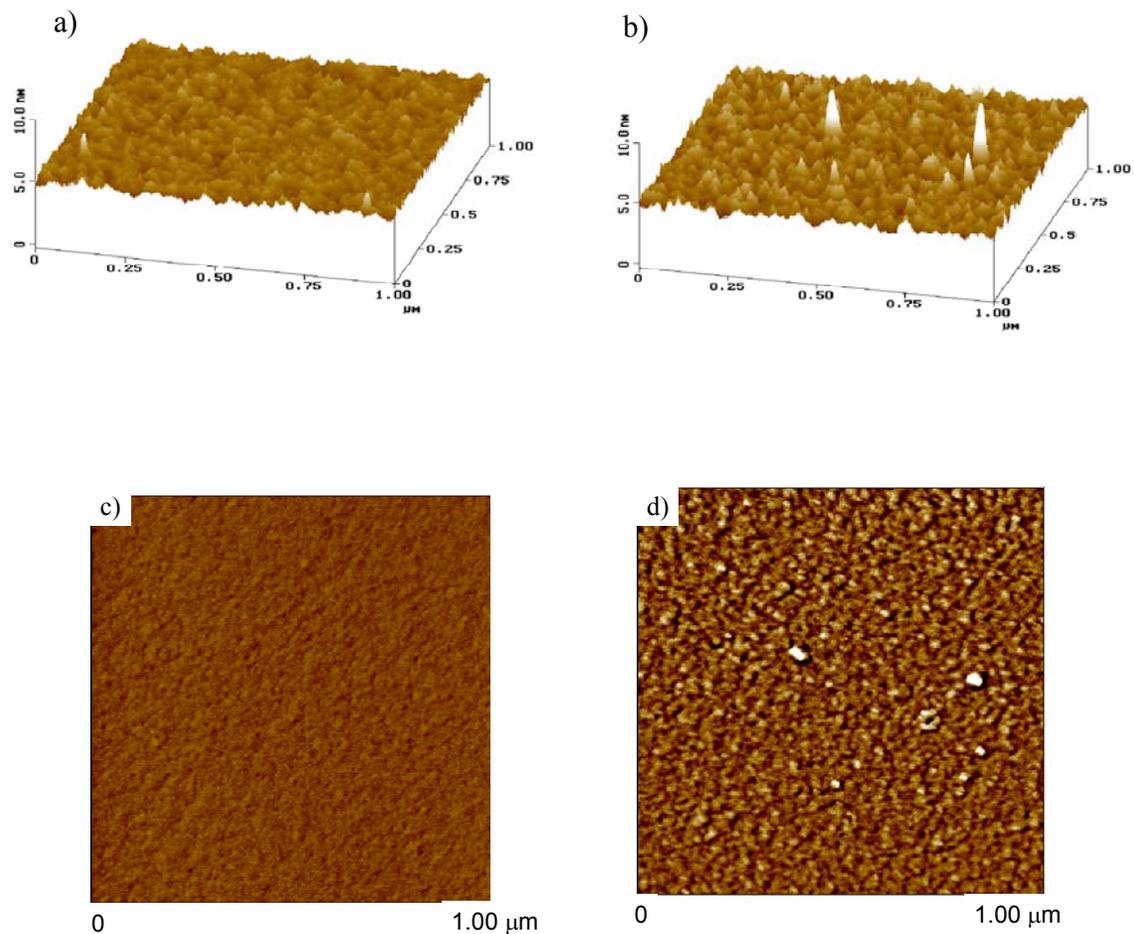


Figure 3-10: Tapping mode AFM topographic (a&b) and phase (c&d) images on silicon/SiO₂ surfaces modified with linear PS-Si(OMe)₃ of M_w = 17,000 g/mol (a&c) and star-branched PS of M_w = 18,500 g/mol (b&d) (height 0-10 nm, phase angle = 0-20 deg). Both surfaces show an RMS roughness value of ~0.28 nm. Surfaces for AFM analysis were prepared by spin coating 1 wt% polymer solutions onto clean silicon wafers, annealing polymer coated surfaces at 150 °C for 12 h and extracting the physically attached polymers by sonication in toluene for 1 h.

The surface features observed in Figure 3-10 for the star-branched polymers are similar to those observed with hyperbranched polymer films,³²⁶ but the roughness of the star-branched PS modified surfaces were lower than those compared to earlier hyperbranched polymer studies. There are two possible explanations for such a difference in the surface roughness values. First, “grafting from” was employed to form the hyperbranched polymer films, which leads to a very high grafting density of chains on the surface. Although all the chains are initiated at the same time, as branching proceeds, chain crowding prevents uniform growth, which leads to a mixture of chain lengths. In contrast, the polymers in our studies were preformed and subsequently deposited on the surface at a lower grafting density. In addition, when compared to a randomly branched structure in the earlier literature, the polymers used for surface modification in our studies were more uniform. As a result, more regular patterns were observed in the present study compared to those reported for the hyperbranched polymers. The tall features that were observed in the present study were attributed to inadvertent dust particles trapped in the film. The mounds observed in this case resemble mushrooms³²⁷ and was attributed to topology-induced reduction in chain grafting density. The depiction in Figure 3-11 explains this effect, where the core-anchored chains are unable to stretch in the vicinity of the incoming chains due to an immobile core unlike the linear polymer analogues.

³²⁶ Mori, H.; Boker, A.; Krausch, G.; Muller, A. H. E. "Surface Grafted Hyperbranched Polymers via Self-Condensing Atom Transfer Radical Polymerization from Silicon Wafers." *Macromolecules* **2001**, 34, 6871-6882.

³²⁷ Milner, S. T. "Polymer Brushes." *Science* **1991**, 251, 905-914.

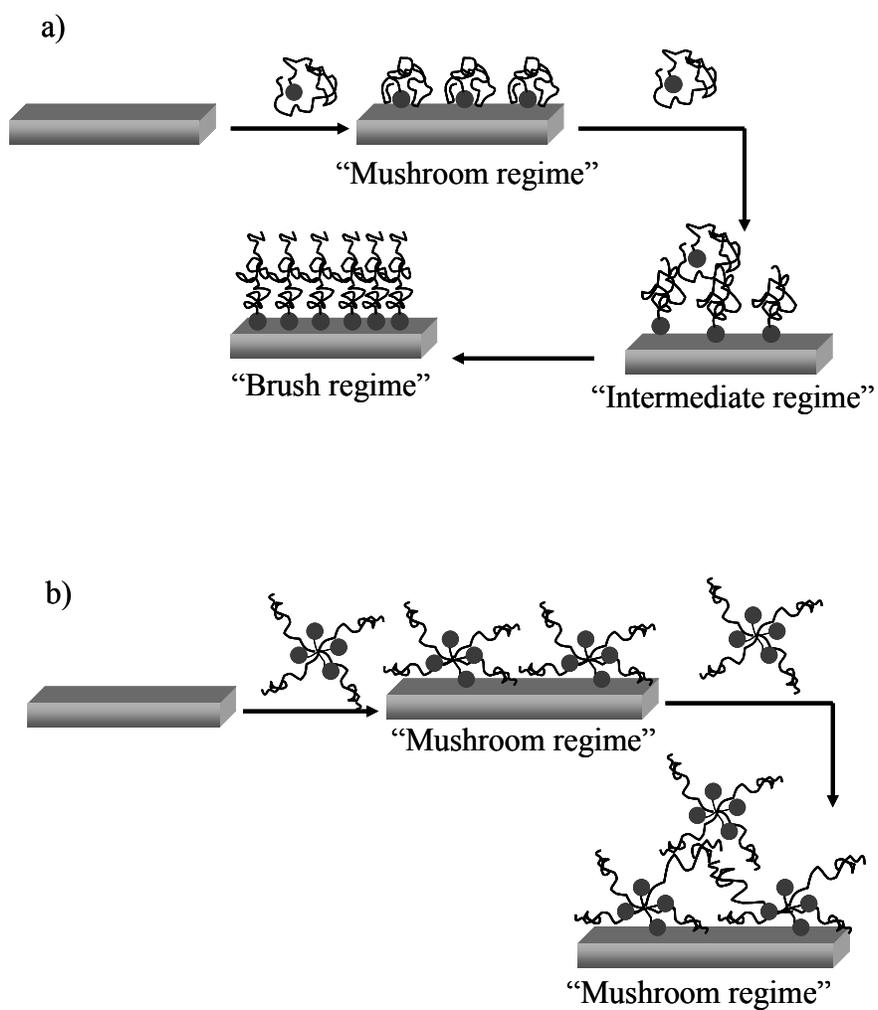


Figure 3-11: Depiction of the formation of (a) brush regime in the case of linear polymer chains, and (b) mushroom regime in the case of star-branched polymers attaching to a solid surface.

In order to prove that the observed topographic features on the star-branched PS modified surfaces corresponded to the mushroom regime, the thickness of the linear and star-branched PS films on silicon/SiO₂ were compared to their respective radii of gyration (R_g), which were obtained in a good solvent (Table 3-8). As seen in Table 3-8, the thicknesses of the linear polymer films are higher than the respective polymer R_g values and " d " $< 2R_g$, which is characteristic of a polymer chain in a stretched brush conformation.^{328, 329} However, the thicknesses of the star-branched PS films were lower than their respective R_g values. In the mushroom regime, the polymer chains have dimensions similar to their unperturbed radii of gyration.³³⁰ Taking into account the swollen dimensions of the polymers in THF, which is a good solvent for PS, the observed similarity in the R_g and thickness values indicated that the star-branched polymer films were in the mushroom regime. Although the comparison of polymer chain dimensions on the surface is made to the chain dimensions in a good solvent, the arguments that hold for swollen chains will also be true for unperturbed chains- in the latter case the chain dimensions are smaller than those of the swollen chains. Any R_g value lower than those shown in Table 3-8 further supports the conclusion that the linear chains were stretched and the star-branched polymers deposited as mushrooms.

³²⁸ Kramer, E. J. "Grafting Kinetics of End-Functional Polymers at Melt Interfaces." *Isr. J. Chem.* **1995**, 35, 49-54.

³²⁹ Penn, L. S.; Huang, H.; Sindhkhedkar, M. D.; Rankin, S. E.; Chittenden, K.; Quirk, R. P.; Mathers, R. T.; Lee, Y. "Formation of Tethered Nanolayers: Three Regimes of Kinetics." *Macromolecules* **2002**, 35, 7054-7066.

³³⁰ Halperin, A.; Tirrell, M.; Lodge, T. P. "Polymer Brushes." *Adv. Polym. Sci.* **1992**, 100, 31-71.

Table 3-8: Comparison of polymer film thickness, R_g , and d values for linear and star-branched PS

Polymer topology	M_n^a	R_g (nm) ^b	Ellipsometric thickness (nm)	Distance between graft points (d) ^c (nm)
Linear PS	3,800	2.3	3.7 ± 0.1	1.21 ± 0.01
Linear PS	9,800	3.2	6.9 ± 0.3	1.44 ± 0.01
Linear PS	17,000	5.5	10 ± 0.1	1.52 ± 0.01
Star PS	13,200*	4.2	2.7 ± 0.2	-
Star PS	13,300*	3.8	3.4 ± 0.3	-

^aSEC conditions: THF, 40 °C, DRI detector, * M_n was derived from MALLS detector. ^bData from the viscosity detector coupled to SEC. ^c $d = 1/(\text{grafting density})^{1/2}$.

It should also be noted that R_g values from intrinsic viscosity measurements for linear polymers are reliable, but the same does not hold for star-branched polymers.³³¹ In order to obtain an estimate of the R_g values for star-branched polymers, a “g” value, where “g” is described as $[\langle R_g^2 \rangle_{br} / \langle R_g^2 \rangle_{lin}]_M$; of 0.5 was assumed, as suggested by Douglas *et al.* and R_g for the star-branched polymers was calculated.^{332, 333} The “g” value of 0.5 is in good agreement with that calculated for a 6-7 arm star-branched macromolecule using the Zimm and Stockmayer equation, which gave a value of 0.45.³¹⁵ The calculated R_g values were similar to those obtained experimentally. Therefore, it was concluded that the star-branched PS film was in the mushroom conformation.

Penn *et al.* have investigated the evolution of various regimes of kinetics during tethering of end-functionalized PS from solution onto silicon/SiO₂ surfaces.³³⁴ They were able to image mushroom, brush, and intermediate shapes. The topography observed for linear PS in our study is relatively smooth compared to their earlier work for PS of similar M_n , which is possibly due to the very low grafting densities observed in their case where tethering was performed in solution. The observed features in the case of star-branched PS modified surfaces were similar to those observed with dendrimer-modified surfaces under monolayer surface coverage conditions.³³⁵ A direct comparison was not performed with other star-branched polymer modified surfaces since an earlier report

³³¹ Wang, W.-J.; Kharchenko, S.; Migler, K.; Zhu, S. "Triple-Detector GPC Characterization and Processing Behavior of Long-Chain-Branched Polyethylene Prepared by Solution Polymerization with Constrained Geometry Catalyst." *Polymer* **2004**, 45, 6495-6505.

³³² Douglas, J. F.; Roovers, J. E. L.; Freed, K. F. "Characterization of Branching Architecture through "Universal" Ratios of Polymer Solution Properties." *Macromolecules* **1990**, 23, 4168-4180.

³³³ Roovers, J. E. L.; Bywater, S. "Preparation and Characterization of Four-Branched Star Polystyrenes." *Macromolecules* **1972**, 5, 384-388.

³³⁴ Huang, H.; Rankin, S. E.; Penn, L. S.; Quirk, R. P.; Cheong, T. H. "Transition from Mushroom to Brush During Formation of a Tethered Layer." *Langmuir* **2004**, 20, 5770-5775.

describing the surface topography of star-branched polymer modified surfaces and comparisons to linear polymers, does not exist. In the recent literature Penn *et al.* compared the kinetics of surface attachment of amine functionalized linear and 4 arm star-PEO of comparable M_n to epoxide-derivatized silica.³³⁶ It was shown that terminally functionalized star-PEO exhibited a higher surface attachment density than linear PEO. This trend is in contrast to our observations in this study. This difference may be attributed to the position of the surface reactive groups, which in the present case was in the star core as compared to the terminal functionality of the star-PEO.

In order to confirm that the observed features were due to stably attached polymer films, surfaces modified with linear and star-branched PS of various M_n were also subjected to Soxhlet extraction in hot toluene for 16 h and characterized using water contact angle measurements, XPS, and AFM. Table 3-9 shows the water contact angle and XPS results obtained on surfaces modified with linear and star-branched PS. Surfaces modified with the linear and star-branched polymers show a high water contact angle and high XPS %C after extraction in hot toluene. In addition, AFM analysis of star-branched PS modified surfaces (Figure 3-12) showed features similar to those observed in Figure 3-10d. These observations confirmed that the surface attached polymers were stable, even during hot toluene extraction.

³³⁵ Hierlemann, A.; Campbell, J. K.; Baker, L. A.; Crooks, R. M.; Ricco, A. J. "Structural Distortion of Dendrimers on Gold Surfaces: A Tapping-Mode AFM Investigation." *J. Am. Chem. Soc.* **1998**, 120, 5323-5324.

³³⁶ Huang, H.; Fulchiero, E. C.; Penn, L. S. "Comparison of Tethering of Linear and Four-Arm Star Poly(Ethylene Oxide)." *Macromolecules* **2005**, 38, 1028-1030.

Table 3-9: Water contact angle values and XPS atomic composition of Soxhlet extracted silicon/SiO₂ surfaces modified with linear and star-branched PS of various M_n

Polymer topology	Polymer M _n (g/mol) ^a	Water contact angle (deg)	Atomic composition (%) ^b		
			%C	%O	%Si
Linear	3,050	89	83	9	8
Linear	6,200	90	94	3	3
Linear	8,900	92	92	4	4
Star	16,400	100	94	3	3
Star	11,700	100	87	7	6

^aSEC conditions: THF, 40 °C, DRI detector. ^{*}MALLS detector. ^bXPS conditions: Mg anode, take-off angle = 45°.

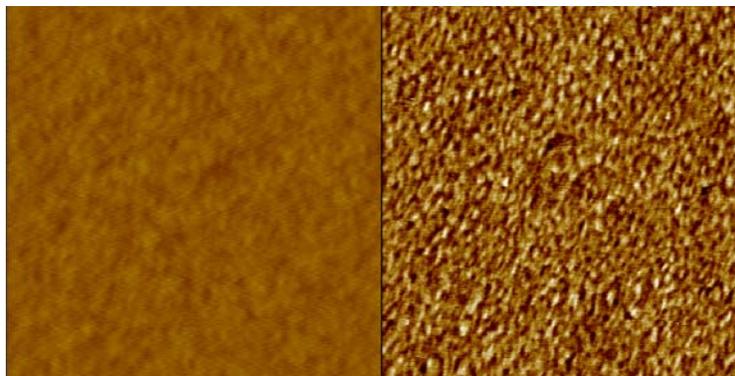


Figure 3-12: Tapping mode AFM topographic (left) and phase (right) images of a Si/SiO₂ surface modified with star-branched PS; $M_w = 22,700$ g/mol (scan area: $1 \mu\text{m}^2$, height: 0-10 nm; phase angle: 0-20 deg).

3.5 Conclusions

Trimethoxysilane-functionalized PS was synthesized using living anionic polymerization, where the polymerization was initiated using *sec*-BuLi and the living polystyryllithium anions were end-capped with CMPTMS. The molar excess CMPTMS that was necessary to obtain quantitatively end-capped PS increased with increasing polymer M_n . PS-Si(OMe)₃ were then hydrolyzed in THF using excess water and subsequently condensed with heat. SEC analysis showed that an average of 6-7 arm star-branched PS was obtained. Branching coefficients (g') that were calculated from the SEC intrinsic viscosity detector data were ~ 0.70 .

Successful modification of silicon/SiO₂ surfaces with star-branched PS was achieved. Despite the steric hindrance associated with the core silanol groups, covalent bonding was established between the star-branched polymers and the silicon/SiO₂ surfaces. AFM analysis of the resulting surfaces showed that star-branched PS modified surfaces present a very different surface topography compared to linear polymers of comparable M_n . Comparison of the film properties of the star-branched and the linear PS modified surfaces with their respective chain dimensions in solution indicated that the star-branched PS assumed a mushroom like conformation and the linear polymer chains were in the moderately stretched brush regime.

3.6 Acknowledgements

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dibutylmagnesium reagents. The authors would also like to thank Mr. Thomas E. Glass for ^{29}Si NMR analysis, Ms. Ann R. Fornof, and Dr. Taigyoo Park for SEC characterization.

CHAPTER 4: Solvent Switchable Silicon Surfaces Obtained via Modification with Novel Amphiphilic Block Copolymers

4.1 Abstract

Silicon/SiO₂ surface modification with novel amphiphilic block copolymers, polystyrene-*b*-poly(acetoxystyrene)-*b*-poly(*tert*-butyl acrylate) (poly(sty-*b*-styOAc-*b*-*t*-BA)) [1], and polystyrene-*b*-poly(2-hydroxyethyl acrylate)-*b*-poly(N,N-dimethylacrylamide) (poly(sty-*b*-HEA-*b*-DMAAm)) [2] from the melt is described. The block copolymers were obtained via nitroxide-mediated polymerization (NMP) through sequential monomer addition. The copolymers were anchored to the surface through the central functionalized block comprising either a long silylated acetoxystyrene (StyOAc) or short HEA blocks. Hydrolysis of the acetoxystyrene block in **1** to 4-hydroxystyrene and subsequent silylation yielded a randomly silylated central block. Following solvent extraction, copolymer **1** modified surfaces were hydrolyzed in acid water to convert the hydrophobic *t*-BA groups to hydrophilic acrylic acid groups. Wetting properties of the block copolymer modified surfaces and the kinetics of block rearrangement after exposure to block selective solvents was investigated using water contact angle measurements. Similarly, the response of copolymer **2** modified surfaces to block selective solvent treatments was studied using contact angle goniometry, AFM, and XPS.

4.2 Introduction

Modification of solid surfaces through grafting of polymers is commonly used to tune properties such as wetting, adhesion, friction, and biocompatibility. In recent years, the use of mixed polymer brushes to generate surfaces, which can respond to external stimuli, has received significant attention. Mixed polymer brushes are polymer films

composed of polymer chains of different chemical compositions grafted onto a surface. Such polymer films are obtained either through grafting of block copolymers, random copolymers, or two different homopolymers in a sequential manner. Such mixed polymer brush modified surfaces comprising polymer chains of significantly different polarities switch their surface energetics upon exposure to different solvents and the chain reorganization leads to different surface wettabilities, and nanomorphologies.

Stamm and coworkers first demonstrated the grafting of mixed homopolymer brushes comprising PS and poly(2-vinylpyridine) (PVP) using both “grafting from” and “grafting to” approaches onto silicon/SiO₂ surfaces using surface tethered azo initiators.^{337, 338} Such mixed polymer brush modified surfaces exhibited reversible changes in wettability, adhesion³³⁹ and surface morphologies following selective solvent treatment. Similarly, mixed polymer brush modified nylon fabrics exhibited extremely large changes in water contact angles (from 150° to complete wetting) after exposure to toluene and acid water, respectively.³⁴⁰ Stamm and coworkers constructed responsive gradient thin films of mixed polyelectrolyte brushes, which were covalently grafted to silicon/SiO₂ surfaces. The gradient films composed of poly(acrylic acid) (PAA) and PVP showed pH responsive changes in wettability.³⁴¹ Zhao *et al.* grafted PS and PMMA by sequential polymerization of PS and PMMA from a mixed ATRP/NMP initiator SAM

³³⁷ Sidorenko, A.; Minko, S.; Schenk-Meuser, K.; Duschner, H.; Stamm, M. "Switching of Polymer Brushes." *Langmuir* **1999**, 15, 8349-8355.

³³⁸ Minko, S.; Patil, S.; Datsyuk, V.; Simon, F.; Eichhorn, K.-J.; Motornov, M.; Usov, D.; Tokarev, I.; Stamm, M. "Synthesis of Adaptive Polymer Brushes via “Grafting to” Approach from Melt." *Langmuir* **2002**, 18, 289-296.

³³⁹ Retsos, H.; Gorodyska, G.; Kiriya, A.; Stamm, M.; Creton, C. "Adhesion between Chemically Heterogeneous Switchable Polymeric Brushes and an Elastomeric Adhesive." *Langmuir* **2005**, 21, 7722-7725.

³⁴⁰ Motornov, M.; Minko, S.; Eichhorn, K.-J.; Nitschke, M.; Simon, F.; Stamm, M. "Reversible Tuning of Wetting Behavior of Polymer Surface with Responsive Polymer Brushes." *Langmuir* **2003**, 19, 8077-8085.

modified surfaces.³⁴² The surfaces showed solvent switchable water contact angles and surface topographies that were dependent on homopolymer chain lengths.³⁴³

Several groups have also reported the grafting of amphiphilic block copolymers to create stimuli responsive surfaces. Zhao and Brittain grafted PS-*b*-PMMA on silicon/SiO₂ surfaces through surface initiated sequential carbocationic/radical polymerization as well as reverse-ATRP/ATRP.^{344, 345} The tethered polymers showed reversible changes in water contact angles upon treatment with block selective solvents. Changes in surface topography following solvent induced rearrangement of the PS and PMMA blocks of the tethered, diblock copolymer was also investigated using AFM and XPS.³⁴⁶ Brittain *et al.* also investigated switchable properties of ABA-type triblock copolymers grafted on silicon/SiO₂ surfaces.³⁴⁷

Iyoda *et al.* used ATRP from surface grafted α -bromoester functionalized trichlorosilanes to tether PMMA-*b*-PAAm to silicon/SiO₂ surfaces.³⁴⁸ Selective solvent treatments resulted in different surface topographies due to solvent induced swelling of the blocks; however, the water contact angles did not change appreciably. Quirk and

³⁴¹ Ionov, L.; Houbenov, N.; Sidorenko, A.; Stamm, M.; Luzinov, I.; Minko, S. "Inverse and Reversible Switching Gradient Surfaces from Mixed Polyelectrolyte Brushes." *Langmuir* **2004**, 20, 9916-9919.

³⁴² Zhao, B. "Synthesis of Binary Mixed Homopolymer Brushes by Combining Atom Transfer Radical Polymerization and Nitroxide-Mediated Radical Polymerization." *Polymer* **2003**, 44, 4079-4083.

³⁴³ Zhao, B. "A Combinatorial Approach to Study Solvent-Induced Self-Assembly of Mixed Poly(Methyl Methacrylate)/ Polystyrene Brushes on Planar Silica Substrates: Effect of Relative Grafting Density." *Langmuir* **2004**, 20, 11748-11755.

³⁴⁴ Zhao, B.; Brittain, W. J. "Synthesis of Tethered Polystyrene-Block-Poly(Methyl Methacrylate) Monolayer on a Silicate Substrate by Sequential Carbocationic Polymerization and Atom Transfer Radical Polymerization." *J. Am. Chem. Soc.* **1999**, 121, 3557-3558.

³⁴⁵ Sedjo, R. A.; Mirous, B., K.; Brittain, W. J. "Synthesis of Polystyrene-Block-Poly(Methyl Methacrylate) Brushes by Reverse Atom Transfer Radical Polymerization." *Macromolecules* **2000**, 33, 1492-1493.

³⁴⁶ Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. "Nanopattern Formation from Tethered PS-*b*-PMMA Brushes Upon Treatment with Selective Solvents." *J. Am. Chem. Soc.* **2000**, 122, 2407-2408.

³⁴⁷ Boyes, S. G.; Brittain, W. J.; weng, X.; Cheng, S. Z. D. "Synthesis, Characterization and Properties of ABA Type Triblock Copolymer Brushes of Styrene and Methyl Acrylate Prepared by Atom Transfer Radical Polymerization." *Macromolecules* **2002**, 35, 4960-4967.

coworkers used *n*-butyllithium initiated anionic polymerization from a surface attached diphenylethylene monolayer to tether hydroxyl-terminated polyisoprene(PI), which was subsequently chain extended with PEO.³⁴⁹ Reversible block switching upon selective solvent treatments was studied using contact angle measurements and XPS.

Brittain and coworkers used both solvent and solvent/thermal stimuli to switch wetting characteristics of surfaces modified with semifluorinated block copolymers.^{350, 351} The block copolymers composed of PS or PMA as the hydrocarbon inner block and several fluoropolymer outer blocks were grafted from silicon/SiO₂ surfaces via surface tethered ATRP initiators. While water contact angle analysis indicated complete block switching, XPS analysis revealed that the block rearrangement was confined to the near-surface region. In the case of thermally induced block rearrangement, the rate of reorganization of the fluorinated block depended on the T_g of the fluorinated block where lower T_g blocks rearranged faster than blocks with higher T_gs.

Tsukruk and coworkers have used Y-shaped polymer brushes, where two incompatible homopolymer chains are attached to a single focal point, to create surfaces exhibiting switchable properties. The homopolymers constituted PS and poly(*t*BA-*co*-AA), which was obtained through hydrolysis of surface grafted poly(*t*-BA). Following selective solvent treatments, the Y-shaped polymer brush-modified surfaces exhibited reversible changes in water contact angle and novel surface topographies consisting of

³⁴⁸ Kong, X.; Kawai, T.; Abe, J.; Iyoda, T. "Amphiphilic Polymer Brushes Grown from the Silicon Surface by Atom Transfer Radical Polymerization." *Macromolecules* **2001**, 34, 1837-1844.

³⁴⁹ Quirk, R. P.; Mathers, R. T.; Cregger, T.; Foster, M. D. "Anionic Synthesis of Block Copolymer Brushes Grafted from a 1,1-Diphenylethylene Monolayer." *Macromolecules* **2002**, 35, 9964-9974.

³⁵⁰ Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. "Synthesis and Characterization of Stimuli-Responsive Semifluorinated Polymer Brushes Prepared by Atom Transfer Radical Polymerization." *Macromolecules* **2004**, 37, 2790-2796.

pinned micelles.^{352, 353} Variation in the tribological properties such as friction coefficient and wear resistance of the surfaces following selective solvent treatment was also studied.^{354, 355} Recently, Zhao and coworkers demonstrated the growth of Y-shaped brushes of PMMA and PS using a combination of ATRP and NMP from surface tethered Y-shaped binary ATRP/NMP initiator.^{356, 357} Grafting of such mixed brushes from surface tethered binary initiator was used to obtain responsive silica particles, which exhibited stable suspensions in both CHCl₃ (non-selective solvent) and MeOH (poor solvent for PS).³⁵⁸

Most of the previous studies that had employed amphiphilic diblock and triblock copolymers to create stimuli responsive surfaces had anchored the polymers through a terminal functionality to the solid surfaces. In this study, surface wettabilities of silicon/SiO₂ surfaces were tuned by using centrally functionalized triblock copolymers, where the central block grafted the polymer to the surface, while the terminal blocks responded to selective solvents. The only previous study using similar polymer

³⁵¹ Granville, A. M.; Boyes, S. G.; Akgun, B.; Foster, M. D.; Brittain, W. J. "Thermoresponsive Behavior of Semifluorinated Polymer Brushes." *Macromolecules* **2005**, 38, 3263-3270.

³⁵² Julthongpiput, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Polymer Brushes: Nanoscale Switchable Surfaces." *Langmuir* **2003**, 19, 7832-7836.

³⁵³ Julthongpiput, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Amphiphilic Brushes with Switchable Micellar Surface Structures." *J. Am. Chem. Soc.* **2003**, 125, 15912-15921.

³⁵⁴ Lemieux, M.; Julthongpiput, D.; Bergman, K. N.; Cuong, P. D.; Ahn, H.-S.; Lin, Y.-H.; Tsukruk, V. V. "Ultrathin Binary Grafted Polymer Layers with Switchable Morphology." *Langmuir* **2003**, 20, 10046-10054.

³⁵⁵ Lemieux, M.; Lin, Y.-H.; Cuong, P. D.; Ahn, H.-S.; Zubarev, E. R.; Tsukruk, V. V. "Microtribological and Nanomechanical Properties of Switchable Y-Shaped Amphiphilic Polymer Brushes." *Adv. Funct. Mater.* **2005**, 15, 1529-1540.

³⁵⁶ Zhao, B.; He, T. "Synthesis of Well-Defined Mixed Poly(Methyl Methacrylate)/Polystyrene Brushes from an Asymmetric Difunctional Initiator-Terminated Self-Assembled Monolayer." *Macromolecules* **2003**, 36, 8599-8602.

³⁵⁷ Zhao, B.; Haasch, R. T.; MacLaren, S. "Self-Reorganization of Mixed Poly(Methyl Methacrylate)/Polystyrene Brushes on Planar Silica Substrates in Response to Combined Selective Solvent Treatments and Thermal Annealing." *Polymer* **2004**, 45, 7979-7988.

³⁵⁸ Li, D.; Sheng, X.; Zhao, B. "Environmentally Responsive "Hairy" Nanoparticles: Mixed Homopolymer Brushes on Silica Nanoparticles Synthesized by Living Radical Polymerization Techniques." *J. Am. Chem. Soc.* **2005**, 127, 6248-6256.

architecture on surfaces was reported by Ward and coworkers using PS-*b*-PS-Si(OEt)₃-*b*-PMMA, where the terminal blocks comprising PS and PMMA were obtained by anionic polymerization.³⁵⁹ The modified surfaces exhibited reversible changes in surface hydrophilicity and adhesion characteristics. However, the blocks studied included PS and PMMA, whose polarities are only moderately different.

This chapter will describe the synthesis of novel amphiphilic centrally functionalized triblock copolymers constituting terminal blocks of significantly different polarities using NMP and silicon/SiO₂ surface modification with the polymers through the “grafting to” approach. In contrast to the anionic polymerization technique, the free radical polymerization technique used in this study requires less stringent purification procedures and allows for the polymerization of a wide variety of functional monomers. Therefore, the synthesis of two different copolymer systems was attempted, where the hydrophobic block was PS, and the hydrophilic block was either a random copolymer of *t*-BA and AA (obtained through hydrolysis of poly(*t*-BA)) or DMAAm. The response of copolymer-modified surfaces to block selective solvents was investigated using contact angle goniometry, AFM, and XPS. Water contact angle analysis was also used to investigate the kinetics of terminal block rearrangement in air and following solvent exposure.

4.3 Experimental

4.3.1 Materials

Styrene (95%, Aldrich), *p*-acetoxystyrene (StyOAc, 95%, Aldrich), *tert*-butyl acrylate (*t*-BA, 95%, Aldrich), and N,N-dimethylacrylamide (DMAAm, 95%, Aldrich)

³⁵⁹ Wang, J. L.; Kara, S.; Long, T. E.; Ward, T. C. "Synthesis of Central Functionalized Asymmetric

were stirred over CaH₂ for 24-48 h and distilled under reduced pressure (0.1 mm Hg, 10 °C) after repeated degassing and freeze-thaw cycles, and stored at -25 °C until further use. 2-Hydroxyethyl acrylate (HEA, 95%, Acros Organic) was purified of the diacrylate and acrylic acid impurities according to a literature procedure,³⁶⁰ and was distilled from molecular sieves under reduced pressure (0.1 mm Hg, 60-70 °C), and stored at -25 °C until further use. 3-Isocyanatopropyltriethoxysilane (IPTES, 95%, Aldrich) was distilled under vacuum (0.1 mm Hg, 50 °C) in the absence of purification reagents. Dibutyltin dilaurate (DBTDL, 95%, Aldrich), N,N-dimethylformamide (DMF, 99.9%, Aldrich), 1,4-dioxane (95%, Aldrich), hydrazine hydrate solution (6.4 mM, Acros Organic), conc. H₂SO₄ (VWR International), NH₄OH (30%, VWR International), H₂O₂ (30%, Aldrich), methanol (EMD Chemicals), dichloromethane (EMD Chemicals), hexane (EMD Chemicals), and conc. HCl (EMD Chemicals) were used as received. THF (EMD Chemicals) was distilled from sodium in the presence of benzophenone immediately prior to use. Millipore milli-Q water was used for surface cleaning. Silicon wafers used as substrates were a generous gift from the Hewlett Packard Company.

4.3.2 Polymer Characterization

Size exclusion chromatography (SEC) data was obtained using a 717 Autosampler system equipped with 3 in-line 5 µm PLgel MIXED-C columns, a Waters 2410 refractive index detector operating at 880 nm, a Wyatt Technology miniDawn[®] multiple angle laser light scattering (MALLS) detector operating at 690 nm and calibrated with polystyrene standards, and a Viscotek Model 270 differential/light

Triblock Copolymers for Surface Modification and Switchable Surface Properties." *J. Polym. Sci., Polym. Chem.* **2000**, 38, 3742-3750.

scattering dual detector. The refractive index increment (dn/dc) was calculated online and was assumed to be similar for all the blocks in the copolymer. SEC measurements were performed at 40 °C in THF at a flow rate of 1 mL/min. ^1H NMR spectroscopy was performed on a Varian UNITY spectrometer at operating at 400 MHz with $\text{CDCl}_3/d_8\text{-THF}$ as solvent.

4.3.3 Surface Characterization

The modified silicon/ SiO_2 surfaces were sonicated in a Branson 1200 ultrasonic generator for 1 h or Soxhlet extracted with hot THF for 5 h. Static water contact angles were measured in the sessile drop mode using a FTA-200 contact angle goniometer with a syringe-driven droplet. The values were measured 30 sec after dispensing the drop to obtain equilibrium values. Contact angles were measured at 4-5 different spots on each surface. XPS was obtained on a Perkin Elmer Model 5400 instrument fitted with a Mg $K\alpha$ X-ray source (1253.8 eV), at a take-off angle of 30°. The anode was operated at 250 W. The 285 eV photoelectron peak of C1s electrons was used as an internal XPS standard. Topographic information on the polymer-modified silicon wafers was obtained using a Digital Instruments Nanoscope III atomic force microscope and software. TAP 150 Si_3N_4 tips with a spring constant of 40 N/m were used and set point ratios of 0.5 to 0.6 were used in the experiments.

4.3.4 Synthesis of Poly(sty-*b*-styOAc-*b*-*t*-BA) (1)

The synthesis of poly(sty-*b*-styOAc-*b*-*t*-BA), shown in Scheme 4-1A, was achieved using sty-DEPN initiated nitroxide mediated polymerization (NMP) via sequential monomer addition. The unimolecular initiator sty-DEPN was synthesized

³⁶⁰ Coca, S.; Jacsieczek, C. B.; Beers, K. L.; Matyjaszewski, K. "Polymerization of Acrylates by Atom Transfer Radical Polymerization. Homopolymerization of 2-Hydroxyethyl Acrylate." *J. Polym. Sci., Part*

according to a literature procedure using 1-bromoethylbenzene and *N-tert*-butyl-*N*-(1-diethyl phosphono-2,2-dimethylpropyl) nitroxide (DEPN).³⁶¹ The first PS block was synthesized by introducing styrene (11 mL, 96 mmol) and sty-DEPN (0.27 g, 0.67 mmol) into a 50 mL round-bottomed flask containing a magnetic stirring-bar and fitted with a septum-cocked three-way glass adaptor that was connected to a vacuum line. The mixture was degassed through multiple freeze-pump-thaw cycles and warmed to room temperature. The degassed solution was then immersed in an oil bath maintained at 110 °C for ~8-12 h corresponding to a styrene conversion of ~75-80%. The reaction was stopped by cooling the flask, and the polymer was isolated by repeated precipitations in 10-fold excess methanol after diluting with THF. The isolated product was dried under vacuum at 100 °C for 24 h and characterized using ¹H NMR spectroscopy and SEC.

The procedure for copolymerization of PS-DEPN with *p*-acetoxystyrene, was similar to the homopolymerization procedure. Degassed *p*-acetoxystyrene (2 g, 13.3 mmol) was added to PS-DEPN macroinitiator (1.3 g, 1 mmol) that was flushed with nitrogen for 15 min. The solution of PS-DEPN in *p*-acetoxystyrene taken in a septum-sealed 50 mL round-bottomed flask was immersed in an oil bath maintained at 110 °C for 6 h (% conversion ~70). After quenching the polymerization by immersing it in cold water, the mixture was diluted with THF and precipitated into 10-fold excess methanol. The copolymer was dried at 100 °C and characterized using ¹H NMR spectroscopy and SEC.

A: Polym. Chem. **1998**, 36, 1417-1428.

³⁶¹ Diaz, T.; Fischer, A.; Jonquière, A.; Brembilla, A.; Lochon, P. "Controlled Polymerization of Functional Monomers and Synthesis of Block Copolymers Using a α -Phosphonylated Nitroxide." *Macromolecules* **2003**, 36, 2235-2241.

Chain extension of the diblock copolymer with *t*-BA monomer was performed as follows. Degassed *t*-BA (1g, 7.8 mmol) was added to a degassed mixture of poly(sty-*b*-styOAc) (1.25 g, 0.05 mmol) and DEPN (0.008 g, 0.02 mmol, 5 mol% excess DEPN with respect to macroinitiator) in a septum-sealed 50 mL round-bottomed flask and heated to 110 °C for 7 h under nitrogen to obtain a conversion of ~30%. The triblock copolymer was isolated by precipitation into 10-fold excess methanol, dried under vacuum at 60 °C for 24 h, and characterized using ¹H NMR spectroscopy and SEC. ¹H NMR (400 MHz, 25 °C in CDCl₃): δ (ppm) 1.17-2.12 (-CH, -CH₂, -CH₃ in styrene, styOAc, and *t*-BA units, b); 2.25 (-OCOCH₃- in styOAc units, s); 6.21-7.23 (aromatic protons of styrene, and styOAc units, b). SEC (THF, 40 °C, MALLS detector): (PS-DEPN)- M_n = 12,600 g/mol, M_w/M_n = 1.05; P(sty-*b*-styOAc)-DEPN- M_n = 23,800 g/mol; M_w/M_n = 1.09; P(sty-*b*-styOAc-*b*-*t*-BA)-DEPN- M_n = 31,600 g/mol; M_w/M_n = 1.06.

4.3.5 Hydrazinolysis of Copolymer 1

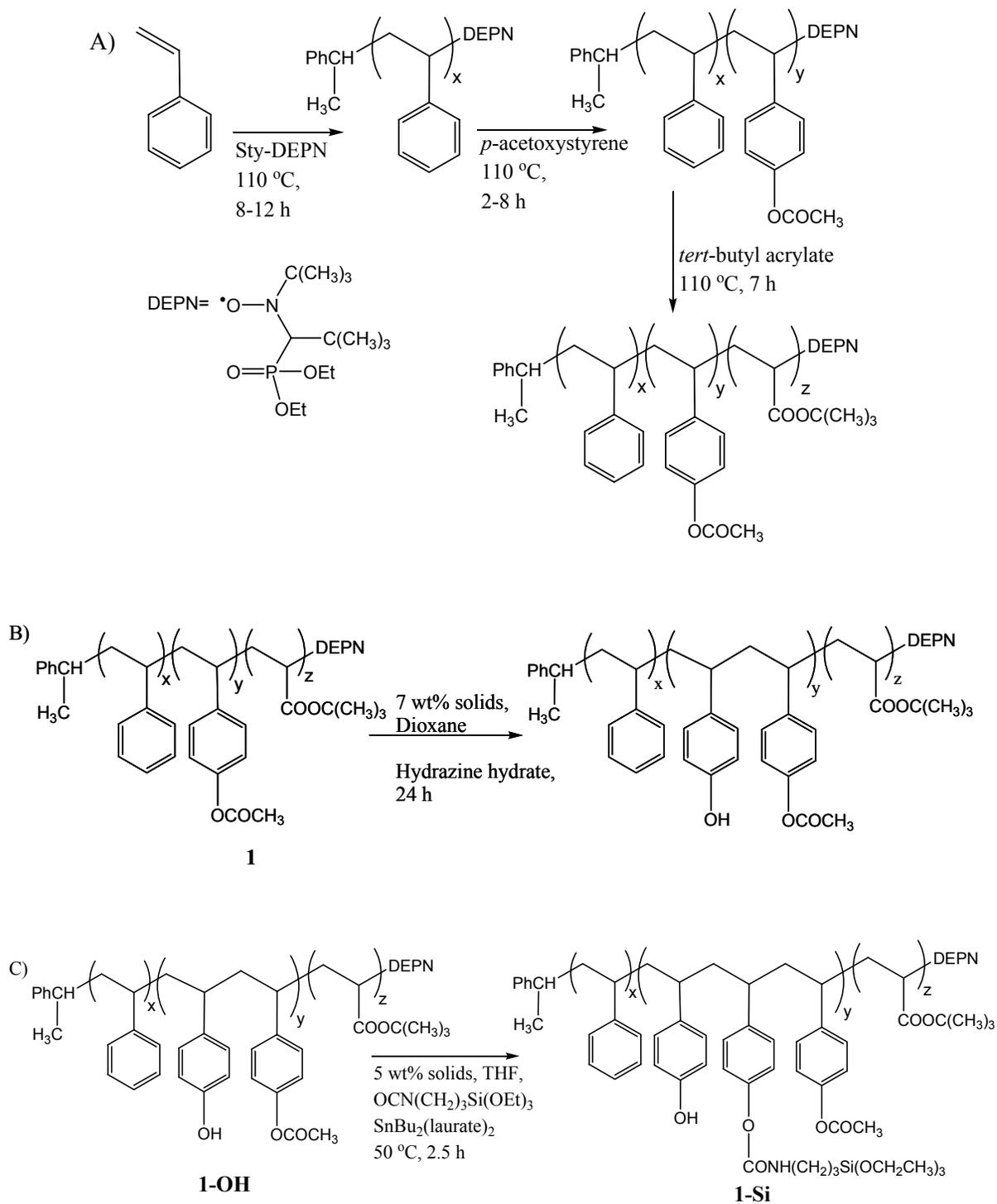
Deacetylation of styOAc units in copolymer **1** was performed using hydrazine hydrate in 1,4-dioxane as shown in Scheme 4-1B.³⁶² Copolymer **1** (0.75 g, 0.024 mmol) was dissolved in 1,4-dioxane (9.7 mL) to form a 7 wt% solution in a 50 mL round-bottomed flask. Hydrazine hydrate (9 eq. with respect to acetoxy groups in **1**, 0.03 mL, 0.22 mmol) was added to the solution, the mixture was purged with nitrogen for 10 min and stirred for 24 h at 25 °C. The partially deacetylated polymer, poly(sty-*b*-styOAc-*co*-styOH-*b*-*t*-BA) (**1-OH**) was isolated by precipitation into 10-fold excess hexane, dried under vacuum at 100°C for 12 h, and characterized using ¹H NMR spectroscopy, and

³⁶² Chen, X.; Jankova, K.; Kops, J.; Batsberg, W. "Hydrolysis of 4-Acetoxy styrene Polymers Prepared by Atom Transfer Radical Polymerization." *J. Polym. Sci., Part A: Polym. Chem.* **1999**, *37*, 627-633.

SEC. ^1H NMR (400 MHz, 25 °C in CDCl_3) : ~40% deacetylation of acetoxy groups;
SEC (THF, 40 °C, MALLS detector): $M_n = 31,600$ g/mol; $M_w/M_n = 1.06$.

4.3.6 Silylation of Copolymer 1-OH

Silylation was performed in a flame dried and septum-sealed 50 mL round-bottomed flask equipped with a magnetic stirring-bar. Copolymer **1-OH** (0.26 g, 0.0082 mmol) was dissolved in dry THF (5.0 mL) to form a 10 wt% solution, to which IPTES (2.5 eq. with respect to phenolic groups in **1-OH**, 0.15 mL, 0.6 mmol) and 2 drops of DBTDL (1 wt% in THF) was added (Scheme 4-1C). The mixture was stirred at 50 °C for 2.5 h and precipitated into 10-fold excess hexane. The isolated product (**1-Si**) was dried at 25 °C for 48 h under vacuum and stored in a desiccator until further use. ^1H NMR (400 MHz, 25 °C in CDCl_3): δ (ppm) 3.23 (-OCO-NH- CH_2 -, m); 3.78 (- $\text{CH}_2\text{Si}(\text{OCH}_2\text{CH}_3)$, m); ~10% silylation of the phenolic groups.



Scheme 4-1: A) Synthesis of poly(sty-*b*-styOAc-*b*-*t*-BA) (**1**), B) hydrazinolysis of **1** to **1-OH**, C) silylation of **1-OH**.

4.3.7 Synthesis of Poly(sty-*b*-HEA-*b*-DMAAm) (2)

PS-DEPN (~70% conversion) was synthesized according to the procedure described earlier. Chain extension of PS-DEPN with HEA was performed as follows. HEA (0.5 g, 4.3 mmol) dissolved in anhydrous DMF (2.2 mL) to form a 30 wt% solution was degassed by repeated freeze-pump-thaw cycles under vacuum. The degassed solution was added to a nitrogen flushed mixture of PS-DEPN (0.5 g, 0.027 mmol) and DEPN (0.0034 g, 0.0014 mmol, 30 mol% excess DEPN with respect to PS-DEPN) in a septum-sealed 50 mL round-bottomed flask and the polymerization was carried out at 115 °C for 1.5 h under nitrogen to a monomer conversion of ~20%. Following polymerization, DMF was removed under reduced pressure; the solid residue was dissolved in THF, precipitated into 10-fold excess 9:1 MeOH/H₂O mixture, and dried at 100 °C for 24 h under vacuum to yield poly(sty-*b*-HEA)DEPN.

Polymerization of DMAAm using poly(sty-*b*-HEA)-DEPN (Scheme 4-2) as macroinitiator was performed in a manner analogous to HEA polymerization. Degassed mixture of DMAAm (2 g, 20.2 mmol) and DMF (2.1 mL) was added to a mixture of diblock copolymer macroinitiator (0.3 g, 0.015 mmol) and DEPN (0.012 g, 2.7 molar excess with respect to macroinitiator) and immersed in an oil bath maintained at 115 °C for 5 h (DMAAm conversion of ~10%). The polymer was isolated by removing DMF under reduced pressure, dissolving the residue in THF, precipitating into excess hexane, and drying at 100 °C for 24 h under vacuum. The polymers obtained after each step were characterized using ¹H NMR spectroscopy and SEC. ¹H NMR (400 MHz, 25 °C in CDCl₃): δ (ppm) 1.06-2.27 (-CH, -CH₂ of styrene, HEA, and DMAAm units, b); 2.28-3.34 (-N(CH₃)₂ of DMAAm unit, b); 3.49-4.41 (-CH₂CH₂OH, -COO-CH₂CH₂- of HEA

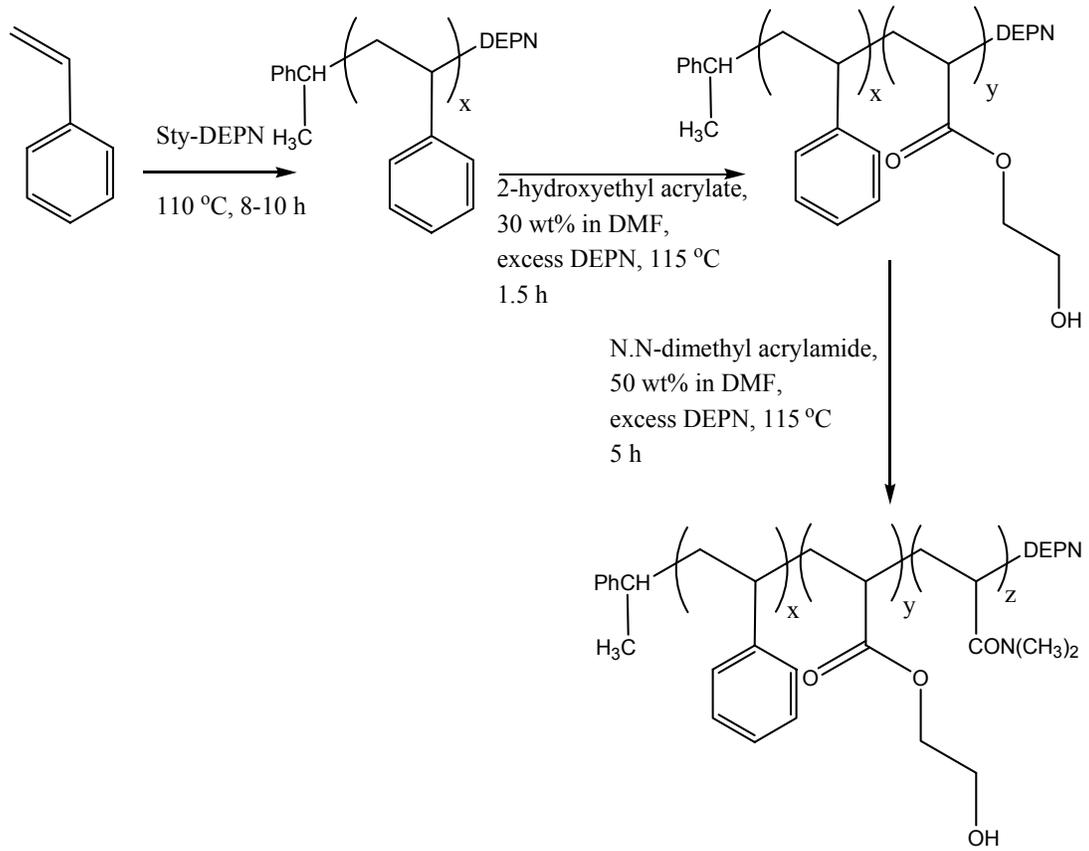
unit, b); 6.01-7.20 (aromatic protons of styrene units; b). SEC (THF, 40 °C, MALLS detector): (PS-DEPN): $M_n = 18,700$ g/mol; $M_w/M_n = 1.05$; poly(sty-*b*-HEA): 19,200 g/mol; $M_w/M_n = 1.18$; poly(sty-*b*-HEA-*b*-DMAAm): 48,000 g/mol; $M_w/M_n = 1.06$.

4.3.8 Substrate Treatment

Silicon wafers were cut into 1 cm² samples and sonicated for 5 min in dichloromethane and 5 min in methanol. The wafers were blown with nitrogen and cleaned with freshly prepared Piranha solution (conc.H₂SO₄:30% H₂O₂; v/v: 70/30) at 90 °C for 1 h, rinsed with milli-Q water, and cleaned with a 30% NH₃:30% H₂O₂:H₂O (v/v/v: 1/1/5) at 60 °C for 15 min. The wafers were then rinsed with milli-Q water several times, blown dry with nitrogen, and immediately modified with the copolymers. (*Caution: Piranha solution reacts violently with many organic materials and should be handled with care.*)

4.3.9 Modification of Silicon/SiO₂ Surfaces with Block Copolymers

Copolymers **1-Si** ($n_{\text{sty}} = 117$, $n_{\text{sty-OAc}} = 77$, $n_{\text{l-BA}} = 43$) and **2** ($n_{\text{sty}} = 177$, $n_{\text{HEA}} = 5$, $n_{\text{DMAAm}} = 67$) were dissolved in THF (1 wt% solution) and spun cast onto clean silicon wafers at 2500 rpm for 1 min. The wafers were then heated in a vacuum oven at 150 °C for 15 h in order to enable the functional groups in the polymers to react with the surface hydroxyls. The wafers were then exhaustively sonicated in THF for ~1 h or Soxhlet extracted with THF for 5 h to remove any physically adsorbed polymer prior to characterization.



Scheme 4-2: Synthesis of poly(sty-*b*-HEA-*b*-DMAAm) (**2**).

4.3.10 Hydrolysis of Surface-grafted Copolymer 1-Si

Silicon wafers coated with copolymer **1** were placed in 1N HCl solution in THF in order to hydrolyze the *tert*-butyl acrylate groups to acrylic acid. Hydrolysis was performed for 17 h or 24 h and surfaces were characterized using XPS to determine the stability of the polymer thin films under the hydrolysis conditions.

4.3.11 Solvent Treatments of Copolymer-modified Surfaces

The surfaces were initially immersed in THF, removed and blown dry with nitrogen, and analyzed using water contact angle measurements. Reversible rearrangement of the surface anchored polymer chains was investigated in solvents of different thermodynamic qualities (methanol and toluene) for the individual blocks over several cycles. For this purpose, the surface was immersed in one particular solvent for a given time, taken out and dried with nitrogen. Water contact angles on the surface immediately following drying were measured at 4-5 different spots. The surfaces were immediately placed in the second solvent for the same time, dried with nitrogen, and the water contact angles were measured. The process was repeated for multiple cycles with solvent immersion alternating between toluene and methanol to assess the extent of reversibility of this switching process. All measurements were carried out in triplicate.

In the case of copolymer **1-Si** modified surfaces, the immersion time in each solvent was 12 min, while in the case of copolymer **2** modified surfaces, the first measurement was done on surfaces that were soaked in a particular solvent for 17 h while for all subsequent measurements, the soaking time in the solvent was 10 min.

4.3.12 Kinetics of Block Rearrangement in Selective Solvents

In order to determine the rate at which the polymer blocks rearranged upon exposure to a favorable solvent, the surfaces were initially soaked in one solvent for 10 min, taken out, and blown dry with nitrogen. After measuring water contact angles immediately following drying, the surfaces were placed in a different solvent for various times and water contact angles were measured after each immersion time. Similarly, the procedure was repeated for the other solvent. All measurements were carried out in triplicate.

Block rearrangement over time in air after solvent exposure was also studied. For this study, the wafers were soaked in a selective solvent for 10-12 min and contact angles were measured immediately after blowing dry with nitrogen and over time as the wafers remained exposed to air at 25 °C.

4.4 Results and Discussions

The amphiphilic copolymers used for silicon/SiO₂ surface modification were synthesized using nitroxide mediated polymerization (NMP). NMP, which belongs to the class of living free radical polymerization strategies was pioneered by Rizzardo *et al.* and Gnanou *et al.*^{363, 364} This process, which involves reversible deactivation of polymeric radicals by stable nitroxides ensures low concentrations of active radicals at a given time during polymerization. Thus, the possibility of radical termination is significantly reduced, leading to well-controlled polymers with narrow molecular weight distributions.

³⁶³ Solomon, D. H.; Rizzardo, E.; Cacioli, P. "Free Radical Polymerization and the Produced Polymers." EP 135280, **1985**.

³⁶⁴ Grimaldi, S.; Finet, J.-P.; Moigne, F. L.; Zeghdaoui, A.; Tordo, P.; Benoit, D.; Fontanille, M.; Gnanou, Y. "Acyclic β -Phosphonylated Nitroxides: A New Series of Counter-Radicals for "Living"/Controlled Free Radical Polymerization." *Macromolecules* **2000**, 33, 1141-1147.

Since the chain ends remain intact as long as the monomer conversion remains low, this technique has been used to synthesize well-defined homo- as well as block copolymers.

4.4.1 Synthesis of poly(sty-*b*-styOAc-*b*-*t*-BA) (1)

In this study, DEPN mediated NMP was used to obtain well-defined amphiphilic triblock copolymers, where the central block was chosen to have functional groups that could react with the hydroxyl groups on silicon/SiO₂ surfaces. One set of functional polymers synthesized were poly(sty-*b*-styOAc-*b*-*t*-BA) (1) obtained by sequential polymerization of styrene, *p*-acetoxystyrene, and *tert*-butyl acrylate. Figure 4-1 shows the ¹H NMR spectra of PS-DEPN, poly(sty-*b*-styOAc)-DEPN, and poly(sty-*b*-styOAc-*b*-*t*-BA)-DEPN. PS-DEPN shows resonances associated with the repeat unit aromatic protons (6.2-7.2 ppm) and the backbone methine and methylene protons (1.17-2.12 ppm). Following chain extension with *p*-acetoxystyrene, a new peak at 2.25 ppm corresponding to the methyl protons of the acetoxy groups was observed. Ratio of the repeat unit acetoxy methyl proton resonance with the aromatic proton resonance indicated the relative molar ratios of *p*-acetoxystyrene and styrene units in the copolymer. Successful polymerization of the third *tert*-butyl acrylate block was confirmed by the appearance of a new peak associated with the methyl protons of the *tert*-butyl groups at 1.43 ppm. The peaks observed between 0.5 and 1 ppm in Figure 4-1a are from the methyl protons of the DEPN mediator, the intensity of which decreases with increasing molecular weights following block copolymerization.

Table 4-1 shows the molecular weights and chemical composition of a series of triblock copolymers 1. All the copolymers displayed narrow molecular weight distributions. The chemical compositions calculated from ¹H NMR agreed well with

those obtained from SEC molecular weights. For the calculation of SEC based molar ratio, the number of repeat units for each block was calculated and compared against the total number of monomer repeat units. For the calculation of NMR based molar ratio, the ratios of all the major peaks associated with the aromatic region, methyl protons of the acetoxy groups at 2.25 ppm, and the aliphatic protons was obtained by integration. Assuming one *p*-acetoxystyrene unit in the copolymer, the relative ratios of styrene and *tert*-butyl acrylate with respect to *p*-acetoxystyrene were calculated and converted to a percent based value.

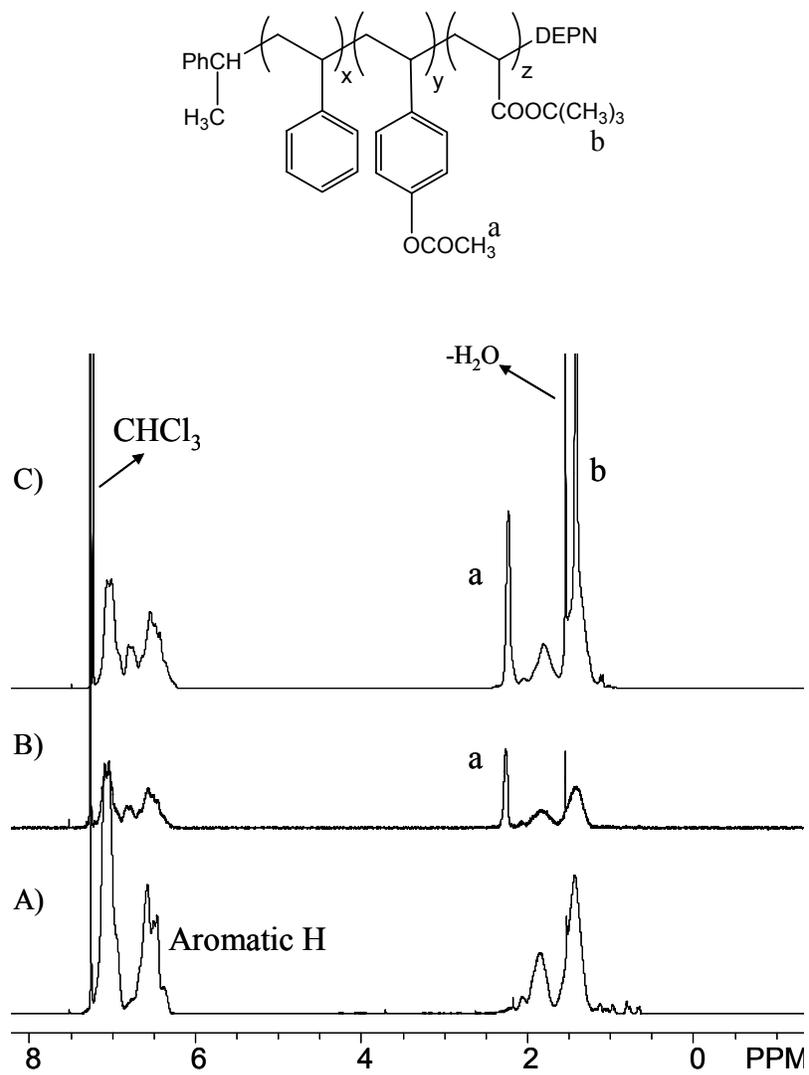


Figure 4-1: ^1H NMR spectra of A) PS-DEPN, B) poly(sty-*b*-styOAc)-DEPN, and C) poly(sty-*b*-styOAc-*b*-*t*-BA).

Table 4-1: Molecular weight and chemical composition data for a series of **1**

M_n^a PS	M_n^a P(styOAc)	M_n^a P(<i>t</i> -BA)	(x:y:z) ^c
(g/mol)	(g/mol)	g/mol	NMR ^d (SEC ^e)
12,500	12,500	5,500	59:24:16 (50:32:18)
12,600	11,200	4,400	53:31:16 (52:30:16)
12,600	11,200	7,800	44:32:23 (48:27:26)
12,600	7,200	10,000	48:26:26 (50:18:32)

^aSEC conditions: THF, 40 °C, MALLS detector. ^b¹H NMR conditions: 400 MHz, 25 °C, CDCl₃. ^cx, y, z refer to the molar ratio of sty:styOAc:*t*-BA units in the copolymer. ^dNMR determination was based on the relative ratios of the peak integrations obtained for resonances between 6.2-7.2, 2.25, and 1.17-2.12 ppm, respectively. ^eSEC determination of x:y:z: $x = n_{\text{sty}}/n$; $y = n_{\text{styOAc}}/n$; $z = n_{\text{t-BA}}/n$, where n_{sty} , n_{styOAc} , $n_{\text{t-BA}}$, refer to the number of repeat units of styrene, *p*-acetoxystyrene, *t*-butyl acrylate, respectively and $n = n_{\text{sty}} + n_{\text{sty-OAc}} + n_{\text{t-BA}}$.

4.4.2 Hydrazinolysis of Copolymer 1

After successful synthesis of narrow distribution triblock copolymers **1**, the acetoxy groups were deacetylated to phenolic groups using hydrazine hydrate. Upon hydrazinolysis, ^1H NMR showed a decrease in the acetoxy methyl proton resonance at 2.25 ppm and the appearance of a new resonance at 7.8 ppm attributed to the phenolic OH, as shown in Figure 4-2b.³⁶⁵ The decrease in the acetoxy methyl proton resonance with respect to the aromatic protons indicated % deacetylation of the styOAc units, which agreed well with the integration for the phenolic OH.

Table 4-2 shows %deacetylation and molecular weight data before and after deacetylation for a series of copolymer **1**. The % deacetylation was between 40 and 80%. SEC traces were monomodal following deacetylation. The loss of the acetoxy groups following hydrazinolysis should have resulted in a decrease in copolymer M_n . However, the calculated decrease in M_n was found to be within the error associated with SEC measurements and thus, a significant change in M_n was not observed after hydrazinolysis. The only exception was sample A, where the M_n doubled following hydrazinolysis; however, the distribution was monomodal, and narrow which indicated that possible hydrogen bonding associations between the phenolic OH groups led to a higher apparent M_n for this polymer.

³⁶⁵ Ito, H.; Willson, C. G.; Fréchet, J. M. J.; Farrall, M. J.; Eichler, E. "Synthesis of Poly(*p*-Hydroxy- α -Methylstyrene) by Cationic Polymerization and Chemical Modification." *Macromolecules* **1983**, 16, 510-517.

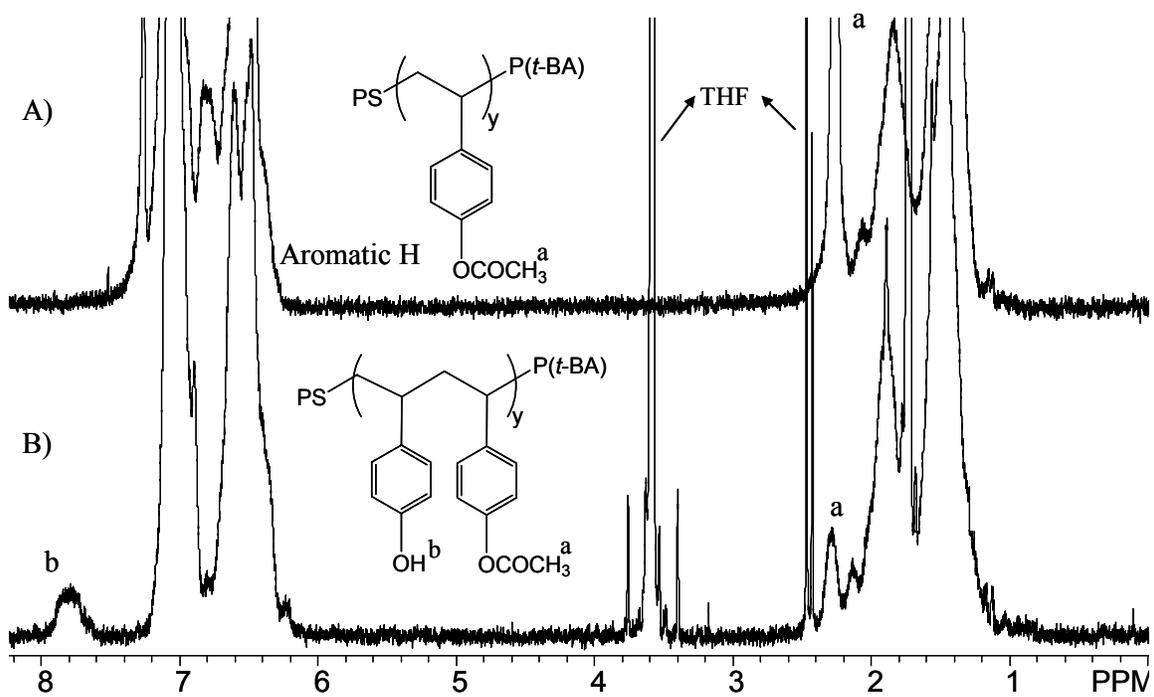


Figure 4-2: ^1H NMR spectra of **1** A) before hydrazinolysis (CDCl_3), and B) after hydrazinolysis ($d_8\text{-THF}$).

Table 4-2: %deacetylation and molecular weight data for a series of copolymer **1** before and after hydrazinolysis

Sample #	%deacetylation ^a	M _n ^b before hydrazinolysis in g/mol (M _w /M _n)	M _n ^b after hydrazinolysis in g/mol (M _w /M _n)
A	80	30,000 (1.13)	56,400 (1.10)
B	50	22,400 (1.04)	26,400 (1.04)
C	40	31,600 (1.06)	32,500 (1.05)

^a1H NMR conditions: 400 MHz, 25 °C in *d*₈-THF. ^bSEC conditions: THF, 40 °C, MALLS detector.

4.4.3 Silylation of Copolymer 1-OH

In order to introduce surface reactive groups in the copolymer, copolymer **1-OH** was silylated using excess IPTES. Sample C shown in Table 4-2 was used for subsequent silylation and surface modification. Figure 4-3 shows the ^1H NMR spectrum of the silylated copolymer. The appearance of three new resonance peaks at 0.6 ppm ($-\text{CH}_2\text{CH}_2\text{-Si-}$), 3.23 ppm ($-\text{O-CO-NH-CH}_2\text{-}$), and 3.79 ppm ($-\text{Si}(\text{OCH}_2\text{CH}_3)_3$) confirmed the successful functionalization of the phenolic OH groups with IPTES. Integration of the peak at 3.79 ppm with the acetoxy methyl protons at 2.25 ppm indicated $\sim 10\%$ silylation of the phenolic OH. Since ^1H NMR for the silylated copolymer was performed in CDCl_3 , residual phenolic OH groups were not observed in the spectrum.

4.4.4 Synthesis of Copolymer 2

The synthetic procedure for copolymer **2** was analogous to that described for copolymer **1**. Figure 4-4 shows the ^1H NMR spectrum of the diblock copolymer poly(sty-*b*-HEA)-DEPN. In addition to the aromatic protons of the styrene units (6.2-7.2 ppm) and the aliphatic protons ($-\text{CH}_2\text{-}$ and $-\text{CH-}$: 1.12-2.17 ppm) of styrene, and HEA, two additional resonances are observed at 3.5-4.5 ppm ($-\text{COO-CH}_2\text{CH}_2\text{OH}$) which confirmed the successful polymerization of HEA from PS-DEPN. Table 4-3 shows mol% HEA and molecular weight data for a series of poly(sty-*b*-HEA). ^1H NMR indicated that the mol% HEA incorporated in the copolymer was relatively low and SEC indicated a narrow polydispersity for the diblock copolymers. The molecular weights for the HEA blocks calculated using ^1H NMR were in good agreement with that obtained from SEC.

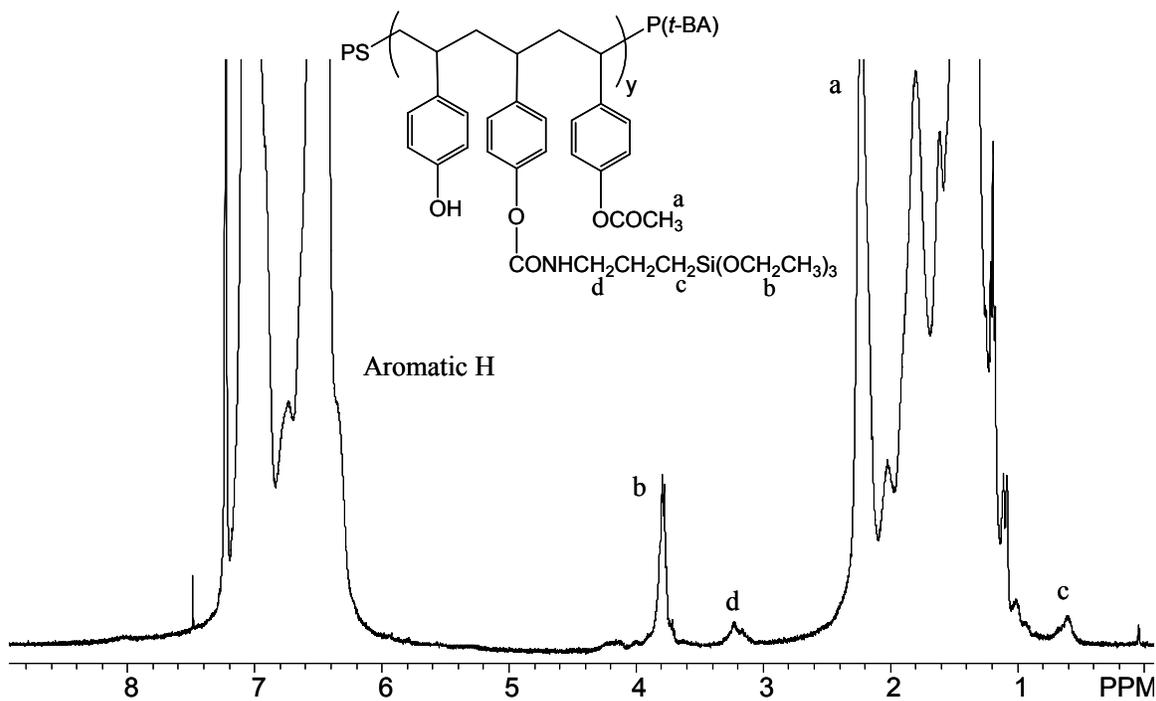


Figure 4-3: ¹H NMR spectrum of poly(sty-*b*-styOAc-*co*-styOH-*b*-*t*-BA) following reaction with IPTES.

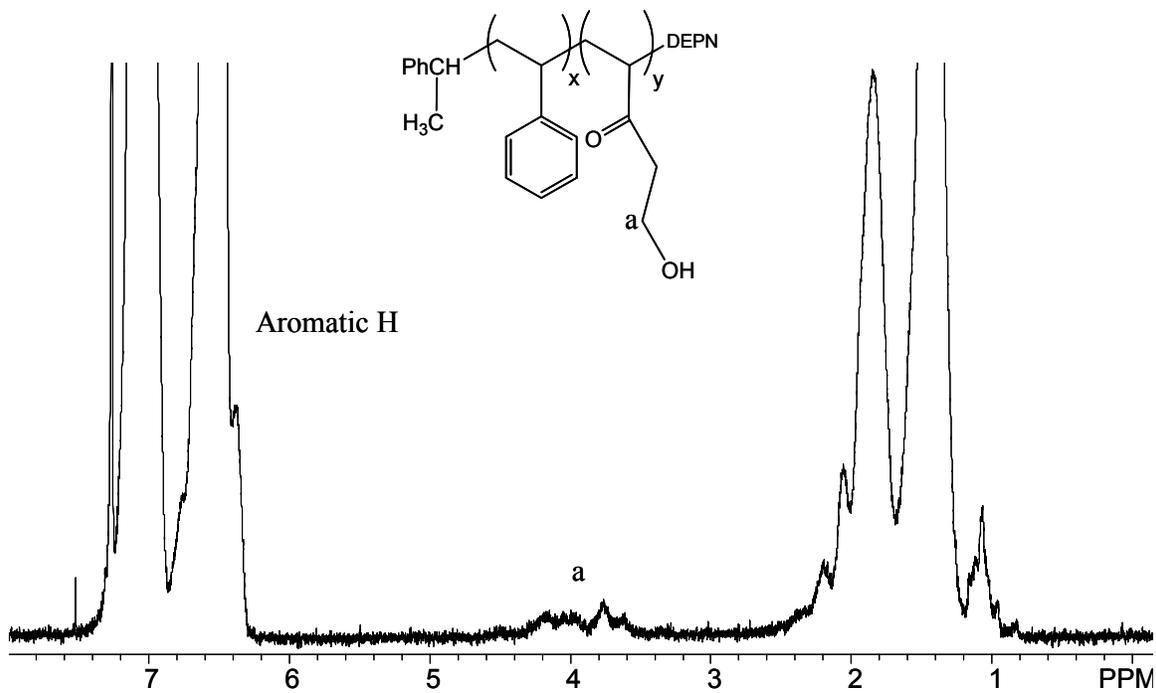


Figure 4-4: ¹H NMR spectrum of poly(sty-*b*-HEA).

Table 4-3: Incorporated mol% HEA and molecular weight data for a series of poly(sty-*b*-HEA)

Sample #	Mol% HEA incorporated ^a	Diblock copolymer M_n^b in g/mol (M_w/M_n)
A	6	20,000 (1.07)
B	4	20,000 (1.18)
C	3	19,600 (1.05)
D	3	19,200 (1.05)

^aRatio of repeat unit methylene protons of HEA unit (3.5-4.5 ppm) to repeat unit aromatic protons (6.3-7.3 ppm). ^bSEC conditions; THF, 40 °C, MALLS detector.

Sample D in Table 4-3 was chain extended with DMAAm to obtain a centrally functionalized amphiphilic triblock copolymer. Since DMAAm has a very high propagation rate constant, it was necessary to add a large excess of free DEPN in order to control its polymerization, which significantly reduced the polymerization rate.³⁶⁶ Figure 4-5 shows the ¹H NMR spectrum of copolymer **2**. In addition to the aromatic and aliphatic proton resonances of the monomer repeat units, and HEA resonances, a new resonance peak between 2.3-3.4 ppm (-CO-N(CH₃)₂) was observed, which confirmed the successful polymerization of DMAAm from poly(sty-*b*-HEA)-DEPN.

SEC on copolymer **2** indicated a very well controlled polymer with a narrow polydispersity ($M_n = 48,000$ g/mol; $M_w/M_n = 1.06$). However, M_n obtained for the DMAAm block from SEC ($M_n \sim 28,000$ g/mol) was significantly higher than that calculated from NMR ($M_n \sim 6,600$ g/mol). This discrepancy is possibly due to interaction between the tertiary amine groups of DMAAm units and the SEC columns leading to spurious results.³⁶⁷ In order to rule out such associations in the NMR solvent, ¹H NMR for copolymer **2** was acquired in solvents of different polarities at different temperatures, all of which gave similar mol% DMAAm in the copolymer. Thus, only NMR M_n was considered for the DMAAm block.

³⁶⁶ Schierholz, K.; Givehchi, M.; Fabre, P.; Nallet, F.; Papon, E.; Guerret, O.; Gnanou, Y. "Acrylamide-Based Amphiphilic Block Copolymers via Nitroxide-Mediated Radical Polymerization." *Macromolecules* **2003**, *36*, 5995-5999.

³⁶⁷ Creutz, S.; Teyssié, P.; Jérôme, R. "Living Anionic Homo- and Block Copolymerization of 2-(Tert-Butylamino)Ethyl Methacrylate." *J. Polym. Sci., Part A: Polym. Chem.* **1997**, *35*, 2035-2040.

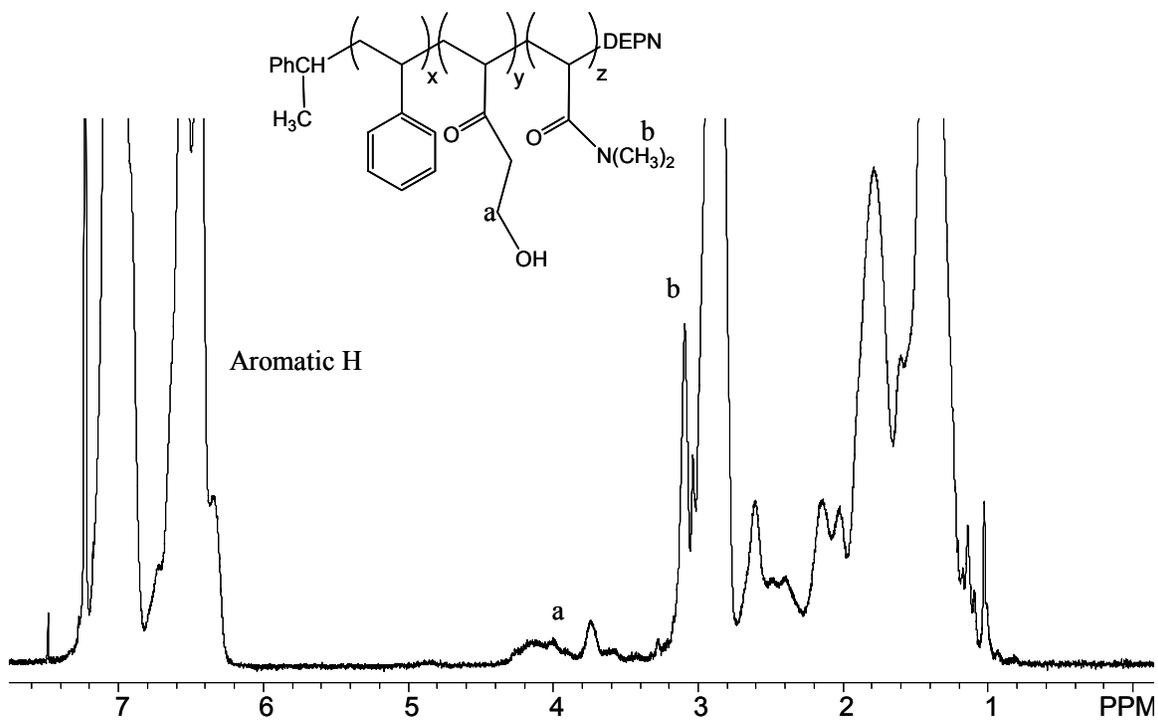


Figure 4-5: ^1H NMR spectrum of copolymer 2.

4.4.5 Silicon/SiO₂ Surface Modification with Copolymer 1-Si

Clean hydrophilic silicon wafers were modified with copolymer **1-Si** from the melt. Following Soxhlet extraction with THF, the modified surfaces showed a water contact angle of $\sim 75^\circ$ (water completely wets clean silicon wafers), indicating a moderately hydrophobic surface; however, these surfaces were not responsive to solvent treatments as both PS and P(*t*-BA) are hydrophobic. It is known that arylurethanes are thermally unstable; however, a high water contact angle on copolymer **1-Si** modified surfaces following solvent extractions indicated that copolymer **1-Si** was stably anchored to the surface. In order to convert the surface grafted hydrophobic copolymer to an amphiphilic system, the *t*-BA groups in the polymer film were hydrolyzed using acid to acrylic acid (AA) for 17 h, or 24 h. Since siloxane linkages formed between the silane modified polymers and the surface hydroxyl groups are also susceptible to acid hydrolysis,³⁶⁸ the surface chemical composition was analyzed using XPS before and after hydrolysis (Figure 4-6). The atomic composition of the surface did not change significantly following hydrolysis, which indicated that the polymer film was stable under the conditions employed for *t*-BA hydrolysis.

After confirming that the copolymer was firmly anchored to the surface, the response of the copolymer coating to various solvent treatments was investigated using water contact angle measurements. The solvents chosen were toluene, a good solvent for PS and methanol, a good solvent for AA containing block. Figure 4-7 shows the changes in water contact angle observed after selective solvent treatments.

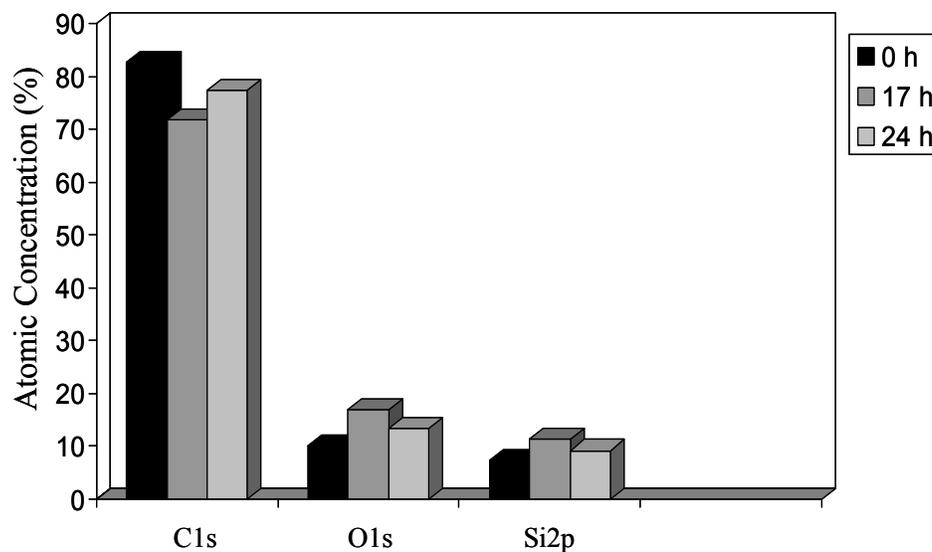


Figure 4-6: XPS atomic composition of silicon/SiO₂ surfaces modified with copolymer 1-Si before (0 h), and after (17 h & 24 h) hydrolysis.

³⁶⁸ Yim, H.; Kent, M. S.; Tallant, D. R.; Garcia, M. J.; Majewski, J. " Hygrothermal Degradation of (3-Glycidoxypropyl)Trimethoxysilane Films Studied by Neutron and X-Ray Reflectivity and Attenuated Total Internal Reflection Infrared Spectroscopy." *Langmuir* **2005**, 21, 4382-4392.

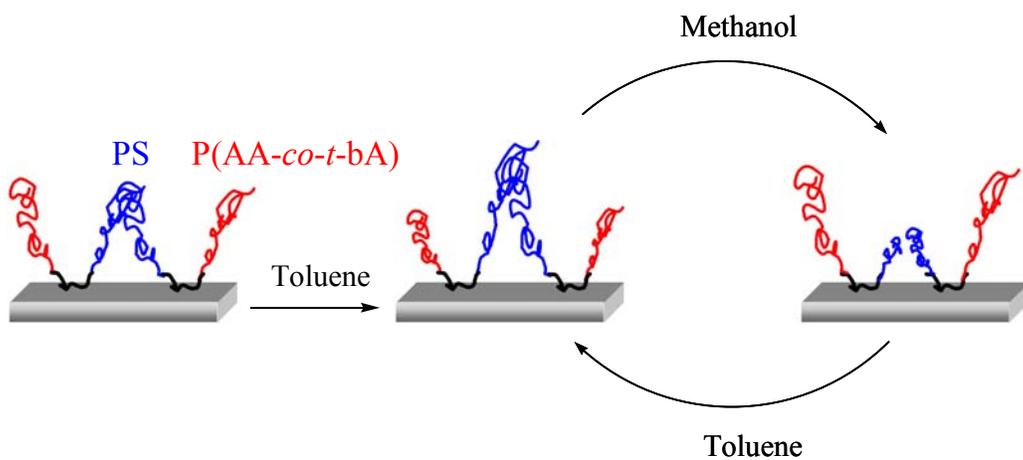
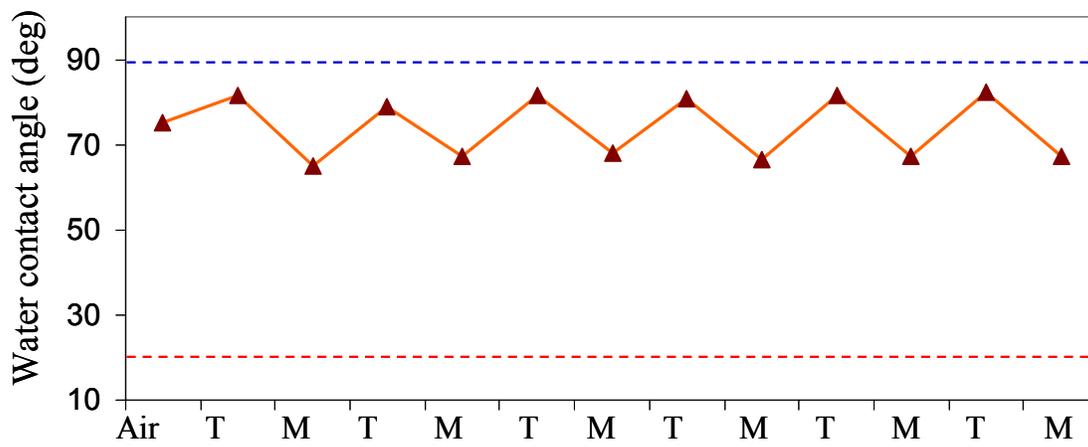


Figure 4-7: Reversible changes in water contact angle (**top**) on copolymer **1-Si** modified silicon/SiO₂ surfaces following exposure to toluene (T), and methanol (M); the blue and red lines indicate the water contact angles observed on neat PS and PAA films. Error in contact angle measurements: $\pm 2^\circ$. Depiction of block rearrangement following selective solvent exposures (**bottom**).

Copolymer **1-Si** modified surfaces show a water contact angle of $\sim 75^\circ$ in air. However, upon immersion in toluene for 12 min, the water contact angle increased to 85° due to rearrangement and segregation of the hydrophobic PS block to the air interface. This preferential segregation of PS to the air interface is due to favorable interaction between PS and toluene. This water contact angle is however, lower than the 90° (Figure 4-7 **top**, blue dotted line) value typically observed on PS modified surfaces possibly due to partial coexistence of the hydrophilic block on the surface. However, methanol immersion promoted surface segregation of the hydrophilic acrylic acid containing block, as shown by a decrease in the water contact angle.

The 65° water contact angle for AA enriched surfaces is higher than that observed for neat PAA films, which is around 15° (Figure 4-7 **top**, red dotted line).³⁶⁹ There could possibly be two reasons for this anomaly. First, due to shorter length of the AA-containing block the coexistence of both PS and AA-containing blocks near the surface is possible, which could lead to higher than expected water contact angle values. However, Tsukruk and coworkers also showed that the minimum water contact angle that was observed on silicon/SiO₂ surfaces modified with a Y-shaped mixed PS-PAA brushes, where $n_{PS} \cong n_{P(AA-co-t-BA)}$ was $\sim 50^\circ$.³⁷⁰ Thus, the length of the AA containing block relative to the PS block does not significantly affect the water contact values. Another more plausible explanation for this anomaly is the incomplete hydrolysis of *t*-BA groups, which could result in higher than expected water contact angle for the AA-containing block. It was shown in the literature that surface hydrolysis of poly(*t*-BA) films was only

³⁶⁹ Coupe, B.; Evangelista, M. E.; Yeung, R. M.; Chen, W. "Surface Modification of Poly(Tetrafluoroethylene-Co-Hexafluoropropylene) by Adsorption of Functional Polymers." *Langmuir* **2001**, 17, 1956-1960.

confined to the near-surface region, while the internal *t*-BA groups were not hydrolyzed even after extended period as a result of spatial constraint in thin films.³⁷¹

The kinetics of rearrangement of the terminal blocks after exposure to selective solvents were also investigated in order to determine if the 12 min immersion time in the solvent was sufficient to promote complete block rearrangement. Figure 4-8a shows the rate of rearrangement of the PS block after exposure to toluene for various times. Initially, the surface was AA enriched following exposure to methanol. Following toluene treatment, AA enriched surface immediately became hydrophobic with a water contact angle of $\sim 85^\circ$ and did not show significant changes even after prolonged exposure to toluene. This indicated that the rearrangement of the PS block following toluene exposure was rapid and instantaneous (Figure 4-8b). A similar profile was observed when PS enriched surface was exposed to methanol, where the water contact angle decreased from 85° to $\sim 65^\circ$ within a few seconds in methanol (Figure 4-8 b & d).

The behavior of the surface anchored triblock copolymers reported in this study is different from the behavior of PS-PAA Y-shaped mixed polymer brushes on silicon/SiO₂ surfaces following toluene and water treatments, where the block rearrangement occurred over an extended period.³⁷² This difference could possibly arise from the anchor length, which in the above-mentioned study was one molecule. On the other hand, in the present study, the central block was significantly long. The longer anchor block might have lead to significantly lower chain grafting density giving the chains sufficient freedom for rapid

³⁷⁰ Julthongpiput, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Polymer Brushes: Nanoscale Switchable Surfaces." *Langmuir* **2003**, 19, 7832-7836.

³⁷¹ Feng, C. L.; Vancso, G. J.; Schönherr, H. "Interfacial Reactions in Confinement: Kinetics and Temperature Dependence of Surface Hydrolysis of Poly(Styrene-*b*-Tert-Butyl Acrylate) Thin Films." *Langmuir* **2005**, 21, 2356-2363.

³⁷² Julthongpiput, D.; Lin, Y.-H.; Teng, J.; Zubarev, E. R.; Tsukruk, V. V. "Y-Shaped Amphiphilic Brushes with Switchable Micellar Surface Structures." *J. Am. Chem. Soc.* **2003**, 125, 15912-15921.

rearrangement upon solvent exposure, as chain grafting density is known to affect the rate of chain reorganization on surfaces.³⁷³ Assuming that the surface grafted copolymer chains were tightly packed with a thickness of ~3 nm as determined using XPS and a bulk density of ~0.977 g/cc (determined based on the molar ratios of the two terminal blocks), approximately 0.1 chains/nm² was obtained for the grafting density. The actual grafting density was however, not determined.

The water contact angle measurements following exposure to block selective solvents also showed that the blocks rearranged in air towards equilibrium structure over time, as shown in Figure 4-9. Surfaces enriched with PS following toluene exposure rearranged slowly over a period of ~12 h to the equilibrium conformation that was observed prior to solvent exposures. Similarly, the AA containing block rearranged over a period of 23 h to the equilibrium conformation, where the water contact angle changed from ~65° to 74°. One possible explanation for this trend, which has not been observed in the literature, could be the greater freedom for chain mobility provided by such long anchor blocks.

³⁷³ Zhao, B.; Brittain, W. J. "Synthesis of Tethered Polystyrene-Block-Poly(Methyl Methacrylate) Monolayer on a Silicate Substrate by Sequential Carbocationic Polymerization and Atom Transfer Radical Polymerization." *J. Am. Chem. Soc.* **1999**, 121, 3557-3558.

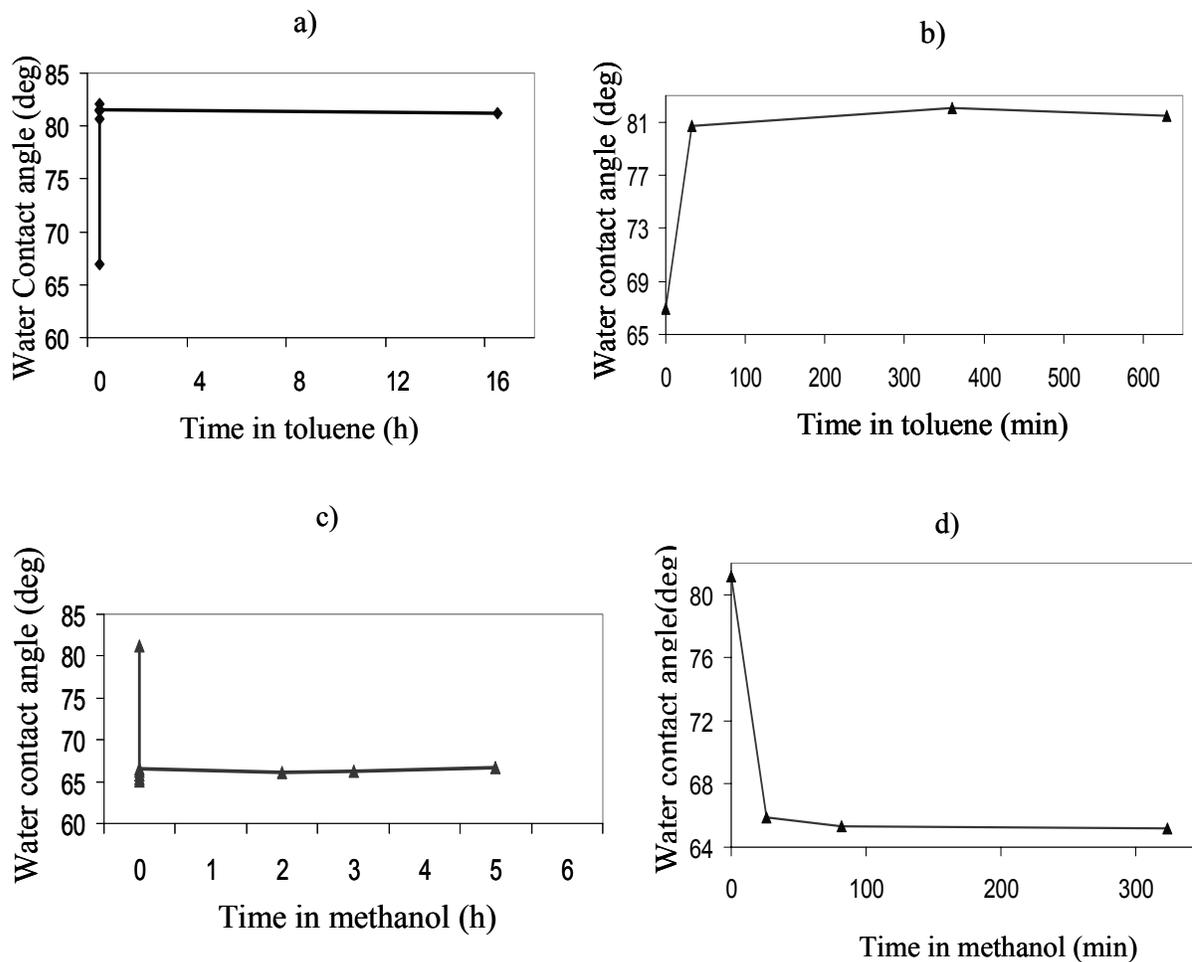


Figure 4-8: Kinetics of rearrangement of PS block after exposure to toluene (**top**) and P(AA-co-t-BA) block after methanol exposure (**bottom**) at longer times (a&c) and shorter times (b&d). Error in contact angle measurements: $\pm 2^\circ$.

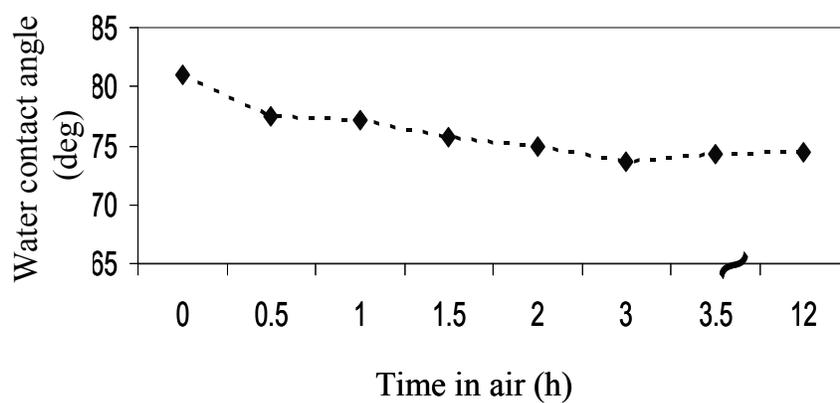
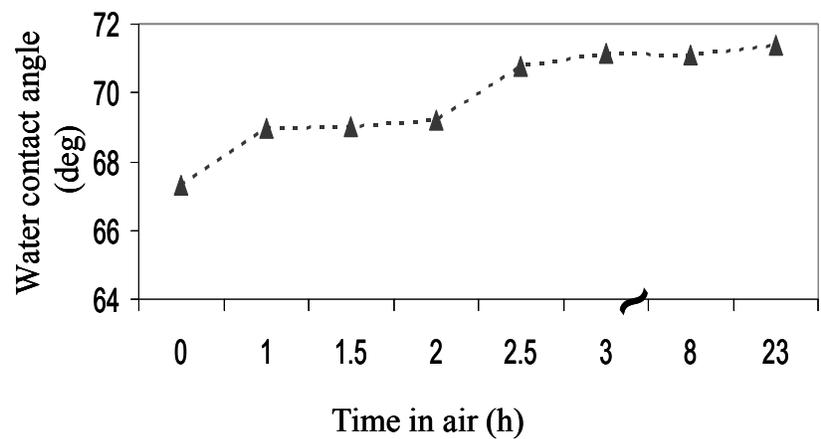


Figure 4-9: Kinetics of reorganization of poly(AA-*co*-*t*-BA) containing block (**top**), and PS block (**bottom**), in air.

4.4.6 Silicon/SiO₂ Surface Modification with Copolymer 2

In order to avoid complications with the surface confinement effects as was observed during the surface hydrolysis of the *t*-BA groups, an alternative system poly(sty-*b*-HEA-*b*-DMAAm), where the amphiphilic copolymer was directly formed in solution was investigated. The use of poly(HEA) as the central block also avoided the additional hydrolysis and functionalization steps that were necessary to introduce surface reactive groups in the poly(styOAc) block of copolymer **1**. Copolymer **2** was anchored to the surface through the hydroxyl groups of HEA,³⁷⁴ and was found to be stable to extensive solvent extractions.

After confirming the stability of the surface anchored copolymer films, the response of the terminal blocks of copolymer **2** to alternating toluene and methanol rinses was studied using water contact angle measurements. The surfaces were initially enriched with one of the blocks by exposure to a selective solvent for ~17 h and the water contact angles were measured. Following this step, water contact angles on surfaces subjected to alternating 10 min solvent exposure was measured over six cycles as shown in Figure 4-10. The surfaces showed a highly reversible switching pattern in water contact angle irregardless of the nature of the surface enriched block. While the PS block exposed to toluene rearranged completely within 10 min exposure, the PDMAAm block rearranged slowly over time and required about 17 h to attain the equilibrium value of ~50°. The slow reorganization of the PDMAAm block was attributed to the short length of the DMAAm block, which therefore required longer time to reach the equilibrium value compared to the longer PS block.

³⁷⁴ Mansky, P.; Liu, Y.; Huang, E.; Russell, T. P.; Hawker, C. J. "Controlling Polymer-Surface Interactions with Random Copolymer Brushes." *Science* **1997**, 275, 1458-1460.

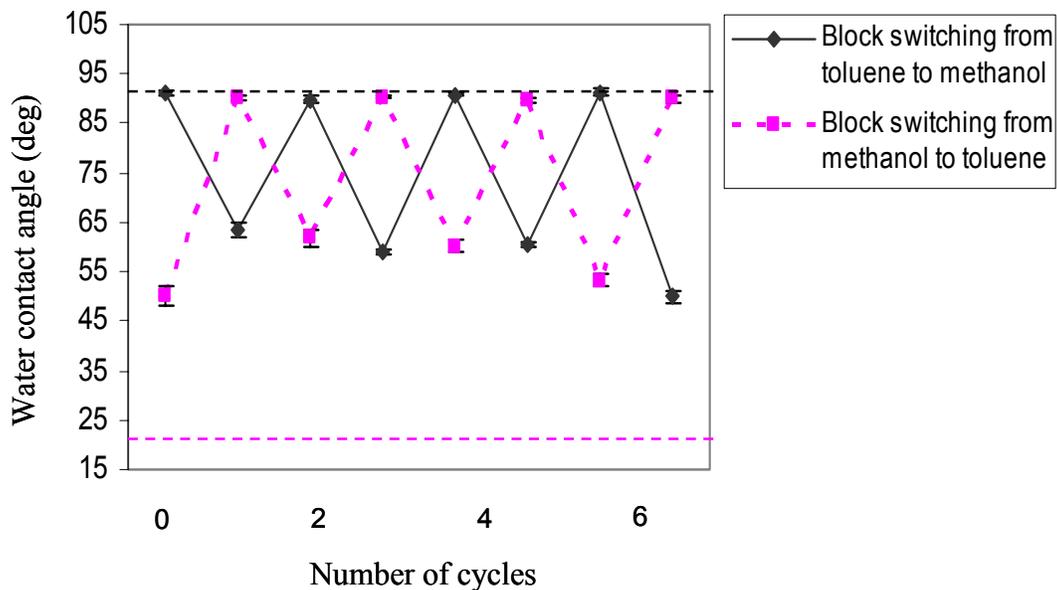


Figure 4-10: Reversible changes in water contact following alternating toluene and methanol exposures (first and last points correspond to solvent exposure for 17 h). The dotted lines represent the water contact angle values on neat PS (black) and PDMAAm (pink) films.

The kinetics of rearrangement of the individual blocks of copolymer **2** in selective solvents was also investigated using water contact angle measurements (Figure 4-11). As seen with copolymer **1**, the block reorganization was rapid and instantaneous even for the short PDMAAm block, which indicated that the central anchor block length plays a crucial role in the reorganization kinetics of the terminal blocks. Thus, the rate at which the copolymer coating responds to external stimuli could be tuned by varying the length of the central anchor point.

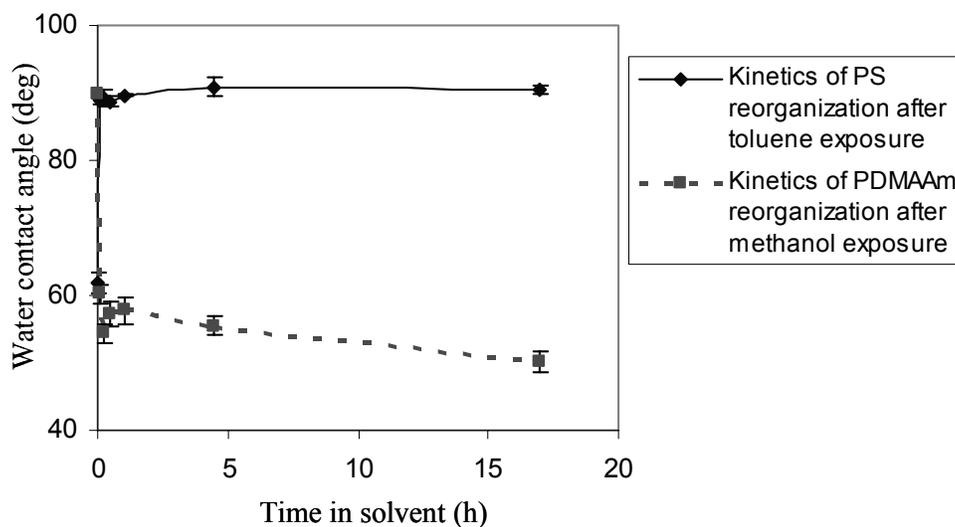


Figure 4-11: Kinetics of reorganization of PS and PDMAAm following exposures to toluene and methanol, respectively.

Earlier studies have shown that mixed polymer brush modified surfaces show a rich array of nanomorphologies following selective solvent treatments. Thus, surface reorganization of the individual blocks following exposure to selective solvents was investigated using AFM. Figure 4-12 shows tapping-mode AFM phase images of surfaces under different conditions. Prior to any solvent exposure the modified surfaces were very smooth, with a roughness value of ~ 0.5 nm (Figure 4-12a) due to the coexistence of both the blocks on the surface (Scheme 4-3a), which is also consistent with the results from water contact angle measurements. After methanol exposure, the phase images (Figure 4-12b) showed largely spherical dimples. The dimples are caused due to the collapse of PS blocks into the film in order to avoid non-favorable interactions with methanol (Scheme 4-3b). AFM section analysis revealed that the dimples were 1-3 nm in depth with lateral dimensions of approximately 50-100 nm, which is significantly larger than the dimension of a single PS chain, which indicated that the collapsed features were probably micellar aggregates.³⁷⁵ However, the roughness values of ~ 0.85 nm on the surfaces following PS chain collapse indicated that the initial films were ultrathin and thus, did not increase the surface roughness significantly.

It was reported that for an asymmetric ($M_{n,PS} > M_{n,PMMA}$) PS-PMMA Y-shaped polymer brushes grafted onto silicon/SiO₂ surfaces, only random variations in surface features with no individual domains were observed upon exposure to good solvent for PMMA, which was the shorter block.³⁷⁶ However, in this study the highly asymmetric polymers still showed phase segregation upon exposure to good solvent for the shorter

³⁷⁵ Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. "Nanopattern Formation from Tethered PS-b-PMMA Brushes Upon Treatment with Selective Solvents." *J. Am. Chem. Soc.* **2000**, 122, 2407-2408.

PDMAAm block. It is known that in addition to polymer M_n , Flory-Huggins interaction parameter between the polymers, between the polymer and the solvent, and density of the grafted chains also influence the surface patterns. Thus, possible reasons for observing dimpled morphology in this study could result from the greater polarity difference between PS and PDMAAm. Therefore, even a small perturbation by exposure to block selective solvent possibly led to greater extent of phase separation in this system in contrast to the literature study involving PS and PMMA. However, the patterns formed were not very regular, which indicated that the segregation was not complete, consistent with water contact angle measurements that indicated the coexistence of both blocks on the surface following methanol treatment.

After exposure to THF, which is a good solvent for both PS and PDMAAm blocks, a ripple like morphology was observed (Figure 4-12c), similar to theoretical and experimental results on symmetric diblock copolymer brushes.^{377, 378} In order to minimize unfavorable heterochain contacts, the grafted chains undergo lateral phase segregation into individual polymer rich domains producing the ripple like morphology, as depicted in Scheme 4-3c.³⁷⁹ The insignificant increase in surface roughness (~1 nm) is again consistent with the deposition of a very thin polymer film. Upon toluene treatment, the surface again became featureless with a roughness value of ~0.55 nm (Figure 4-12d) because of vertical segregation of the blocks where PDMAAm was collapsed into the

³⁷⁶ Zhao, B.; Haasch, R. T.; MacLaren, S. "Solvent-Induced Self-Assembly of Mixed Poly(Methyl Methacrylate)/Polystyrene Brushes on Planar Silica Substrates: Molecular Weight Effect." *J. Am. Chem. Soc.* **2004**, 126, 6124-6134.

³⁷⁷ Marko, J. F.; Witten, T. A. "Correlations in Grafted Polymer Layers." *Macromolecules* **1992**, 25, 296-307.

³⁷⁸ Zhao, B.; Brittain, W. J.; Zhou, W.; Cheng, S. Z. D. "Nanopattern Formation from Tethered PS-b-PMMA Brushes Upon Treatment with Selective Solvents." *J. Am. Chem. Soc.* **2000**, 122, 2407-2408.

³⁷⁹ Zhulina, E.; Balazs, A. C. "Designing Patterned Surfaces by Grafting Y-Shaped Copolymers." *Macromolecules* **1996**, 29, 2667-2673.

film while PS completely segregated to the air interface, as shown in Scheme 4-3d. Such a vertical segregation occurs only when one of the blocks has a favorable interaction with the surface, which is possible between the polar PDMAAm block and the hydrophilic silicon/SiO₂ surface. The AFM observations are also consistent with the water contact angle values observed following various solvent treatments.

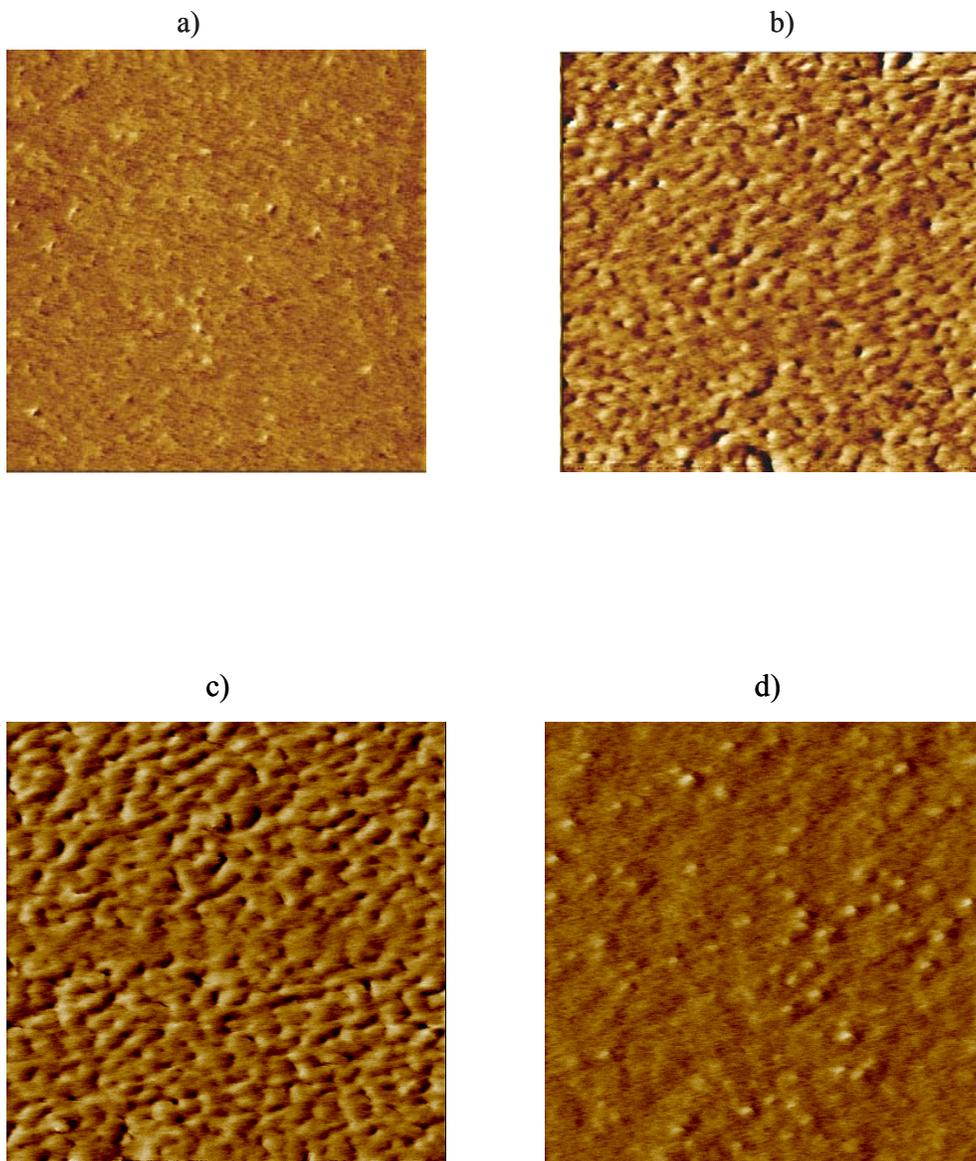
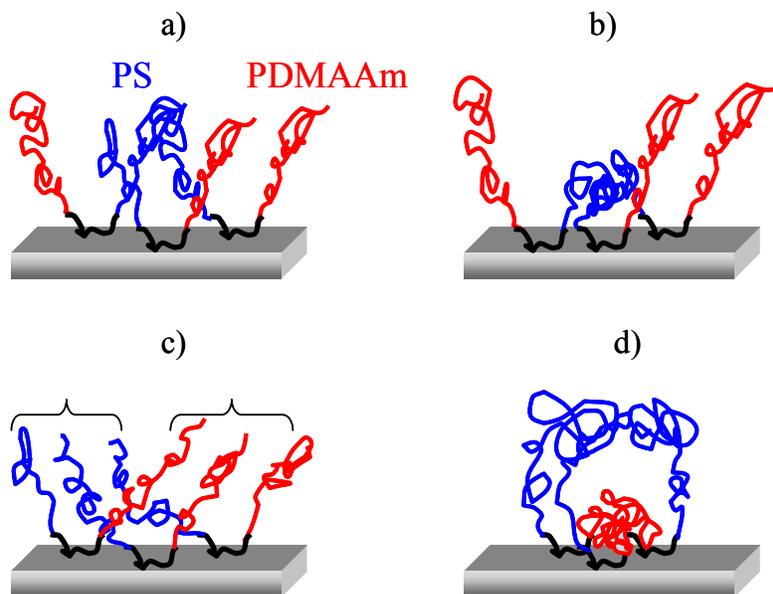


Figure 4-12: Tapping-mode AFM phase images of copolymer **2** modified silicon/SiO₂ surfaces in air a) before solvent treatment, b) after methanol treatment, c) after THF treatment, d) after toluene treatment (scan area = 1 μ m², phase angle = 0-25 deg).



Scheme 4-3: Depiction of the formation of various nanomorphologies on silicon/SiO₂ surfaces modified with copolymer **2** a) before solvent exposure, b) after methanol exposure, c) after THF exposure, and d) after toluene exposure.

Surface atomic compositions following various solvent exposures for copolymer **2** modified surfaces were investigated using XPS. Table 4-4 shows the XPS atomic compositions of copolymer-modified surfaces before and after solvent treatments. The as-modified surface shows ~85% C. Based on the molecular weights of the styrene, HEA, and DMAAm blocks ($M_{n,PS} = 18,700$ g/mol, $M_{n,HEA} = 540$ g/mol; $M_{n,DMAAm} = 6,600$ g/mol), the theoretical C/O should be ~22. However, the ratio calculated from XPS is ~9, which indicated that there was a significant contribution from the underlying silicon/SiO₂ surfaces even at the shallow analysis angle of 30°, which is also consistent with the appearance of Si2p photoelectron peaks associated with the surface. This indicated that the films were ~2-3 nm in thickness. Following toluene treatment, C increased to 93%, which indicated the segregation of PS to the air interface. The toluene swollen PS chains also increased the film thickness moderately as indicated by a decrease in %Si from the underlying substrate. An opposite trend was observed when the surface was immersed in methanol, where the C decreased to 78% while the N increased to 3.5%. The C/N ratio of 22 on surface was however, higher than that expected from the chemical composition of DMAAm, which is ~5. In addition, the %O and %Si increased following methanol treatment, which showed that the collapse of PS to the surface decreased the apparent film thickness and therefore increased the contribution from the surface atoms. However, the trend in surface atomic composition clearly showed preferential segregation of the PS and the PDMAAm blocks following selective solvent exposures consistent with the water contact angle results.

Table 4-4: XPS atomic composition of silicon/SiO₂ surfaces modified with copolymer **2** before and after selective solvent exposures

Surface treatment	Atomic composition (%) ^a			
	%C	%O	%N	%Si
As-modified	84	9	2	5
After toluene exposure	92	3	2	3
After methanol exposure	78	11	4	7

^aXPS conditions: Mg anode, take-off angle = 30°.

4.5 Conclusions

Centrally functionalized amphiphilic triblock copolymers comprising PS as the hydrophobic block and different hydrophilic blocks were synthesized using nitroxide-mediated polymerization. The central functional block constituting either a long silylated hydroxystyrene block (**1**) or a short 2-hydroxyethyl acrylate block (**2**) was used to graft the copolymers to silicon/SiO₂ surfaces from the melt. Silicon/SiO₂ surfaces modified with copolymers **1** and **2** exhibited reversible changes in water contact angle following block selective solvent treatments. Investigation of the kinetics of block rearrangement in selective solvents indicated that the copolymers showed rapid and instantaneous reorganization upon selective solvent exposure. XPS analysis of copolymer **2** modified surfaces also confirmed block rearrangement upon selective solvent treatment consistent with the water contact angle results. AFM on copolymer **2** modified surfaces showed interesting surface morphologies after various solvent exposures, which was attributed to vertical/lateral segregation or micellar aggregation of the terminal blocks. Surfaces that were modified with copolymer **1** comprising long anchor block also exhibited block reorganization in air.

4.6 Acknowledgements

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Chapter 5: Multiple Hydrogen Bonding for Reversible Polymer-Surface Adhesion

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5.1 Abstract

Specific and reversible adhesion of a terminal thymine-functionalized polystyrene (PS-thymine) was demonstrated for a silicon/SiO₂ surface with complementary adenine recognition sites. A novel adenine containing triethoxysilane (ADPTES), which was suitable for covalent attachment to silanol containing surfaces, was synthesized in one-step from adenine and 3-isocyanatopropyltriethoxysilane (IPTES). ¹H and ¹³C NMR spectroscopy and fast atom bombardment mass spectroscopy confirmed the chemical structure, and ²⁹Si NMR spectroscopy indicated the absence of any premature hydrolysis of the alkoxy silane derivative. X-ray photoelectron spectroscopy (XPS) and water contact angle measurements indicated attachment of PS-thymine to silicon/SiO₂ surfaces that were modified with a mixture of ADPTES and 3-mercaptopropyltriethoxysilane (MPTES). PS-thymine attachment was not observed to surfaces that were modified with only MPTES. The exclusive attachment of PS-thymine to an ADPTES/MPTES modified surface confirmed hydrogen bonding mediated adenine-thymine association to silicon/SiO₂ surfaces containing a sufficiently low concentration of adenine recognition sites. While PS-thymine attachment to the ADPTES/MPTES modified surfaces was insensitive to THF rinsing, the PS-thymine was completely removed from the surface upon DMSO rinsing due to disruption of the adenine-thymine hydrogen bonding with a more polar aprotic solvent. PS-thymine was successfully reattached to the

ADPTES/MPTES modified surface following DMSO rinse demonstrating the solvato-reversible nature of the adenine-thymine association.

5.2 Introduction

Molecular recognition, which is defined as the specific interaction between multiple molecules without the involvement of covalent bonding forms the basis of supramolecular organization in biological systems.³⁸⁰ Non-covalent interactions such as electrostatic, hydrogen bonding, host-guest, and π - π stacking are often of central importance in molecular recognition.³⁸¹ Although relatively weak, these directional, multivalent interactions lead to self-assembly of molecules into complex hierarchies with well-defined functional superstructures. Lehn and co-workers first developed self-assembly strategies based on molecular recognition to construct synthetic materials with unique physical properties.³⁸²

Molecular recognition sites on surfaces enables the preparation of functional surfaces for a myriad of applications ranging from electronics and optics to sensors and catalysis. Thus, in recent years several studies have used the SAM technique to obtain surfaces modified with the desired molecular recognition groups.³⁸³ Surface modification with molecules that are capable of non-covalently interacting with molecules in solution opens up exciting new prospects, particularly in the field of sensors and nanodevices.

³⁸⁰ Lehn, J.-M., "Supramolecular Chemistry: Concepts and Perspectives." VCH: Weinheim, **1995**.

³⁸¹ Lindoy, I. F.; Atkinson, M. F., " Self-Assembly in Supramolecular Systems." RSC: Cambridge, **2000**.

³⁸² Lehn, J.-M. "Supramolecular Chemistry-Scope and Perspectives Molecules, Supermolecules, and Molecular Devices (Nobel Lecture)." *Angew. Chem. Int. Ed. Eng.* **1988**, *27*, 89-112.

³⁸³ Ulman, A. "Formation and Structure of Self-Assembled Monolayers." *Chem. Rev.* **1996**, *96*, 1533-1554.

Several studies described the use of receptor-ligand interactions such as biotin-avidin,³⁸⁴ antibody-antigen,³⁸⁵ and carbohydrate-lectin³⁸⁶ on surfaces for biosensing, affinity chromatography, and molecular organization. Similarly, extensive literature exists on surface tethered nucleic acids for use as biosensors for forming microarrays and for the reversible assembly of nanoparticles.^{387, 388} However, the complexity associated with biological molecules makes their functionalization with suitable surface reactive groups demanding and expensive. On the other hand, the use of specific non-covalent interactions such as host-guest complexation, hydrogen/electrostatic interactions on a surface presents a simple route for creating surfaces with tunable chemical and physical properties.

Previous efforts have employed molecular recognition groups on surfaces including selective inclusion complexation and ionic/hydrogen bonding interactions.³⁸⁹ Several groups have used cyclodextrin (CD) based host-guest interactions³⁹⁰ as model membrane receptors and chemical sensors.^{391, 392, 393} Electrostatic interactions between

³⁸⁴ Salem, A. K.; Chao, J.; Leong, K. W.; Searson, P. C. "Receptor-Mediated Self-Assembly of Magnetic Nanoparticles." *Adv. Mater.* **2004**, 16, 268-271.

³⁸⁵ Jung, S.-H.; Son, H.-Y.; Yuk, J. S.; Jung, J.-W.; Kim, K. H.; Lee, C.-H.; Hwang, H.; Ha, K.-S. "Oriented Immobilization of Antibodies by a Self-Assembled Monolayer of 2-(Biotinamido)Ethanethiol for Immunoarray Preparation." *Colloids Surf., B* **2006**, 47, 107-111.

³⁸⁶ Anilyte, J.; Liesiene, J.; Niemeyer, B. "Evaluation of Cellulose-Based Biospecific Adsorbents as a Stationary Phase for Lectin Affinity Chromatography." *J. Chromatogr. B* **2006**, 831, 24-30.

³⁸⁷ Rogers, P. H.; Michel, E.; Bauer, C. A.; Vanderet, S.; Hansen, D.; Roberts, B. K.; Calvez, A.; Crews, J. B.; Lau, K. O.; Wood, A.; Pine, D. J.; Schwartz, P. V. " Selective, Controllable, and Reversible Aggregation of Polystyrene Latex Microspheres Via DNA Hybridization." *Langmuir* **2005**, 21, 5562-5569.

³⁸⁸ Peelen, D.; Smith, L. M. "Immobilization of Amine-Modified Oligonucleotides on Aldehyde-Terminated Alkanethiol Monolayers on Gold." *Langmuir* **2005**, 21, 266-271.

³⁸⁹ Maeda, Y.; Fukuda, T.; Yamamoto, H.; Kitano, H. "Regio- and Stereoselective Complexation by a Self-Assembled Monolayer of Thiolated Cyclodextrin on a Gold Electrode." *Langmuir* **1997**, 13, 4187-4189.

³⁹⁰ Madison, P. H.; Long, T. E. "Carbohydrate/Monomer Complexes in Aqueous Polymerizations: Methylated- α -Cyclodextrin Mediated Aqueous Polymerization of Hydrophobic Methacrylic Monomers." *Biomacromolecules* **2000**, 1, 615-621.

³⁹¹ Endo, H.; Hirabayashi, T. D.; Morokoshi, S.; Ide, M. G.; Kitano, H. "Orientational Effect of Surface-Confining Cyclodextrin on the Inclusion of Bisphenols." *Langmuir* **2005**, 21, 1314-1321.

amines and carboxylic acids have also found use in the immobilization of nanoparticles/nanorods on surfaces^{394, 395} and formation of tunable mixed nanoparticle composites.^{396,}

397, 398

Surface studies involving hydrogen bonding association has mostly involved small molecules.^{399, 400} Crooks *et al.* investigated carboxylic acid SAMs on gold as sensors for vapors of organic acids as well as bases.⁴⁰¹ In the case of interaction between the acid SAMs and organic base vapors, the vapor phase molecules readily desorbed upon nitrogen purging, which indicated a relatively weak interaction between the sensor and probe molecules.⁴⁰² Rogers *et al.* used tetrapyridylporphyrins that were capable of forming multiple hydrogen bonds with carboxyl terminated SAMs to obtain stable

³⁹² Sabapathy, R. C.; Bhattacharya, S.; Cleland, W. E.; Hussey, C. L. "Host-Guest Complexation in Self-Assembled Monolayers: Inclusion of a Monolayer-Anchored Cationic Ferrocene-Based Guest by Cyclodextrin Hosts." *Langmuir* **1998**, *14*, 3797-3807.

³⁹³ Chen, Y.; Banerjee, I. A.; Yu, L.; Djalali, R.; Matsui, H. "Attachment of Ferrocene Nanotubes on α -Cyclodextrin Self-Assembled Monolayers with Molecular Recognitions." *Langmuir* **2004**, *20*, 8409-8413.

³⁹⁴ Gole, A.; Sainkar, S. R.; Sastry, M. "Controlled Organization of Carboxylic Acid Derivatized Colloidal Silver Particles on Amine-Terminated Self-Assembled Monolayers." *Chem. Mater.* **2000**, *12*, 1234-1239.

³⁹⁵ Gole, A.; Orendorff, J.; Murphy, J. "Immobilization of Gold Nanorods onto Acid-Terminated Self-Assembled Monolayers via Electrostatic Interactions." *Langmuir* **2004**, *20*, 7117-7122.

³⁹⁶ Boal, A. K.; Galow, T. H.; Ilhan, F.; Rotello, V. M. "Binary and Ternary Polymer-Mediated "Bricks and Mortar" Self-Assembly of Gold and Silica Nanoparticles." *Adv. Funct. Mater.* **2001**, *11*, 461-465.

³⁹⁷ Galow, T. H.; Boal, A. K.; Rotello, V. M. "A "Building Block" Approach to Mixed-Colloid Systems through Electrostatic Self-Organization." *Adv. Mater.* **2000**, *12*, 576-579.

³⁹⁸ Auer, F.; Scotti, M.; Ulman, A.; Jordan, R.; Sellergren, B.; Garno, J.; Liu, G.-Y. "Nanocomposites by Electrostatic Interactions: 1. Impact of Sublayer Quality on the Organization of Functionalized Nanoparticles on Charged Self-Assembled Layers." *Langmuir* **2000**, *16*, 7554-7557.

³⁹⁹ Arias, F.; Godínez, L. A.; Wilson, S. R.; Kaifer, A. E.; Echegoyen, L. "Interfacial Hydrogen Bonding. Self-Assembly of a Monolayer of a Fullerene-Crown Ether Derivative on Gold Surfaces Derivatized with an Ammonium-Terminated Alkanethiolate." *J. Am. Chem. Soc.* **1996**, *118*, 6086-6087.

⁴⁰⁰ Garcia-Lopez, J. J.; Zapotoczny, S.; Timmerman, P.; van Veggel, F. C. J. M.; Vansco, G. J.; Crego-Calama, M.; Reinhoudt, D. N. "Growth of Individual Hydrogen-Bonded Nanostructures on Gold Monolayers." *Chem. Commun.* **2003**, 352-353.

⁴⁰¹ Sun, L.; Kopley, L. J.; Crooks, R. M. "Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules: Hydrogen-Bonding Interactions." *Langmuir* **1992**, *8*, 2101-2103.

⁴⁰² Yang, H. C.; Dermody, D. L.; Xu, C.; Ricco, A. J.; Crooks, R. M. "Molecular Interactions between Organized Surface-Confined Monolayers and Vapor-Phase Probe Molecules.8. Reactions between Acid-Terminated Self-Assembled Monolayers and Vapor-Phase Bases." *Langmuir* **1996**, *12*, 726-735.

porphyrin functionalized gold surfaces.⁴⁰³ Rotello *et al.* demonstrated recognition between gold surfaces that were patterned with diacyl-2,6-diaminopyridine (DAP) and an electroactive ferrocene-terminated uracil in solution using STM.⁴⁰⁴ Competitive adsorption between ferrocene and alkyl uracil led to the reversible tuning of the electroactivity of the surface.

Polymers that exhibit reversible interactions with a solid surface hold considerable potential as releasable coatings, and smart adhesives. In addition, the capability to reversibly attach polymers to solid surfaces enables tunable surface energetics. Polymers that were functionalized with hydrogen bonding groups were assembled onto complementary surfaces in order to direct nanoparticle assembly and tune surface characteristics, primarily through triple hydrogen bonding interactions between thymine-triazine/diaminopyridine.^{405, 406, 407, 408, 409}

Although complementary triple hydrogen bonding thymine-DAP/triazine as well as self-complementary UPy based quadruple hydrogen bonding interactions were studied

⁴⁰³ Krishnamohan Sharma, C. V.; Broker, G. A.; Szulczewski, G. J.; Rogers, R. D. "Self-Assembly of Freebase- and Metallated-Tetrapyridylporphyrins to Modified Gold Surfaces." *Chem. Commun.* **2000**, 1023-1024.

⁴⁰⁴ Credo, G. M.; Boal, A. K.; Das, K.; Galow, T. H.; Rotello, V. M.; Feldheim, D. L.; Gorman, C. B. "Supramolecular Assembly on Surfaces: Manipulating Conductance in Noncovalently Modified Mesoscale Structures." *J. Am. Chem. Soc.* **2002**, 124, 9036-9037.

⁴⁰⁵ Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; -Albrecht, T. T.; Russell, T. P.; Rotello, V. M. "Self-Assembly of Nanoparticles into Structured Spherical and Network Aggregates." *Nature* **2000**, 404, 746-748.

⁴⁰⁶ Boal, A. K.; Gray, M.; Ilhan, F.; Clavier, G. M.; Kapitzky, L.; Rotello, V. M. "Bricks and Mortar Self-Assembly of Nanoparticles." *Tetrahedron* **2002**, 58, 765-770.

⁴⁰⁷ Sanyal, A.; Norsten, T. B.; Oktay, U.; Rotello, V. M. "Adsorption/Desorption of Mono- and Diblock Copolymers on Surfaces Using Specific Hydrogen Bonding Interactions." *Langmuir* **2004**, 20, 5958-5964.

⁴⁰⁸ Norsten, T. B.; Jeoung, E.; Thibault, R. J.; Rotello, V. M. "Specific Hydrogen-Bond-Mediated Recognition and Modification of Surfaces Using Complementary Functionalized Polymers." *Langmuir* **2003**, 19, 7089-7093.

⁴⁰⁹ Jeoung, E.; Carroll, J. B.; Rotello, V. M. "Surface Modification via a 'Lock and Key' Specific Self-Assembly of Polyhedral Silsesquioxane (POSS) Derivatives to Modified Gold Surfaces." *Chem. Commun.* **2002**, 1510-1511.

earlier, hydrogen bonding interaction on surfaces using DNA base pairs has not received significant attention. In addition to exhibiting high specificity, these interactions also have reasonable thermal stability. Earlier studies had investigated the influence of DNA base pairs on the properties of polymers functionalized with these groups.^{410, 411} A limited number of earlier studies have employed adenine-thymine interactions on surfaces. A relevant manuscript described the assembly of zeolites that were functionalized with thymine groups to adenine functionalized glass surfaces.⁴¹²

This chapter will describe an investigation of the stability and reversibility of DNA base pair mediated association between a polymer and silicon/SiO₂ surface. In the current study, silicon/SiO₂ surfaces were modified with adenine using a novel adenine-derivatized triethoxysilane. PS containing a single, terminal, complementary thymine group was obtained via a *sec*-butyllithium (*sec*-BuLi) initiated living anionic polymerization of styrene and subsequent termination with ethylene oxide.⁴¹³ Thymine was subsequently introduced at the PS chain end using a two-step Michael addition based synthetic strategy.⁴¹⁴ Reversible attachment of the PS-thymine to the adenine functionalized silicon/SiO₂ surface was probed using XPS and water contact angle measurements.

⁴¹⁰ Overberger, C. G.; Inaki, Y. "Graft Copolymers Containing Nucleic Acid Bases and L- α -Amino Acids." *J. Polym. Sci., Polym. Chem.* **1979**, 17, 1739-1758.

⁴¹¹ Yamauchi, K.; Lizotte, J. R.; Long, T. E. "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002**, 35, 8745-8750.

⁴¹² Park, J. S.; Lee, G. S.; Lee, Y.-J.; Park, Y. S.; Yoon, K. B. "Organization of Microcrystals on Glass by Adenine-Thymine Hydrogen Bonding." *J. Am. Chem. Soc.* **2002**, 124, 13366-13367.

⁴¹³ Quirk, R. P.; Mathers, R. T.; Wesdemiotis, C.; Arnould, M. A. "Investigation of Ethylene Oxide Oligomerization During Functionalization of Poly(Styryl)Lithium Using Maldi-Tof Ms and Nmr." *Macromolecules* **2002**, 35, 2912-2918.

⁴¹⁴ Yamauchi, K.; Lizotte, J. R.; Long, T. E. "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules Via a Michael Addition." *Macromolecules* **2002**, 35, 8745-8750.

5.3 Experimental

5.3.1 Materials

3-isocyanatopropyltriethoxysilane (IPTES, 95%, Aldrich) was vacuum distilled in the absence of purification reagents (0.1 mm Hg, 30 °C). Styrene (Aldrich) was stirred over CaH₂ for 3-4 days, distilled under vacuum (0.1 mm Hg, 10 °C) after repeated degassing and freeze-thaw cycles, and stored at -25 °C. Styrene was vacuum distilled from dibutylmagnesium (DBM) under similar conditions immediately prior to polymerization. DBM (25% solution in heptane, FMC Corporation Lithium Division), *sec*-butyllithium (*sec*-BuLi, 1.4 M in cyclohexane, Aldrich), ethylene oxide (99%, Aldrich), anhydrous DMSO (Aldrich), potassium *tert*-butoxide (Aldrich), methanol (EMD Chemicals), dichloromethane (EMD Chemicals), conc. H₂SO₄ (VWR International), NH₄OH (30%, VWR International), H₂O₂ (30%, EMD Chemicals), and 3-mercaptopropyltriethoxysilane (MPTES, 95%, Gelest, Inc.) were used as received. Cyclohexane (EMD Chemicals) was distilled from sodium immediately prior to use. Adenine and thymine (Aldrich) were dried overnight in a vacuum oven at 60 °C. CHCl₃ (EMD Chemicals) for surface modification was dried over CaH₂ and distilled immediately prior to use. Millipore milli-Q water was used for surface cleaning. Silicon wafers used as the substrates were a generous gift from Hewlett-Packard Company.

5.3.2 Material Characterization

Size exclusion chromatography (SEC) data was obtained using a 717 Autosampler system equipped with 3 in-line 5 μm PLgel MIXED-C columns, a Waters 2410 refractive index detector operating at 880 nm, a Wyatt Technology miniDawn[®] multiple angle laser light scattering (MALLS) detector operating at 690 nm and

calibrated with polystyrene standards, and a Viscotek Model 270 differential/light scattering dual detector. The refractive index increment (dn/dc) was calculated online. SEC measurements were performed at 40 °C in THF at a flow rate of 1 mL/min. ^1H , ^{13}C , and ^{29}Si NMR spectroscopy were performed on a Varian UNITY spectrometer at 400 MHz, 100 MHz, and 79.5 MHz respectively with CDCl_3 as solvent. Fast atom bombardment mass spectrometry (FAB-MS) was achieved using a Fissons Instruments VG Quattro.

5.3.3 Surface Characterization

The modified silicon/ SiO_2 surfaces were sonicated in a Branson 1200 ultrasonic generator for 1 h. Static water contact angles were measured in the sessile drop mode using a FTA-200 contact angle goniometer with a syringe-driven droplet. The values were measured 30 sec after dispensing the drop to obtain equilibrium values. Contact angles were measured at 4-5 different spots on each surface. XPS was obtained on a Perkin Elmer Model 5400 instrument fitted with a Mg $K\alpha$ X-ray source (1253.8 eV), at a take-off angle of 30°. The anode was operated at 250 W. The 285 eV photoelectron peak of C1s electrons was used as an internal XPS standard.

5.3.4 Synthesis of Adenine-functionalized Triethoxysilane (ADPTES)

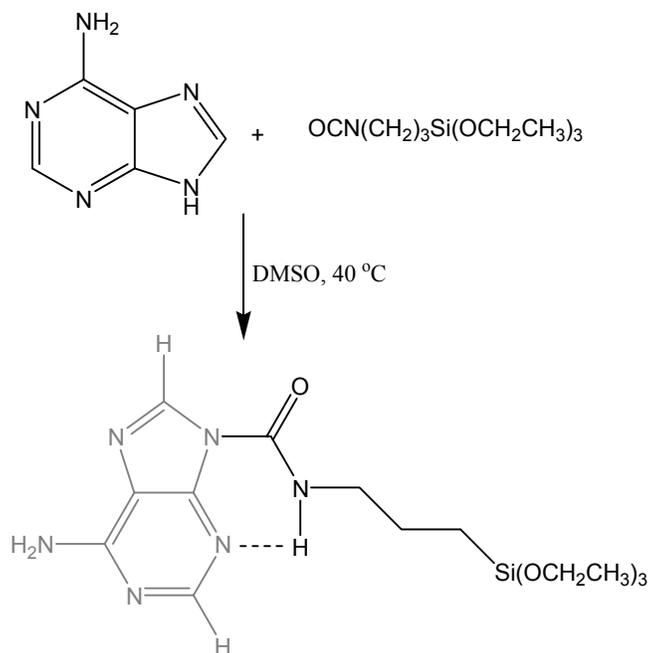
The synthesis of ADPTES involved the reaction of adenine with IPTES in anhydrous DMSO as shown in Scheme 5-1. All glassware was rigorously cleaned and flame dried. Dry adenine (2g, 14.8 mmol) was dissolved in anhydrous DMSO (30 mL) at 145 °C under nitrogen in a septum-sealed 100 mL round-bottomed flask. IPTES (4 mL, 16.2 mmol, 1.1 equivalents) was dissolved in anhydrous DMSO (10 mL) in a 100 mL septum-sealed round-bottomed flask. The adenine solution was slowly added to a

room temperature solution of IPTES using a double-tipped needle (cannula) over 30 min. The mixture was allowed to stir for an additional 2 h to ensure complete reaction. DMSO was removed under vacuum and the solid product was dissolved in CHCl_3 and passed through Celite. The solid was then recrystallized from cold toluene. The product was isolated in ~20 % yield. ^1H NMR (400 MHz, 25 °C in CDCl_3): δ (ppm) 0.73 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}-$: 2H, t); 1.23 ($-\text{Si}(\text{OCH}_2\text{CH}_3)_3$: 9H, t); 1.81 ($-\text{CH}_2\text{CH}_2\text{CH}_2\text{Si}-$: 2H, m); 3.50 ($-\text{CH}_2\text{NH}-\text{CO}-$: 2H, q); 3.84 ($-\text{Si}(\text{OCH}_2\text{CH}_3)_3$: 6H, q); 5.84 ($-\text{NHCONH}-$: 2H, s); 8.36 ($-\text{N}=\text{CH}-\text{NH}-$: 1H, s); 8.52 ($-\text{N}-\text{CH}=\text{N}-$: 1H, s); 8.93 ($-\text{N}=\text{CH}-\text{NH}-$: 1H, s). ^{13}C NMR (100 MHz, 25 °C in CDCl_3): δ (ppm) 7.28, 17.9, 22.6, 42.2, 58.1, 119.6, 138.8, 147.8, 148.6, 152.7, 155.5. $m/z = 382.18$ (theoretical: 382.5).

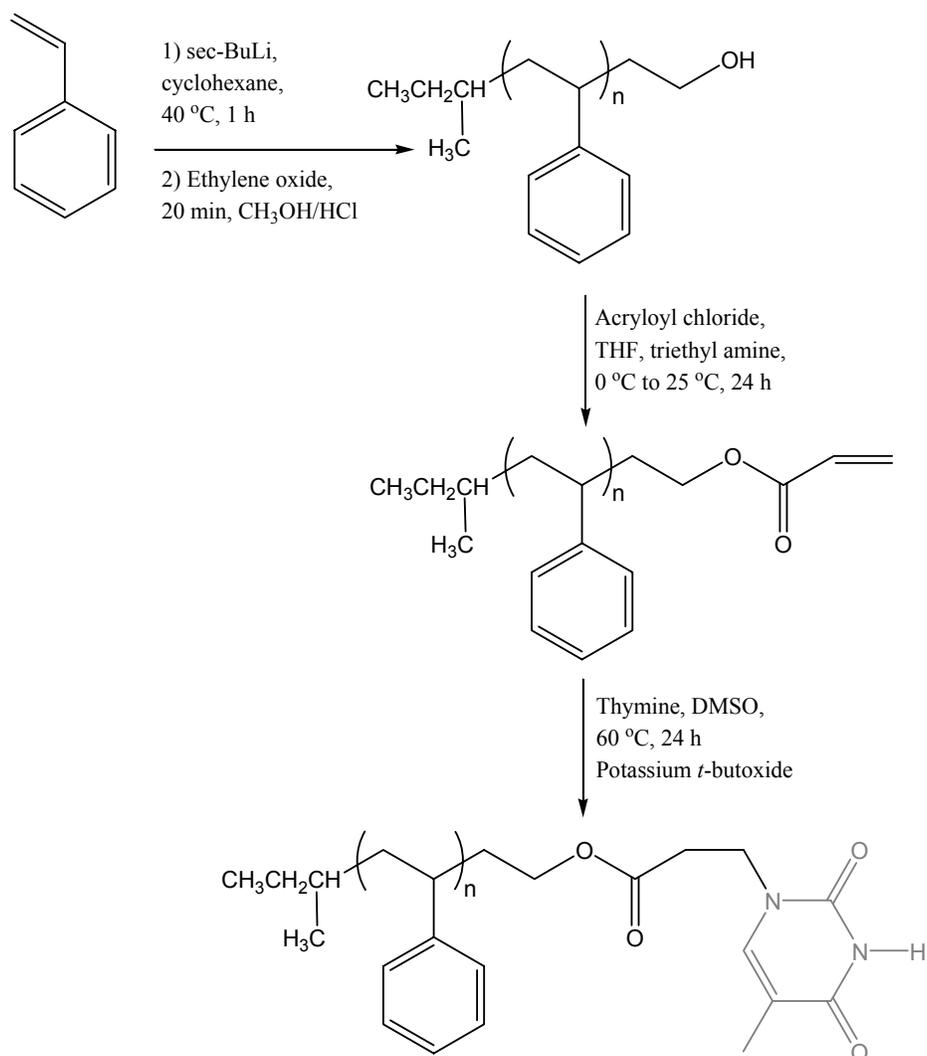
5.3.5 Synthesis of Thymine-functionalized Polystyrene (PS-thymine)

Thymine-functionalized PS was obtained according to a literature procedure⁴¹⁵ as shown in Scheme 5-2. Hydroxy-terminated polystyrene (PS-OH) was synthesized via anionic polymerization of styrene initiated with *sec*-BuLi in cyclohexane at 40 °C. The living anions were end-capped with ethylene oxide. Acrylation of PS-OH and subsequent reaction with thymine was performed according to a literature procedure.⁴¹⁵ The PS-thymine product was characterized using ^1H NMR spectroscopy.

⁴¹⁵ Yamauchi, K.; Lizotte, J. R.; Long, T. E. "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002**, 35, 8745-8750.



Scheme 5-1: Synthesis of ADPTES with selective coupling to the secondary amine; the adenine group is shown in gray.



Scheme 5-2: Synthesis of thymine-functionalized PS; the thymine group is shown in gray.

5.3.6 Substrate Treatment

Silicon wafers were cut into 1 cm² samples and sonicated for 5 min in dichloromethane and 5 min in methanol. The wafers were blown with nitrogen and cleaned with freshly prepared Piranha solution (conc.H₂SO₄:30% H₂O₂; v/v: 70/30) at 90 °C for 1 h, rinsed with milli-Q water, and cleaned with a 30% NH₃:30% H₂O₂:H₂O (v/v/v: 1/1/5) at 60 °C for 15 min. The wafers were then rinsed with milli-Q water several times, blown dry with nitrogen, and immediately immersed in the alkoxy silane solution and allowed to stir for a given time. (*Caution: Piranha solution reacts violently with many organic materials and should be handled with care.*)

5.3.7 Covalent Modification of Silicon/SiO₂ Surfaces and Polymer Treatment

Freshly cleaned silicon wafers were modified with a 5 mM solution of [25:75; mol/mol] ADPTES/MPTES in CHCl₃ for 6 h and subsequently sonicated 3 times in CHCl₃ to remove any physisorbed material. Surface modification exclusively with MPTES and ADPTES was carried out under similar conditions. Wafers were characterized after each modification step using XPS and water contact angle measurements. The alkoxy silane-modified surfaces were immersed in a 5 mM solution of PS-thymine (M_n = 2,010 g/mol) or PS-OH (M_n = 4,200 g/mole) for 24 h and exhaustively rinsed with both CHCl₃ and THF.

5.4 Results and Discussion

5.4.1 Synthesis of ADPTES and PS-thymine

A novel adenine-containing alkoxy silane was synthesized in a single step via the reaction of adenine with IPTES (Scheme 5-1). ¹H and ¹³C NMR spectroscopy and FAB-MS confirmed the chemical structure of the isolated product. Characteristic ¹H NMR

resonances associated with the adenine groups were observed at 5.84 ppm (-NHCONH-), 8.36 ppm (-N=CH-NH-), 8.52 ppm (-N-CH=N-), and 8.93 ppm (-N=CH-NH-) in addition to resonances associated with the triethoxysilane, which confirmed successful derivatization (Figure 5-1). ²⁹Si NMR spectra for both IPTES and ADPTES exhibited a single alkoxy silane Si resonance similar to the precursor alkoxy silane (IPTES) and confirmed the absence of any alkoxy silane hydrolysis (Figure 5-2) since any hydrolysis or condensation of the ethoxy silane group would have resulted in a pronounced shift in the Si resonance to lower or higher field, respectively.⁴¹⁶

Figure 5-3 shows the representative ¹H NMR spectra of hydroxyl-, acrylated-, and thymine-functionalized PS. The disappearance of the resonance at 3.29 ppm (CH₂OH; Figure 5-3a) following reaction with acryloyl chloride and appearance of four new resonances (-COOCH₂- at 3.82 ppm, CH₂=CH- at 5.74 ppm, 5.97 ppm, and 6.24 ppm; Figure 5-3b) confirmed quantitative acrylation. Upon reaction with thymine, the three olefinic proton resonances associated with the acrylate double bonds disappeared and a new peak at 7.78 ppm (-CO-NH-CO-, Figure 5-3c) appeared.

⁴¹⁶ Kelts, L. W.; Armstrong, N. J. "A Silicon-29 NMR Study of the Structural Intermediates in Low pH Sol-Gel Reactions." *J. Mater. Res.* **1989**, 4, 423-430.

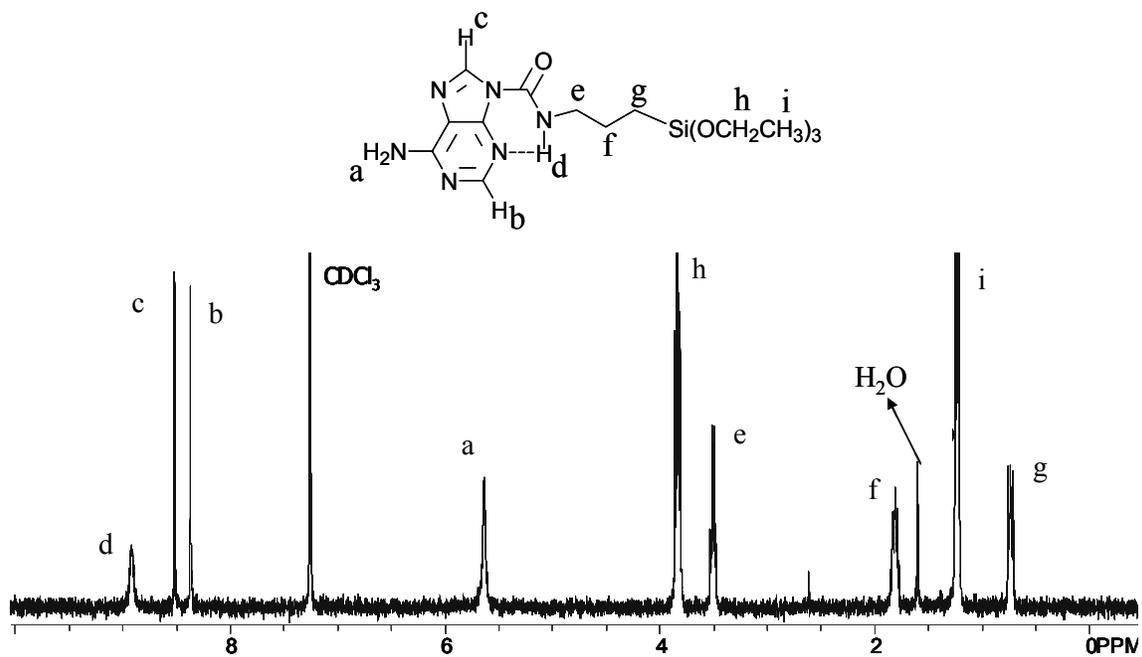


Figure 5-1: ¹H NMR spectrum of adenine-functionalized triethoxysilane (ADPTES).

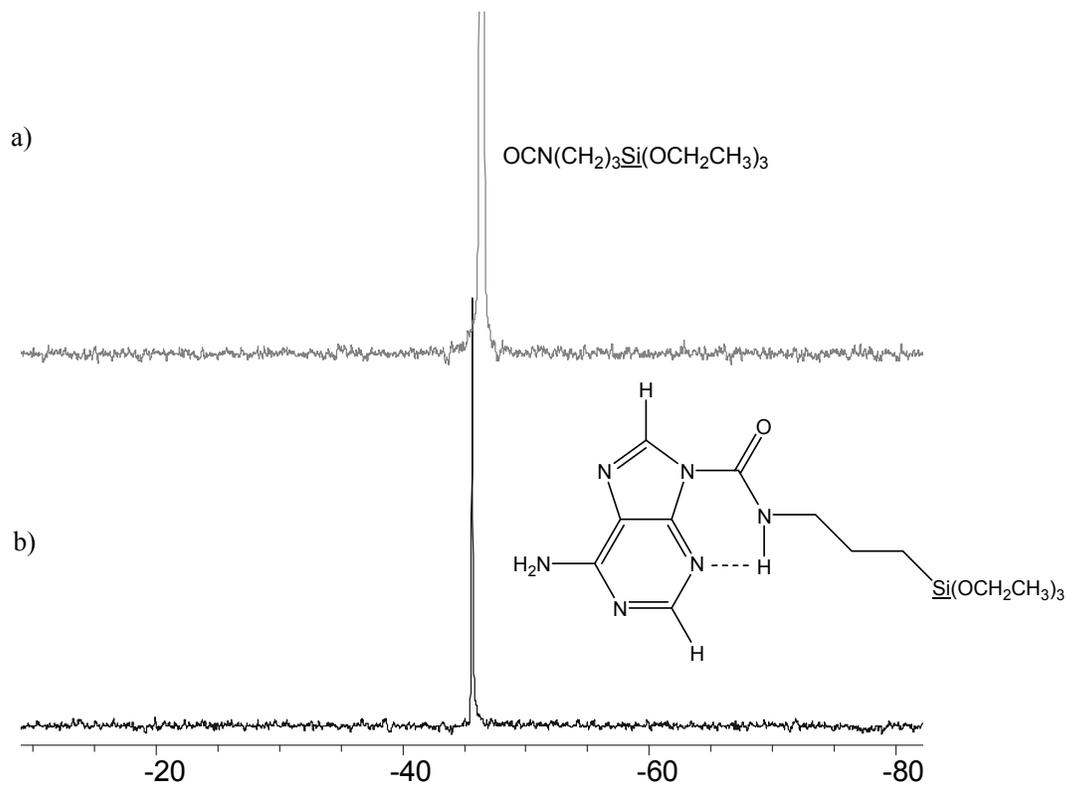


Figure 5-2: ^{29}Si NMR spectra in 16 wt% CDCl_3 containing 0.06 M $\text{Cr}(\text{acac})_3$ of a) IPTES, and b) ADPTES.

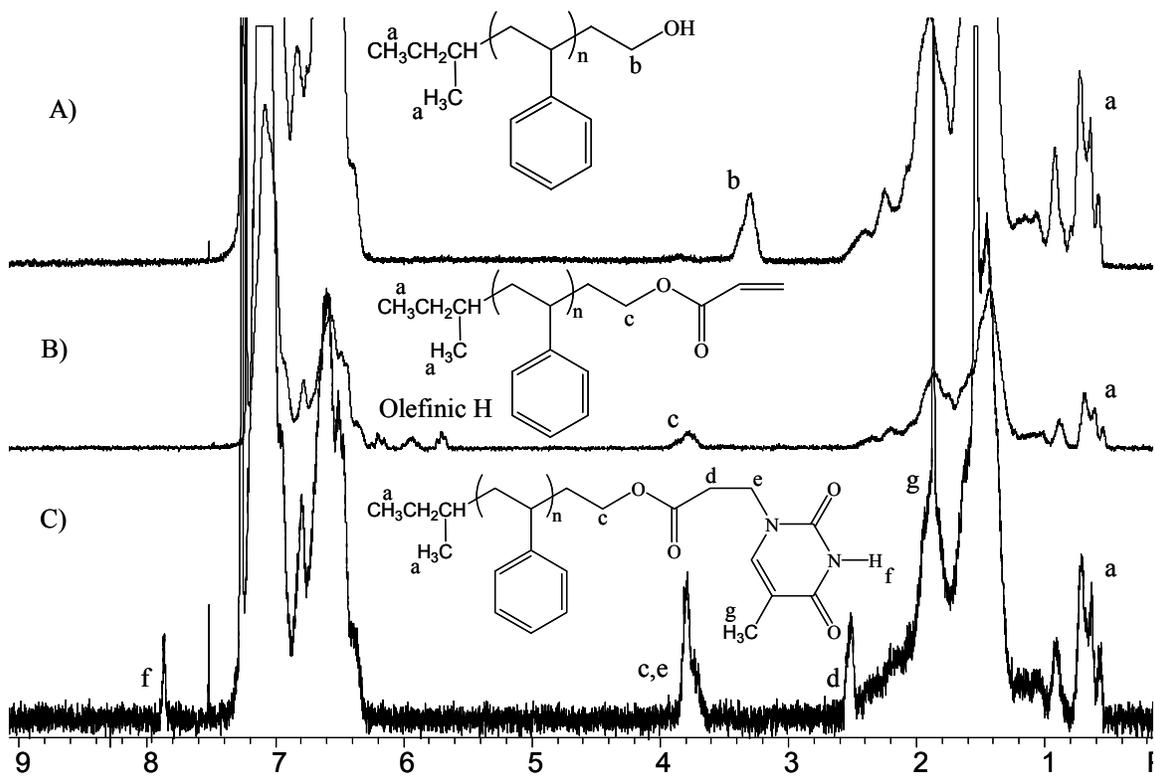


Figure 5-3: ^1H NMR of A) PS-OH, B) acrylated PS, and C) PS-thymine.

Tables 5-1, and 5-2 summarize the molecular weights and % functionalization of a series of PS-OH, acrylated PS, and PS-thymine, respectively. The sample designation in Tables 5-1 and 5-2 refer to the same polymers that were taken through various functionalization steps. Low molecular weight PSOH exhibited quantitative functionalization; however, as PSOH molecular weight increased, only partial acrylation was achieved and thus, functionalization with thymine was not attempted for higher M_n PS.

Table 5-1: Molecular weight, % end-capping, and % functionalization data for a series of PSOH and acrylated-PS

Sample designation	PSOH			Acrylated PS	
	NMR M_n^a (g/mol)	SEC M_n^b (g/mol) (M_w/M_n)	% end- capping ^c	NMR M_n^a (g/mol)	% functionalization ^d
A	1,750	1,670 (1.08)	100	2,160	93
B	1,900	2,000 (1.05)	100	2,050	96
C	3,060	3,280 (1.03)	100	3,300	90
D	4,200	4,020 (1.05)	97	4,610	87
E	14,300	14,700 (1.01)	80	16,200	78

^aRatio of repeat unit aromatic proton resonance to initiator methyl protons. ^bSEC conditions: THF, 40°C, DRI detector. ^cRatio of terminal methylene protons of ethylene oxide unit at 3.28 ppm to initiator methyl protons. ^dRatio of olefinic protons of acrylate unit at 5.74 ppm to initiator methyl protons.

Table 5-2: Molecular weight, and % functionalization data for a series of PS-thymine

Sample designation	NMR M_n^a (g/mol)	SEC M_n^b in g/mol (M_w/M_n)	% end-capping ^c
A	2,230	2,010 (1.07)	94
B	2,340	2,190 (1.05)	96
C	3,500	2,960 (1.09)	100
D	4,670	4,600 (1.06)	100

^aRatio of repeat unit aromatic proton resonance to initiator methyl protons. ^bSEC conditions: THF, 40°C, DRI detector. ^cRatio of methylene protons adjacent to ester oxygen and ring nitrogen at 3.8 ppm to initiator methyl protons.

5.4.2 Specific Recognition between PS-thymine and Silicon/SiO₂ Surfaces Modified with ADPTES Mixture

Freshly cleaned silicon/SiO₂ surfaces were modified with a mixture of ADPTES/MP TES at a molar ratio of 1:3 from a CHCl₃ solution. Anhydrous CHCl₃ was used to eliminate both premature hydrolysis of the ethoxysilane groups and multilayer formation.⁴¹⁷ MP TES was used as a diluent to lower the concentration of adenine groups on the surface. Dilution of the adenine groups was considered as earlier literature have shown that the exclusive presence of molecular recognition groups on solid surfaces hinders the recognition phenomenon.^{418, 419}

Although photoelectron peaks associated with N were not observed on silicon/SiO₂ surfaces that were coated with MP TES, XPS analysis of the silicon/SiO₂ surface detected N1s photoelectron peaks after treatment with the ADPTES/MP TES mixture, as shown in Figure 5-4, which indicated successful adenine functionalization. The principal N1s core level peak exhibited a binding energy of 399.9 eV, which was similar to literature values.⁴²⁰

⁴¹⁷ Moon, J. H.; Shin, J. W.; Kim, S. Y.; Park, J. W. "Formation of Uniform Aminosilane Thin Layers: An Imine Formation to Measure Relative Surface Density of the Amine Groups." *Langmuir* **1996**, 12, 4621-4624.

⁴¹⁸ Häussling, L.; Ringsdorf, H.; Schmitt, F.-J.; Knoll, W. "Biotin-Functionalized Self-Assembled Monolayers on Gold: Surface Plasmon Optical Studies of Specific Recognition Reactions." *Langmuir* **1991**, 17, 1837-1840.

⁴¹⁹ Wang, Z.-H.; Jin, G. "Silicon Surface Modification with a Mixed Silane Layer to Immobilize Proteins for Biosensor with Imaging Ellipsometry." *Colloids Surf., B* **2004**, 34, 173-177.

⁴²⁰ Herne, T. M.; Tarlov, M. J. "Characterization of DNA Probes Immobilized on Gold Surfaces." *J. Am. Chem. Soc.* **1997**, 119, 8916-8920.

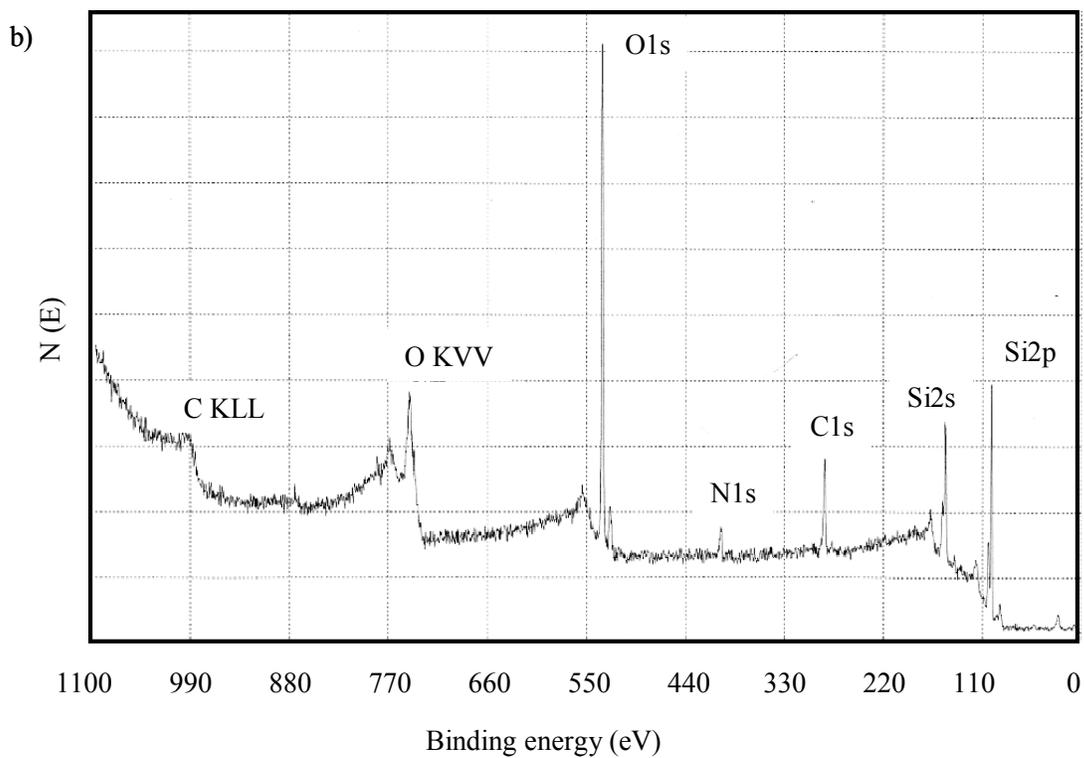
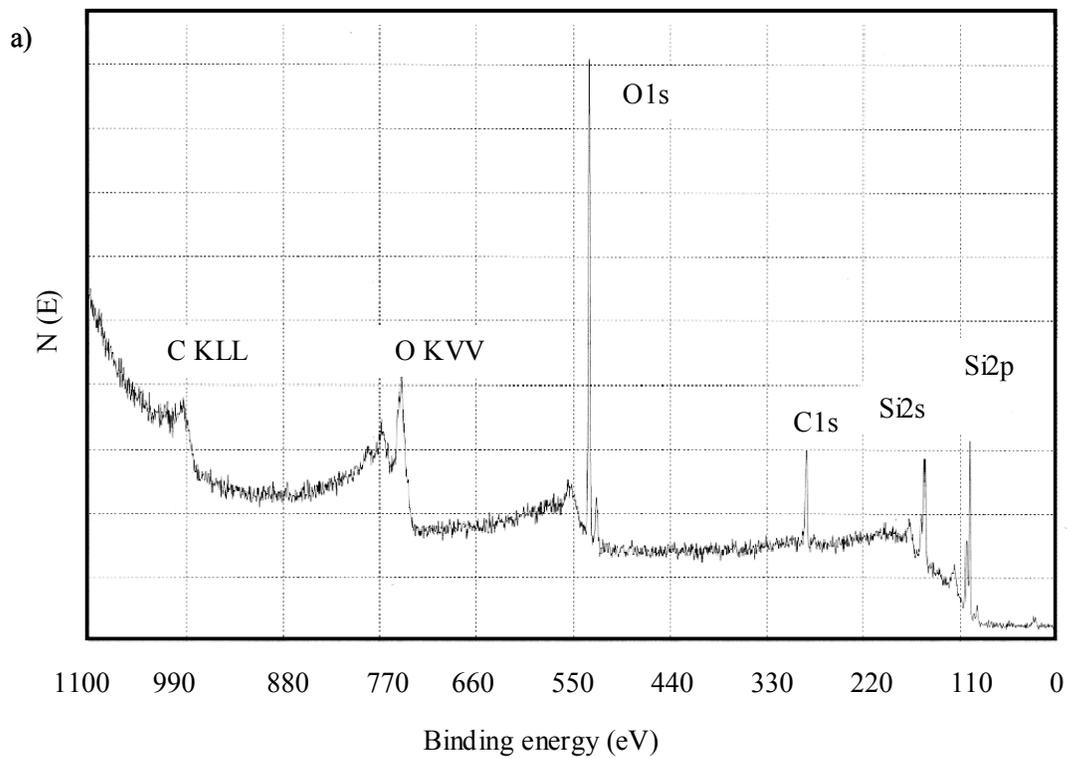


Figure 5-4: XPS survey spectra of silicon/SiO₂ surfaces modified with a) MPTES, and b) ADPTES/MPTES.

The XPS elemental composition of MPTES and ADPTES/MPTES-coated silicon/SiO₂ surfaces are shown in Table 5-3. It was not possible to quantify the mercapto groups on the surface due to the susceptibility of -SH groups to oxidation under ambient conditions.⁴²¹ Also, it was not possible to avoid oxidation of the mercapto groups despite performing reactions and storing the samples in the absence of light. The sulfur region in XPS spectrum showed two peaks centered at 163.4 eV and 168.3 eV attributed to -SH groups and oxidized by-products species, respectively.⁴²² However, the latter peak at 168.3 eV, was predominant, which indicated that most mercapto groups were oxidized under the experimental conditions. The S2p photoelectron peak also indicated some residual sulfuric acid that was used in the cleaning procedure, this led to further difficulty in estimating the actual concentration of the mercapto sites on the surface.

The C/N ratio was calculated based on the atomic compositions given in Table 5-3 for the surface modified with the mixture before polymer deposition, and were higher than expected based on the chemical composition of ADPTES, which further indicated co-deposition of MPTES on the surface. However, it was not possible to determine the actual ratio of N/S on the surface due to the above-mentioned reasons. However, based on C/N ratio of 3.7 and the chemical composition of the alkoxysilanes, it was estimated that there was 1 ADPTES for every 4.4 MPTES on the surface. This ratio is higher than the theoretical ratio based on solution composition, which would ideally give a C/N ratio

⁴²¹ Liu, J.; Hlady, V. "Chemical Pattern on Silica Surface Prepared by UV Irradiation of 3-Mercaptopropyltriethoxy Silane Layer: Surface Characterization and Fibrinogen Adsorption." *Colloids Surf., B* **1996**, 8, 25-37.

⁴²² Liu, J.; Hlady, V. "Chemical Pattern on Silica Surface Prepared by UV Irradiation of 3-Mercaptopropyltriethoxy Silane Layer: Surface Characterization and Fibrinogen Adsorption." *Colloids Surf., B* **1996**, 8, 25-37.

of 3:1, assuming complete hydrolysis of the ethoxy groups. Preferential chemisorption of the mercapto compound⁴²³ on the surface was disregarded based on the following justification. For the MPTES coated surface, the C/S ratio that was calculated from XPS was 6, which is higher than the expected ratio of 3 calculated from the chemical composition of MPTES. Such a high ratio for C/S was observed for surfaces coated with mercaptopropyltrimethoxysilane and MPTES and was attributed to the presence of carbon impurities.⁴²⁴ A similar trend was observed for surfaces coated with ADPTES, where the surfaces showed a C/N ratio of 2.8 compared to the expected value of 1.5. Thus, the higher C/N ratio than expected from the relative concentrations of the two silanes in solution in the case of ADPTES and the mixture was attributed to the presence of carbon contamination.

The atomic compositions of the MPTES- and ADPTES/ MPTES-coated surfaces following PS-thymine treatment and solvent rinse are also listed in Table 5-3. The atomic %C on silicon/SiO₂ surfaces that were modified with the ADPTES/MPTES mixture increased following exposure to the PS-thymine solution, while the MPTES-modified surface showed no change. Assuming one ADPTES molecule for every three MPTES molecules on the surface, the recognition of PS-thymine by every ADPTES molecule would lead to a C/N ratio of 23. This ratio corresponds to a relative increase of ~20 compared to the ADPTES/MPTES modified surface prior to PS-thymine exposure. Table 5-3 shows a C/N ratio of 7 following PS-thymine exposure corresponding to a relative increase of ~4, which indicated only 20% recognition of PS-thymine by the

⁴²³ Heise, A.; Stamm, M.; Rauscher, M.; Duschner, H.; Menzel, H. "Mixed Silane Self Assembled Monolayers and Their in Situ Modification." *Thin Solid Films* **1998**, 327-329, 199-203.

surface anchored adenine groups. The simultaneous deposition of silanes on a surface often leads to randomly distributed species on the surface, which possibly results in some phase segregation of the two silanes. This could therefore lead to some surface regions abundant in ADPTES and close proximity of the ADPTES molecules in this region could limit their accessibility to the incoming PS-thymine. As a result, quantitative attachment of PS-thymine to all the surface-bound adenine groups was not observed.

The %O and %Si on the ADPTES/MP TES-modified surface also decreased upon exposure to PS-thymine solution, which further confirmed the hydrogen-bond mediated attachment of PS-thymine to the ADPTES/MP TES-modified surface illustrated in Figure 5-5.

⁴²⁴ Hu, M.; Noda, S.; Okubo, T.; Yamaguchi, Y.; Komiyama, H. "Structure and Morphology of Self-Assembled 3-Mercaptopropyltrimethoxysilane Layers on Silicon Oxide." *Appl. Surface Sci.* **2001**, 181, 307-316.

Table 5-3: XPS elemental composition of MP TES, and ADPTES/MP TES modified silicon/SiO₂ surface before and after PS-thymine treatment

XPS photoelectron peak ^a	Binding energy (eV)	Atomic composition (%)			
		MP TES modified ^b		ADPTES/MP TES modified ^c	
		Before	After ^d	Before	After ^d
C1s	285.0	29	27	20	33
O1s	532.3	35	37	36	30
Si2p	102.7; 99.0	31	31	35	28
N1s	399.9	-	-	4	5
S2p	163.4; 168.3	5	5	5	4

^aXPS conditions: Mg anode, take-off angle = 30°. ^bSurface modification with MP TES: 5mM MP TES in CHCl₃, 6 h, extracted with CHCl₃. ^cSurface modification with ADPTES/MP TES mixture: 5mM ADPTES/MP TES (1:3 molar ratio) in CHCl₃, 6 h, extracted with CHCl₃. ^dSurface modification with PS-thymine: 5mM PS-thymine in CHCl₃, 24 h, extracted with CHCl₃/THF.

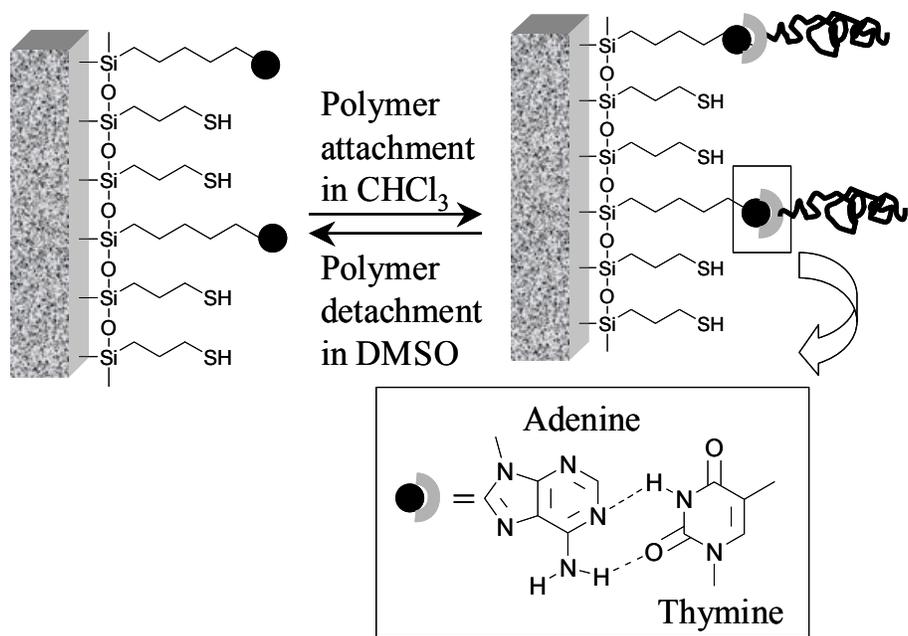


Figure 5-5: Depiction of proposed molecular recognition between an ADPTES/MP TES modified silicon/SiO₂ surface and a thymine-functionalized polymer.

When the surface was modified only with ADPTES, XPS atomic %C did not reveal polymer attachment as shown in Table 5-4, which suggested the role of steric hindrance in molecular recognition in a similar fashion to the earlier literature.^{425, 426} Water contact angle measurements further supported XPS data.

Static water contact angle results for MPTES, ADPTES, ADPTES/MPTES modified surfaces before and after PS-thymine treatment are summarized in Table 5-5. The water contact angle on a freshly cleaned silicon wafer was nearly 0° as the water drop spread to completely wet the surface, and upon modification with MPTES, the contact angle increased to 35°. Earlier studies have shown that surfaces with a uniform layer of MPTES show a water contact angle of 60°, however upon oxidation, the contact angle decreased to approximately 20°.⁴²⁷ The water contact angle on the MPTES coated surfaces in our study was intermediate between the two contact angle values reported above, which suggested partial oxidation of the surface mercapto groups in a consistent fashion with the XPS observation. When the surfaces were modified with the ADPTES/MPTES mixture, the surfaces showed a water contact angle of 40°, while the surface modified with neat ADPTES alone had a water contact angle of approximately 47°. This suggested that the former surface had a higher concentration of MPTES groups as the water contact angle was closer to values for a MPTES coated surface.

⁴²⁵ Häussling, L.; Ringsdorf, H.; Schmitt, F.-J.; Knoll, W. "Biotin-Functionalized Self-Assembled Monolayers on Gold: Surface Plasmon Optical Studies of Specific Recognition Reactions." *Langmuir* **1991**, *17*, 1837-1840.

⁴²⁶ Wang, Z.-H.; Jin, G. "Silicon Surface Modification with a Mixed Silane Layer to Immobilize Proteins for Biosensor with Imaging Ellipsometry." *Colloids Surf., B* **2004**, *34*, 173-177.

⁴²⁷ Liu, J.; Hlady, V. "Chemical Pattern on Silica Surface Prepared by UV Irradiation of 3-Mercaptopropyltriethoxy Silane Layer: Surface Characterization and Fibrinogen Adsorption." *Colloids Surf., B* **1996**, *8*, 25-37.

Table 5-4: XPS elemental composition of ADPTES modified silicon/SiO₂ surface before and after PS-thymine treatment

XPS photoelectron peak (eV) ^a	Atomic composition (%)	
	Before ^b	After ^c
C1s	28	27
O1s	32	33
N1s	31	31
Si2p	9	9

^aXPS conditions: Mg anode, take-off angle = 30°. ^bSurface modification with ADPTES: 5mM ADPTES in CHCl₃, 6 h, extracted with CHCl₃. ^cSurface modification with PS-thymine: 5mM PS-thymine in CHCl₃, 24 h, extracted with CHCl₃/THF.

Table 5-5: Water contact angle on MPTES, ADPTES, and ADPTES/MPTES silicon/SiO₂ surfaces before and after PS-thymine treatment

Surface	Water contact angle (deg)	
	Before	After
MPTES modified surfaces	35 ± 4	40 ± 3
ADPTES modified surfaces	47 ± 3	45 ± 4
ADPTES/MPTES modified surfaces	40 ± 5	54 ± 6

Following exposure of the ADPTES/MPTES-modified silicon/SiO₂ surface to the PS-thymine solution, the water contact angle increased to 54° (Table 5-5), which indicated successful PS-thymine attachment, while the MPTES-coated surface showed insignificant change. The 15° increase in water contact angle that was observed on ADPTES/MPTES following PS-thymine treatment is similar to earlier reports on the attachment of POSS-DAP to thymine modified gold surfaces through DAP-thymine interaction.⁴²⁸ In comparison, neat PS films on solid surfaces have a higher water contact angle of 90°.⁴²⁹ The lower 54° water contact angle of the PS-thymine treated surface was attributed to attachment of PS-thymine to adenine groups randomly dispersed on the surface, which gives rise to heterogeneous polymer coverage.

On the other hand, modification of ADPTES/MPTES coated surfaces with PS-OH, which contained weaker hydrogen bonding hydroxyl groups, showed insignificant polymer attachment following THF rinse as shown in Figure 5-6, which further confirmed the absence of any non-specific polymer adsorption on adenine coated surfaces. Studies with polymers containing non-complementary bases such as cytosine were not attempted because of limited solubility of cytosine at reaction conditions for thymine functionalized PS. Attempts to investigate the influence of M_n were not successful due to less efficient chain end functionalization at molecular weights higher than 10,000 g/mol. Oxidation of the residual mercapto groups on surfaces that were modified with the neat MPTES or ADPTES/MPTES and subjected to polymer

⁴²⁸ Jeoung, E.; Carroll, J. B.; Rotello, V. M. "Surface Modification via a 'Lock and Key' Specific Self-Assembly of Polyhedral Silsesquioxane (POSS) Derivatives to Modified Gold Surfaces." *Chem. Commun.* **2002**, 1510-1511.

⁴²⁹ Zhao, B.; Brittain, W. J. "Synthesis of Polystyrene Brushes on Silicate Substrates via Carbocationic Polymerization from Self-Assembled Monolayers." *Macromolecules* **2000**, 33, 342-348.

modification, was negligible and insignificantly contributed to any error in the measurements.

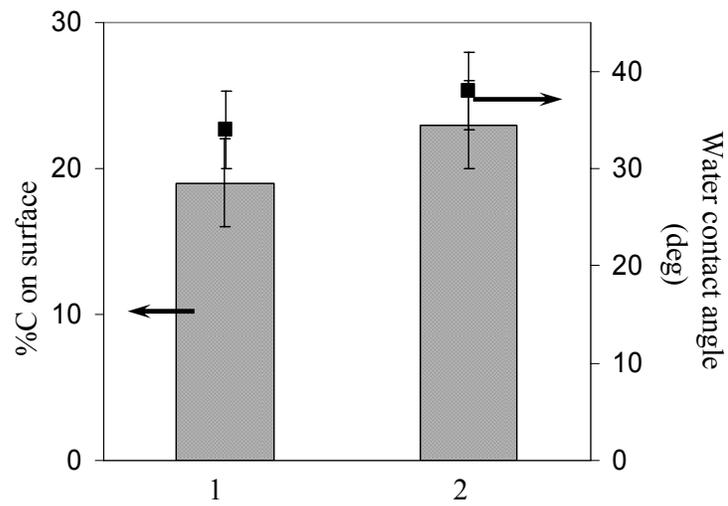


Figure 5-6: Variation in XPS %C (bars) and water contact angle (solid squares) on silicon/SiO₂ surfaces modified with ADPTES/MP TES 1) before, and 2) after PS-OH treatment.

5.4.3 Reversible Association between PS-thymine and Surfaces Modified with ADPTES Mixture

Despite non-uniform coverage, the PS coatings remained amenable to reversibility due to the hydrogen bonding attachment points. Elevated temperatures and moderate/strong polar solvents are known to disrupt adenine-thymine hydrogen bonding in solution. Linear PS with DNA base pairs at a single chain end was found to undergo dissociation at 95 °C in toluene.⁴³⁰ Overberger and coworkers have prepared grafted and branched poly(ethyleneimine)s that were functionalized with DNA base pairs, and the influence of solution pH, polymer structure and flexibility, and relative position of the hydrogen-bonding groups on the dissociation of adenine-thymine/adenine-uracil interactions was studied.⁴³¹ All these factors were found to influence the temperature of dissociation, which was found to be between 45 °C and 90 °C. Park *et al.* suggested that the onset of adenine-thymine dissociation occurred on surfaces at 55 °C.⁴³² In this study, the stability of hydrogen bonding directed polymer association on a surface towards solvents was evaluated. The PS-thymine hydrogen bonded to the surface adenine groups remained stable despite multiple rinses with THF, which is a moderately polar solvent. Similarly enhanced stability toward CHCl₃ was reported for surface-anchored pyrimidinone dimers relative to pyrimidinone dimers in solution.⁴³³ However, as shown in Figure 5-7a, a decreased %C and lower water contact angle were observed following

⁴³⁰ Yamauchi, K.; Lizotte, J. R.; Long, T. E. "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002**, 35, 8745-8750.

⁴³¹ Overberger, C. G.; Inaki, Y.; Nambu, Y. "Graft Copolymers of Nucleic Acid Bases on Polyethyleneimine: Interaction of the Polymers." *J. Polym. Sci., Polym. Chem.* **1979**, 17, 1759-1769.

⁴³² Park, J. S.; Lee, G. S.; Lee, Y.-J.; Park, Y. S.; Yoon, K. B. "Organization of Microcrystals on Glass by Adenine-Thymine Hydrogen Bonding." *J. Am. Chem. Soc.* **2002**, 124, 13366-13367.

⁴³³ Zou, S.; Zhang, Z.; Forch, R.; Knoll, W.; Schönherr, H.; Vansco, G. J. "Tunable Complex Stability in Surface Molecular Recognition Mediated by Self-Complementary Quadruple Hydrogen Bonds." *Langmuir* **2003**, 19, 8618-8621.

rinses with the more polar DMSO (sample 3), which indicated disruption of the adenine-thymine hydrogen bonds and loss of PS-thymine from the silicon/SiO₂ surface.

As observed earlier for solutions, the adenine-thymine associations were completely reversible on a surface, and it was possible to reattach PS-thymine to the surface adenine groups following the DMSO wash. The reattachment of PS-thymine was confirmed using XPS and water contact angle measurements as shown in Figure 5-7a. A surface that was modified with a 1:3 mixture of ADPTES/ MPTES subjected to a second PS-thymine treatment following DMSO rinse (sample 4), showed increased %C and water contact angle showing that PS-thymine re-attached to the surface-bound adenine groups. The water contact angle increased from 39° to 51° upon association of the PS-thymine to surface-bound adenine (Figure 5-7a). A second DMSO rinse (sample 5) disrupted the adenine-thymine hydrogen bonding, which resulted in the removal of PS-thymine and a decrease in the water contact angle to 38°. A similar trend in XPS %Si, as shown in the bottom right corner of Figure 5-7b, further confirmed the solvent dependent reversible association between PS-thymine and surface adenine groups. The DNA base pair mediated reversible association between polymer and surface therefore demonstrates the utility of molecular recognition groups to reversibly switch the chemical properties and wetting characteristics of a silicon/SiO₂ surface without any detectable hysteresis. Such non-covalent interactions between a polymer and a surface as shown in this study, allows for surface modification with polymers of varied chemical composition and topology for design flexibility and performance optimization.

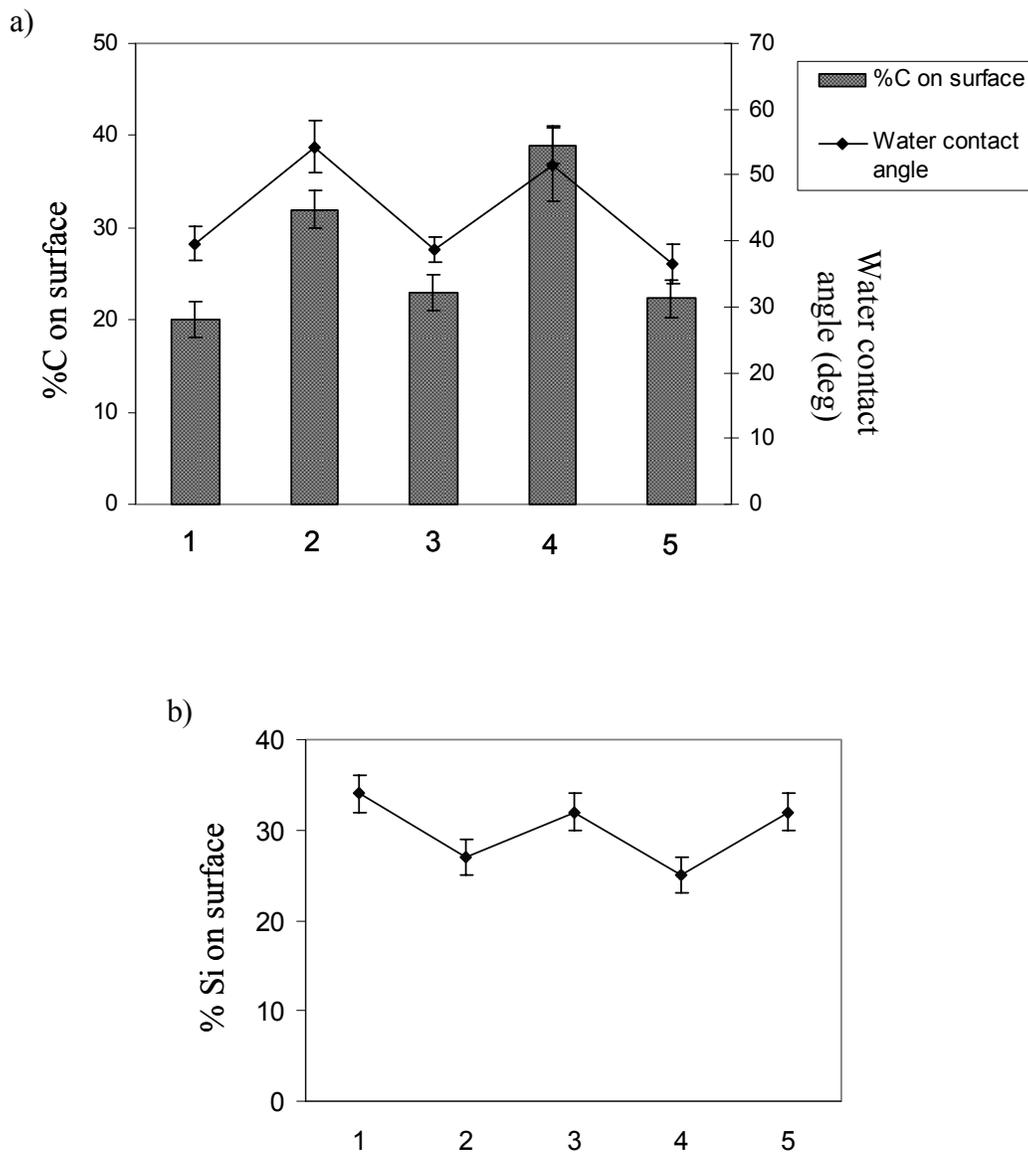


Figure 5-7: (a) XPS atomic %C and water contact angles and (b) XPS atomic %Si on silicon/SiO₂ surfaces after (1) ADPTES/MPTES modification, (2) PS-thymine treatment/THF rinse, (3) first DMSO rinse, (4) second PS-thymine treatment/THF rinse, (5) second DMSO rinse.

5.5 Conclusions

A novel adenine-derivatized triethoxysilane (ADPTES) was successfully used to modify a silicon/SiO₂ surface with adenine groups, and a thymine-functionalized PS was applied to adenine-modified surfaces from solution to investigate the capability of surface adenine groups to recognize and bind to thymine end-capped PS. Exclusive ADPTES-modification of the surface resulted in very poor recognition of the complementary PS-thymine presumably due to steric hindrance and self-association on the surface. Silicon/SiO₂ surfaces treated with a mixture of ADPTES and a 3-mercaptopropyltriethoxysilane (MPTES) diluent, however, exhibited a high affinity for the PS-thymine, while neat MPTES modification did not lead to any recognition. Absence of non-specific polymer adsorption on ADPTES/MPTES coated surfaces was further confirmed using a weakly hydrogen bonding PS-OH, which showed insignificant attachment to surfaces that were modified with the mixture. The hydrogen bonding between the complementary adenine and thymine groups were stable in THF but disrupted in DMSO. Water contact angle measurements and XPS analysis demonstrated reversible association between the PS-thymine and the surface adenine groups based on solvent wash.

5.6 Acknowledgements

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CHAPTER 6: Hydrogen Bonding between Adenine-modified Surfaces and Terminal Thymine-functionalized Polystyrene: Influence of Surface Adenine Concentration on Polymer Recognition

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Viswanathan, K.; Ward, T. C.; Long, T. E. "Hydrogen Bonding between Adenine-modified Surfaces and Terminal Thymine-functionalized Polystyrene: Influence of Surface Adenine Concentration on Polymer Recognition." Unpublished work copyright (2006) American Chemical Society.

6.1 Abstract

The influence of surface adenine concentration on the adhesion of terminal thymine-functionalized polystyrene (PS-thymine) to a silicon/SiO₂ surface that was modified with adenine-functionalized triethoxysilane (ADPTES) was investigated. The surface adenine concentration was systematically varied via co-deposition of a non-hydrogen bonding diluent. Two different silanes, i.e. 2-diphenylphosphinoethyltriethoxysilane (DPPETES) and 3-mercaptopropyltriethoxysilane (MPTES), were used as the diluents. The compositions of the silicon/SiO₂ surfaces modified with different ratios of ADPTES to DPPETES were determined using XPS and agreed well with the ADPTES to DPPETES molar ratios in solution. XPS and water contact angle measurements revealed that modification of surfaces exclusively with the diluents did not result in significant PS-thymine attachment. However, at low surface adenine concentrations, PS-thymine attachment increased with adenine concentration, reached a maximum. At higher surface adenine concentrations, PS-thymine attachment decreased with increasing adenine concentration. A similar trend was observed for surfaces that were modified with a mixture of ADPTES and MPTES. PS-thymine attachment to silicon/SiO₂ surfaces modified with a 1:2 ratio of ADPTES to DPPETES

was insensitive to THF rinsing, however, the PS-thymine was completely removed from the adenine-modified surface upon rinsing with the more polar DMSO.

6.2 Introduction

Molecular recognition sites on solid surfaces provide a platform for tuning the chemical and physical properties of a surface in a reversible and “on-demand” fashion. In addition, molecular recognition sites on surfaces enable the preparation of functional surfaces for a range of emerging applications.^{434, 435, 436} Thus, modified surfaces that contained a variety of molecular recognition groups were obtained using the well established functionalized thiols and alkoxy- or chlorosilane self-assembled monolayers (SAM).^{437, 438}

Mixed monolayers are widely used to obtain surfaces with a controlled concentration of a particular functionality via either co-deposition of an inert non-functional diluent or mixing of functionalities in a tailored proportion.⁴³⁹ Such mixed monolayers are obtained using competitive chemisorption, successive chemisorption, or Langmuir-Blodgett techniques.^{440, 441, 442, 443, 444} Earlier studies have shown that dilution

⁴³⁴ Mbindyo, J. K. N.; Reiss, B. D.; Martin, B. R.; Keating, C. D.; Natan, M. J.; Mallouk, T. E. "DNA Directed Assembly of Gold Nanoparticles on Complementary Surfaces." *Adv. Mater.* **2001**, 13, 249-254.

⁴³⁵ Cui, Y.; Wei, Q. Q.; Park, H. K.; Leiber, C. M. "Nanowire Nanosensors for Highly Sensitive and Selective Detection of Biological and Chemical Species." *Science* **2001**, 293, 1289-1292.

⁴³⁶ Endo, H.; Hirabayashi, T. D.; Morokoshi, S.; Ide, M. G.; Kitano, H. "Orientational Effect of Surface-Confined Cyclodextrin on the Inclusion of Bisphenols." *Langmuir* **2005**, 21, 1314-1321.

⁴³⁷ Bain, C. D.; Evall, J.; Whitesides, G. M. "Formation of Monolayers by the Coadsorption of Thiols on Gold: Variation in the Head Group, Tail Group, and Solvent." *J. Am. Chem. Soc.* **1989**, 111, 7155-7164.

⁴³⁸ Ulman, A., "An Introduction to Ultrathin Organic Films." Academic Press: Boston, **1991**.

⁴³⁹ Fadeev, A. Y.; McCarthy, T. J. "Binary Monolayer Mixtures: Modification of Nanopores in Silicon-Supported Tris(Trimethylsiloxy)Silyl Monolayers." *Langmuir* **1999**, 15, 7238-7243.

⁴⁴⁰ Wirth, M. J.; Fatunmbi, H. O. "Horizontal Polymerization of Mixed Trifunctional Silanes on Silica: A Potential Chromatographic Stationary Phase." *Anal. Chem.* **1992**, 64, 2783-2786.

⁴⁴¹ Offord, D. A.; Griffin, J. H. "Kinetic Control in the Formation of Self-Assembled Mixed Monolayers on Planar Silica Substrates." *Langmuir* **1993**, 9, 3015-3025.

⁴⁴² Mathauer, K.; Frank, C. W. "Binary Self-Assembled Monolayers as Prepared by Successive Adsorption of Alkyltrichlorosilanes." *Langmuir* **1993**, 9, 3446-3451.

of the molecular recognition groups leads to better recognition in the case of biotin-streptavidin, enzyme-substrate, and antibody-antigen interactions.^{445, 446}

A few reports in the literature have investigated the influence of the surface concentration of proteins and carbohydrates and their association with complementary groups in solution. Knoll and coworkers studied the influence of biotin mole fraction (χ_b) on the assembly of successive layers of proteins and antibodies in mixed SAM. Biotin concentration was systematically varied and surface plasmon resonance (SPR) spectroscopy was used to characterize the adsorption of successive layers of proteins.⁴⁴⁷ Streptavidin, which was deposited as the second layer, showed maximum adsorption at a biotin mole fraction (χ_b) of 0.1. Adsorption decreased with a further increase in χ_b due to steric hindrance. A similar trend was observed for the successive layers of antibodies and proteins that were deposited on the biotin bound streptavidin. In a similar study, Stayton *et al.* investigated the influence of biotinylated SAM structure and surface concentration on streptavidin binding using SPR.⁴⁴⁸ An ordered SAM that allowed close packing of the biotin groups led to very low streptavidin binding, while a more disordered SAM showed higher fractions of bound streptavidin. However, the interaction in the disordered SAM was irreversible due to unfavorable surface bound protein-protein interactions.

⁴⁴³ Huang, J. Y.; Song, K. J.; Lagoutchev, A.; Yang, P. K.; Chuang, T. J. "Molecular Conformation and Nanomechanics of Self-Assembled Alkylsiloxane Monolayers." *Langmuir* **1997**, 13, 58-64.

⁴⁴⁴ Ge, S.; Takahara, A.; Kajiyama, K. "Phase Separated Morphology of an Immobilized Organosilane Monolayer Studied by a Scanning Probe Microscope." *Langmuir* **1995**, 11, 1341-1346.

⁴⁴⁵ Häussling, L.; Ringsdorf, H.; Schmitt, F.-J.; Knoll, W. "Biotin-Functionalized Self-Assembled Monolayers on Gold: Surface Plasmon Optical Studies of Specific Recognition Reactions." *Langmuir* **1991**, 17, 1837-1840.

⁴⁴⁶ Wang, M.; Liechti, K. M.; Wang, Q.; White, J. M. "Self-Assembled Silane Monolayers: Fabrication with Nanoscale Uniformity." *Langmuir* **2005**, 21, 1848-1857.

⁴⁴⁷ Spinke, J.; Liley, M.; Guder, H.-J.; Angermaier, L.; Knoll, W. "Molecular Recognition at Self-Assembled Monolayers: The Construction of Multicomponent Multilayers." *Langmuir* **1993**, 9, 1821-1825.

⁴⁴⁸ Pérez-Luna, V. H.; O'Brien, M. J.; Opperman, K. A.; Hampton, P. D.; López, G. P.; Klumb, L. A.; Stayton, P. S. "Molecular Recognition between Genetically Engineered Streptavidin and Surface-Bound Biotin." *J. Am. Chem. Soc.* **1999**, 121, 6469-6478.

Reversible association was possible with the ordered SAM, and the biotin mol fraction that corresponded to maximum recognition was ~0.15. Stayton and coworkers also found that the recognition between biotinylated SAMs that were diluted with either methyl- or oligoethylene-terminated thiols showed a broad maximum as the biotin surface coverage was increased before slowly decreasing at high biotin surface coverage.⁴⁴⁹

Whitesides and coworkers studied the reversible adsorption of anhydrase enzyme to alkanethiolate mixed SAM with varying concentrations of benzenesulfonamide, and exclusive presence of benzenesulfonamide on the gold surface led to irreversible association between the surface and the enzyme.⁴⁵⁰ Houseman and Mrksich investigated the influence of gold surface immobilized N-acetyl glucosamine (GLcNAc) density on enzymatic glycosylation using radio labeled galactose. Maximum galactose incorporation occurred at a 0.7 GLcNAc mole fraction; however, the reaction yield decreased significantly at higher concentrations.⁴⁵¹ Chi et al. studied the influence of precursor oligonucleotide surface concentration on the enzymatic polymerization of DNA bases.⁴⁵² The polymerization proceeded to a significant extent only on surfaces modified with a mixed SAM, which prevented steric crowding around the precursor oligonucleotides and enhanced the polymerization rate of the monomers. Frederix and coworkers studied the performance of a mixed SAM comprising 16-mercapto-1-

⁴⁴⁹ Nelson, K. E.; Gamble, L.; Jung, L. S.; Boeckl, M. S.; Naeemi, E.; Golledge, S. L.; Sasaki, T.; Castner, D. G.; Campbell, C. T.; Stayton, P. S. "Surface Characterization of Mixed Self-Assembled Monolayers Designed for Streptavidin Immobilization." *Langmuir* **2001**, *17*, 2807-2816.

⁴⁵⁰ Mrksich, M.; Grunwell, J. R.; Whitesides, G. M. "Biospecific Adsorption of Carbonic Anhydrase to Self-Assembled Monolayers of Alkanethiolates That Present Benzenesulfonamide Groups on Gold." *J. Am. Chem. Soc.* **1995**, *117*, 12009-12010.

⁴⁵¹ Houseman, B. T.; Mrksich, M. "The Role of Ligand Density in the Enzymatic Glycosylation of Carbohydrates Presented on Self-Assembled Monolayers of Alkanethiolates on Gold." *Angew. Chem. Int. Ed. Eng.* **1999**, *38*, 782-785.

⁴⁵² Chi, Y. S.; Jung, Y. H.; Choi, I. S.; Kim, Y.-G. "Surface-Initiated Growth of Poly D(A-T) by *Taq* DNA Polymerase." *Langmuir* **2005**, *21*, 4669-4673.

hexadecanoic acid (16-MHD) and 11-mercapto-1-undecanol (11-MUOH) as an antibody-antigen affinity biosensor. The amounts of covalently bound antibody and its corresponding antigen recognition reached a maximum at a 5 mol% concentration of surface acid groups.⁴⁵³

Solid surfaces were also modified with groups exhibiting non-covalent yet specific interactions such as selective inclusional complexation and hydrogen bonding interactions to assemble small molecules on gold/silica surfaces.^{454, 455, 456, 457, 458} Several groups have also reported the assembly of polymers on surfaces through hydrogen bonding interactions.^{459, 460, 461, 462} In all of these studies, the surface concentration of the hydrogen bonding groups was diluted with non-functional diluents in order to increase the distance between the hydrogen bonding groups on the solid surface and thereby enhance the association between the surface bound recognition groups and the

⁴⁵³ Frederix, F.; Bonroy, K.; Laureyn, W.; Reekmans, G.; Campitelli, A.; Dehaen, W.; Maes, G. "Enhanced Performance of an Affinity Biosensor Interface Based on Mixed Self-Assembled Monolayers of Thiols on Gold." *Langmuir* **2003**, *19*, 4351-4357.

⁴⁵⁴ Maeda, Y.; Kitano, H. "Inclusional Complexation by Cyclodextrins at the Surface of Silver as Evidenced by Surface-Enhanced Resonance Raman Spectroscopy." *J. Phys. Chem.* **1995**, *99*, 487-488.

⁴⁵⁵ Sun, L.; Kepley, L. J.; Crooks, R. M. "Molecular Interactions between Organized, Surface-Confined Monolayers and Vapor-Phase Probe Molecules: Hydrogen-Bonding Interactions." *Langmuir* **1992**, *8*, 2101-2103.

⁴⁵⁶ Krishnamohan Sharma, C. V.; Broker, G. A.; Szulczewski, G. J.; Rogers, R. D. "Self-Assembly of Freebase- and Metallated-Tetrapyrrolylporphyrins to Modified Gold Surfaces." *Chem. Commun.* **2000**, 1023-1024.

⁴⁵⁷ Garcia-Lopez, J. J.; Zapotoczny, S.; Timmerman, P.; van Veggel, F. C. J. M.; Vansco, G. J.; Crego-Calama, M.; Reinhoudt, D. N. "Growth of Individual Hydrogen-Bonded Nanostructures on Gold Monolayers." *Chem. Commun.* **2003**, 352-353.

⁴⁵⁸ Zou, S.; Zhang, Z.; Forch, R.; Knoll, W.; Schönherr, H.; Vansco, G. J. "Tunable Complex Stability in Surface Molecular Recognition Mediated by Self-Complementary Quadruple Hydrogen Bonds." *Langmuir* **2003**, *19*, 8618-8621.

⁴⁵⁹ Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; Albrecht, T. T.; Russell, T. P.; Rotello, V. M. "Self-Assembly of Nanoparticles into Structured Spherical and Network Aggregates." *Nature* **2000**, *404*, 746-748.

⁴⁶⁰ Norsten, T. B.; Jeoung, E.; Thibault, R. J.; Rotello, V. M. "Specific Hydrogen-Bond-Mediated Recognition and Modification of Surfaces Using Complementary Functionalized Polymers." *Langmuir* **2003**, *19*, 7089-7093.

⁴⁶¹ Boal, A. K.; Gray, M.; Ilhan, F.; Clavier, G. M.; Kapitzky, L.; Rotello, V. M. "Bricks and Mortar Self-Assembly of Nanoparticles." *Tetrahedron* **2002**, *58*, 765-770.

⁴⁶² Sanyal, A.; Norsten, T. B.; Oktay, U.; Rotello, V. M. "Adsorption/Desorption of Mono- and Diblock Copolymers on Surfaces Using Specific Hydrogen Bonding Interactions." *Langmuir* **2004**, *20*, 5958-5964.

complementary groups in solution. However, a systematic investigation of the diluent concentration on the extent of hydrogen bonding mediated recognition was not reported in these earlier studies.

This chapter will describe a systematic investigation of the influence of surface adenine concentration on PS-thymine recognition. MPTES and DPPETES were used as diluents in order to determine the influence of diluent structure on the recognition process. DPPETES served as an excellent XPS tag due to the presence of phosphorus and was used to correlate the silane composition in solution with the modified surface composition. XPS and water contact angle measurements were used to investigate the attachment of PS-thymine to the homo/mixed SAM modified surfaces.

6.3 Experimental

6.3.1 Materials

Methanol (EMD Chemicals), dichloromethane (EMD Chemicals), tetrahydrofuran (THF, EMD Chemicals), dimethylsulfoxide (DMSO, EMD Chemicals), conc. H_2SO_4 (VWR International), NH_4OH (30%, VWR International), H_2O_2 (30%, EMD Chemicals), 3-mercaptopropyltriethoxysilane (MPTES, 95%, Gelest, Inc.), and 2-diphenylphosphinoethyltriethoxysilane (DPPETES, Gelest, Inc.) were used as received. CHCl_3 (EMD Chemicals) for surface modification was dried over CaH_2 and distilled immediately prior to use. Millipore milli-Q water was used for surface cleaning. Silicon wafers were a generous gift from the Hewlett-Packard Company.

6.3.2 Surface Characterization

The modified silicon/ SiO_2 surfaces were sonicated in a Branson 1200 ultrasonic generator for 1 h. Static water contact angles were measured in the sessile drop mode

using a FTA-200 contact angle goniometer with a syringe-driven droplet. The values were measured 30 sec after dispensing the drop to obtain equilibrium values. Contact angles were measured at 4-5 different spots on each surface. XPS data was obtained at a 30° take-off angle on a Perkin Elmer Model 5400 instrument fitted with a Mg K α X-ray source (1253.8 eV). The anode was operated at 250 W. The 285 eV C1s photoelectron peak was used as an internal XPS standard.

6.3.3 Substrate Treatment

Silicon wafers were cut into 1 cm² samples and sonicated for 5 min in dichloromethane and 5 min in methanol. The wafers were blown with nitrogen and cleaned with freshly prepared Piranha solution (conc.H₂SO₄:30% H₂O₂; v/v: 70/30) at 90 °C for 1 h, rinsed with milli-Q water, and cleaned with a 30% NH₃:30% H₂O₂:H₂O (v/v/v: 1/1/5) at 60 °C for 15 min. The wafers were then rinsed with milli-Q water several times, blown dry with nitrogen, and immediately immersed in the alkoxy silane solution and allowed to stir for a given time. (*Caution: Piranha solution reacts violently with many organic materials and should be handled with care.*)

6.3.4 Covalent Modification of Silicon/SiO₂ Surfaces

Freshly cleaned silicon wafers were modified with a 5 mM solution of various ratios of ADPTES/MPTES or ADPTES/DPPETES in CHCl₃ for 6 h and subsequently sonicated 3 times in CHCl₃ to remove any physisorbed material. Surface modification exclusively with MPTES, DPPETES, and ADPTES was performed under similar conditions. Surfaces were characterized after each modification step using XPS and water contact angle measurements.

6.3.5 PS-thymine Treatment

The synthesis of PS-thymine was described earlier in detail.⁴⁶³ The alkoxy silane-modified surfaces were immersed in a 5 mM solution of PS-thymine ($M_n = 2,010$ g/mol) in CHCl_3 for 24 h and exhaustively rinsed with both CHCl_3 and THF.

6.4 Results and Discussion

In the previous chapter, the solvato-reversible association between ADPTES coated surfaces and PS-thymine was reported. Surfaces modified exclusively with ADPTES did not show any significant PS-thymine attachment, and maximum PS-thymine recognition occurred when the surface bound ADPTES groups were diluted. Dilution of the surface bound adenine groups was accomplished via competitive chemisorption of MPTES and ADPTES onto silicon/ SiO_2 surfaces (Figure 6-1).

⁴⁶³ Yamauchi, K.; Lizotte, J. R.; Long, T. E. "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002**, 35, 8745-8750.

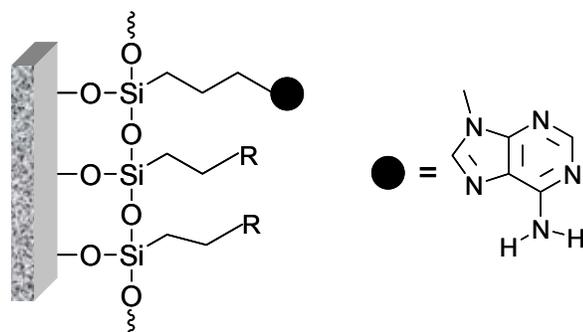


Figure 6-1: Depiction of the co-deposition of ADPTES and the diluent on a silicon/SiO₂ surface, where R is -CH₂SH in the case of MPTES and -PPh₂ in the case of DPPETES.

6.4.1 Silicon/SiO₂ Surface Modification with ADPTES/DPPTES Mixtures

The relative ratio of ADPTES to MPPTES in the modifying solution was 1:3, and XPS analysis was used to determine the relative ratios of ADPTES to MPPTES on the mixed SAM modified silicon/SiO₂ surfaces. The predominant S2p peak was centered at 168.0 eV corresponding to oxidized sulfur species, indicating that most of the mercapto groups were oxidized under the experimental conditions (Figure 6-2b).⁴⁶⁴ This peak overlapped with the S2p photoelectron peak from residual sulfuric acid that was used in the cleaning procedure (Figure 6-2a). Thus, estimating the actual concentration of mercapto sites on the surface proved difficult. Therefore, in order to assess the concentration of ADPTES/diluent on the surface, phosphorus-containing DPPETES was used as an alternative diluent. Since the P2p peak does not overlap with any known contamination, DPPETES served as a good XPS tag.

⁴⁶⁴ Viswanathan, K.; Ozhalici, H.; Elkins, C. L.; Heisey, C.; Ward, T. C.; Long, T. E. "Multiple Hydrogen Bonding in Reversible Polymer Surface Adhesion." *Langmuir* **2006**, 22, 1099-1105.

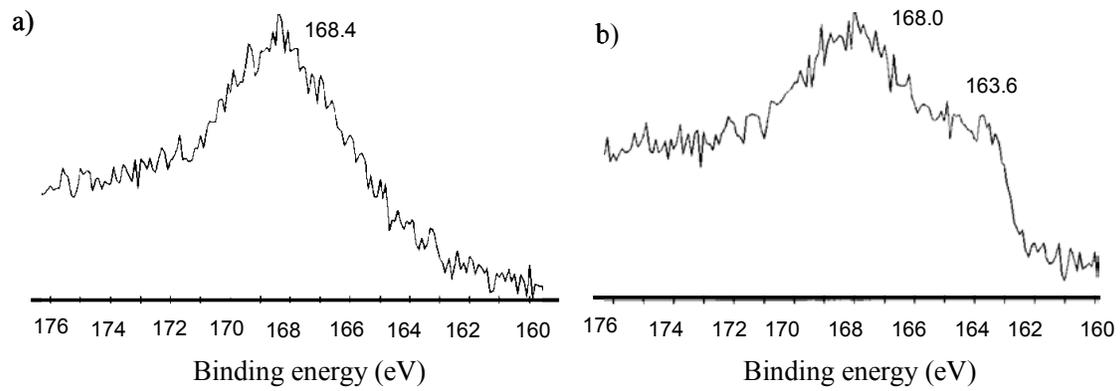


Figure 6-2: XPS wide scan spectra of S_{2p} region on a) clean silicon/SiO₂ surface, and b) MPTES-modified silicon/SiO₂ surface.

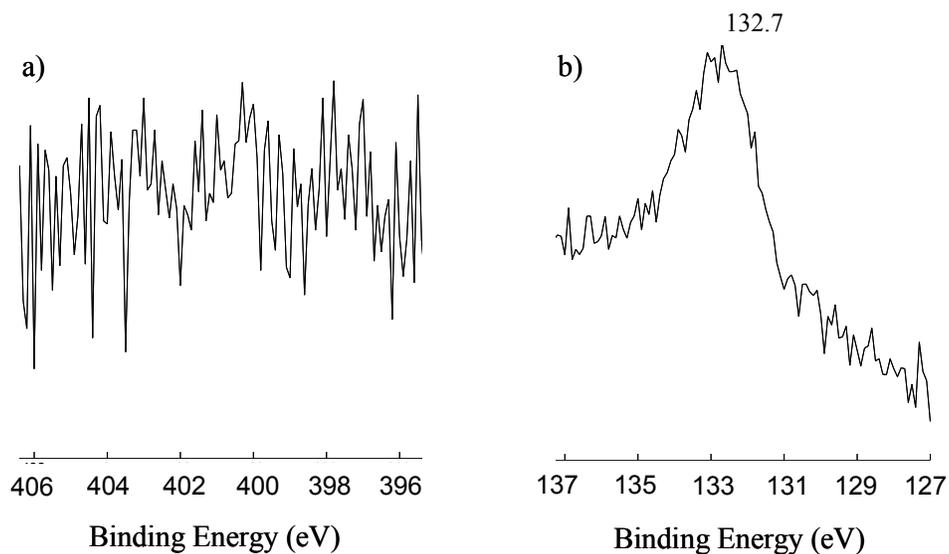
While XPS analysis of a surface modified exclusively with DPPETES showed a P2p peak at 132.7 eV (Figure 6-3b) and no N1s peak (Figure 6-3a), XPS analysis of a surface modified with a 1:5 mixture of ADPTES to DPPETES showed a P2p peak at 132.8 eV due to the diphenyl phosphine groups (Figure 6-3d) and a N1s peak at 399.9 eV due to the adenine groups (Figure 6-3c), which is consistent with earlier literature on surfaces modified with DNA bases.^{465, 466} Similarly, the P2p photoelectron peak observed at 132.8 eV binding energy is consistent with the presence of P bound to organic groups.⁴⁶⁷ The presence of both P and N confirmed the co-deposition of ADPTES and DPPETES on the surface. Thus, the XPS N/P ratio was used to determine the relative concentrations of ADPTES to DPPETES on the modified surface.

⁴⁶⁵ Herne, T. M.; Tarlov, M. J. "Characterization of DNA Probes Immobilized on Gold Surfaces." *J. Am. Chem. Soc.* **1997**, 119, 8916-8920.

⁴⁶⁶ Wang, J.; Rivas, G.; Jiang, M.; Zhang, X. "Electrochemically Induced Release of DNA from Gold Ultramicroelectrodes." *Langmuir* **1999**, 15, 6541-6545.

⁴⁶⁷ Mould, J. F.; Stickle, W. F.; Sobol, P. E.; Bomben, K. D., "Handbook of X-Ray Photoelectron Spectroscopy." Physical Electronics, Inc.: Minnesota, **1995**.

DPPETES modified silicon/SiO₂ surfaces



1:5 ADPTES/DPPETES modified silicon/SiO₂ surfaces

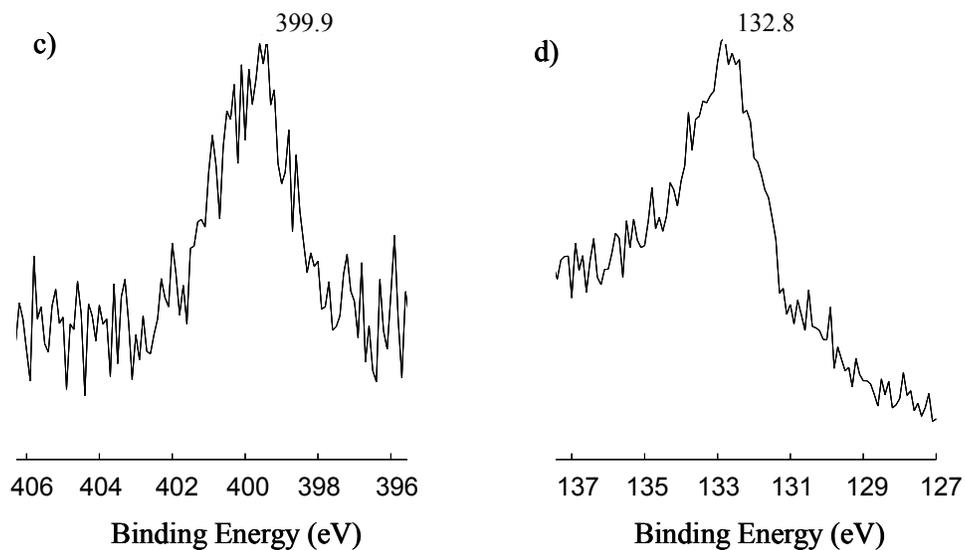


Figure 6-3: XPS wide scan spectra of a) & c) N1s region, and b) & d) P2p region on modified silicon/SiO₂ surfaces.

Silicon/SiO₂ surfaces modified with various molar ratios of ADPTES and DPPETES from solution were analyzed using XPS to determine the respective surface compositions (Tables 6-1 and 6-2). The atomic compositions of silicon/SiO₂ surfaces modified with various ratios of ADPTES and DPPETES are shown in Table 6-1. The molar ratio of ADPTES/DPPETES groups and the mol% adenine groups on the modified surfaces were calculated based on the XPS N/P ratio (Table 6-2). One ADPTES contributes 6 N atoms and one DPPETES contains 1 P atom. Thus, when deposited in a 1:3 ADPTES:DPPETES molar ratio, and assuming equivalent surface and solution composition, a N/P ratio of 2:1 is expected. Indeed as seen in Table 6-2, the XPS N/P ratio was also 2:1, indicating the presence of three DPPETES molecules for every one ADPTES molecule corresponding to 25 mol% adenine. The good agreement between the solution and surface composition indicated the absence of preferential chemisorption of a silane over the other.^{468, 469} The only anomaly was observed for the 1:1 mixture, where an excess of DPPETES was deposited on the surface. Excess deposition of one component during competitive adsorption of binary mixtures of silanes is known in the literature.^{470, 471}

In order to estimate the distance between the surface attached adenine groups, an average of 5 hydroxyl groups/nm² was assumed, which gives an average distance of

⁴⁶⁸ Wirth, M. J.; Fatunmbi, H. O. "Horizontal Polymerization of Mixed Trifunctional Silanes on Silica: A Potential Chromatographic Stationary Phase." *Anal. Chem.* **1992**, *64*, 2783-2786.

⁴⁶⁹ Mathauer, K.; Frank, C. W. "Binary Self-Assembled Monolayers as Prepared by Successive Adsorption of Alkyltrichlorosilanes." *Langmuir* **1993**, *9*, 3446-3451.

⁴⁷⁰ Offord, D. A.; Griffin, J. H. "Kinetic Control in the Formation of Self-Assembled Mixed Monolayers on Planar Silica Substrates." *Langmuir* **1993**, *9*, 3015-3025.

⁴⁷¹ Heise, A.; Stamm, M.; Rauscher, M.; Duschner, H.; Menzel, H. "Mixed Silane Self Assembled Monolayers and Their in Situ Modification." *Thin Solid Films* **1998**, *327-329*, 199-203.

~0.44 nm between the hydroxyl groups.⁴⁷² If each silane molecule attaches through three hydroxyl groups to the surface, the distance between the head groups of the surface anchored silane molecules will be approximately 1.32 nm. The average distance between the adenine groups will then be approximately 2.46 nm, 5.28 nm, and 7.98 nm for ADPTES/DPPETES ratios of 1:1, 1:3, and 1:5, respectively.

Table 6-1: XPS atomic composition of silicon/SiO₂ surfaces modified with various ratios of ADPTES and DPPETES from solution

Molar ratio of ADPTES: DPPETES in solution	Atomic composition (%) ^a				
	C1s	O1s	Si2p	N1s	P2p
1:0	28	32	31	9	0
1:1	30	32	30	6	2
1:3	27	34	33	4	2
1:5	32	33.5	29	3	2.5
0:1	32	34	31	-	3

^aXPS conditions: Mg anode, take-off angle = 30°.

⁴⁷² McCafferty, E.; Wightman, J. P. "Determination of the Concentration of Surface Hydroxyl Groups on Metal Oxide Films by a Quantitative XPS Method." *Surf. Interface Anal.* **1998**, 26, 549-564.

Table 6-2: Correlation between solution and surface compositions determined using XPS N/P and C/N ratios for silicon/SiO₂ surfaces modified with various ratios of ADPTES/DPPETES from solution

Molar ratio of ADPTES: DPPETES in solution	Surface composition ^a					
	N/P	Molar ratio of ADPTES: DPPETES ^a	Adenine ^b (mol%)	C/N	Molar ratio of ADPTES: DPPETES ^b	Adenine ^c (mol%)
1:1	3	1:2	33	5	1:1.5	40
1:3	2	1:3	25	6.8	1:2.3	30
1:5	1.2	1:5	17	10.7	1:4	20

^aXPS conditions: Mg anode, take-off angle = 30°. ^bcalculated based on XPS N/P ratio. ^ccalculated based on XPS C/N ratio.

The XPS C/N ratio was similarly used to determine the mol% adenine on the modified surfaces. Assuming complete hydrolysis of the triethoxysilyl groups, one ADPTES contributes 9 C atoms and one DPPETES contributes 11 C atoms. Thus, when deposited in a 1:3 ADPTES:DPPETES molar ratio, a C/N ratio of 8.5:1 is expected. As seen in Table 6-2, the observed C/N ratio is 6.8, which corresponds to 31 mol% adenine on the surface. It was observed that the mol% adenine calculated using C/N ratio was higher than the mol% determined using N/P ratio. This result is reasonable considering that the XPS atomic composition for DPPETES modified surfaces gave a C/P ratio of 10, which is lower than the theoretical value of 14 that was used for the calculation of mol% adenine. Assuming every DPPETES contributes only 10 C atoms, the surface composition based on XPS C/N ratio gives 2.8 DPPETES molecules for every one ADPTES molecule, which is in agreement with the 1:3 ADPTES/DPPETES ratio from solution. Thus, both N/P and C/N ratios confirm that an increase in the ADPTES ratio in solution results in an increase in the mol% adenine that is deposited on the surface.

6.4.2 Association between ADPTES/DPPETES-modified Silicon/SiO₂ Surfaces and PS-thymine

After confirming the random nature of the silane deposition, the influence of surface adenine concentration on the extent of PS-thymine recognition was investigated. Silicon/SiO₂ surfaces that were modified with mixtures containing different ratios of ADPTES to DPPETES were further modified with PS-thymine. Following PS-thymine modification, the surfaces were exhaustively rinsed with CHCl₃/THF, which is a good solvent mixture for PS-thymine prior to XPS and water contact angle measurements. Shown in Figure 6-4 is the %C on surface as determined using XPS and water contact

angle results on surfaces that were modified with various ratios of ADPTES/DPPETES before and after PS-thymine modification.

A clear trend was observed between the mol% adenine deposited on the surface and the extent of PS-thymine attachment as shown in Figure 6-4. A surface modified exclusively with DPPETES showed insignificant polymer attachment. The surface treated with the 17 mol% adenine solution did not show a discernible difference in XPS %C; however, a small increase in water contact angle was observed, which may indicate a low level of PS-thymine attachment. The low extent of PS-thymine attachment was attributed to the low surface adenine concentration. When the surface adenine concentration was increased to 25 mol%, an increased XPS %C and water contact angle suggested an increase in PS-thymine attachment. The hydrogen bonding interactions of the adenine and thymine groups are complementary as shown previously, and PS-OH with only moderate hydrogen bonding capability did not associate to the surface adenine groups.⁴⁷³ As the adenine concentration on the surface was increased to 50 mol% , PS-thymine attachment decreased as a result of steric crowding around the molecular recognition groups, which is also consistent with earlier literature studies.^{474, 475} Finally, modification of surfaces exclusively with ADPTES resulted in negligible polymer attachment in a consistent fashion to studies reported by other groups.⁴⁷⁶

⁴⁷³ Viswanathan, K.; Ozhalici, H.; Elkins, C. L.; Heisey, C.; Ward, T. C.; Long, T. E. "Multiple Hydrogen Bonding in Reversible Polymer Surface Adhesion." *Langmuir* **2006**, *22*, 1099-1105.

⁴⁷⁴ Spinke, J.; Liley, M.; Guder, H.-J.; Angermaier, L.; Knoll, W. "Molecular Recognition at Self-Assembled Monolayers: The Construction of Multicomponent Multilayers." *Langmuir* **1993**, *9*, 1821-1825.

⁴⁷⁵ Pérez-Luna, V. H.; O'Brien, M. J.; Opperman, K. A.; Hampton, P. D.; López, G. P.; Klumb, L. A.; Stayton, P. S. "Molecular Recognition between Genetically Engineered Streptavidin and Surface-Bound Biotin." *J. Am. Chem. Soc.* **1999**, *121*, 6469-6478.

⁴⁷⁶ Chi, Y. S.; Jung, Y. H.; Choi, I. S.; Kim, Y.-G. "Surface-Initiated Growth of Poly D(A-T) by *Taq* DNA Polymerase." *Langmuir* **2005**, *21*, 4669-4673.

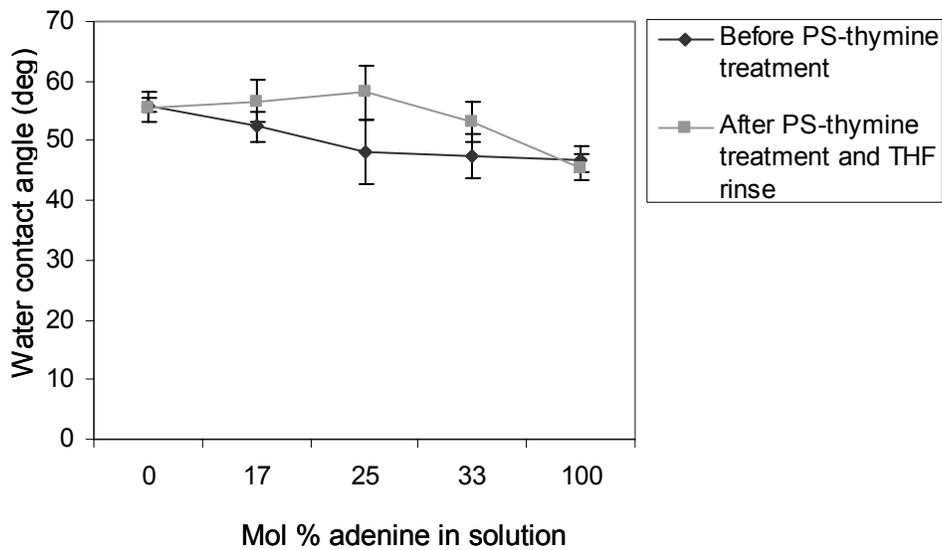
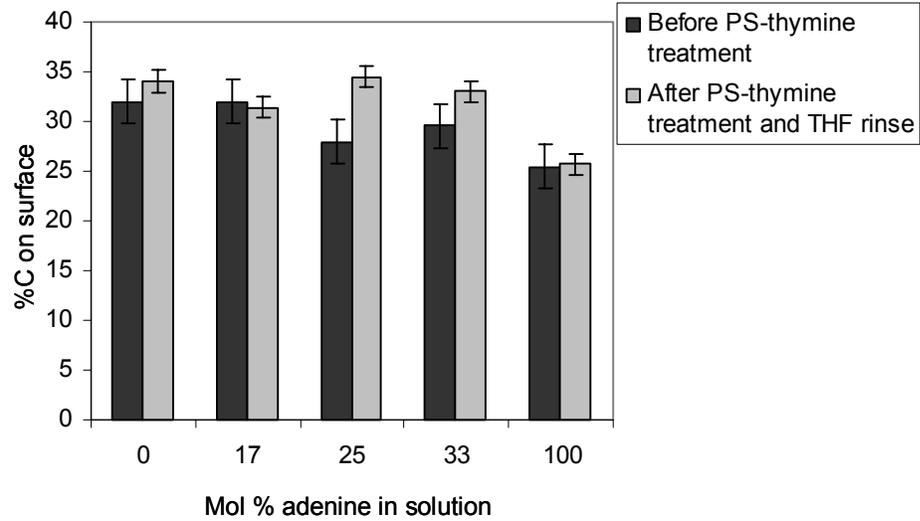


Figure 6-4: Influence of surface adenine concentration on the extent of PS-thymine recognition by silicon/SiO₂ surfaces modified with ADPTES/DPPETES mixtures, studied using XPS %C (**top**) and water contact angle (**bottom**).

The solvato-reversible nature of the association between the ADPTES/DPPETES modified surfaces and the PS-thymine was studied using water contact angle measurements in order to confirm the hydrogen bonding mediated attachment of the PS-thymine to the adenine modified surfaces. The water contact angle results on surfaces modified with a 1:2 ADPTES/DPPETES mixture are shown in Figure 6-5. The water contact angle increased moderately following PS-thymine attachment and THF rinse (b), which is in good agreement with that observed in Figure 6-4. Although water contact angle following PS-thymine attachment was not significantly higher, it was still outside the experimental error confirming that the observed increase in contact angle for water was because of PS-thymine attachment. Following a second rinse with DMSO, a solvent capable of disrupting hydrogen bonding, the water contact angle decreased (c) to a value similar to that observed on surfaces prior to PS-thymine treatment (a). This polar solvent switchable PS-thymine attachment suggested that the PS-thymine interacted with the surface bound adenine groups through hydrogen bonding.

6.4.3 PS-thymine Recognition by Silicon/SiO₂ Surfaces Modified with Various Mixtures of ADPTES/MP TES

Silicon/SiO₂ surfaces were also modified with a mixture comprising various ratios of ADPTES and a second diluent MP TES to determine the influence of surface adenine concentration and diluent structure on the extent of PS-thymine attachment, and XPS and water contact angle results are summarized in Figure 6-6. As noted earlier, due to the susceptibility of the mercapto groups towards oxidation, it was not possible to quantify the surface composition of this mixture. Therefore, the XPS %C and water contact angle values measured on the modified surfaces before and after PS-thymine attachment, as shown in Figure 6-6, were plotted against the theoretical adenine composition in solution

assuming similar solution and surface compositions. Surfaces modified with the ADPTES/MPTES mixtures exhibited similar trends to those modified with the ADPTES/DPPETES mixtures.

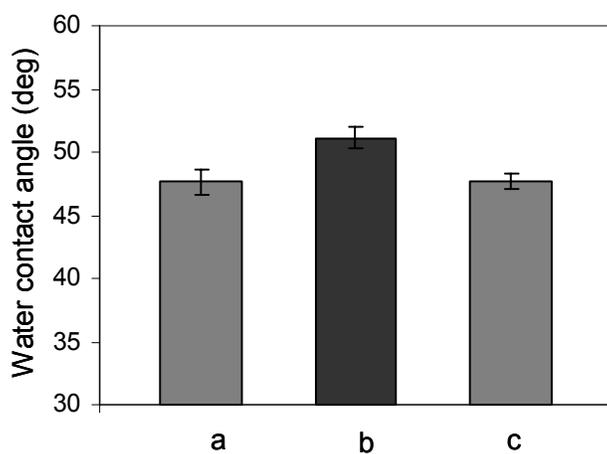


Figure 6-5: Water contact angle values on silicon/SiO₂ surfaces modified with a 1:2 mixture of ADPTES/DPPETES mixture: a) before PS-thymine treatment, b) after PS-thymine treatment and THF rinse, c) after PS-thymine treatment, THF rinse, and DMSO rinse.

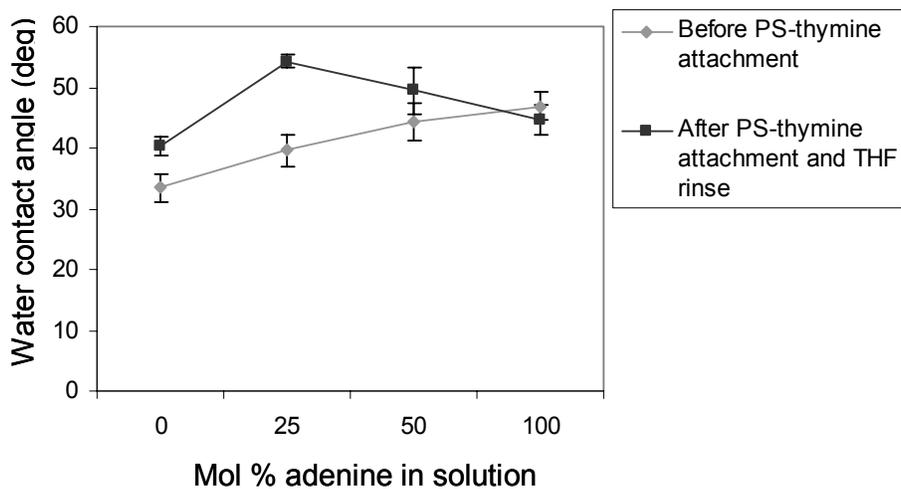
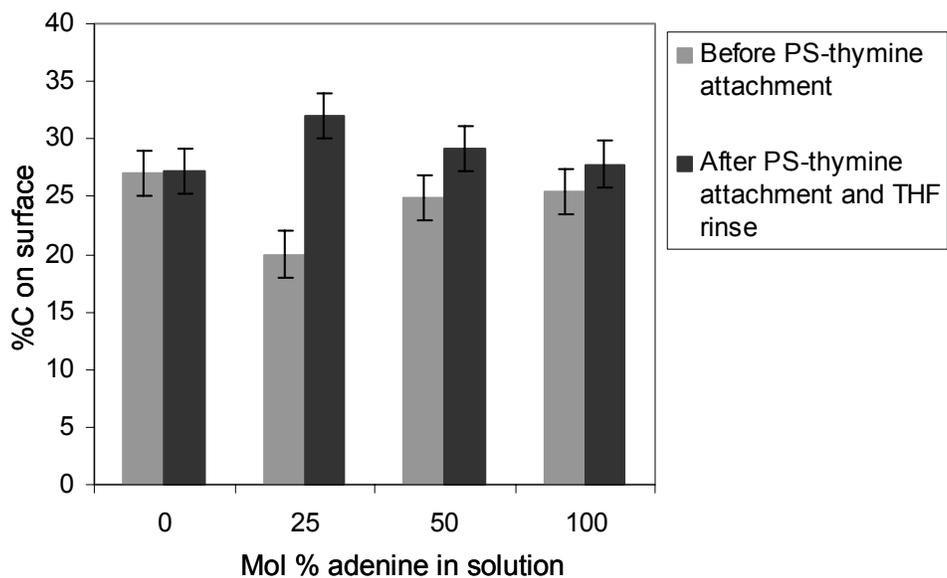


Figure 6-6: Influence of surface adenine concentration on the extent of PS-thymine recognition by silicon/SiO₂ surfaces modified with ADPTES/MP TES mixtures, studied using XPS %C (**top**) and water contact angle (**bottom**).

XPS (Figure 6-6 (top)) and water contact angle analysis (Figure 6-6 (bottom)) indicated that maximum PS-thymine association was observed for surfaces modified with 25 mol% adenine and decreased with further increase in adenine concentration. The exclusive presence of either MPTES or ADPTES on the surface led to negligible PS-thymine attachment. The amount of PS-thymine attached to a 1:3 ADPTES/MPTES (25 mol% adenine) modified surfaces was significantly higher than that observed in the case of surfaces comprising 1:3 ADPTES/DPPETES (25 mol% adenine). It is known that monolayer structure influences the molecular recognition process at surfaces and spatial constraint near the receptor leads to decreased recognition.⁴⁷⁷ Thus, based on previously reported studies, we believe that when MPTES was used as the diluent, the small mercapto head group did not create spatial constraint near the adenine groups. However, when DPPETES was used as the diluent, the bulky diphenyl phosphine group of DPPETES hindered recognition around the adenine groups leading to lower levels of PS-thymine attachment.

6.5 Conclusions

Silicon/SiO₂ surfaces were modified with various mixtures of adenine-triethoxysilane (ADPTES) and 2-diphenylphosphinoethyltriethoxysilane (DPPETES). XPS N/P ratios indicated no preferential deposition, and the ADPTES/DPPETES compositions of the modified surfaces were similar to the solution compositions. The exclusive presence of either the DPPETES diluent or the ADPTES did not lead to significant PS-thymine attachment. Also low or high concentrations of surface ADPTES

⁴⁷⁷ Motesharei, K.; Myles, D. C. "Molecular Recognition on Functionalized Self-Assembled Monolayers of Alkanethiols on Gold." *J. Am. Chem. Soc.* **1998**, 120, 7328-7336.

resulted in only moderate PS-thymine attachment. However, modification with 25 mol% ADPTES, led to significant PS-thymine attachment. Water contact angle analysis of surfaces that were modified with 1:2 ADPTES/DPPETES and exposed to the PS-thymine solution showed polymer attachment following THF rinse. Subsequent DMSO rinse removed the PS-thymine from the surface. This confirmed the hydrogen-bonding mediated attachment between the PS-thymine and the adenine-modified surface. Surfaces that were modified with various ratios of ADPTES and 3-mercaptopropyltriethoxysilane (MPTES) showed a similar trend to ADPTES/DPETES modified surfaces. However, a higher level of PS-thymine attachment was observed for surfaces that were modified with 1:3 ADPTES/MPTES compared to surfaces modified with 1:3 ADPTES/DPPETES, which was attributed to less spatial constraint near the surface adenine groups due to the relatively small size of the mercapto groups.

6.6 Acknowledgements

This material is based upon work supported by the U.S. Army Research Laboratory and the U.S. Army Research Office under contract/grant number DAAD19-02-1-0275 Macromolecular Architecture for Performance (MAP) MURI. The authors would also like to thank FMC Lithium Division for the donation of alkyllithium and dibutylmagnesium reagents.

CHAPTER 7: DNA Base-pair Mediated Attachment of Methacrylate Random Copolymers to Silicon/SiO₂ Surfaces

7.1 Abstract

A novel thymine containing trimethoxysilane (TTMS) was synthesized in one-step from thymine and 3-acryloxypropyltrimethoxysilane (APTMS). ¹H and ¹³C NMR spectroscopy and fast atom bombardment mass spectroscopy (FAB-MS) confirmed the chemical structure. However, ¹H NMR and ²⁹Si NMR spectroscopy indicated some extent of premature hydrolysis of the alkoxy silane derivative. Specific adhesion of adenine containing methacrylate random copolymers to thymine-functionalized silicon/SiO₂ surfaces from the melt was investigated using XPS, water contact angle measurements, and ellipsometry. The adenine containing copolymers were synthesized via conventional free radical copolymerization of 2-ethylhexyl methacrylate (EHMA) with a novel adenine-methacrylate (AIEMA) monomer. The copolymer attachment resulted in a hydrophobic surface. However, the attached copolymers were not completely removed from the surface upon polar solvent rinses. Control studies with other SAM systems containing anhydride groups indicated some extent of covalent attachment of the copolymers to the modified surfaces.

7.2 Introduction

Self-assembled polymeric films offer significant advantages compared to other conventional surface modification techniques. There are many approaches for modifying solid surfaces with polymers, including physisorption, covalent attachment, and electrostatic adsorption. Covalent grafting of polymer chains is generally preferred due

to the stability of the resultant polymer coatings.⁴⁷⁸ However, covalent modification strategies typically lead to irreversible changes on surfaces.

In recent years, reversible surface modification with polymers through non-covalent hydrogen bonding interactions has received widespread attention. The use of reversible hydrogen bonding sites on surfaces provides a platform for tuning both the chemical and physical properties of a surface in a reversible and “on-demand” fashion. For example, Rotello and co-workers used nanoparticles and polymers functionalized with complementary hydrogen bonding groups such as thymine and triazine to form extended nanoparticle aggregates.^{479, 480} The nature and degree of substitution of the hydrogen bonding groups controlled the morphology of the nanoparticle aggregates. Rotello and co-workers also demonstrated hydrogen-bond mediated attachment of diaminopyridine (DAP)-derivatized polyhedral oligomeric silsesquioxanes (POSS) to thymine-functionalized gold surfaces.⁴⁸¹ Reversible adsorption/desorption of DAP containing homopolymers and diblock copolymers to/from thymine functionalized gold surfaces was also investigated.^{482, 483} In the case of block copolymers containing hydrogen bonding groups, the functionalized block length controlled the amount of polymer adsorbed on the surface, while the chemical composition of the unfunctionalized

⁴⁷⁸ Advincula, R. C.; Brittain, W. J.; Caster, K. C.; R  he, J., "Polymer Brushes." Wiley-VCH: Weinheim, **2004**; p 483.

⁴⁷⁹ Boal, A. K.; Ilhan, F.; DeRouchey, J. E.; -Albrecht, T. T.; Russell, T. P.; Rotello, V. M. "Self-Assembly of Nanoparticles into Structured Spherical and Network Aggregates." *Nature* **2000**, 404, 746-748.

⁴⁸⁰ Boal, A. K.; Gray, M.; Ilhan, F.; Clavier, G. M.; Kapitzky, L.; Rotello, V. M. "Bricks and Mortar Self-Assembly of Nanoparticles." *Tetrahedron* **2002**, 58, 765-770.

⁴⁸¹ Jeoung, E.; Carroll, J. B.; Rotello, V. M. "Surface Modification via a 'Lock and Key' Specific Self-Assembly of Polyhedral Silsesquioxane (POSS) Derivatives to Modified Gold Surfaces." *Chem. Commun.* **2002**, 1510-1511.

⁴⁸² Norsten, T. B.; Jeoung, E.; Thibault, R. J.; Rotello, V. M. "Specific Hydrogen-Bond-Mediated Recognition and Modification of Surfaces Using Complementary Functionalized Polymers." *Langmuir* **2003**, 19, 7089-7093.

⁴⁸³ Sanyal, A.; Norsten, T. B.; Oktay, U.; Rotello, V. M. "Adsorption/Desorption of Mono- and Diblock Copolymers on Surfaces Using Specific Hydrogen Bonding Interactions." *Langmuir* **2004**, 20, 5958-5964.

block dictated the properties of the modified surfaces. Several groups have studied the properties of polymers that were functionalized with DNA base pairs.^{484, 485, 486} Interactions between DNA base pairs are highly specific and exhibit reasonable thermal stability. A recent study has described the assembly of thymine-functionalized zeolites to adenine functionalized glass surfaces.⁴⁸⁷ However, the use of DNA base pairs to attach polymers to solid surfaces has not received significant attention.

This chapter will describe DNA base pair mediated association between a random copolymer and a silicon/SiO₂ surface from the melt. Silicon/SiO₂ surfaces were modified with thymine using a novel thymine-derivatized trimethoxysilane. All earlier literature in which hydrogen bonding groups were used to attach polymers to solid surfaces primarily employed polystyrene derivatives ($T_g > 100$ °C) and solution modification approaches. The low T_g adenine containing copolymers, as described in this study were synthesized via conventional free radical copolymerization of 2-ethylhexyl methacrylate (EHMA) and a novel adenine containing methacrylate monomer (AIEMA). The melt phase attachment of the copolymers to the thymine-modified silicon/SiO₂ surface was characterized using contact angle measurements, XPS, and ellipsometry.

⁴⁸⁴ Overberger, C. G.; Inaki, Y. "Graft Copolymers Containing Nucleic Acid Bases and L- α -Amino Acids." *J. Polym. Sci., Polym. Chem.* **1979**, 17, 1739-1758.

⁴⁸⁵ Yamauchi, K.; Lizotte, J. R.; Long, T. E. "Synthesis and Characterization of Novel Complementary Multiple-Hydrogen Bonded (CMHB) Macromolecules via a Michael Addition." *Macromolecules* **2002**, 35, 8745-8750.

⁴⁸⁶ Lutz, J.-F.; Thünemann, A. F.; Rurack, K. "DNA-Like "Melting" of Adenine- and Thymine-Functionalized Synthetic Copolymers." *Macromolecules* **2005**, 38, 8124-8126.

⁴⁸⁷ Park, J. S.; Lee, G. S.; Lee, Y.-J.; Park, Y. S.; Yoon, K. B. "Organization of Microcrystals on Glass by Adenine-Thymine Hydrogen Bonding." *J. Am. Chem. Soc.* **2002**, 124, 13366-13367.

7.3 Experimental

7.3.1 Materials

3-acryloxypropyltrimethoxysilane (APTMS, 95%, Gelest, Inc.) was vacuum-distilled from neat (0.1 mm Hg, 30 °C). 2-ethylhexyl methacrylate (EHMA, 97%, Aldrich) was passed through activated basic alumina to remove the inhibitor. 3-(triethoxysilyl)propylsuccinicanhydride (95%, Gelest, Inc.), 2-isocyanatoethyl methacrylate (IEMA, 99% Aldrich), AIBN (98% Aldrich) and anhydrous DMSO (99% Aldrich), conc. H₂SO₄ (VWR International), NH₄OH (30%, VWR International), H₂O₂ (30%, Aldrich), methanol (EMD Chemicals) and dichloromethane (EMD Chemicals) were used as received. The polymerization solvent THF (EMD Chemicals) was used as received. Silicon/SiO₂ surface modification was carried out in CHCl₃ (EMD Chemicals), which was freshly distilled from CaH₂ (Aldrich). Thymine (99%, Aldrich) and adenine (99%, Aldrich) were dried in vacuum oven at 60 °C overnight prior to use. Milli Q water was used for surface cleaning. Silicon wafers used as the substrates were a generous gift from Hewlett Packard Company.

7.3.2 Material Characterization

Size exclusion chromatography (SEC) data was obtained using a 717 Autosampler system equipped with 3 in-line 5 μm PLgel MIXED-C columns, a Waters 2410 refractive index detector operating at 880 nm, a Wyatt Technology miniDawn[®] multiple angle laser light scattering (MALLS) detector operating at 690 nm and calibrated with polystyrene standards, and a Viscotek Model 270 differential/light scattering dual detector. The refractive index increment (dn/dc) was calculated online. SEC measurements were performed at 40 °C in THF at a flow rate of 1 mL/min. ¹H, ¹³C,

and ^{29}Si NMR spectroscopy were performed on a Varian UNITY spectrometer at 400 MHz, 100 MHz, and 79.5 MHz respectively with CDCl_3 as solvent. Fast atom bombardment mass spectrometry (FAB-MS) was achieved using a Fissons Instruments VG Quattro.

7.3.3 Surface Characterization

The modified silicon/ SiO_2 surfaces were sonicated in a Branson 1200 ultrasonic generator for 1 h. Static water contact angles were measured in the sessile drop mode using a FTA-200 contact angle goniometer with a syringe-driven droplet. The values were measured 30 sec after dispensing the drop to obtain equilibrium values. Contact angles were measured at 4-5 different spots on each surface. XPS was obtained on a Perkin Elmer Model 5400 instrument fitted with a Mg $K\alpha$ X-ray source (1253.8 eV), at a take-off angle of 30° . The anode was operated at 250 W. The 285 eV photoelectron peak of C1s electrons was used as an internal XPS standard. Ellipsometric data were obtained on a Beaglehole ellipsometer with a He-Ne laser ($\lambda=632.8$ nm) and an angle of incidence of 70° . Refractive indices of 1.5 were used for SiO_2 , thymine, and copolymer layers, in the calculation of polymer layer thickness. In order to determine the thickness of the silane and the copolymer layer, thickness of the original SiO_2 layer, which was determined using clean silicon wafers was subtracted from the thickness values calculated following silane and copolymer modification.

7.3.4 Synthesis of Thymine-functionalized Trimethoxysilane (TTMS)

The synthesis involved the reaction of APTMS with thymine in the presence of catalytic amount of potassium *tert*-butoxide in anhydrous DMSO under nitrogen as shown in Scheme 7-1. All glassware was rigorously cleaned and flame dried. Dry

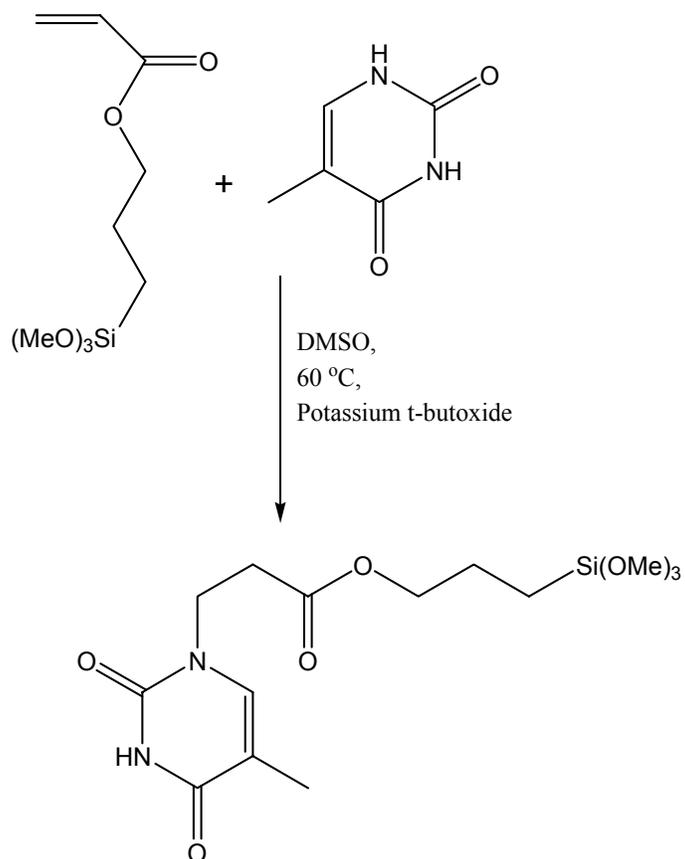
thymine (1g, 7.9 mmol, 2 eq.), APTMS (0.9 mL, 3.95 mmol), and potassium *tert*-butoxide (10 mg) mixture in DMSO (15mL) was stirred at 60 °C for 24 h. After the reaction, DMSO was removed under vacuum and the solid product was isolated in ~70% yield. The product was characterized using NMR spectroscopy and FAB-MS. ¹H NMR (400 MHz, 25 °C in CDCl₃): δ (ppm) 0.56 (-CH₂CH₂CH₂Si-: 2H, t); 1.58 (-CH₂CH₂CH₂Si-: 2H, m); 1.72 (-CH=C-CH₃: 3H, s); 2.67(-CH₂COO-: 2H, t); 3.44 (-Si(OCH₃)₃: 9H, s); 3.83 (-N-CH₂-CH₂-OCO-): 2H, t); 3.95 (-N-CH₂-CH₂OCO-: 2H, t); 7.48 (-N-CH=C-: 1H, s); 11.2 (-CO-NH-CO-: 1H, s). ¹³C NMR (100 MHz, 25 °C in CDCl₃): δ (ppm) 4.77, 11.8, 21.4, 32.6, 44.5, 50.1, 66.4, 109.8, 141.2, 150.3, 163.8, 170.9. m/z = 360.1; 329.1 (theoretical: 360.4).

7.3.5 Synthesis of Adenine-derivatized Methacrylate Monomer (AIEMA) and Poly(EHMA-co-AIEMA)

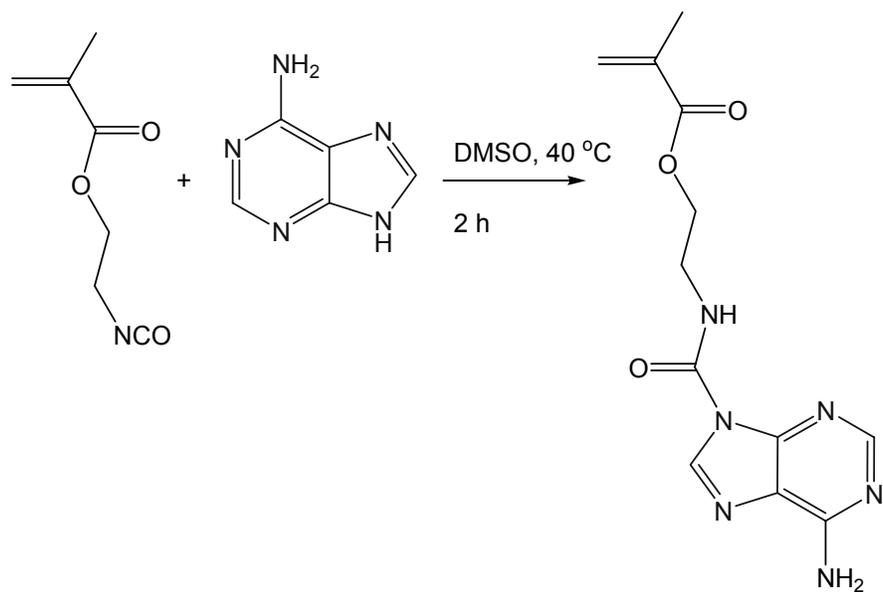
The synthesis of the monomer involved the reaction of adenine with the isocyanate group of IEMA (1.1 eq) in anhydrous DMSO as shown in Scheme 7-2. All reactions were conducted under dry conditions in nitrogen. Dry adenine (2g, 14.8 mmoles) was dissolved in anhydrous DMSO (30 mL) at 145 °C under nitrogen. IEMA (4 mL, 16.2 mmoles, 1.1 equivalents) was dissolved in anhydrous DMSO (10 mL) in a 100 mL round-bottomed flask. The adenine solution was slowly added to a room temperature solution of IEMA using a double-tipped needle (cannula) over 30 min. The mixture was allowed to stir for an additional 2 h to ensure complete reaction. DMSO was removed under vacuum, the solid residue was dissolved in methanol and the solution was allowed to cool down in the refrigerator. The product was isolated by filtering off the methanol and washing the solid with cold methanol. The product was isolated in ~20 % yield and characterized using NMR spectroscopy. ¹H NMR (400 MHz, 25 °C in CDCl₃):

δ (ppm) 1.87 ($\text{CH}_2=\text{CH}-\text{CH}_3$: 3H, s); 3.7 ($-\text{CH}_2-\text{NH}-\text{CO}-$: 2H, m); 4.28 ($-\text{COO}-\text{CH}_2-\text{CH}_2-$: 2H, t); 5.7, 6.09 ($-\text{CH}_2=\text{C}-\text{CH}_3$: 2H, s); 7.69 ($-\text{NH}_2-\text{C}=\text{N}=-$: 2H, s); 8.23 ($-\text{N}=\text{CH}-\text{N}=-$: 1H, s); 8.54 ($-\text{N}=\text{CH}-\text{N}-$: 1H, s); 9.09 ($-\text{CH}_2-\text{CH}_2-\text{NH}-$: 1H, t). ^{13}C NMR (100 MHz, 25 °C in CDCl_3): δ (ppm) 17.9, 38.8, 62.6, 119.7, 125.8, 135.5, 138.7, 147.9, 148.7, 152.7, 155.3, 166.6.

AIBN initiated conventional free radical polymerization was used to synthesize the random copolymers. THF was used as the polymerization solvent as AIEMA was found insoluble in most solvents that are commonly used for free radical polymerization. Mixture of EHMA (5.6mL, 25 mmol, 95 mol%), AIEMA (0.38g, 1.3 mmol, 5 mol%) and AIBN (0.025g, 0.05 wt%) was dissolved in THF (80 mL) and heated to 60 °C for 24 h. The polymers were isolated first by removing THF under vacuum, dissolving the residue in CHCl_3 and precipitating in a 10-fold excess of 9:1 MeOH/ H_2O mixture. The polymers were dried in vacuum oven at 50 °C for 48 h and characterized by SEC and NMR spectroscopy. ^1H NMR (400 MHz, 25 °C in d_8 - THF): δ (ppm) 0.5-2.2 ($-\text{CH}$, $-\text{CH}_2$, $-\text{CH}_3$ in EHMA and AIEMA units, b); 3.5-4.2 ($-\text{CH}_2\text{COO}-$, $-\text{CH}_2-\text{NH}-$ in EHMA and AIEMA units, b); 7.5 ($\text{NH}_2-\text{C}=\text{N}-$, s), 8.2 ($-\text{C}=\text{N}-\text{CH}=\text{N}-$, s), 8.5 ($-\text{NH}=\text{CH}-\text{N}-$, s), and 9.2 ($-\text{NH}=\text{CH}-\text{N}-$, s).



Scheme 7-1: Synthesis of TTMS.



Scheme 7-2: Synthesis of AIEMA.

7.3.6 Substrate Treatment

Silicon wafers were cut into 1 cm² samples and sonicated for 5 min in dichloromethane and 5 min in methanol. The wafers were blown with nitrogen and cleaned with freshly prepared Piranha solution (conc.H₂SO₄:30% H₂O₂; v/v: 70/30) at 90 °C for 1 h, rinsed with milli-Q water, and cleaned with a 30% NH₃:30% H₂O₂:H₂O (v/v/v: 1/1/5) at 60 °C for 15 min. The wafers were then rinsed with milli-Q water several times, blown dry with nitrogen, and immediately immersed in the alkoxy silane solution and allowed to stir for a given time. (*Caution: Piranha solution reacts violently with many organic materials and should be handled with care.*)

7.3.7 Modification of Silicon/SiO₂ Surfaces with TTMS and Random Copolymers

Substrate treatment was as described earlier. Freshly cleaned silicon wafers were modified with a 5mM solution APTMS in CHCl₃ for 24 h and sonicated 3 times in CHCl₃ to remove any physically adsorbed materials. 1 wt% random copolymer solutions were then spun cast onto thymine modified wafers at 2500 rpm and annealed at 65°C in vacuum oven for 8 h. Wafers after each step were exhaustively rinsed with solvents and characterized using XPS, contact angle, and ellipsometry.

7.4 Results and Discussions

7.4.1 Synthesis of TTMS

A novel thymine-containing trimethoxysilane was synthesized in a single step via the reaction of thymine with IEM (Scheme 7-1). ¹H and ¹³C NMR spectroscopy and FAB-MS confirmed the chemical structure of the isolated product. Characteristic ¹H NMR resonances associated with the thymine groups were observed at 11.2 ppm (-CO-NHCO-), 7.48 ppm (-N-CH=C-), and 1.72 ppm (CH₂=CH-CH₃), in addition to the

resonances of trimethoxysilane with complete disappearance of the olefinic resonances between 5.8 and 6.3 ppm, which confirmed successful derivatization (Figure 7-1).

It was not possible to avoid premature hydrolysis and condensation of the methoxysilyl groups during the product workup. Integration of the methoxysilyl proton resonance at 3.44 ppm with methylene protons of $-\text{Si}-\text{CH}_2-$ at 0.56 ppm indicated ~20% hydrolysis. In addition, ^{29}Si NMR spectra for TTMS (Figure 7-2), exhibited two Si resonances at -42 ppm (similar to APTMS precursor) and -52 ppm. The ratio of the two Si resonances was 84:16, which indicated that 16% of the methoxysilyl group had undergone condensation that shifted the Si resonance slightly upfield. This result is consistent with the ^1H NMR observations. However, since major component of TTMS was the unhydrolyzed product, it was used for modifying silicon/ SiO_2 surfaces.

7.4.2 Synthesis of Poly(EHMA-co-AIEMA)

Conventional free radical polymerization was used to synthesize random copolymers of EHMA and AIEMA. ^1H NMR spectra of AIEMA is shown in Figure 7-3. In addition to the olefinic proton resonances at 5.5 ppm and 6.1 ppm, adenine resonances at 7.5 ppm ($\text{NH}_2-\text{C}=\text{N}-$:2H, s), 8.2 ppm ($\text{C}=\text{N}-\text{CH}=\text{N}-$: 1H, s), 8.5 ppm ($-\text{NH}=\text{CH}-\text{N}-$: 1H, s), and 9.2 ppm ($-\text{NH}=\text{CH}-\text{N}-$: 1H, s) was observed. Due to the limited solubility of AIEMA, it was difficult to incorporate greater than 7 mol% AIEMA in the copolymers. Figure 7-4 shows the ^1H NMR spectrum of a random copolymer of EHMA and AIEMA. In addition to the backbone methylene protons (between 0.5 and 2.0 ppm) and side chain methyl and ester methylene protons (between 3.5 and 4.5 ppm), four resonances associated with the adenine groups were observed at 7.5 ppm, 8.2 ppm, 8.5 ppm, and 9.2 ppm.

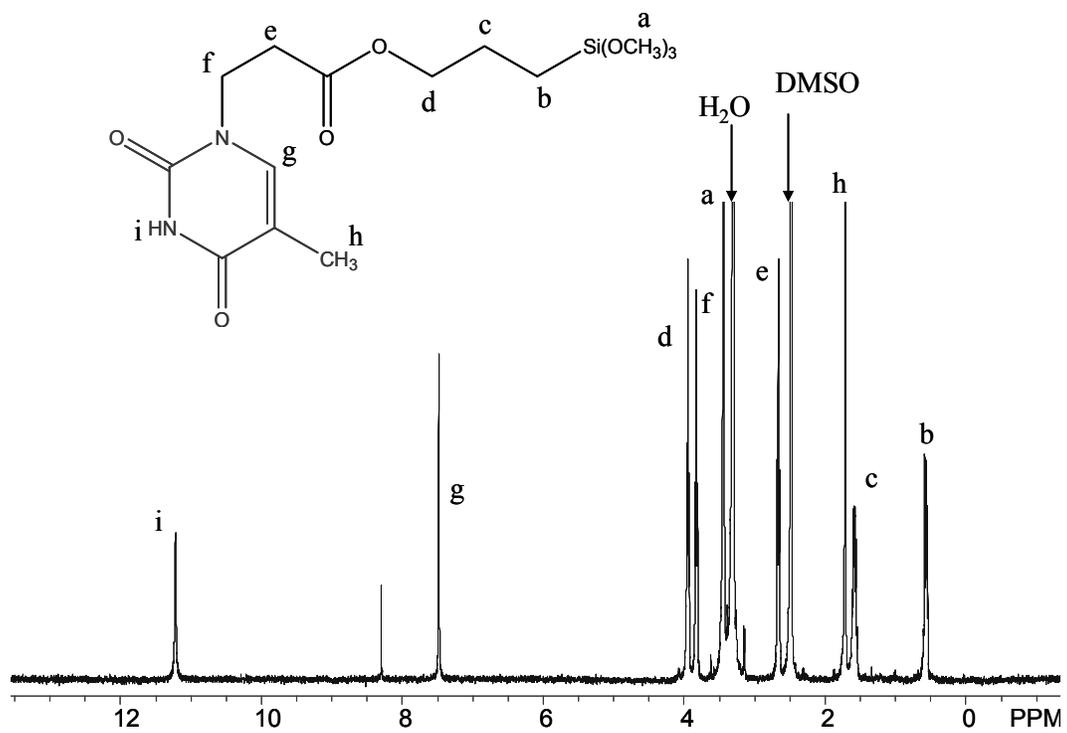


Figure 7-1: ¹H NMR spectrum of TTMS in *d*₆-DMSO.

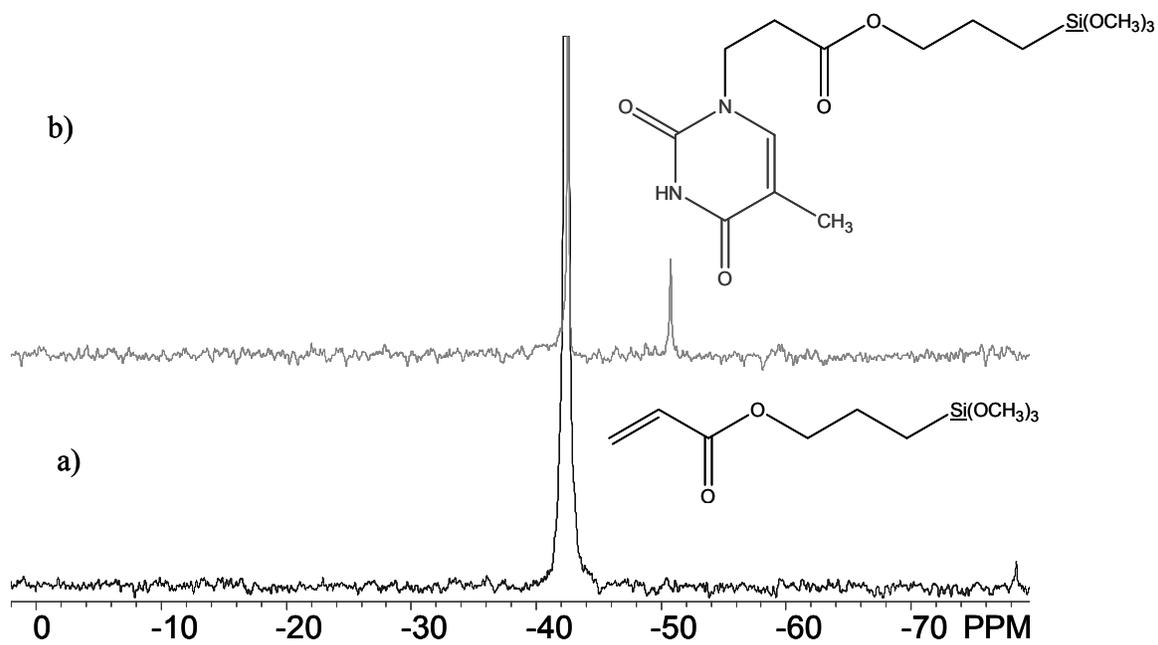


Figure 7-2: ^{29}Si NMR spectra of 16 wt% CDCl_3 solution containing 0.06 M $\text{Cr}(\text{acac})_3$ a) APTMS, and b) TTMS.

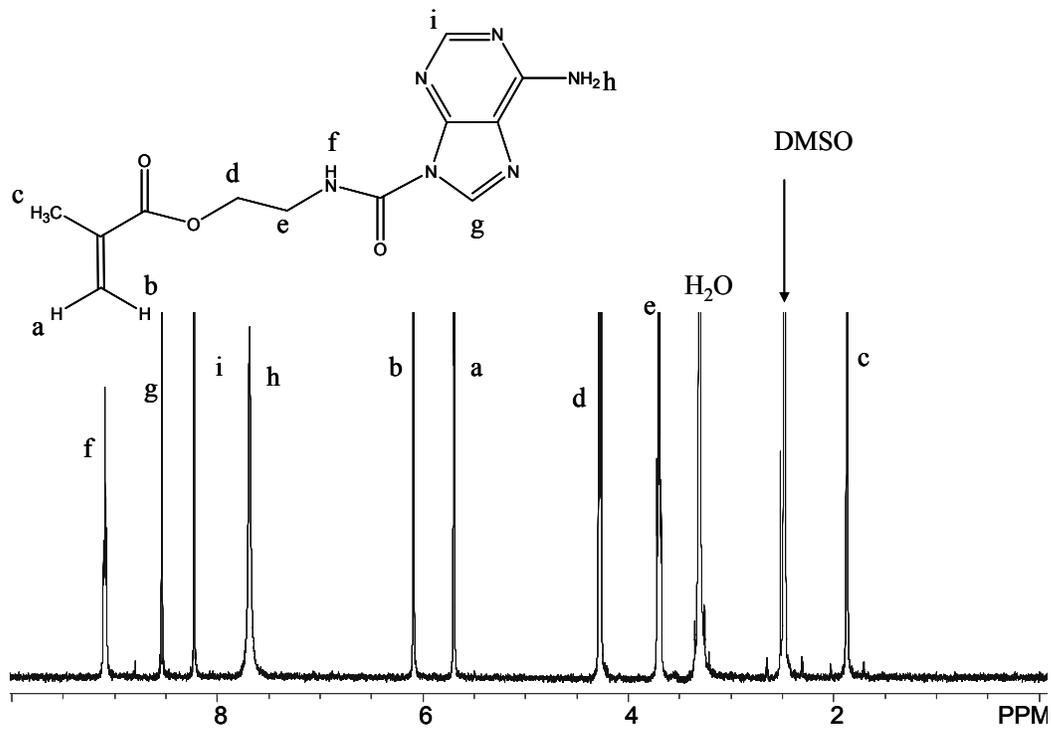


Figure 7-3: ¹H NMR spectra of AIEMA.

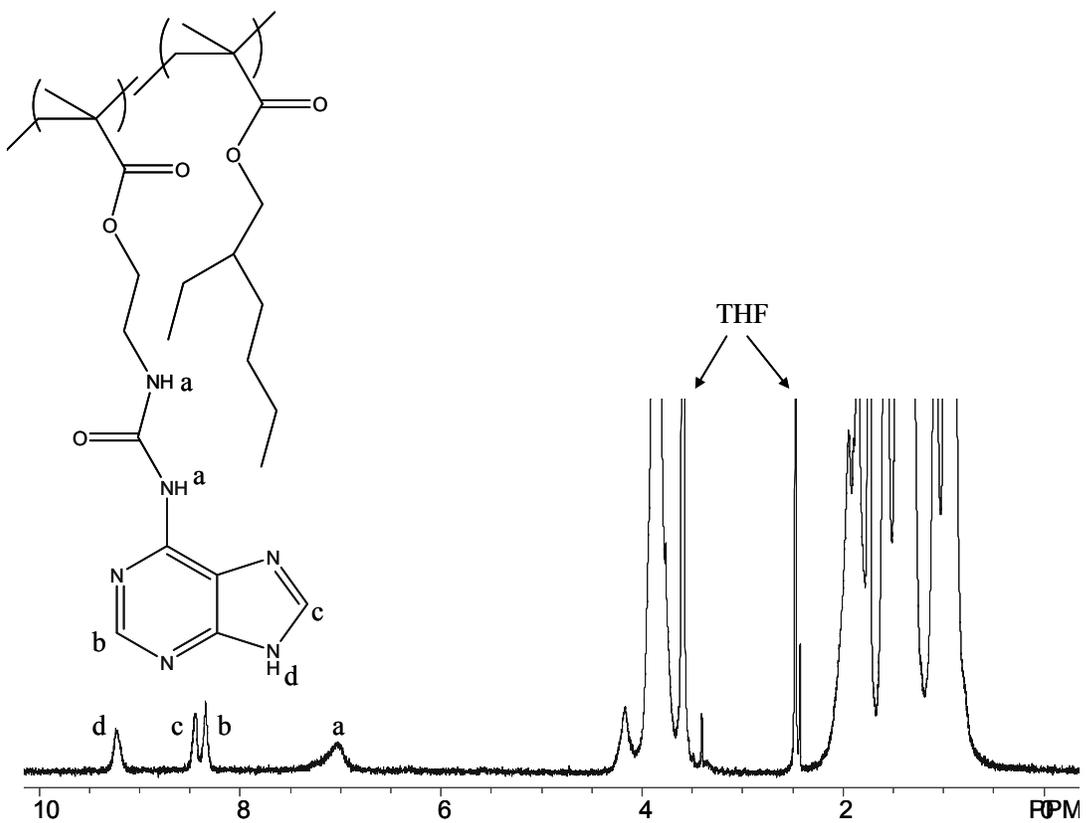


Figure 7-4: ^1H NMR spectra of a random copolymer of EHMA and AIEMA in d_8 -THF.

Table 7-1 shows the molecular weight and chemical composition data for a series of copolymers containing different levels of adenine. The mol% adenine in the copolymer was close to the feed composition and the polydispersities were between 1.5 and 2. As shown in Table 7-1, it was possible to vary the mol% adenine incorporated in the copolymer and the molecular weights by varying the feed composition and the initiator concentration, respectively.

Table 7-1: Molecular weight, and chemical composition data for a series poly(EHMA-*co*-AIEMA)

Sample designation (Copolymer-mol% AIEMA- M_n)	Mol% AIEMA targeted	SEC M_n^a (g/mol) (M_w/M_n)	Mol% AIEMA incorporated ^b
Co-1-145k	1	145,000 (1.68)	1.0
Co-3-19k	3	19,000 (1.90)	2.5
Co-3-71k	3	71,000 (2.51)	2.2
C-3-114k	3	114,000 (1.90)	2.6
Co-5-20k	5	19,700 (2.09)	3.5
Co-5-103k	5	103,000 (2.06)	4.3
Co-7-47k	7	47,000 (2.20)	6.2
Co-7-69k	7	69,000 (2.11)	7.0

^aSEC conditions: THF, 40 °C, MALLS detector. ^b¹H NMR conditions: 400 MHz, 25 °C, *d*₈-THF; ratio of adenine proton resonance at 8.5 ppm to EHMA and AIEMA ester methylene protons between 3.5 and 4.5 ppm.

7.4.3 Silicon/SiO₂ Surface Modification with TTMS and Poly(EHMA-co-AIEMA)

Park et al. reported the only previous synthesis of a thymine-functionalized alkoxysilane in a study that involved the assembly of thymine-functionalized zeolites onto adenine-functionalized surfaces.⁴⁸⁸ In the present research, a novel thymine-derivatized trimethoxysilane (TTMS) was used to modify silicon/SiO₂ surfaces from solution. Modification of the surfaces with TTMS was confirmed using XPS and water contact angle measurements. The XPS atomic composition and water contact angle values for a clean silicon/SiO₂ surface before and after modification with TTMS are listed in Table 7-2. Nitrogen was not detected on the clean surface, however, the silicon/SiO₂ surface that was treated with TTMS contained 5 atomic% N, which confirmed the presence of adsorbed TTMS. The principal N1s photoelectron had a binding energy between 400.2 and 400.4 eV, which was consistent with earlier literature for thymine multilayers.⁴⁸⁹ The contact angle measurements indicated a similar trend. The water contact angle on the clean silicon/SiO₂ surface was essentially 0°, and the contact angle increased to 45° following silane modification, which indicated a moderately hydrophobic surface.

After confirming the successful modification of silicon/SiO₂ surfaces with TTMS, the attachment of adenine containing random copolymers to surface bound thymine groups was investigated. The copolymers were spun cast onto modified silicon/SiO₂ surfaces, annealed at 65 °C for 8 h, and immediately extracted with THF for 1 h. The 8 h annealing time was sufficient to obtain maximum copolymer attachment.

⁴⁸⁸ Park, J. S.; Lee, G. S.; Lee, Y.-J.; Park, Y. S.; Yoon, K. B. "Organization of Microcrystals on Glass by Adenine-Thymine Hydrogen Bonding." *J. Am. Chem. Soc.* **2002**, 124, 13366-13367.

⁴⁸⁹ Petrovykh, D. Y.; Kimura-Suda, H.; Tarlov, M. J.; Whitman, L. J. "Quantitative Characterization of DNA Films by X-Ray Photoelectron Spectroscopy." *Langmuir* **2004**, 20, 429-440.

Table 7-2: XPS atomic composition and water contact angle data on clean silicon/SiO₂ surface before (blank) and after modification with TTMS

Surface	Atomic composition (%) ^a				Water contact angle (deg)
	C1s	O1s	N1s	Si2p	
Blank	17 ± 1	42 ± 3	-	41 ± 3	~ 0
TTMS	32 ± 3	37 ± 2	5 ± 1	26 ± 5	45

^aXPS conditions: Mg anode, take-off angle = 30°.

Figure 7-5 shows the change in ellipsometric film thickness of thymine-modified silicon/SiO₂ surfaces following attachment of poly(EHMA-co-AIEMA) of M_n 19,000g/mol, 70,000 g/mol, and 115,000 g/mol, each functionalized with ~3 mol% AIEMA. While the film thickness for the surfaces modified with TTMS was approximately constant, the film thickness of copolymer modified surfaces increased with increasing copolymer M_n. However, the relative increase in copolymer film thickness was significantly lower than the corresponding increase in copolymer M_n, which indicated that the copolymer deposited in a flat conformation on the surface, possibly due to multiple contacts as depicted in Figure 7-6. Due to the multi-point attachment, it was not possible to calculate the grafting density of the surface attached polymer chains.

Table 7-3 shows the XPS %C and water contact angle data on thymine-modified surfaces before and after copolymer treatment. Significantly higher %C was observed for surfaces modified with the copolymers, with the highest amount observed in the case of Co-3-70k. The copolymer attachment also resulted in a hydrophobic surface. In contrast, thymine-modified surfaces treated with poly(EHMA) (M_n = 74,000 g/mol) containing no adenine groups, showed insignificant polymer attachment following annealing and THF extraction (Figure 7-7). This confirmed that the adenine groups were responsible for anchoring the copolymer to the surface.

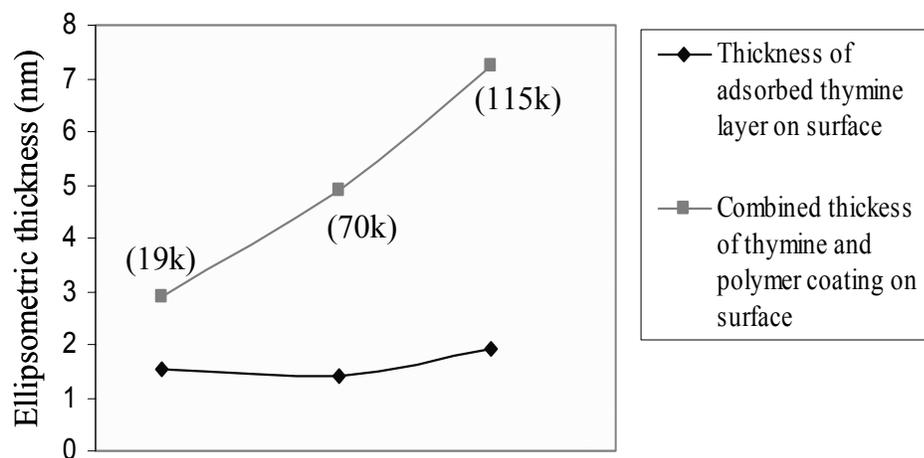


Figure 7-5: Influence of copolymer M_n (shown in parenthesis) on the ellipsometric thickness of copolymer coated and thymine-modified surfaces; the copolymers were functionalized with 3 mol% adenine.

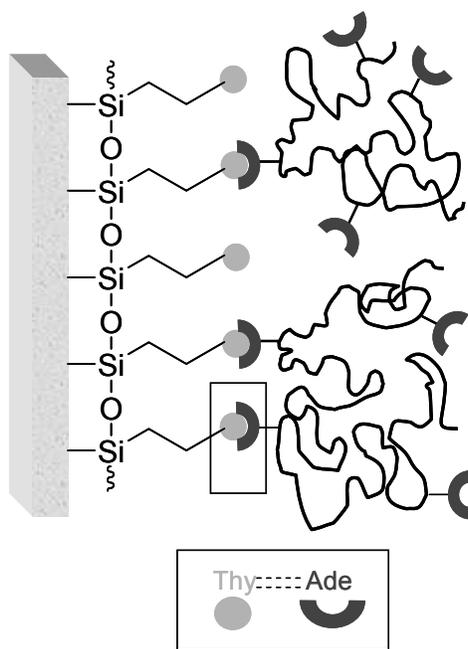


Figure 7-6: Depiction of poly(EHMA-co-AIEMA) adsorption onto thymine-modified silicon/SiO₂ surface.

Table 7-3: XPS atomic composition and water contact angle data on silicon/SiO₂ surfaces modified with thymine, before and after treatment with Co-3 of various M_n

Polymer designation	(XPS %C) ^a		Water contact angle (deg)	
	Before	After	Before	After
Co-3, 19k	41 ± 2	56 ± 2	47 ± 1	83 ± 5.0
Co-3, 70k	40 ± 2	75 ± 2	47 ± 1	87 ± 3
Co-3, 115k	40 ± 2	65 ± 2	47 ± 1	84 ± 4

^aXPS conditions: Mg anode, take-off angle = 30°.

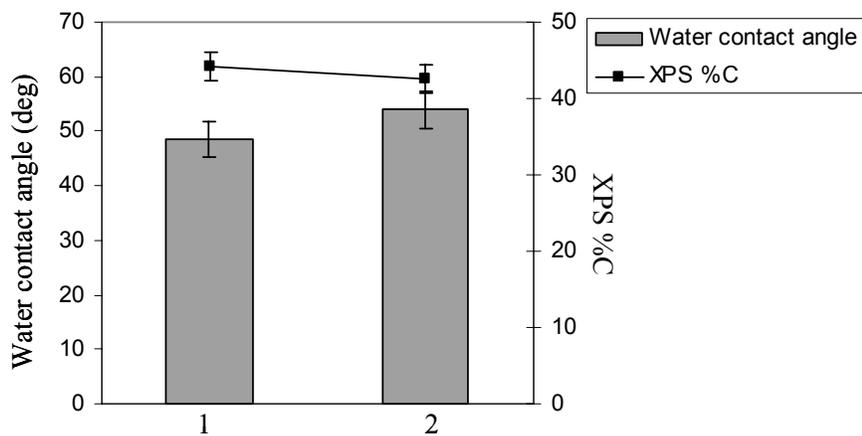


Figure 7-7: Water contact angle and XPS %C on thymine-modified silicon/SiO₂ surfaces before (1), and after (2) poly(EHMA) treatment and THF extraction.

7.4.4 Influence of Solvent on Poly(EHMA-*co*-AIEMA) Attachment to Thymine-modified Surfaces

After confirming the attachment of adenine containing methacrylate copolymers to thymine-functionalized surfaces, the influence of solvent polarity and temperature on the association was investigated. Table 7-4 shows the water contact angle and ellipsometric data on thymine-modified surfaces before and after treatment with Co-3-19k following several solvent treatments. Both water contact angle and ellipsometric thickness decreased following treatment with THF/DMSO, which indicated partial removal of the copolymer. However, subsequent solvent rinses at 25 °C and elevated temperatures did not completely remove the copolymer from the surface. These observations indicated that the copolymer was partially attached to the surfaces through stable covalent linkages.

Table 7-4: Water contact angle and ellipsometric thickness data on thymine-modified silicon/SiO₂ surfaces after treatment with Co-3-19k

Thin film characterization technique	Thymine-modified surface				
	Before copolymer treatment	After copolymer treatment ^a			
		THF	(3:2) THF/DMSO	(3:2) THF/DMSO	Toluene 110 °C (5 h)
Water contact angle (deg)	47 ± 1	83 ± 5	62 ± 6	62 ± 6	62 ± 6
Ellipsometric thickness (nm)	3.55 ± 0.16	4.41 ± 0.27	4.07 ± 0.26	4.14 ± 0.26	4.12 ± 0.26

^aCopolymer treatment conditions: Co-3-19k spun cast at 2,500 rpm, annealed at 65 °C for 8 h, extracted with THF for 1 h.

It was also found that the neat copolymers crosslinked upon annealing, the time and temperature of crosslinking depended on the chemical composition of the copolymer. As the AIEMA content increased, the copolymers crosslinked at lower temperatures and shorter annealing times. Copolymers containing 3 mol% AIEMA (Co-3) were found to crosslink at 85 °C after 8 h of annealing possibly due to thermal imidation reactions. Such thermal imidation aided crosslinking between amines/amides and acid/esters in SAM and multilayer thin films has been reported in the literature.^{490, 491}

A control study was therefore performed with 3-(triethoxysilyl)propylsuccinicanhydride modified silicon/SiO₂ surfaces. Following copolymer treatment, the modified surfaces showed enhanced %C and water contact angle (Figure 7-8), which indicated that the copolymers were covalently attached to the surface, possibly through imidization reaction with the surface anhydride groups that also explains the crosslinking observed in the copolymers.

⁴⁹⁰ Fryxell, G. E.; Rieke, P. C.; Wood, L. L.; Englehard, M. H.; Williford, R. E.; Graff, G. L.; Campbell, A. A.; Wiacek, R. J.; Lee, L.; Halverson, A. "Nucleophilic Displacements in Mixed Self-Assembled Monolayers." *Langmuir* **1996**, 12, 5064-5075.

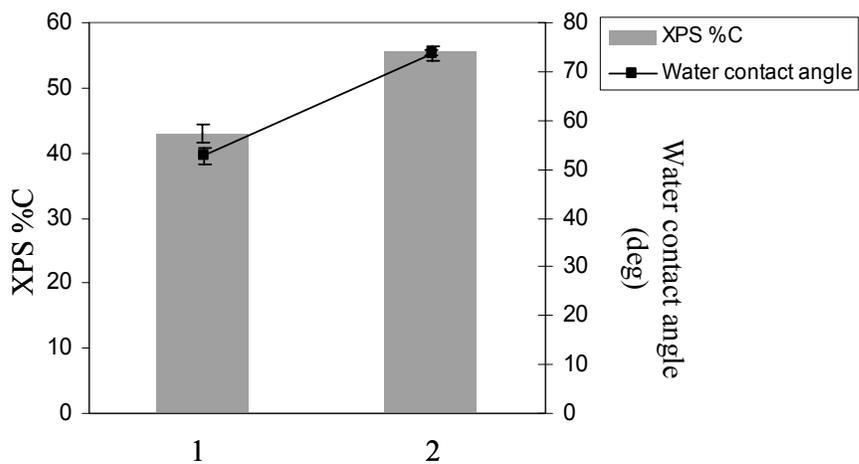


Figure 7-8: XPS %C and water contact angle on succinic anhydride modified silicon/SiO₂ surfaces (1) before, and (2) after Co-3-19k treatment.

⁴⁹¹ Yang, S. Y.; Rubner, M. F. "Micropatterning of Polymer Thin Films with Ph-Sensitive and Cross-Linkable Hydrogen-Bonded Polyelectrolyte Multilayers." *J. Am. Chem. Soc.* **2002**, 124, 2100-2101.

7.5 Conclusions

A novel thymine-derivatized trimethoxysilane (TTMS) was successfully used to modify a silicon/SiO₂ surface with thymine groups. Adenine-functionalized random copolymers were applied to thymine-modified silicon/SiO₂ surfaces from the melt. The adenine-functionalized random copolymers were synthesized through free radical polymerization of 2-ethylhexyl methacrylate (EHMA) and a novel methacrylate monomer, AIEMA. The chemical composition of the copolymer was similar to the feed composition. Surface modification with a series of copolymers containing 3 mol% AIEMA and various molecular weights were attempted. While non-functionalized homopolymer did not adsorb onto thymine-modified surfaces, XPS, and ellipsometric analysis showed significant attachment of adenine containing copolymers to thymine-modified surfaces. Water contact angle measurements also indicated a significantly hydrophobic surface after copolymer attachment. However, polar solvent rinse could effect only partial removal of the surface attached copolymers. A control study on the attachment of adenine-functionalized copolymers to succinic anhydride modified surfaces indicated that possible side reactions such as imidization during copolymer annealing step led to covalent anchoring of the copolymers to the surface.

7.6 Acknowledgements

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CHAPTER 8: OVERALL CONCLUSIONS

Polymer modification of solid surfaces has emerged as one of the most promising approaches for tailoring a number of surface properties such as wettability, adhesion, biocompatibility, friction, etc. Compared to small molecules, the use of polymers as surface modifiers enables control over many variables such as film thickness, chemical composition and areal density of functional groups. The use of living polymerization in particular has allowed the synthesis of a variety of well-defined functional polymers of various composition and topologies. The research effort primarily involved the design of novel macromolecules using living polymerization strategies to achieve functional and stimuli responsive silica surfaces.

Several studies have reported employing dendrimers and highly branched polymers for introducing large densities of functional groups on surfaces. In this research, we demonstrated silica surface modification with simple and novel star-branched polymers containing functionalities in the core, achieved through the hydrolysis and condensation of trimethoxysilane endgroups of well-defined anionically synthesized PS. Earlier studies have mainly reported the influence of polymer topology on the capability of star-PEG modified surfaces in preventing protein adhesion. However, none of the studies had undertaken a detailed microscopic investigation of surfaces modified with star-branched polymers. Star-branched modifiers provide functional and relatively well-defined model systems for probing surface properties compared to ill-defined highly branched systems and synthetically challenging dendrimers. Using such simple star-shaped macromolecules, we showed that while the macroscopic properties were relatively unaffected by polymer topology; microscopic differences were, observed

between the linear and star-branched polymer modified surfaces. A model explaining the formation of the observed surface features was proposed.

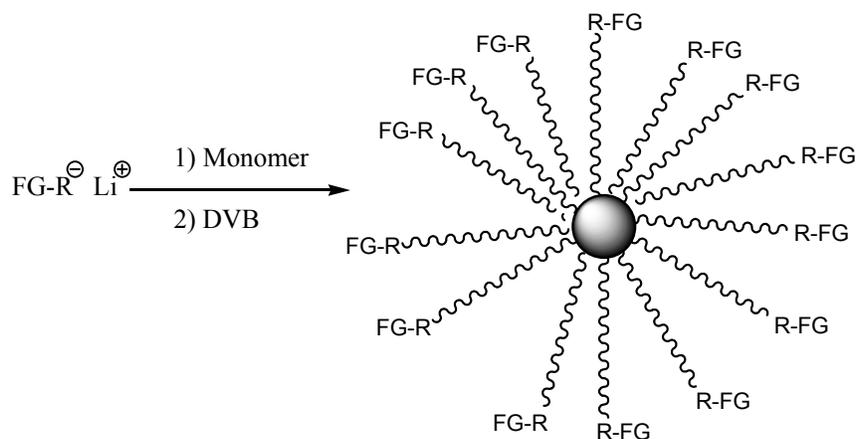
A living polymerization strategy was also used to synthesize amphiphilic triblock block copolymer constituting hydrophobic polystyrene and different hydrophilic terminal blocks. The central functionalized block covalently anchored the copolymers to silica surfaces. The amphiphilic copolymers exhibited stimuli responsive changes in surface wettabilities due to selective solvent induced reorganization of the terminal hydrophobic/hydrophilic blocks. Only limited studies in the literature had reported kinetic analysis of block reorganization upon selective solvent treatments. The novel block copolymers investigated in this study exhibited highly reversible switching of surface hydrophobicity following alternating solvent exposures. Kinetic analysis of block reorganization in selective solvents indicated the process was rapid and instantaneous. Such a rapid switching in surface properties was not reported previously and was attributed to the additional freedom available to the surface grafted copolymers provided by the long central functional blocks. Copolymers containing significantly long central functionalized blocks exhibited unique behavior, where chain rearrangement was also observed in air. Thus, it was shown for the very first time that high T_g polymer chains are capable of rearranging in the melt state, provided sufficient freedom exists for such a reorganization process. Unlike all earlier reports, which had employed densely grafted terminally attached block copolymers, or mixed homopolymers, the novel polymer architecture described in this study provides an easy and convenient way of tuning the chain reorganization profiles. The flexibility was achieved by tailoring the central block lengths of the triblock copolymers.

In contrast to the covalent modification approaches, which often lead to permanent modification of surfaces, a non-covalent modification approach to create renewable surfaces exhibiting “universal” adhesion properties was also investigated. The non-covalently associating motifs employed in this study were multiple hydrogen bonding DNA bases, adenine and thymine. Living anionic polymerization was used to obtain thymine-functionalized PS, while adenine modification of surfaces was achieved using a novel adenine-functionalized alkoxy silane. All previous studies investigating polymer association to surfaces through multiple hydrogen bonding associations were performed on gold surfaces. Our study describing the solvato-reversible polymer coating was the first demonstration on silica surfaces. Control studies with weakly hydrogen bonding polymers confirmed the absence of any non-specific polymer adsorption on adenine-modified surfaces. We also presented the first systematic investigation of the influence of surface concentration of the multiple hydrogen bonding groups on the extent of polymer recognition by the modified surfaces. These studies revealed that maximum polymer attachment was observed at a particular adenine concentration, above and below which the attachment significantly decreased. It was also shown that the structure of the diluent species used to space out the surface bound adenine groups influenced the polymer attachment density significantly and thus, demonstrated the need for proper choice of the diluent to obtain optimal polymer attachment.

CHAPTER 9: Suggested Future Work

9.1 Surface Modification with Branched Polymers

This study investigated a simple and convenient route for obtaining functionalized star-branched polymers, which were subsequently used to modify solid surfaces. However, the polymers obtained had short oligomeric arms and do not therefore display significant mechanical integrity. It is therefore necessary to obtain functionalized star-branched macromolecules with significantly higher arm molecular weights and functionalities. One of the approaches that could be used to obtain such highly functionalized star-branched macromolecules with longer arm lengths would be to use living anionic polymerization with functional initiators and the well-known divinylbenzene coupling chemistry. This could lead to well-defined star-branched macromolecules of different chemical compositions containing a number of peripheral functional groups, as depicted in Scheme 9-1.



FG-functional group: $-\text{OH}$, $-\text{NH}_2$

Scheme 9-1: Synthesis of highly functionalized star-branched macromolecules using functionalized alkyllithium initiated living anionic polymerization and DVB coupling approach.

Modification of solid surfaces with the functionalized star-branched macromolecules can lead to significantly different surface topography as was shown with the low molecular weight star-branched polymers in this study. Since it was shown that star-branched macromolecules primarily deposit as mushrooms compared to brush structure seen with the linear polymers, the well-spaced star-branched functional polymer chains could possibly serve as better adhesion promoters for surface supported polymer films compared to the highly stretched linear polymers. The well-defined and functional star-branched macromolecules could serve as better alternatives for obtaining functional surfaces with good performance attributes than the randomly branched hyperbranched polymers or dendrimers, which lack mechanical properties.

9.2 Switchable Surfaces Obtained through Modification with Amphiphilic Block Copolymers

Surface modification with novel centrally functionalized amphiphilic triblock copolymers demonstrated that such systems could find application as stimuli responsive coatings capable of altering solid surface properties reversibly in response to external stimuli. The copolymers synthesized had a very short hydrophilic block. It would be interesting to investigate the extent of switching observed for block copolymers constituting hydrophobic and hydrophilic blocks of equal lengths. The copolymers anchored through the functionalized central block exhibited rapid and instantaneous switching of surface wettability compared to studies reported in the literature. A systematic analysis of the influence of the central block length on the kinetics of switching would be interesting. This analysis could therefore be used to determine the cut-off length, and in turn the critical grafting density, at which the brush reorganization profile changes from a gradual variation to an instantaneous recovery.

The living free radical polymerization approach, which gives access to monomers bearing a variety of functional groups, could be used to design novel amphiphilic copolymers. Copolymers constituting blocks that could respond to gaseous and water-based analytes in a selective manner would be interesting for use as environmentally friendly model reversible column/membrane materials.

9.3 Multiple Hydrogen Bonding between Polymers and Surfaces

This study had demonstrated the use of base pairing between adenine and thymine for reversibly attaching PS-thymine to adenine-functionalized silicon/SiO₂ surfaces. The oligomeric PS used in this study served only as a model system to prove that such reversible hydrogen bonding groups can confer universal adhesion properties to surfaces. All the reversibility studies were performed with organic solvents. The design of water-soluble polymers, such as PEO functionalized with the DNA bases could lead to polymeric coatings that are pH reversible. The synthesis of DNA base functionalized linear low T_g polymers bearing multiple functional groups can enhance polymer coverage on surfaces and lead to thermally reversible polymeric coatings. The extension of this modification strategy to functionalize three-dimensional surfaces could be employed to construct novel organic-inorganic nanocomposites with pH/solvent/ temperature tunable physical and mechanical properties.