SYNTHESIS AND CHARACTERIZATION OF NANOSCALE POLYMER FILMS GRAFTED TO METAL SURFACES

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SYNTHESIS AND CHARACTERIZATION OF NANOSCALE POLYMER FILMS GRAFTED TO METAL SURFACES

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
Doctor of Philosophy
Materials Science and Engineering

by
Yuriy Galabura
August 2014

Accepted by:
Dr. Igor Luzinov, Committee Chair
Dr. Stephen Foulger
Dr. O. Thompson Mefford
Dr. Scott Husson
Dr. Ruslan Burtovyy
ABSTRACT

Anchoring thin polymer films to metal surfaces allows us to alter, tune, and control their biocompatibility, lubrication, friction, wettability, and adhesion, while the unique properties of the underlying metallic substrates, such as magnetism and electrical conductivity, remain unaltered. This polymer/metal synergy creates significant opportunities to develop new hybrid platforms for a number of devices, actuators, and sensors.

This present work focused on the synthesis and characterization of polymer layers grafted to the surface of metal objects. We report the development of a novel method for surface functionalization of arrays of high aspect ratio nickel nanowires/micronails. The polymer "grafting to" technique offers the possibility to functionalize different segments of the nickel nanowires/micronails with polymer layers that possess antagonistic (hydrophobic/hydrophilic) properties. This method results in the synthesis of arrays of Ni nanowires and micronails, where the tips modified with hydrophobic layer (polystyrene) and the bottom portions with a hydrophilic layer (polyacrylic acid). The developed modification platform will enable the fabrication of switchable field-controlled devices (actuators). Specifically, the application of an external magnetic field and the bending deformation of the nickel nanowires and micronails will make initially hydrophobic surface more hydrophilic by exposing different segments of the bent nanowires/micronails.

We also investigate the grafting of thin polymer films to gold objects. The developed grafting technique is employed for the surface modification of Si/SiO₂/Au
microprinted electrodes. When electronic devices are scaled down to submicron sizes, it becomes critical to obtain uniform and robust insulating nanoscale polymer films. Therefore, we address the electrical properties of polymer layers of poly(glycidyl methacrylate) (PGMA), polyacrylic acid (PAA), poly(2-vinylpyridine) (P2VP), and polystyrene (PS) grafted to the Si/SiO$_2$/Au microprinted electrodes. The polymer layers insulated under normal ambient conditions can display a significant increase in conductivity as the environment changes. Namely, we demonstrate that the in-plane electrical conductivity of the grafted polymer layers grafted to Au and SiO$_2$ surfaces can be changed by at least two orders of magnitude upon exposure to water or organic solvent vapors. The conductive properties of all the grafted polymer films under study are also significantly enhanced with temperature increase. The observed phenomenon makes possible the chemical design of polymer nanoscale layers with reduced or enhanced sensitivity to anticipated changes in environmental conditions. Finally, we show that the observed effects can be used in a micron-sized conductometric-transducing scheme for the detection of volatile organic solvents.

This research also includes the study of nanoscale-level actuation with grafted polymer films and polymer/gold nanoparticles systems-grafted composites. First, we investigate the nanoscale-level actuation with polymer films. To this end, we use “grafting to” approach to synthesize PGMA thin polymer film (80–200 nm). Then, film is swollen in a good solvent and freeze-dried until the solvent is sublimated, thereby creating grafted polymer nanofoam that exhibits shape memory properties. We demonstrate nanoscale actuation using the developed system. In addition, we show that
the modification of the PGMA nanofoam with low molecular weight polystyrene allows response tuning of the porous polymer film.

Furthermore, we incorporate gold nanoparticles (5 nm) into a thin PGMA layer (80 nm) to fabricate a PGMA/gold nanoparticles grafted composite film. The PGMA/gold nanoparticles grafted nanofoam is synthesized following the same procedure developed for the fabrication of the PGMA nanofoam. We demonstrate the shape-memory properties and nanoscale-level actuation of the developed system. Moreover, we investigate the change in the optical signal of the developed system as a function of temperature arising from the localized surface plasmon resonance and plasmon coupling effects of the gold nanoparticles. We envision that the change in optical properties upon actuation can be utilized to develop platforms for new off-line sensing devices.
DEDICATION

I dedicate this dissertation to my parents, Oksana and Dmytro Galabura, who have always believed in me. Their support, love, and encouragement have sustained me throughout my life. Thank you for your patience and all the sacrifices you made. Without you, this day would have never come.
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CHAPTER ONE

INTRODUCTION

It is difficult to imagine a world where humans could function without metals and metal alloys. These materials' unique properties, such as excellent electrical and heat conductivity, magnetism, and ductility, make them invaluable resources in modern society.

Throughout the centuries, metals have been the subject of intensive studies for the oldest branch of materials science—metallurgy. However, things have changed in the late 19th and early 20th centuries, when the use of metallic materials spread into numerous areas of science and technology.¹ For example, in electronics, energy fields, and aeronautics, metals and metal alloys are used in combination with other materials, such as polymers and ceramics. The development of metal/polymer composite materials is a classic example of this growing synergy between metals and polymers. In this technology, the properties of metals and polymers are combined to produce materials as lightweight as plastics, but capable of conducting heat and electricity.

Further, the deposition of thin polymer films on metal surfaces has created a number of new opportunities. For example, the biocompatibility of a titanium implant is dramatically improved by depositing a very thin polyethylene glycol film on the implant's surface.²⁻³ A polymer layer only a few nanometers thick is required to induce this desired property. Nanoscale polymer layers grafted to metal surfaces can be used to modulate adhesion, lubrication, wettability, friction, and biocompatibility of the underlying substrate.

¹, ², ³
The grafting of ultrathin polymer layers to metal surfaces has presented great opportunities, where the properties of metals (e.g., magnetism and electrical conductivity) and the properties of ultrathin polymer films can be combined to construct hybrid platforms for various devices, actuators, and sensors.

The goal of this research is fabrication and characterization of polymer nanolayers (brushes) deposited on metal surfaces (nickel and gold) by the "grafting to" method, with the prospective possibility of integrating developed systems into active microfluidic and sensing devices. To this end, the methodology for the modification of flat model metal surfaces was first developed. Next, the approach used for the modification of flat metal surfaces was employed to modify complex (3D) nickel structures (nanowires, micronails), microprinted gold electrodes, and nanoparticles.

The work is structured as follows: Chapter 2 of this dissertation gives a literature overview of the methods used to modify the metal surfaces. It also provides descriptions of the methods used for the synthesis of the grafted polymer nanoscale films and their characterization and utilization for the surface modification of metals. Chapter 3 provides descriptions of the experimental techniques used. Chapter 4 focuses on the synthesis and characterization of ultrathin polymer films grafted to the model surfaces of nickel and gold. Specifically, we will discuss the permanent grafting of carboxy-terminated PS, polyethylene glycol (PEG), P2VP, and PAA from the melt onto gold and nickel model surfaces employing PGMA as a macromolecular anchoring layer. Chapter 5 describes the methodology for the surface functionalization of different segments of nickel nanofibers/micronails with polymer layers of antagonistic natures. The method is
based on a combination of the step-by-step etching of silicone (PDMS) matrix incorporating nickel nanowires/micronails and the "grafting to" technique. The technique of step-by-step controllable etching of the silicone matrix allowed us to expose certain segment of the surface of nickel nanofibers/micronails for polymer grafting. The "grafting to" technique allowed us to modify the surface with polymer layers via the macromolecular anchoring layer approach. This approach resulted in the modification of different segments of nanowires/micronails with different polymers. Namely, the tips of the nanowires/micronails were modified with a hydrophobic PS layer, and the bottom portion with a hydrophilic polyacrylic acid film.

Chapter 6 examines the electrical properties of the ultrathin polymer layers grafted to the surface of microprinted gold electrodes. Specifically, layers of PGMA, PS, PAA, and P2VP with thicknesses of 10–20 nm were grafted to the gold surfaces. The polymer layers insulating at normal ambient conditions displayed significant increase in conductivity as they were exposed to the vapors of organic solvents and water. This phenomenon allowed us to design nanoscale polymer layers with reduced or enhanced sensitivity to anticipated changes in environment. The observed effects can be employed in the micron-sized conductometric transducing scheme for the detection of volatile organic solvents and water vapor.

The first part of Chapter 7 focuses on the synthesis and characterization of the shape-memory grafted nanofoams. We employed the "grafting to" technique to obtain an 80–200-nm anchored and cross-linked film of PGMA. The film was swollen in chloroform and freeze-dried to produce a nanofoam. The grafted nanofoam had
properties of a shape-memory material, exhibiting gradual mechanical contraction at the nanometer scale as the temperature was increased. The epoxy functionalities in the PGMA film were used for grafting low molecular weight PS. We demonstrated that the mechanical response of the grafted nanofoam could be tuned by grafting low molecular weight polymers.

We envision that the shape-memory grafted nanofoams can be utilized as a platform for developing unattended off-line sensing devices. To prove this concept, in the second part of Chapter 7 we focus on the synthesis, characterization, and actuation of the grafted PGMA/gold nanoparticles composite nanofoam. Specifically, gold nanoparticles were incorporated into the cross-linked PGMA film. Then, the PGMA/gold nanoparticles nanofoam was fabricated following the same procedure developed to fabricate the PGMA nanofoam. We tracked changes in the optical response of the system as a function of temperature (before foaming, after foaming, and after thermal actuation). The excitation of the gold nanoparticles with visible light led to characteristic extinction (absorption and scattering) bands. The position of the absorption bands depended on the nanoparticles environment. Thus, by changing the environment of gold nanoparticles (foaming/collapsing cycles) we were able to detect changes in the extinction bands. This alteration of the optical response can be monitored post-facto through UV-vis spectroscopy.

In conclusion, this dissertation provides the fundamentals for the synthesis and characterization of nanoscale polymer layers employed for the modification of metal surfaces.
References


CHAPTER TWO
LITERATURE REVIEW

This research is devoted to the synthesis and characterization of nanoscale polymer films employed in the surface modifications of metals. Therefore, the study requires an understanding of the grafting concepts and behaviors of nanoscale polymer films. An understanding of the basics of metal surface/polymer interactions and metal surface chemical reactivity is also important.

This chapter provides a brief overview of the techniques and materials employed for metal surface modifications. In addition, nanoscale polymer layer preparation techniques and behavior are presented in this chapter to summarize the state-of-the-art technology in the field of surface modification.

2.1 Methods of metal surface modification: Introduction

Various modern approaches have been used to modify metal surfaces. The modification techniques can be divided into two major categories: physical and chemical.¹ Surface modification by physical methods can be accomplished by high-power laser treatment,²,³ plasma treatment,⁴ ionic plasma deposition,⁵ chemical vapor deposition,⁶ ion beam bombardment,⁷,⁹ and physical vapor deposition.¹⁰,¹¹ Physical methods of surface modification offer certain advantages over chemical methods; for instance, by making it easier to conduct and control modifications. In addition, the methods are environmentally safe and clean, do not require the use of chemical solutions, and require no liquid waste disposal. The subject of physical methods of surface
modification is very vast.\textsuperscript{12-15} Because the present research focuses on the chemical methods of surface modification, the analysis of physical methods is beyond the scope of this literature review. Therefore, this review focuses on the recent progress in chemical methods to modify the surface properties of metals. The review is composed of two sections. Section 1 centers on low molecular weight compounds utilized for metal surface modifications: silanes, thiols, fatty carboxylic acids, and derivatives of the phosphoric and phosphonic acids that form self-assembled monolayers (SAM) when anchored to the surface of metal/metal oxides.\textsuperscript{16} SAMs have generated great interest in surface modification research due to their molecular order, versatility, simplicity, and processing flexibility.\textsuperscript{17} Section 2 describes macromolecular compounds employed for the surface modification of metals. Thin polymer films, polymer brushes, and techniques of polymers deposition are described in this section.

2.2 Low molecular weight compounds for the surface modification of metals

2.2.1 Silanes

Silanes are silicon-based compounds that possess: (a) a hydrolytically sensitive center-hydrolyzable group that can react with inorganic substrates, such as metal oxides, to form stable covalent bonds; and (b) an organic substitution-organofunctional group that alters the physical properties of treated surfaces\textsuperscript{18,19} (Fig. 2.1). Organofunctional silanes are often used in the modification of metal surfaces. Silane-based chemical modification is commonly called silane coupling treatment.\textsuperscript{20}
There is a broad variety of commercially available silanes that can be used for metal surface modifications, such as alkoxy silanes \( [R_{4-n}\text{Si}(OR^*)_n; \ R^*=\text{Me, Et}] \), hydrogenosilanes \( [R_{4-n}\text{SiH}_n] \), and chlorosilanes \( [R_{4-n}\text{SiCl}_n] \).

![Diagram of silane molecule]

**Figure 2.1.** Structure of the silane molecule

The greatest advantages of the silanes are their ability to bear different functional groups and the simplicity of their deposition/attachment to the metal/metal oxide surface. However, the use of silanes in surface modifications requires the fulfillment of one precondition—presence of the oxide layer; this is because silanes have high bonding affinity to various metal oxide surfaces.

Alkoxy silanes and chlorosilanes react with metal oxide surfaces through the condensation reaction with the hydroxyl groups.\(^{19}\) The majority of the widely used organosilanes have one organic substituent and three hydrolyzable substituents (alkoxy or chloride). Initially, there is hydrolysis of the three labile groups (Fig. 2.2 A). In the vast majority of surface treatment applications, the alkoxy or chloride groups are hydrolyzed to form silanol functionalities. Next, one silanol functionality reacts with the hydroxyl group present on the metal oxide surface while others participate in the intermolecular
condensation reaction (Fig. 2.2 B and C). These reactions can occur sequentially or simultaneously with the initial hydrolysis step. As a result, there is usually only one bond from each silicon of the organosilane to the substrate surface at the interface. The two remaining silanol groups are present in either condensed or free form. The organofunctional group remains available for covalent reactions or physical interactions with other compounds.

![Diagram](image)

**Figure 2.2.** Steps of the chemical reaction of silanes with a substrate surface

The work of Castricum et al. reported on the employment of organochlorosilanes for hydrophobization of the Al₂O₃ surface.²¹ Chlorotriphenyl silane, tert-butylchlorodimethyl silane, and chlorotrimethyl silane were used to modify the surfaces
which is rich in hydroxyl groups. The hydrolysis of the chloride groups and subsequent condensation with the surface hydroxyl groups resulted in successful functionalization of the surface with hydrophobic moieties. In another example, Jeon et al. developed the method of microcontact printing of alkylchlorosiloxanes on several metal/oxide surfaces, such as Al/Al₂O₃, TiN/TiO, and ITO.²²

It is important to note that the reactions of chlorosilanes or alkoxy silanes with oxides presented on metal surfaces result in the release of HCl or alcohol that can alter the surfaces. For example, Rendi De Palma et al. observed complete disintegration of magnetic ferrite nanoparticles during surface modification with chlorosilanes due to the liberation of HCl.²³ To address this issue, Ido et al. developed and implemented another method of chemical surface modification for Al₂O₃ and TiO₂ substrates, where hydrosilanes were utilized as effective surface modifiers.²⁴ The result of silane/substrate coupling was the liberation of hydrogen that is non-corrosive to metals and oxides.

### 2.2.2 Organosulfur compounds: Thiols

Organosulfur compounds have high chemical affinity toward the surfaces of transition metals.²⁵,²⁶ The compounds reported in the literature included alkyl sulfides, alkyl disulfides, thiophenols, cysteines, xanthenes, and thioureas.²⁷ The most prominent category of organosulfur compounds employed in the metal surface modifications are thiols. Thiols contain the carbon-bonded sulfhydryl group (R-SH) that is responsible for the bonding of the thiol molecule to the metal surface, while the R-functional group is responsible for the interaction of the metal surface with other phases (Fig. 2.3). The
interaction between the surface of gold and alkanethiols is the most studied and best understood. The presumed adsorption chemistry between thiols and gold surface is shown in Figure 2.4. Thiols can interact with metal surfaces in two ways. The intact thiol molecules can be adsorbed or the molecules can be chemisorbed, resulting in the formation of metal thiolites. The chemisorption results in cleavage of the S-H bond.

![Figure 2.3. Structure of the thiol molecule](image)

The surface modification of gold with alkanethiols was extensively studied by the George Whitesides Research Group. For instance, Bain et al. developed the method of tuning and controlling the hydrophilicity and acidity of the gold surface. Their approach was based on the chemisorption of a mixture of undecanethiol and 11-mercaptoundecanoic acid. The result of the adsorption was the formation of densely packed, oriented monolayers. These monolayers exposed the polar carboxylic groups and non-polar methyl groups at the interface. The wettability and acidity of the surface were controlled by varying the ratio between the two components in the mixture.
A number of papers have reported the modifications of other metals with thiols. For example, Doty et al. developed approaches to stabilize water suspensions of Ag nanoparticles based on surface modifications of the nanoparticles with thiolalicylated polyethylene glycol. Extremely stable water suspensions of Ag nanoparticles were produced. The suspensions were able to withstand high NaCl (≥ 2M) concentrations and a pH range of 1–14. These experimental developments opened the door for the biological applications of the water suspensions of Ag nanoparticles. Moreover, adsorption of thiols provides significant protection for the metal surface against oxidation. For example, Laibinis et al. studied self-assembled monolayers derived from the adsorption of n-alkanethiols onto freshly evaporated copper surfaces. The presence of the monolayer slowed the oxidation of the surface. In addition, the monolayers formed by long-chain alkanethiols were more effective at preventing surface oxidation than were the monolayers formed by short-chain alkanethiols.
2.2.3 Carboxylic acids

Long-chain carboxylic acids have been widely used in the surface modification of metals. There are three possible mechanisms for immobilization of carboxylic acids on metal surfaces. The first is based on the chemisorption of acid molecules and involves the formation of surface salts. The driving force for this mechanism is the reaction between oxide (hydroxide) that is naturally present on the surface of many metals and carboxylic groups and are able to generate protons; that is, a base/acid reaction on the surface. The general requirement for the reaction is the presence of oxide on the metal surface. The result of the reaction is the formation of surface salts between carboxylate anion and the surface metal cation. The second mechanism is realized through a proton transfer to a lattice oxygen atom presented on the surface. The third mechanism involves physisorption of acid molecules with no proton transfer.

Lim et al. provided a representative example for studying adsorption of carboxylic acids on metal oxide surfaces. The adsorption of stearic acid onto the aluminum surface was investigated. The study revealed that stearic acid binds to the alumina surface via monodentate and bidentate interactions (Fig. 2.5). The kinetics of stearic acid desorption was also studied. A time-dependent desorption profile of stearic acid provided evidence of the presence of areas with different levels of adsorption affinity on the alumina surface.

Dote et al. conducted an interesting study on the adsorption of stearic acid on a surface of gold and aluminum. The relationship between the chemistry of the surface and the mechanism of the immobilization of the stearic acid was established.
Figure 2.5. Schematics of the binding of molecules of fatty carboxylic acids to the substrate surface; monodentate interaction (image A); bidentate interaction (image B)

The acid was chemisorbed on the aluminum oxide substrate, and the acidic proton was dissociated from the acid to form the surface salts. However, on gold, where there are no strong acid-base interactions, the acid was physisorbed. The structure and packing densities of the layers of the carboxylic acids adsorbed onto the surfaces; factors that influenced them were the subject of the work of Tao et al.43 The researchers studied the monolayers of fatty carboxylic acids \( \text{C}_n\text{H}_{2n+1}\text{COOH} \ n=2-18, 22 \) formed on the surfaces of Ag, Cu, and Al. The structure formed by the monolayers was highly dependent on the nature of the metal surface, as well as the chain length of the acid involved in the surface modification. It was established that the surface determined the geometry of the head group and packing density. The chain length also affected the packing density and conformation of the chains in the layer. The Ag surface provided a setting for highly ordered arrays of acid molecules. The acid molecules dissociated completely on the surface of the Ag. Two oxygen atoms of the carboxylate anion bound to the surface
almost symmetrically. On the surfaces of aluminum and copper, the acid molecules also
dissociated, but the carboxylate anions bound asymmetrically. The result of this
interaction led to a lower packing density and less order, especially for short-chain acid
molecules. As the chain lengthened, the cohesive interaction pulled the chains up into a
normal orientation to the surface plane.

![Diagram of phosphonate interaction with a substrate surface]

**Figure 2.6.** Schematics of phosphonate interaction with a substrate surface; monolayer
formation (image A); polycondensation reaction (image B)

### 2.2.4 Organophosphorus compounds

Organic derivatives of phosphoric and phosphonic acids, such as monoalkyl
phosphoric acid, phenylphosphonic acid, their ethyl esters, and their trimethylsilyl esters,
have been extensively used for the modification of metal surfaces. As with silanes, the
major requirement for the attachment of the phosphonates groups to the surface is the presence of the native or grown metal oxide layer. Modification of the metal surface with derivatives of phosphoric or phosphonic acids creates metal-oxygen-phosphorus bonds. For example, the modification of the Ti surface results in Ti-O-P bonds. An important difference between the silanes and phosphonates chemistry is that phosphonates only undergo reactions with surface OH groups, but do not undergo a homocondensation reaction. Thus, they do not form P-O-P bonds. However, depending on the reaction conditions (T, pH, and concentration), the condensation process can compete with the surface modification (Fig. 2.6).

The surfaces of different oxides have been modified using phosphonates. For example, Holland et al. investigated the binding of 2-carboxyethanephosphonic acid (CEPA) and phenylphosphonic acid (PPA) to a SnO$_2$ surface by solid-state $^{31}$P NMR. The observations confirmed strong interactions between the SnO$_2$ surface and the phosphonic acid groups. In addition, $^1$H MAS NMR spectroscopy displayed a complete absence of the acidic protons of the phosphonic acid groups, strongly supporting the formation of P-O-Sn linkages. The results indicated primarily a bidentate and tridentate phosphonic acid bonding configuration at the SnO$_2$ surface for both CEPA and PPA molecules (Fig. 2.7).
2.3 Modification of the surface with polymers

Polymers are also widely used for the surface modifications of metals. They are excellent candidates for several reasons: (a) they can form films of variable thicknesses, thus providing control over a number of functional groups; (b) they have better and more tailorable mechanical properties compared to low molecular weight compounds; (c) they offer a wide variety of functional groups to choose from; and (d) they can serve as stimuli-responsive materials. Originally, polymer thin films were created through physical adsorption of polymer chains on the surface of interest. The nature of the interactions between the polymer and the surface in these coatings is usually noncovalent. Thus, the performance of physisorbed polymer layers reduces over an extended period due to the erosion of the coating under application conditions. To overcome these shortcomings, it is necessary to chemically bind the polymers to the surface. For this purpose, densely grafted polymer layers are the most valid candidates. They have the same set of advantages as SAM. Moreover, covalently grafted polymer systems are chemically and mechanically more robust than SAM or physically adsorbed polymer chains. In addition, they provide a higher degree of synthetic flexibility and the potential...
to fabricate active and responsive interfaces. The second part of this literature review focuses on the theory, synthesis, and characterization of chemically grafted polymer layers. This part presents a description of the behavior of polymers and the methods employed for their fabrication.

2.3.1 Theory of densely anchored polymer layers

The term polymer "brush" refers to the dense ensemble of polymer chains attached by one end to the substrate.\textsuperscript{49,52-54} The density of tethering for polymer chains is so high that, in a good solvent, polymer chains are forced to stretch away from the surface to avoid overlapping. For the stretching, the distance between the tethering points should be less than the radius of the gyration of the polymer chain. The conformation of macromolecules when the chains are stretched away from the surface in the direction normal to the grafting surface is different from the conformation of the polymer chains in solution where the chains adopt random-walk conformations (Table 2.1).\textsuperscript{49}

Alexander was the first researcher to conduct a theoretical analysis of polymer brushes.\textsuperscript{55} Up to date, the internal structure of polymer brushes was widely studied by numerical and analytical self-consistent field (SCF) calculations and by computer simulations.\textsuperscript{56-59}

Table 2.1. Polymer chain size in the brush and solution\textsuperscript{51}

<table>
<thead>
<tr>
<th>Solvent/Polymer chain state</th>
<th>Tethered polymer chain</th>
<th>Free polymer chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>Good solvent</td>
<td>$L/a \sim N(a/d)^{2/3}$</td>
<td>$R_g \sim N^{3/5}$</td>
</tr>
<tr>
<td>Theta solvent</td>
<td>$L/a \sim N(a/d)$</td>
<td>$R_g \sim N^{1/2}$</td>
</tr>
<tr>
<td>Bulk state</td>
<td>$L/a \sim N^{2/3}$</td>
<td>$R_g \sim N^{1/2}$</td>
</tr>
</tbody>
</table>
Polymer chains densely tethered to the surface have two tendencies when immersed in a good solvent.\textsuperscript{52} First, they attempt to maximize their entropy by adopting random-walk configuration. This should lead to shorter, dense brush layers and result in strong overlapping among the undeformed coils. The overlapping increases the monomer–monomer unit contacts and the corresponding interaction energy ($F_{\text{int}}$). Second, densely tethered polymer chains in contact with a good solvent would like to be wet by it, thus forming tall sparse brushes. This leads to a decrease in configurational entropy, which is unfavorable. As a result, when the distance between two adjacent tethered chains is much smaller than the radius of the polymer chain gyration, both tendencies cannot be met. Polymer chains respond by choosing equilibrium height $L$ of the brush, where the two forces are balanced. Stretching lowers the interaction energy per chain $F_{\text{int}}$ at the price of high elastic free energy $F_{\text{el}}$. The interplay of these two terms determines the equilibrium thickness of the grafted layer.\textsuperscript{49,52}

In his work, Alexander considered the flat, nonadsorbing surface to which monodisperse polymer chains were tethered.\textsuperscript{55} The minimization of the free energy of the polymer chain with respect to thickness $L$ gave the following equation:

$$\frac{L}{a} \approx N \left( \frac{a}{d} \right)^{2/3}$$  \hspace{1cm} (2.1)

where $L$- is layer thickness, $a$- average segment diameter, $d$- distance between grafting points, and $N$- degree of polymerization. The most important conclusion from equation 2.1 is that equilibrium thickness of the polymer brushes varies linearly with the degree of
polymerization. This is opposite to the behavior of free polymer chain in a good solvent where the dimension of the polymer chain varies with N in a relationship of $R_g \sim N^{3/5}$. Table 2.1 shows comparison of scaling behavior of the polymer chains in brushes and free coils at good solvent, theta solvent and at a bulk state. To conclude, polymer chains in the polymer brushes exhibit extended conformations. The degree of deformation depends on the environmental conditions. This phenomenon provides an opportunity to not just tune but also to control and switch the properties of the surfaces on demand.

Polymer chains can be tethered to different interfaces, such as solid-liquid, liquid-liquid, and solid-air. They can be chemically bonded to the solid surface or attached through physical adsorption. Figure 2.8 illustrates a classification of the polymer systems comprising the polymer brushes.
Figure 2.8. Examples of the polymer systems comprising polymer brushes\textsuperscript{51}

Polymer brushes drew significant attention in the 1950s when they were first used to stabilize nanoparticles.\textsuperscript{61-63} It was found that polymer brushes could be used to control adhesion,\textsuperscript{64} lubrication,\textsuperscript{65} protein, wettability,\textsuperscript{68,69} and cell interactions with surfaces.\textsuperscript{66,67}

2.3.2 Methods of synthesis of polymer brushes

The tethering of polymer chains to surfaces can be reversible or irreversible.\textsuperscript{49} For reversible tethering, physical adsorption of homopolymers or block copolymers is utilized. For example, with block copolymers used, one block that strongly interacts with a surface is adsorbed while another block dangles above the surface, thus forming the
brush structure.\textsuperscript{70,71} Covalent tethering of the polymer chains can be conducted using two approaches: "grafting to" or "grafting from". In the "grafting to" approach, synthesized polymer molecules with reactive functional groups chemically react with complementary functionalities that are present on the surface.\textsuperscript{72-74} In the "grafting from" approach, an initiator is first attached to the surface, followed by surface-initiated polymerization.\textsuperscript{75,76} Despite the resulting high layer thickness, the "grafting from" approach is more demanding for highly controlled reaction conditions.

### 2.3.3 Physical adsorption

The physical adsorption of the polymer chains on a solid surface is a reversible process and can be achieved by the self-assembly of block or graft copolymers. These copolymers can be adsorbed in the presence of a selective solvent or surface, resulting in a selective solvation or adsorption respectively.\textsuperscript{49} The grafting density of the polymer chains and all other characteristics of the polymer layer formed upon physical adsorption of the polymer chains are controlled by thermodynamics.\textsuperscript{77} Figure 2.9 illustrates the scheme of the polymer brush fabrication by physical adsorption of polymer chains on a solid surface.
Figure 2.9. Representation of the physical adsorption of the polymer chains on a substrate surface

The major factors that control the adsorption of macromolecules and the structure of the polymer layer include the concentration of the polymer and molecular weights. The polymer/solvent, polymer/surface affinity and selectivity, and the ratio between the blocks responsible for adsorption (anchor) and brush formation (buoy) are also important factors.⁷⁸,⁷⁹
The preparation of polymer brushes by physical adsorption is not difficult. However, this method of brush formation has significant drawbacks. For example, the polymer brushes exhibit thermal and solvolitic instabilities. When heated above glass transition temperature, these polymer brushes dewet, thus forming heterogeneous systems. To overcome these drawbacks, polymer chains should be covalently attached to the surface using "grafting from" and "grafting to" techniques.

### 2.3.4 'Grafting from' approach

The "grafting from" approach is based on the polymerization reaction conducted from the surface to generate tethered chains. Prior to polymerization, the initiator species are immobilized on the substrate surface. The entire surface of a substrate can potentially be covered with a layer of grafted polymer chains. The method allows the preparation of polymer brush layers of high thickness and grafting density. Figure 2.10 schematically shows the "grafting from" method for the synthesis of polymer brushes. Free, controlled, anionic and cationic, ring-opening polymerizations can be utilized for the "grafting from" approach.

Glow discharge is one of the easy and convenient methods to introduce initiating radical species on a surface. For example, Ito et al. employed glow discharge in the presence of oxygen to introduce a peroxide species on the surface of a porous polymer membrane composed of polyethylene and polytetrafluoroethylene.
Acrylamide, 3-carbamoyl-1-(p-vinylbenzyl) pyridinium chloride and mixtures of two monomers were graft-polymerized on the surface of the porous polymer membrane to investigate the water permeation as a function of the ionic strength of the solution. It was revealed that the rate of water permeation could be influenced by the ionic strength of the solution. The rate of water permeation was also affected by the addition of the oxidant or reductant solution. The change in permeability was reversible and occurred immediately with the changing ionic strength. The reduced rate of water permeation at lower ionic strengths could be attributed to the contraction of the grafted polymer chains because of the primary salt effect. The rapid response was characteristic of this material because of the polymer brushes' direct contact with the environment. In addition, in the absence of the NaCl, the permeation rate through the grafted membrane increased as result of the addition of reductant solution. This was most likely a result of the formation of an insoluble polymer complex.
Many studies have investigated the "grafting from" method, where conventional radical polymerization from the surface was utilized to grow polymer chains. For instance, Tsubokawa et al. developed a solvent-free method of free radical graft polymerization from the surface of silica. The introduction of initiator onto the silica nanoparticles surface was achieved by the reaction of the amino groups presented on a surface of silica nanoparticles with 4,4-azobis(4-cyanopentanoic chloride) (ACPC) in the presence of pyridine. Then, the grafting of hyperbranched poly(amidoamine) (PAMAM) was successfully achieved from gas phase.

To achieve better control over the polymer molecular weight and polydispersity, "controlled/living" types of polymerization can be used. These techniques allow grafting of block copolymers to a variety of surfaces.

Matyjaszewski et al. developed an effective methodology for conducting atom-transfer radical-polymerization (ATRP) from a surface. Conventional atom-transfer radical polymerization was carried out in rigorously deoxygenated systems to prevent oxygen from trapping the propagating radicals. The scientists also reported a new method of ATRP that could be performed in the presence of limited amount of air and with a very small (typically ppm) amount of copper catalyst together with an appropriate reducing agent. This technique was successfully applied to the preparation of densely grafted polymer brushes (poly(n-butyl acrylate) homopolymer and poly(n-butyl acrylate)-block-polystyrene copolymer) on silicon wafers (0.4 chains/nm^2). This simple method of grafting well-defined polymers did not require any special equipment and could be carried out in vials or jars without deoxygenation.
To conclude, the "grafting from" approach presents many opportunities to the field of surface modification. However, the approach has some drawbacks. The main disadvantages are initiator efficiency, the limitation of initiator surface coverage, and the rate of monomer diffusion through already synthesized polymer films. In most cases, it is difficult to determine and control the exact molecular weight of the grafted polymer. There is also broad molecular weight distribution for the grafted chains that occurs due to less control over the polymerization compared to the bulk. The side reactions during "grafting from" synthesis are more important than the bulk polymerization because of high local concentration of the polymer chains. In addition, the modification procedure is quite complex and must be strictly followed to obtain the desired results.49,94,95

2.3.5 "Grafting to" approach

The "grafting to" approach is based on the attachment of preformed, end-functionalized polymer chains to a suitable substrate surface under appropriate conditions to form a tethered polymer brush.49 This method involves chemical reactions between end-functionalized polymer chains and complementary groups on the surface. End-functionalized polymers can be synthesized by free radical, controlled, cationic, anionic, ring-opening polymerization. Several methods can be used for the surface functionalization, such as plasma (corona, glow discharge) treatments, SAMs, and chemisorptions of the thin films of the reactive polymers. The "grafting to" can be performed either from solution or melt.49,96 Figure 2.11 represents the schematics of the "grafting to" approach.
Koutsos et al. synthesized the set of thiol terminated polystyrenes by anionic polymerization and studied their attachment to a gold surface. Polystyrene chains were adsorbed from toluene solution. AFM was utilized to study the chains conformation in bad solvent (water). Polymer chains showed two structural regimes in bad solvent conditions. A third structural regime has been observed when the adsorption was conducted from poor solvent conditions\textsuperscript{97}.

Figure 2.11. Representation of the "grafting to" approach of polymer chains tethering to the surface

Frank et al. reported a simple and effective way to photochemically attach thin polymeric layers to solid surfaces. The system was based on a photoreactive benzophenone derivative 4-(3′-chlorodimethylsilyl) propyloxybenzophenone that was bound to the SiO\textsubscript{2} surface by a silane anchor. The silane was immobilized on the SiO\textsubscript{2} surface at room temperature from toluene solutions. Then, polystyrene (PS) films were spin coated on top of the benzophenone derivative and the formed platform was
illuminated with UV light. As a result, thin (≤ 16 nm) films of PS were fabricated on the surface.

Luzinov et al. developed a method for grafting thin polymer films to the various surfaces employing a macromolecular anchoring layer approach.\textsuperscript{94,98-100} The method was based on the use of polyglycidyl methacrylate (PGMA) as a reactive anchoring interface. Various end-functionalized polymers were grafted to the reactive anchoring layer through the reaction between complementary groups.\textsuperscript{72,94,101} For example, this approach was used to graft carboxy- and anhydride-terminated polystyrene chains to the surface of a silicon wafer from the melt. The grafting was governed by the steric factor associated with the free volume available between the macromolecules of PS grafted to the surface. Low diffusion at the interface limited the further increase of grafting density with high molecular weight polymers.\textsuperscript{94}

The "grafting to" approach has many advantages. First, it is relatively easy to graft well-defined polymer chains to surfaces. A disadvantage of the "grafting to" approach is the low thickness of the polymer layer compared to what is achieved using the "grafting from" method. However, to change and control the surface properties, a high thickness is not always required. Surface parameters, such as wettability, adhesion, biocompatibility, and friction, can be improved by forming a covalently attached thin polymer film with a thickness of just a few nanometers.\textsuperscript{49,72,94,101,102}
2.3.6 Physical adsorption, "grafting from" and "grafting to" approaches in the modification of metal surfaces

The physical adsorption of block copolymers on the surface of metal nanoparticles has been successfully used to enhance their dispersability in a solvent.\textsuperscript{103,104} For instance, Tony Azzam et al. studied the stabilization of gold and palladium nanoparticles in a dispersion by a place exchange reaction between tetraoctylammonium bromide (TOAB) and poly(ethylene oxide)-b-polystyrene-b-poly(4-vinylpyridine) (PEO-b-PS-b-P4VP) triblock copolymer.\textsuperscript{105} The block copolymer was synthesized by atom-transfer radical polymerization. The displacement of the TOAB by block copolymer was mediated by strong coordination forces between the polyvinylpyrrolidone (PVP) block and the nanoparticle surface. In addition, the displacement of the low molecular weight compound TOAB with the block copolymer increased entropy, thus the exchange reaction was an entropically favored process. The prepared complex exhibited greatly improved stability. Self-assembly in water after the ligand exchange resulted in micellar structures of $\sim 20$ nm (electron microscopy) with the metal NP found located on the surface of the micelles. The stability of the nanoparticles in water depended greatly on the grafting density of the copolymer. The dispersions of the nanoparticles with high grafting density of polymer chains exhibited high stability (more than 6 mo.) compared to the dispersions of nanoparticles with low grafting density.

A considerable number of studies have been dedicated to grafting polymers to and from metal surfaces.\textsuperscript{106-110} For instance, Wei et al. studied surface modifications of Au, Ag, and Pd nanoparticles with nanothin polymer films.\textsuperscript{109} They employed a high affinity
of Au, Ag, and Pd to thiol compounds and grafted thiol-terminated poly(N-isopropylacrylamide) (PNIPAM) polymer chains to the nanoparticles surface utilizing the "grafting to" approach. First, a solution of thiol-terminated PNIPAM in water was prepared. Then, noble metals nanoparticles were synthesized in the presence of HS-PNIPAM. Polymer chains were grafted in situ to the surface to form core-corona nanoparticles. The resulting nanoparticles were well dispersible in water and organic solvents, such as chloroform, DMF, toluene, and ethanol. Moreover, they exhibited thermal sensitivity in water dispersions and showed a cloud point temperature of 32 °C.

An intriguing variation of the "grafting from" approach was developed by Ignatova et al.64 These scientists modified the surface of stainless steel with ultrathin polymer layers employing a "two-step grafting from" procedure. First, poly (2-phenyl-2-(2,2,6,6-tetramethyl-piperidin-1-yloxy)-ethylacrylate) film was tethered to the surface by electrografting. Then, nitroxide-mediated polymerization of 2-(dimethylaminoethyl) acrylate, styrene, or n-butyl acrylate was initiated from the electrografted polyacrylate chains. The grafted polymers were quaternized to endow them with antibacterial properties. Peeling tests revealed a strong adhesion of the grafted polymer films to the steel surface. Moreover, the quaternized copolymers showed excellent antibacterial properties and low affinity toward fibrinogen adsorption. These characteristics made the grafted polymers excellent candidates for antibacterial and antifouling coatings for stainless steel orthopedic and dental implants.

Wang et al. developed a method of surface modification of gold nanoparticles by employing a combination of "grafting to" and "grafting from" approaches.75 These
researchers reported the synthesis of Janus gold nanoparticles (AuNP) that were functionalized with two different types of polymer chains on opposite sides. Figure 2.12 shows the schematics of the surface modification. Thiol-terminated polyethylene oxide (HS-PEO) was crystallized from the solution into lamellar single crystals with a typical thickness of 12 nm. The thiol groups were located on the surfaces of the crystals (Fig. 2.12, images a and b). The AuNPs were immobilized on the surface of the HS-PEO crystals due to a strong chemical affinity between the gold and the thiol groups (Fig. 2.12, image c). Next, the thio-terminated initiator 11-mercaptoundecyl 2-bromo-2-methylpropionate was immobilized on the "free" surface of AuNPs through the ligand exchange reaction, resulting in asymmetric PEO/AuNP/initiator complexes (Fig. 2.12, image d). Atom-transfer radical polymerization was then performed from the AuNPs' surface modified with initiator. Polymethyl methacrylate was successfully synthesized on the AuNPs' surface (Fig. 2.12, image e). The final step comprised the dissolution of the HS-PEO single crystals (Fig. 2.12, image f). To verify the synthesis of the Janus AuNPs, the polymers were cleaved from the surface and analyzed by gel permeation chromatography (GPC). Two peaks were obtained from the elution curve. The first was ascribed to polymethyl methacrylate (PMMA) and the second to HS-PEO. This method was successfully employed to modify noble metals nanoparticles with different polymers.
In conclusion, a review of the literature demonstrated progress in the area of surface modifications of metals. The results to date showed the accumulation of solid expertise in employing low molecular weight compounds that are able to form self-assembled monolayers (SEM) for modifications of noble metal surfaces. Ultrathin polymer films (brushes) are also extensively used for these modifications. However, in the literature, the practice of using polymer films in surface modifications was mostly limited to the functionalization of noble metals.

The literature review showed a lack of practical methods for surface modification of transition metals utilizing the "grafting to" approach. New reliable methods for surface modification of transition metals, such as Ni, Fe, and Co, should be developed.
2.5 References


10. Größner-Schreiber, B.; Herzog, M.; Hedderich, J.; Dück, A.; Hannig, M.; Griepentrog, M., Focal adhesion contact formation by fibroblasts cultured on surface-


CHAPTER THREE
EXPERIMENTAL

3.1 Chemical reagents used

Hydrogen peroxide \([\text{H}_2\text{O}_2]\):

Company Identification: Acros Organics
MSDS Name: Hydrogen Peroxide (30% in Water) (Without Stabilizer), Reagent ACS
CAS Number: 7722-84-1

Sulfuric acid 98% \([\text{H}_2\text{SO}_4]\):

Company Identification: Acros Organics
MSDS Name: Sulfuric Acid, Reagent ACS
CAS Number: 7664-93-9

Chloroform:
Company Identification: VWR International LLC
MSDS Name: Chloroform, ACS
CAS Number: 67-66-3

Toluene:
Company Identification: Acros Organics
MSDS Name: Toluene, Reagent ACS
CAS Number: 108-88-3

Methyl ethyl ketone [MEK]:
Company Identification: Acros Organics
MSDS Name: 2-Butanone, 99+%
CAS Number: 78-93-3

Ethanol:
Company Identification: Mallinckrodt Baker Inc.
MSDS Name: Reagent Alcohol, ACS
CAS Number: 64-17-5

Methanol:
Company Identification: VWR International LLC
MSDS Name: Methanol, ACS
CAS Number: 67-56-1

Acetone:
Company Identification: VWR International LLC
MSDS Name: Acetone, ACS
CAS Number: 67-64-1

N-Methyl-2-pyrrolidone [NMP]:
Company Identification: Alfa Aesar
MSDS Name: N-Methyl-2-pyrrolidone, 99+% 
CAS Number: 872-50-4

Ether:
Company Identification: VWR International LLC
MSDS Name: Ether, Stabilized; ACS
CAS Number: 60-29-7
**Succinic anhydride:**

Company Identification: Sigma-Aldrich

MSDS Name: Succinic Anhydride

CAS Number: 108-30-5

**N,N-Dimethylformamide [DMF]:**

Company Identification: Acros Organics

MSDS Name: N,N-Dimethylformamide, 99%

CAS Number: 68-12-2

**Tetrabutylammonium fluoride 70% solution in water [TBAF]:**

Company Identification: Sigma-Aldrich

MSDS Name: Tetrabutylammonium Fluoride

CAS Number: 429-41-4

---

### 3.2 Polymers used for surface modifications

**Polyglycidyl methacrylate [PGMA] (Structure 3.1)**

The PGMA (M$_n$=176000 g/mole, PDI=2.7) was synthesized by solution radical polymerization and purified by multiple precipitations in ether following the procedure described elsewhere.$^{1,2}$
Carboxy-terminated polystyrene [PS] (Structure 3.2)

The carboxy-terminated polystyrene \((M_n=48000 \text{ g/mole, PDI}=1.05)\) was purchased from Polymer Source Inc., Canada.

Carboxy-terminated poly (2-vinyl pyridine) [P2VP] (Structure 3.3)

The carboxy-terminated poly (2-vinyl pyridine) \((M_n=53000 \text{ g/mole, PDI}=1.06)\) was purchased from Polymer Source Inc., Canada.
Carboxy-terminated polyethylene glycol [PEG] (Structure 3.4)

Polyethylene glycol monomethyl ether, with $M_n=5000$ g/mole was obtained from Sigma-Aldrich and modified with succinic anhydride to form a carboxy-terminated derivative following procedure reported elsewhere\(^1\).

Polyacrylic acid [PAA] (Structure 3.5)

The PAA from Sigma-Aldrich was precipitated from water solution with acetone, dried in a vacuum, and dissolved in methanol to prepare the dip-coating solution.
3.3 Principle experimental and characterization techniques

3.3.1 Dip coating

Dip coating is a process where the substrate is immersed in a solution and then withdrawn at a constant speed. The sample withdrawal can be done under atmospheric or other gas conditions. The withdrawal speed and the viscosity of the solution determine the coating thickness. If the withdrawal speed is such that the shear rates keep the system in the Newtonian regime, the coating thickness can be calculated by the Landau-Levich equation:

\[ h = 0.944 \times \left( \frac{\eta v}{\rho g} \right)^{1/2} \times \left( \frac{\eta v}{\sigma} \right)^{1/6}, \]  

(3.1)

where \( \eta \) is the dynamic viscosity of the solvent, \( v \) is the withdrawal speed, \( \rho \) is the liquid density, \( g \) is the acceleration gravity, and \( \sigma \) is the liquid surface tension. In this work, an operating speed adjusted to approximately 4 mm/sec was used for polymer film deposition. A Mayer Feintechnik D-3400 dip coater was placed in a clean room to avoid contamination of the samples with dust particles. Figure 3.1 represents the procedure of the coating with dip-coating apparatus.

![Figure 3.1. Procedure for coating substrate with dip-coating apparatus](image)

Figure 3.1. Procedure for coating substrate with dip-coating apparatus.
3.3.2 Ellipsometry

Ellipsometry is an optical technique that measures the dielectric properties (refractive index) of thin films. It can be used to evaluate the thickness, refractive index, extinction coefficient, surface roughness, and composition of thin films. Typically, ellipsometry measures the change in the polarization state of light reflected from the surface of a sample.\(^5\)

\[
\tan(\Psi) e^{i\Delta} = \frac{R_p}{R_s} \quad (3.2)
\]

The measured values are expressed as \(\Psi\) and \(\Delta\). These values are related to the ratio of the Fresnel reflection coefficients \(R_p\) and \(R_s\) for \(p\)- and \(s\)-polarized light respectively. Because ellipsometry measures the ratio of two values, it can be highly accurate and very reproducible. From equation (3.2), the ratio is seen to be a complex number; therefore, it contains "phase" information in \(\Delta\), which makes the measurement very sensitive. Figure 3.2 shows how a linearly polarized input beam is converted to an elliptically polarized reflected beam.\(^5\) For any angle of incidence greater than 0° and less than 90°, \(p\)-polarized and \(s\)-polarized light will be reflected differently.

**Figure 3.2.** Schematic of the geometry of the ellipsometer\(^5\)
The coordinate system used to describe the ellipse of polarization is the $p$-$s$ coordinate system. The $s$-direction is taken to be perpendicular to the direction of propagation and parallel to the sample surface. The $p$-direction is taken to be perpendicular to the direction of propagation and contained in the plane of incidence.

The ellipsometry was performed with a COMPEL automatic ellipsometer (InOmTech, Inc.) at a $70^\circ$ angle of incidence. Five measurements were taken for each sample. For all the experiments in the current research, the compensator was kept on for thickness values less than 11 nm and removed for thickness values greater than 14 nm. For thickness values between 11 and 14 nm (both limits included), the average value of the thickness with and without the compensator was used.

### 3.3.3 Contact angle measurements

When liquid is placed on the surface, it either spreads or beads up. The shape of the liquid drop is determined by the surface tension of the liquid and the surface. The contact angle of the liquid droplet is defined as the angle formed by the intersection of the liquid-solid interface and the liquid-vapor interface (Fig. 3.3).

As described by Young, the contact angle of a liquid drop on an ideal solid surface is defined by the mechanical equilibrium of the drop under the action of three interfacial tensions.\(^7,8\)

\[
\gamma_{lv} \cos \theta_Y = \gamma_{sv} - \gamma_{sl},
\]

(3.3)
where $\gamma_{lv}$, $\gamma_{sv}$, and $\gamma_{sl}$ represent the liquid-vapor, solid-vapor, and solid-liquid interfacial tensions, respectively, and $\cos \theta_Y$ is the contact angle. Thus, the equilibrium contact angle is governed by the force balance at the three phase boundaries (Fig. 3.3), as defined by equation (3.3).

The contact angle is very sensitive to the chemical composition of the top layer and is a relatively simple, inexpensive, and reliable technique for characterizing polymer surfaces. In this work, the static contact angle measurements were performed using a contact angle goniometer (Kruss, Model DSA10). Three measurements were taken for each sample. The calculation of the contact angle was made using the tangent method. The contact angle measurements were made with deionized (DI) water (pH 6.0) and a static time of 30 sec before the angle measurement.

![Figure 3.3](image)

**Figure 3.3.** Illustration of contact angles formed by liquid drops on a smooth, homogeneous surface

### 3.3.4 Atomic force microscopy (AFM)

Atomic force microscopy is the technique used to obtain information on surface topography and properties (roughness, morphology, electrical, and magnetic properties, and the size of surface features) of the different substrates.
In AFM, a sharp probe (tip) is moved across the surface of the sample, while the probe-surface interaction is monitored to produce an image. Depending on the feedback signal, AFM has three primary modes of operation: the contact, non-contact, and tapping modes (Fig. 3.4).

The AFM studies were performed on a Dimension 3100 microscope (Digital Instruments, Inc.). The tapping mode was used to study the surface morphology of the samples in ambient air. Silicon tips with nominal spring constants of 45 N/m were used to scan the surfaces with a 1-Hz rate.

Figure 3.4. Schematics of the AFM operation

3.3.5 Plasma generator

Plasma modification is an effective method to introduce surface functional groups on polymers without modifying the bulk properties. A typical plasma environment consists of charged and neutral species, such as electrons, ions, and radicals. The plasma generator used in this work was obtained from Harrick Scientific Corporation (Model
It is a compact, radio frequency (13.54MHz), glow discharge apparatus. It has a 3”-diameter by 7”-long chamber and a removable cover. The chamber has two hoses for connection to the vacuum source and the introduction of the gas required for the sample treatments. The plasma treatments were done at 0.2-mtorr pressure. The generator power switch was set at 18 W.

### 3.3.6 Scanning electron microscopy (SEM)

In SEM, a focused beam of high-energy electrons interacts with the surface of solid specimens producing signals that are sensed by a detector, thereby revealing information about the sample, including its texture, chemical composition, crystalline structure, and orientation of crystals.

A Hitachi S-4800 high-resolution scanning electron microscope (FE-SEM) and two variable pressure scanning electron microscopes (SU6600 and SU3400) in the Advanced Materials Research Laboratory (AMRL) (Research Park, Clemson University), were used for scanning purposes. High-vacuum and variable pressure regimes were used in the sample analyses. Figure 3.5 represents the optics schematics of the SEM.

Energy Dispersive X-Ray spectroscopy integrated into the SU6600 and SU3400 systems was used to track the changes in the chemical compositions after grafting the polymer layers.
3.3.7 Transmission electron microscopy (TEM)

In TEM, a focused beam of high-energy electrons is transmitted through an ultra-thin specimen. While traveling through, electrons interact differently with various parts of the specimen. Some parts of the specimen scatter electrons and appear as dark areas on the image. The image is brighter where electrons are not scattered.\textsuperscript{15}

High-resolution Scanning Transmission Electron Microscope HD2000 and Transmission Electron Microscope 9500 in the AMRL were used for scanning purposes. \textbf{Figure 3.6} represents the schematics of the TEM optics.\textsuperscript{16}
3.4 Characterization of the polymer films

Several parameters were calculated, such as surface coverage ($\Gamma$), grafting density ($\Sigma$), and distance between grafting sites ($D$), for the characterization of the polymer layers.\textsuperscript{17} The surface coverage (adsorbed amount) (mg/m$^2$) was calculated from the ellipsometry thickness $h$ (nm) and density (g/cm$^3$) of the polymer using the following equation:

$$\Gamma = h \times \rho$$  \hspace{1cm} (3.4)

The density of PGMA (1.08 g/cm$^3$) was assumed to be the same as for the poly (propyl methacrylate).\textsuperscript{18} The density data for PEG (1.12 g/cm$^3$), PAA (1.14 g/cm$^3$), PS (1.05 g/cm$^3$), and P2VP (1.06 g/cm$^3$) were provided by a supplier. It was assumed that the density of the thin polymer films was the same as the density of bulk polymers.
The chain density, $\sum$ (chain/nm$^2$), which is the inverse of the average area per adsorbed chain, was determined using the following equation:

$$
E = \frac{\Gamma \times N_d \times 10^{-21}}{M_n} = \frac{(6.023 \times \Gamma \times 100)}{M_n}
$$

(3.5)

The distance between grafting sites was determined by employing the equation:

$$
D = \left(\frac{4}{\pi \times E}\right)^{1/2}
$$

(3.6)

All the above parameters were calculated from the measured ellipsometric thicknesses. Thus, errors in $\Gamma$ and $\sigma$, which were proportional to the thicknesses, should not have exceeded 10%. The error in $D$ should also not have exceeded 10%.

The end-to-end distance of the unperturbed polymer chains was calculated by the following equation:

$$
\langle r^2 \rangle^{1/2} = a \times N^{1/2},
$$

(3.7)

where $N$ - is the degree of polymerization and $a$ - is a statistical segment length. The statistical segment length for PGMA, PS, and P2VP was assumed to be the same as for poly (methyl methacrylate) (0.6 nm).$^{19}$ The statistical segment length used in calculations for PEG was equal to 0.29 nm$^1$.

The radius of gyration of unperturbed polymer chains $R_g$ was calculated using the following equation:

$$
R_g = a \times \left(N/6\right)^{1/2}
$$

(3.8)

The root-mean-square roughness (RMS) of the samples was computed from the topographical AFM images recorded in the tapping mode using Nanoscope version
5.3.0r3.sr3 software (Veeco Instruments Inc.). The RMS is the standard deviation of the feature height (Z) values within a given area. The formula used to calculate RMS is \(^{20}\):

\[
RMS = \sqrt{\frac{\sum_{i=1}^{N}(Z_i - Z_{\text{ave}})^2}{N}}, \quad (3.9)
\]

where \(Z_{\text{ave}}\) is the average Z value within the given area, \(Z_i\) is the current Z value, and \(N\) is the number of points within a given area.
3.5 References


7. T. Young, Philos. Trans. R. Soc. Lond. 95, 65 (1805).


CHAPTER FOUR
GRAFTING OF NANOSCALE POLYMER LAYERS TO THE MODEL SURFACES OF NICKEL AND GOLD

4.1 Introduction

The aim of this portion of the research was the fabrication, characterization, and understanding of polymer nanolayers grafted to metal surfaces (nickel and gold). Specifically, this section reports a methodology for the modification of flat model metal surfaces with nanothin polymer films utilizing the "grafting to" approach. The grafting of homogeneous nanothin polymer films to metal surfaces presents significant opportunities. It allows the establishment of the conditions necessary for polymer grafting, such as temperature and time. In addition, when grafted to the flat surface of homogeneous polymer films, it can be examined straightforwardly by AFM, ellipsometry, and goniometry (wettability measurements). For instance, AFM and ellipsometry have been used for thickness analysis of the thin polymer films grafted to silicon wafers and other surfaces. Many important film characteristics, such as roughness, grafting density, and distance between grafting sites, can be calculated from the measured values.

In our investigations, the model studies were performed on nickel- and gold-coated silicon wafers. The developed methodology was then transferred to the surface modification of more complex systems, such as nickel nanowires, micronails, and microprinted gold electrodes. The developed method of Ni and Au surface modification was based on the "grafting to" approach. This is an effective approach of polymer

chains tethering. The number of polymers with different properties, such as PS, P2VP, PEG, and PAA, were grafted to the model surfaces employing PGMA as an intermolecular anchoring layer. The synthesized nanothin polymer films were analyzed and characterized by means of ellipsometry, AFM, and goniometry.

4.2 Experimental

4.2.1 Model surface of nickel

Initially, the grafting of the polymer layers to the nickel-coated silicon wafers (model surface) was investigated. Highly polished, single crystal silicon wafers were cleaned in an ultrasonic bath for 30 min, placed in a hot "piranha solution" (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1 h, and then rinsed several times with high-purity water. Next, nickel was sputtered on the surface of the silicon wafers (100-nm thickness) using a vacuum deposition system built in Dr. Chumanov's laboratory (Department of Chemistry, Clemson University). The model samples were plasma activated at a high intensity level (18 W) for 5 min. Next, the samples were rinsed with high-purity DI water and dried under a stream of ultrapure nitrogen.

The PGMA film was deposited on the model surface by dip coating from 3.0 wt% chloroform solution, dried, and then aged overnight. The unbounded polymer was removed from the surface by multiple washings with chloroform. Additionally, the sample was annealed for 10 min at 120 ºC to stabilize and cross-link the PGMA layer.
To study the effects of temperature on the grafting of PGMA films, the same experimental sequence was employed (deposition, annealing, and rinsing). The samples were annealed for 1 h at 60, 72, 96, and 120 °C respectively.

The initial film of carboxy-terminated PS was dip coated from 1.0 wt% methyl ethyl ketone solution onto wafers modified with the PGMA anchoring layer (2.0 nm). The specimens were annealed overnight in a preheated 120 °C vacuum oven to facilitate the reaction between the carboxy end groups of polystyrene and the epoxy-modified substrate. At high temperatures, the carboxylic groups were able to react with the epoxy groups of the PGMA layer. The unbounded polymer was removed by multiple washings with methyl ethyl ketone.

The polyacrylic acid film was dip coated from a 1.0 wt% methanol solution onto the wafers modified with the PGMA anchoring layer. The grafting was conducted inside an incubator at 36 °C. The unbounded polymer was extracted by multiple washings with methanol and high-purity DI water.

The carboxy-terminated PEG powder was deposited onto the surface of a clean glass slide and was covered with the silicon wafer modified by the PGMA primary layer. The specimens were placed in a vacuum oven at 115 °C for 2 h to allow the end groups to anchor to the epoxy-modified substrate. The unbounded PEG was removed by multiple washings with chloroform.

The thickness and water contact angle measurements were performed to evaluate the coverage of the model surface with the grafted polymer films. The AFM studies were carried out to evaluate the morphology of the layers.
4.2.2 Model surface of gold

Initially, the grafting of the polymer layers to gold-coated glass slides (model surface) was investigated. Plain glass microscopy slides were cleaned in an ultrasonic bath for 30 min, placed in a hot "piranha solution" (3:1 concentrated sulfuric acid/30% hydrogen peroxide) for 1 h, and were then rinsed several times with high-purity water. Next, a thin film of gold (100.0 nm) was sputtered on the substrate surface. The samples were plasma treated at a high intensity level (18 W) for 5 min to remove contaminations. The samples were then rinsed with high-purity DI water and dried under a stream of ultrapure nitrogen.

The PGMA film was deposited on the model surface by dip coating from 0.2 wt% chloroform solution and left to dry at room temperature. Next, the PGMA was annealed at 120 °C under a vacuum for 1 h. The unbounded polymer was removed by multiple washings with chloroform.

For the grafting, the polymer films were deposited by dip coating on a PGMA layer following the same experimental sequence employed in the modification of the Ni samples (deposition, annealing, and rinsing). Solutions of PAA in methanol, P2VP, and PS in chloroform were used. Detailed experimental conditions are presented in Table 4.1.

Table 4.1. Parameters of the grafting of polymer layers to the model surface of Au

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Annealing temperature (°C)</th>
<th>Annealing time, (h)</th>
<th>Solvent rinse</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>120</td>
<td>1</td>
<td>Chloroform</td>
</tr>
<tr>
<td>PS</td>
<td>120</td>
<td>0.5</td>
<td>Chloroform</td>
</tr>
<tr>
<td>PAA</td>
<td>38</td>
<td>2</td>
<td>Methanol/Water</td>
</tr>
<tr>
<td>P2VP</td>
<td>120</td>
<td>0.5</td>
<td>Chloroform</td>
</tr>
</tbody>
</table>
The thickness and water contact angle measurements were performed to evaluate the coverage of the model surface with the polymer films. The AFM studies were carried out to evaluate the morphology of the grafted polymer layers.

4.3 Results and discussion

4.3.1 Model surface of nickel

To select the proper conditions of PGMA layer deposition, we followed the established procedure employed for the modification of silicon wafers. The surface of the nickel film sputtered on the silicon wafers was covered with a PGMA macromolecular anchoring layer. The layer could not be removed from the surface after the solvent treatment, suggesting that PGMA was chemically bonded to the surface due to a reaction between epoxy functionalities of the anchoring layer and the surface hydroxyl groups. The thickness of the PGMA anchoring layer was 2.0±1.0 nm. The deposited amount \( \Gamma \) of PGMA was 2.2 mg/m\(^2\), and the grafting density was 0.007 chain/nm\(^2\) with a corresponding surface concentration of epoxy groups was \( \approx 9 \) groups/nm\(^2\).

The thickness of the PGMA layer (and, therefore, the surface coverage \( \Gamma \)) grafted to the nickel surface was identical to the thickness of the PGMA layer grafted to the silicon wafers (2.5 nm). Thus, assuming the same reactivity of the epoxy groups for both batches of PGMA (used to modify silicon and nickel), we concluded that the reactivity of the nickel and silicon oxide surfaces was similar at room temperature grafting. Additionally, we studied the effect of temperature on the grafting of PGMA to the nickel
surface. The thickness of the grafted PGMA demonstrated linear dependence on temperature (Fig. 4.1).

![Graph showing linear relationship between thickness and temperature](image)

**Figure 4.1.** Thickness of the PGMA grafted to the model surface of Ni as a function of temperature; error bars indicate standard deviation

Polystyrene molecules were grafted to the PGMA macromolecular anchoring layer via the reaction between the epoxy groups presented in each repeating unit of the PGMA chain and the carboxylic groups presented at the end of the polystyrene chains. The selected conditions (time and temperature) for the polystyrene grafting were based on the research of Iyer et al.\textsuperscript{11} The thickness of the grafted polystyrene layers was
10.0±2.0 nm (Table 4.2). The adsorbed amount $\Gamma$ of polystyrene was 10.5 mg/m$^2$, which corresponded to 0.13 chain/nm$^2$. Because the distance between the grafting sites (D=3.2 nm) was smaller than the radius of the gyration ($R_g=13.9$ nm) of the polymer chain, the polystyrene layer was in the "brush regime" and would eventually form a brush in a good solvent.

**Table 4.2.** Characteristics of the polymer layers grafted to the model surface of Ni

<table>
<thead>
<tr>
<th>Polymer/Parameter</th>
<th>$M_n$, Da</th>
<th>$\rho$, g/cm$^3$</th>
<th>$h$, nm</th>
<th>$\Gamma$, mg/m$^2$</th>
<th>RMS, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Ni</td>
<td>59</td>
<td>7.81</td>
<td>100.0±5.0</td>
<td>781</td>
<td>1</td>
</tr>
<tr>
<td>PGMA</td>
<td>176 000</td>
<td>1.08</td>
<td>2.0±1.0</td>
<td>2.16</td>
<td>0.5</td>
</tr>
<tr>
<td>PAA</td>
<td>100 000</td>
<td>1.14</td>
<td>6.0±0.4</td>
<td>6.84</td>
<td>0.3</td>
</tr>
<tr>
<td>PS</td>
<td>48 000</td>
<td>1.05</td>
<td>10.0±2.0</td>
<td>10.5</td>
<td>0.3</td>
</tr>
<tr>
<td>PEG</td>
<td>5000</td>
<td>1.12</td>
<td>13.5±1.0</td>
<td>15.12</td>
<td>1.6</td>
</tr>
</tbody>
</table>

Under the conditions used, the thickness of the PS layer grafted to the model nickel surface was close to the thickness of the PS layer synthesized on a silicon wafer (15.0±2.0 nm) by Iyer et al.$^{11}$ Thus, it could be concluded that the reactivity of the PGMA macromolecular layer grafted to the nickel model surface was close to the reactivity of the PGMA layer grafted to silicon wafer.

The polyacrylic acid chains reacted with the PGMA macromolecular layer through the reaction between the epoxy groups of PGMA and the carboxylic groups presented in each repeating unit of PAA. In our experiments, we used the research of Hoy as a reference and guide for grafting the PAA nanoscale films.$^{16}$ The thickness of the
PAA layers measured by ellipsometry was 6.0±0.4 nm (Table 4.2). Therefore, the adsorbed amount $\Gamma$ of the PAA was 6.8 mg/m$^2$, which corresponded to 0.04 chain/nm$^2$.

We determined that grafting PAA layers to the model surfaces of nickel followed the trend established by Hoy.$^{16}$ Specifically, our results revealed that the thickness of the grafted PAA film was close to the thickness of the PAA-block-PS copolymer films synthesized by Hoy. Therefore, we supported the conclusion that the amount of PAA grafted to the surface is determined by the high availability of the reactive carboxy groups presented in the PAA chains and not by the time and temperature of the grafting.$^{16}$

Zdyrko studied carboxy-terminated PEG grafting from a melt onto silicon substrates modified with PGMA. The conditions selected for the PEG grafting in this work were close to those employed for anchoring PEG onto silicon wafers.

The carboxy-terminated polyethylene glycol PEG chains were attached to the model nickel surface that was previously activated with a macromolecular anchoring layer PGMA (h=6.0 nm). The thickness of the PEG layer was 13.5±1.0 nm and closely matched the results of Zdyrko et al.$^2$ The adsorbed amount $\Gamma$ of PEG was 15.1 mg/nm$^2$, and the calculated grafting density was equal to 1.8 chain/nm$^2$. As established by Zdyrko et al., such a high grafting density could be explained by a more extended interphase between the PEG and PGMA chains segments (loops and tails).$^{17}$ Thus, immersed in a good solvent, the PEG layer would form a brush because the distance between the grafting sites (D=0.8 nm) is smaller than the PEG chain's radius of gyration ($R_g=2.4$ nm).

The morphology of the pristine nickel surface changed after the polymer layers were attached (Fig. 4.2). The AFM studies showed that the PGMA, PS, and PAA layers
were smooth and homogeneous on a micro and nanoscale with RMS roughness less than 0.5 nm for $1\times1$-μm scanned areas (pristine Ni RMS=1.0 nm). However, the AFM analysis revealed a higher value of RMS roughness for the PEG-grafted layer (1.6 nm). This phenomenon was associated with the formation of domains composed of PEG crystals formed by the fraction of grafted macromolecules.$^{2,18}$

Figure 4.2. AFM images of the polymer layers grafted to the model Ni surface; size of AFM images is $1\times1$ μm; vertical scale is 5 nm (Ni, PGMA, PS, and PAA) and 20 nm (PEG)

The contact angle measurements allowed us to estimate the screening of the model surface by deposited polymer layers (Fig. 4.3). The contact angle of the pristine nickel model surface was equal to $78.0\pm3.0^\circ$. The droplet of water completely wetted the surface when treated with plasma. The value of the contact angle of the nickel surface covered with PGMA layers increased to $60.0\pm2.0^\circ$. This result was similar to data obtained for PGMA grafted to the silicon surface. Thus, the model surface of nickel was uniformly modified with the PGMA layer.
Due to the hydrophobicity of the PS layers, the surface modified with PS was expected to exhibit high contact angle values. The measured contact angle values (88.0±2.0°) indicated complete coverage of the model surface previously functionalized with PGMA by PS macromolecules. The value of the contact angle of the model surface modified with PAA was 6.0±1.0°. The result showed there was a sufficient amount of PAA chains on the nickel surface. The model surface modified with PEG exhibited a contact angle value of 38.0±3.0°. A low contact angle value confirmed the sufficient coverage of the model surface with the hydrophilic PEG layer.
4.3.2 Model surface of gold

The conditions of polymer grafting onto the model gold surfaces were also based on the conditions for grafting the polymer films onto the silicon wafers. We followed the methodologies developed by our group over the last 15 years.\textsuperscript{2,11,12,16,17,21}

The PGMA layer anchored to the model surface of gold could not been removed by multiple washings with a good solvent (chloroform). We hypothesized that the attachment of the PGMA chains to the surface of the gold occurred through a reaction between the thiol groups on the gold surface and the epoxy functionalities of PGMA. We assume that the thiol functionalities on the surface of the gold is was a result of the chemisorption of hydrogen sulfide naturally present in ambient air. The thickness of the PGMA layer was 12.0±1.0 nm; thus, the conditions selected for the PGMA grafting resulted in successful grafting of the polymer layer.

The PS grafting to the model surface of gold was based on the methodology developed by Iyer et al.\textsuperscript{11} It could be concluded that selected conditions for PS grafting resulted in the successful attachment of PS to the PGMA layer previously deposited on the model surface. However, comparing our results with data obtained by Iyer et al., we observed a deviation in the thickness of the grafted PS layer. The rate of grafting is governed by kinetic factors and is substantially enhanced by increasing of polymer mobility\textsuperscript{22}. Therefore, polymer chains mobility is a function of temperature. Thus, the discrepancy in the thickness of the grafted PS layer can be explained by lower temperature of grafting (120 °C as compared to 150 °C) employed in our experiments\textsuperscript{11}. On the other hand, the glass transition temperature of bulk PS is 100 °C.\textsuperscript{23} Therefore, at
120 °C, the PS chains had enough mobility to diffuse and find reactive sites on the surface.

In the PAA grafting, the conditions resulted in successful tethering of PAA chains to the PGMA layer.24 The measured thickness of the grafted PAA film was identical to the thickness of the PAA film attached to the model surface of nickel.

The conditions employed in the P2VP grafting were based on research by Chyasnavichyus.25 The glass transition temperature of bulk P2VP film is equal to 93 °C.26 The temperature of 120 °C was used to enhance chains mobility and facilitate grafting. The polymer grafting conditions resulted in the successful synthesis of the P2VP layer.

The polymer layers of PS, PAA, and P2VP grafted to the macromolecular anchoring layer were analyzed, and the layer characteristics (grafting amount, grafting density, and distance between grafting sites) were calculated. All the parameters of the grafted polymer layers are presented in Table 4.3. Since the distance between grafting sites (D) for the PS and P2VP chains was much smaller than the radius of gyration (R_g), the grafted polymers would have assumed "brush" conformation had they been immersed in a good solvent.
Table 4.3. Characteristics of the polymer layers grafted to the model surface of gold

<table>
<thead>
<tr>
<th>Polymer/Parameter</th>
<th>Mₙ, Da</th>
<th>ρ, g/cm³</th>
<th>h, nm</th>
<th>Γ, mg/m²</th>
<th>RMS, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>Au</td>
<td>197</td>
<td>19.3</td>
<td>110.0±5.0</td>
<td>2123</td>
<td>2</td>
</tr>
<tr>
<td>PGMA</td>
<td>176 000</td>
<td>1.08</td>
<td>12.1±1.0</td>
<td>13.07</td>
<td>0.6</td>
</tr>
<tr>
<td>PS</td>
<td>48 000</td>
<td>1.05</td>
<td>7.0±1.0</td>
<td>7.35</td>
<td>0.6</td>
</tr>
<tr>
<td>PAA</td>
<td>100 000</td>
<td>1.14</td>
<td>6.0±1.0</td>
<td>6.84</td>
<td>0.3</td>
</tr>
<tr>
<td>P2VP</td>
<td>53 000</td>
<td>1.06</td>
<td>8.0±1.0</td>
<td>8.48</td>
<td>0.4</td>
</tr>
</tbody>
</table>

The AFM images showed that the surface of the pristine gold film was altered by the polymer films grafting. The RMS roughness of the surface decreased from 2.6 to 0.6 nm after attaching the anchoring layer of PGMA (Fig. 4.4). The AFM analysis revealed that the grafted polymer layers were uniform and homogeneous with RMS roughness less than 1 nm on the micro and nanoscales.

Figure 4.4. AFM images of the polymer layers grafted to the model Au surface; size of AFM images is 1×1 μm; vertical scale is 20 nm (Au) and 10 nm (PGMA, PS, PAA, and P2VP)

The modification with polymer layers changed the wettability of the model surface by water (Fig. 4.5). The contact angle of the pristine gold surface was equal to
35.0±2.0°. The value changed to 60.0±1.0° after the PGMA grafting, suggesting complete coverage of the surface. Among the grafted polymers, PS was the most hydrophobic. The value of the contact angle for the model surface was 93.0±1.0° after the PS layer was attached. These results were in agreement with the data previously reported by Iyer et al.\textsuperscript{11} The PAA is a hydrophilic polymer. Thus, the lowest value of the contact angle was observed after the attachment of the polymer layer (18.0±1.0°). The presence of the P2VP on the substrate surface resulted in a 50.0±1.0° contact angle.

\textbf{Figure 4.5.} Values of the static contact angle for the Au surface before and after modification with PGMA, PS, PAA, and PEG layers, respectively
4.4 Conclusion

The model nickel and gold surfaces were successfully modified with robust, pinhole-free, nanothin polymer films. The macromolecular anchoring layer was deposited to obtain reactive layers with a significant number of epoxy groups. The different polymer films were then grafted to the surface using the "grafting to" technique. The polymer chains were covalently attached through the reaction between the epoxy functionalities of the PGMA and the complementary carboxylic groups presented as functional units within the grafted polymer chains.

The conditions employed for grafting the polymer layers to the Ni and Au model surfaces resulted in successful fabrication of the nanoscale polymer films. Moreover, the measured thickness (grafting density) of the polymer films grafted to the model surfaces was similar to the thickness of those grafted to the silicon substrates. Therefore, the selected conditions can be used for the permanent attachment of polymer macromolecules to the surfaces of Ni and Au objects.
4.5 References


CHAPTER FIVE

POINTED MODIFICATION OF NICKEL NANOWIRES AND MICRONAILS

5.1 Introduction

Arrays/forests of supported high-aspect-ratio 1D nano/microstructures composed of metals and ceramics are of great interest in academic and practical fields because of their unique properties. These structures also offer great promise for a number of existing and emerging applications, such as room temperature UV nanolayers, magnetic gas and biosensors, field emission electron emitters, dye-sensitized and quantum-dots-sensitized quantum cells, electrodes for electron implants, photoelectrochemical cells, liquid repelling and antifouling surfaces. In a number of applications, control over the surface chemistry of the 1D nano/microstructures is crucial to ensure their performance. For example, in nanowire-based liquid repelling surfaces for which wetting properties cannot be linked to only a single parameter (geometry), the interactions of the liquid with the solid surface must be taken into account. Thus, the wetting behavior can be changed and controlled by functionalizing the surface. The surface modification of nanofiber arrays can provide an interface for protonation/deprotonation or specific ligand/receptor binding reactions, as well as further fabrication of nanofiber-based pH and biomolecular nanosensors.

A promising technique for the precise tuning of surface properties involves the deposition of nanoscale polymer layers that are chemically tethered to the surface. Macromolecules at the interface can be anchored to the surface in a variety of
configurations. Densely tethered polymer chains that are grafted by one end form brush-like layers.\textsuperscript{19,21,22} By tuning the brush parameters (grafting density, chain length, polydispersity, and chemical composition) the properties of the layer can be carefully regulated. For instance, one of the most interesting applications is the regulation of interactions between synthetic materials and biological substances (proteins, cells, and microorganisms), which is important for the development of biomedical materials (implants, drug delivery systems). For example, polyethylene glycol brushes are well known for their antifouling properties.\textsuperscript{23,24}

In this chapter, we report the effective technique of surface functionalization of arrays of high-aspect-ratio nickel magnetic nanowires/micronails. The technique involves the functionalization of different segments of nickel nanowires/micronails with polymer layers that possess antagonistic properties (hydrophobic/hydrophilic) by employing the "grafting to" method based on the macromolecular anchoring layer approach.\textsuperscript{20,25-27} More specifically, we demonstrate the functionalization of nanowires/micronails tips with a hydrophobic polymer layer (polystyrene) and a layer of the hydrophilic polymer (polyacrylic acid) at the bottom portion (Fig. 5.1). The established method of surface functionalization opens the door to a wide range of possible localized modifications with different polymer combinations. This, in turn, opens a pathway for an abundance of potential applications. For example, nanowires/micronails tips can be modified with an antifouling polymer layer of poly (ethylene glycol) methyl ether methacrylate, while the bottom part can contain ligands responsible for cell adhesion and proliferation (e.g., biotin, RGD).\textsuperscript{28-32} The application of the external magnetic field and
nanowires/micronail bending deformation will make initially antifouling surface prone for cell adhesion by exposing functional molecules to the interface. Thus, the described system should release and hide functional molecules upon receiving external commands (turning the magnetic field on or off) in a preprogrammed manner.

![Diagram of nickel nanowires functionalized with hydrophobic and hydrophilic layers](image)

**Figure 5.1.** Schematic of an array of nickel nanowires functionalized with a hydrophobic polystyrene layer and hydrophilic polyacrylic acid layer before and after application of an external magnetic field.

### 5.2 Experimental

#### 5.2.1 Synthesis of arrays of nickel nanowires/micronails

The synthesis of arrays of nickel nanowires was conducted by Grigoryev et al. in Professor Minko's group at Clarkson University (Nanostructured Materials Group).
Anodized aluminum oxide (AAO) (pore diameter 200 nm, 60-μm thickness) and track-etch polycarbonate (PC) membranes (pore diameter 1 μm, 30-μm thickness) were used for the synthesis of the arrays/forests of magnetic nickel nanowires/micronails by the electrodeposition technique.14,15

The AAO templates were used for the fabrication of nickel nanowires arrays, while PC track-etched templates were used for the fabrication of nickel micronails arrays respectively. The membranes were covered with a conductive electrode (cathode) on one side, and an electrolyte containing Ni²⁺ ions were allowed to contact the electrode only through the membrane pores. The deposition of nanowires/micronails was conducted in the potentiostatic regime employing a three-electrode cell and an electrolytic bath containing Ni²⁺ ions.15 The pore confinement led to the formation of nickel wires in the membrane. To fabricate the arrays of micronails, the electrodeposition within the pores of the PC template was not stopped when the fiber’s tips reached the top of the membrane. Therefore, the fibers growth was no longer restricted by the pore walls, and the mode of growth changed from 1D to 3D. As a result, hemispherical caps formed on the membrane surface.

5.2.2 Surface modification of nickel nanowires arrays fabricated in the aluminum oxide membrane

The AAO membranes were dissolved in a 10 w/v% solution of KOH for 1 h. The samples were then carefully rinsed with methanol and high-purity water. Air plasma was used to activate the surface of the nanowires. Plasma treatments were done at 0.2-torr
pressure. The generator power switch was set at 18 W. Next, the nanowire arrays were rinsed carefully with ultrapure DI water and then dried. The ultrathin PGMA film was deposited on the surface of the nanofibers using a 3 w/v%-chloroform solution following the procedure developed for the modification of the model nickel surface (Chapter 4, p. 64). The unbounded polymer was removed from the surface by multiple washings with chloroform. The surface of the nickel nanowires was then modified with a layer of PAA following the procedure developed on a nickel model surface (Chapter 4, p. 64)

The PDMS resin (Sylgard 184) mixed with a curing agent (10:1 by mass) was poured directly onto the nickel nanowires arrays. The resin uniformly spread, covering the arrays. Next, the sample was cured at 80 °C for 1 h. Thus, the nickel nanowires arrays already modified with PAA were entrapped in the PDMS matrix. The PDMS film with the wires was detached from the electrode surface. The surface of the film in contact with the electrode was further treated.

To expose certain segments of the nanowires for modification, the procedure for controlled wet etching of PDMS was developed. A solution of tetrabuthylammonium fluoride (1:30 by mass) (TBAF) (Aldrich) in N-methyl-2-pirrolidinone was used as an etchant agent.\textsuperscript{33-35} The silicone underwent depolymerization catalyzed by the presence of the fluoride ion.\textsuperscript{36} The etching rate was determined by measuring the weight loss of a silicone sample after each etching step.

The nickel nanowires arrays entrapped in the silicone matrix were immersed in TBAF solution and gently agitated during etching. The agitation was required to replenish the etchant at the sample surface. The etching rate was controlled by the
reaction time. The sample was carefully rinsed several times with acetone (VWR) and high-purity DI water after the etching. The uncovered segments of the nanowires with lengths of \( \approx 1 \, \text{μm} \) were treated in a plasma cleaner and washed again with high-purity DI water. Next, the exposed segments of nickel nanowires were modified with a PGMA anchoring layer and then by the PS layer, following the procedure developed for the modification of model surfaces (Chapter 4, p. 64). The carboxy-terminated PS was melt grafted under a vacuum at 120 °C. The sample was rinsed several times with methyl ethyl ketone to extract the unattached polymer. Finally, the PDMS matrix was etched further to expose the nickel nanowires surface that was initially modified with PAA. After the PDMS etching, the samples were washed multiple times with acetone and high-purity water, and then dried.

5.2.3 Surface modification of arrays of nickel micronails fabricated in the polycarbonate membrane

A polycarbonate track-etched membrane was partially etched in air plasma. The plasma treatments were done at 0.2-torr pressure. The generator power switch was set at 12 W. The rest of membrane was dissolved in chloroform. Next, the nickel micronails arrays were cleaned in air plasma to remove PC residues and to activate the surface.

The surface of the nickel micronails was activated by grafting a reactive layer of PGMA. The surface was further functionalized with the layer of PAA according to the procedure developed for model surfaces (Chapter 4, p. 64). The nickel micronails were
separated farther apart than were the nickel nanofibers deposited within the pores of the AAO membranes. Thus, the aggregation of the nickel micronails was not observed.

The PDMS resin (Sylgard 184) mixed with a curing agent (10:1 by mass) was directly deposited dropwise onto the nickel micronails arrays. The resin was uniformly spread, covering the nickel micronails arrays. Then, the sample was cured at 80 °C for 1 h. Thus, the nickel micronails arrays were entrapped in the PDMS matrix. The procedure for controllable wet etching of silicone was employed to expose certain micronails segments for surface functionalization. The caps of the nickel micronails were exposed for modification with the PGMA anchoring layer and hydrophobic PS film. Next, the PDMS matrix was etched to expose the stems of the micronails already modified with the hydrophilic PAA layer. Finally, the samples were rinsed with acetone and high-purity DI water, and dried.

The morphology of the nickel nanowires/micronails arrays was examined by scanning electron microscopy (SEM). Polymer layers attached to the surface of the nickel nanowires were visualized by transmission electron microscopy (TEM). Energy dispersive X-ray spectroscopy was used to measure the carbon content on the surface of the nickel nanowires/micronails after the polymer layer grafting. The water contact-angle measurements were conducted to evaluate the screening of the nanowires/micronails by the thin polymer films.
5.3 Results and discussion

5.3.1 Entrapment of forests of Ni nanowires in the PDMS matrix

In the previous chapter, it was shown that the model surface of nickel was successfully modified by grafting the nanoscale polymer films. The methodology used in the model study (Chapter 4, p. 64) was successfully employed for the surface functionalization of the arrays of nanowires/micronails.

It was observed that, after dissolving the aluminum oxide template, arrays of high-aspect-ratio nanowires aggregated near the fiber tips due to strong capillary forces between them during sample drying. (Fig. 5.2, left column).

Scheme 5.1. Representation of the fabrication of the reverse replica of the arrays of Ni nanowires: step 1 – nanowires have been entrapped into the PDMS matrix; step 2 – matrix has been flipped; step 3 – electrode has been removed and PDMS matrix etched

However, at the bottoms, the nanowires were mechanically attached to the sputtered electrode (cathode) and they remained separated (Scheme 5.1). To modify not aggregated, bottom, separated portion of the nickel nanowires, they were entrapped in the PDMS matrix and a reversed replica of the sample was used for further modification
(Scheme 5.1, steps 1 and 2). To expose the specific segment of nanowires/micronails at the desired length for surface functionalization, the methodology for controllable etching of the PDMS matrix was developed (Scheme 5.1, step 3). The electrode (cathode) was removed prior to the PDMS etching and surface functionalization.

**Figure 5.2.** SEM images of arrays of nickel nanowires and micronails

**5.3.2 Controlled etching of the PDMS matrix**

PDMS is known for its thermal and chemical stability. However, in certain conditions, PDMS undergoes depolymerization reactions. In our work, a solution of TBAF in NMP (N-methyl pyrrolidinone) was used as a source of fluoride ions to etch the silicone matrix and expose certain segments of the nanowires/micronails for surface functionalization. TBAF is widely used in organic synthesis for removing silyl ether
The fluoride ion $\text{F}^-\text{F}$ is a powerful nucleophile agent for silicone due to the ion's small size (little steric barrier to attack a silicon atom) and the strength of the Si-F bond.\textsuperscript{46} In the presence of fluoride ions, the PDMS underwent chain cleavage between crosslinks. This process was accompanied by a depolymerization. Both processes led to a decrease in molecular weight of the polymer (Scheme 5.2).

![Scheme 5.2. Representation of the depolymerization reaction that occurs during PDMS etching with tetra butyl ammonium fluoride (TBAF)](image)

It was crucial to investigate the kinetics of PDMS etching to enable the exposure of the nickel nanowires/micronails segments of predetermined lengths. Figure 5.3
represents the thickness of etched material as a function of time. Thus, with the determined etching rate of the PDMS matrix, the segments of nickel nanowires/micronails of certain lengths could be exposed for modification.

![Figure 5.3](image.png)

**Figure 5.3.** Etched thickness of the PDMS film as a function of time

### 5.3.3 Stability of PAA and PS layers in etching solution

The developed method for the controllable wet etching of the PDMS inspired an additional question: *What is the stability of the PAA and PS layers, and can they withstand treatment with the etchant agent tetrabuthylammonium fluoride?* To answer this question, we conducted a set of experiments on the model nickel surfaces. The
PDMS film was deposited and cured on top of a PAA layer that was previously attached to the model surface through the PGMA anchoring layer. Next, the silicone was removed from the model surface by etching with a TBAF solution. The sample was then rinsed and dried.

We examined changes in the thickness, water contact angle, and morphology of the PAA layer before the PDMS deposition and after the complete etching of the PDMS. Moreover, we allowed the model surface to contact the etchant for an additional 60 min to inspect the stability of the PAA layer after direct contact with the TBAF solution. The model surface modified with the PS layer was immersed into the solution of TBAF for 60 min to investigate the stability of the PS film. Thickness, water contact angle, and layer morphology were examined before and after the interaction of the PS film with the etchant.

![AFM images of PAA and PS layers before (A, C) and after (B, D) TBAF treatment respectively; size of the AFM images is 1x1 µm; vertical scale is 10 nm](image)

**Figure 5.4.** AFM images of PAA and PS layers before (A, C) and after (B, D) TBAF treatment respectively; size of the AFM images is 1x1 µm; vertical scale is 10 nm

**Figure 5.4** reveals the morphology of the PAA and PS layers before (images A and C) and after (images B and D) the TBAF treatment. The surface of the polymer layers was homogeneous and smooth, with RMS roughness less than 1 nm before and
after the samples interacted with the etchant. The AFM images show that the morphology and texture of the polymer layers were not significantly affected by the etchant. Moreover, we did not detect any significant changes in the thickness or water contact angles for the polymer films (Fig. 5.5). To conclude, the grafted layers of PAA and PS were robust, stable, and able to withstand the conditions of silicone etching with TBAF.

![Graph showing thickness comparison between PAA and PS](image)

<table>
<thead>
<tr>
<th>Water Contact Angle</th>
<th>PAA</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Before TBAF treatment</td>
<td>0</td>
<td>92±3.6</td>
</tr>
<tr>
<td>After TBAF treatment</td>
<td>0</td>
<td>93±1.4</td>
</tr>
</tbody>
</table>

**Figure 5.5.** Water contact-angle analysis and ellipsometry measurements before and after TBAF treatment for model surfaces modified with PAA and PS
5.3.4 Surface functionalization of nickel nanowires with nanoscale polymer films

The surface of the nickel nanowires was functionalized with PGMA and PAA layers following the procedure developed for model nickel surfaces (Chapter 4, p. 64). Ellipsometry could not be used to measure the thickness of the grafted polymer layers due to high surface roughness. To overcome this challenge, energy dispersive X-ray spectroscopy (EDS) was utilized to track the carbon content after each step of the modification. The optimum accelerating voltage (kV) was determined by the tracked element. To obtain adequate intensity, it needed to be no less than twice the highest excitation energy Ec (keV) of the element of interest. An accelerating voltage of 10 kV was used during the analysis. An increase in the carbon content from 2.8% for unmodified nanowires (carbon originates from environment), to 3.8% and 12.5%, manifested the functionalization of the surface of the nickel nanowires with the PGMA and PAA layers respectfully (Fig. 5.6 A).

![Figure 5.6](image.png)

**Figure 5.6.** Energy dispersive spectroscopy analysis of arrays of Ni nanowires (A) and micronails (B) before and after modification with PGMA and PAA layers
Next, the nickel nanowires arrays modified with PAA were entrapped in the PDMS matrix. We aimed to expose the tips of the Ni nanowires at lengths of 1 μm for surface functionalization with the PS film. The SEM analysis revealed the arrays of nickel nanowires entrapped within the PDMS matrix before the etching (Fig. 5.7, image A) and after the etching (Fig. 5.7, image B). The length of the exposed tips of the individual nanowires was approximately 1 μm. The tips were sequentially modified with the PGMA and PS polymer layers.

We employed TEM analysis to visualize the PAA and PS layers attached to the surface of the Ni nanowires (Fig. 5.7, images C, D, and E). The TEM images show individual nanowires modified with PAA and PS. The thickness of the polymer films was 5–6 and 10–12 nm for the PAA and PS layers respectively. The TEM visualization techniques proved the screening of the surface of nickel nanowires with the polymer films.
Figure 5.7. SEM images of arrays of Ni nanowires entrapped in the PDMS matrix (A); tips of Ni nanowires partially exposed for modification (B); TEM images of single Ni nanowires before modification (C); after modification by PGMA and PAA (D); and after modification by PGMA and PS (E).

As discussed above, the step-by-step etching of the PDMS film with arrays of nanowires entrapped within it allowed us to accomplish two goals: (1) to modify different segments of nanowires with different polymer layers and (2) to overcome the phenomenon of nanowires aggregation by functionalizing the bottom, separated portion of the nanowires that were mechanically attached to the sputtered electrode (cathode). When the tips of the nickel nanowires were modified with PS, the PDMS matrix was etched further to expose the hydrophilic segments. SEM imaging revealed the aggregation of nickel nanowires (Fig. 5.8, images A and B). The presence of a nanothin layer of a hydrophobic polymer (PS) on the nanowire surfaces did not prevent their
aggregation due to high density and close positioning of the nanowires to one another. Despite this, the major goal was achieved. The developed method resulted in the functionalization of different segments of nickel nanowires with polymer layers of an antagonistic nature.

![Image](image.jpg)

**Figure 5.8.** SEM images of arrays of Ni nanowires after further etching of the PDMS matrix (hydrophobic and hydrophilic segments are opened)

### 5.3.5 Surface functionalization of nickel micronails with PGMA and PAA nanoscale polymer films

At the next stage of our study, we employed other templates for the fabrication of nickel nanowires where pores were distributed far enough away from one another to avoid aggregation. Track-etch polycarbonate (PC) membranes (pore diameter 1 μm, thickness 30 μm) with pores density of $2 \times 10^5$ cm$^{-2}$ were employed for the synthesis of self-standing forests of nickel nail-like micronails.$^{15}$ The pore confinement led to the deposition of nickel fibers within the template. As the fibers tips reached the top of the PC membrane, the growth was no longer restricted by the pores walls, resulting in the formation of hemispherical nickel caps on the membrane surface (**Fig. 5.9 A**).
The dissolution of a polycarbonate track-etch membrane in a good solvent (chloroform, dimethylformamide) is typically accompanied by significant swelling of the polymer. It causes the disconnection of the micronails from the supporting substrate due to development of strong osmotic pressures within the swelling polymer. To overcome this challenge, the PC template was partially etched in air plasma (Fig. 5.9, image B). The rest of the membrane was dissolved in chloroform (Fig. 5.9, images C and D). The PC membrane residues were removed by additional air plasma treatment. The SEM analysis revealed freestanding forests of nickel micronails after the PC membrane was removed.

The surface of the nickel micronails was modified with PGMA and PAA polymer layers following the procedure developed on the model surfaces (Chapter 4, p. 64).
first activated the surface by attaching a primary macromolecular anchoring layer of PGMA. Then, the surface was modified with a hydrophilic polymer layer of PAA. The PAA has the carboxylic group present in each repeating unit. At 40 °C, they reacted with the complementary epoxy groups of the PGMA, forming ester bonds.\textsuperscript{47} Thus, the PAA layer was covalently attached to the micronails surface.

EDS was utilized to track the carbon content after every step of the modification. An increase in carbon content from 3\% for unmodified micronails, to 5.3\% and 8.2\%, manifested in the functionalization of the surface of the nickel micronails with the PGMA and PAA layers respectfully (Fig. 5.2 B).

The contact-angle analysis of the nickel micronails surface with no additional functionalization revealed that they demonstrated superhydrophobic properties with an apparent contact angle $\geq 150.0^\circ$. The water contact angle on a flat nickel surface was equal to 78.0±3.0°. The superhydrophobicity of forests of nickel micronails is caused by the reentrant geometry of the interface.\textsuperscript{14,15,48-57} It creates an energy barrier for the immediate transition of water droplets from the Cassie-Baxter regime to the Wenzel state. Even the latter corresponds to the minimum surface energy, and the transition from Cassie to Wenzel is energetically favorable (for flat surfaces with water contact angle < 90.0°).\textsuperscript{58,59} The Cassie-Baxter state describes the situation when a water droplet is suspended on the top of microstructures. The Wenzel state describes the situation when a water droplet is in full contact with a microstructure surface.

When a water droplet was placed on the sample surface, it remained attached to the substrate at a relatively small number of points on the caps of the micronails, as if
supported by a thin air layer rather than a substrate. The transition from the Cassie to Wenzel states occurred when the water droplet was forced to penetrate the reentrant surface by applying downward force on a water droplet (Fig. 5.10, Schemes 1 and 2, image B). We conducted measurements of water contact angle when Cassie-Wenzel transition occurred to evaluate changes in surface energy after functionalization with the PGMA and PAA layers. The water contact angle was equal to 58.0±0.7° before surface functionalization, 84.0±2.3° after modification with PGMA, and 25.0±5.5° after modification with the hydrophilic PAA layer, respectively (Fig. 5.10; Schemes 1 and 2, image C; Scheme 3, image B). The wetting behavior changed after the micronails surface was functionalized with layers of PGMA and PAA. Figure 5.11 represents the measured static water contact angles when the surface functionalization with PGMA and PAA were conducted.
Figure 5.10. Dynamics of the change of water contact angle on a surface of Ni micronails before modification (Scheme 1), and after modification with PGMA (Scheme 2) and PAA (Scheme 3)

In the non-modified surface, and after PGMA grafting, the phenomenon of superhydrophobicity was observed. Next, we forced the transition from the water repelling to the wetting state by applying downward force to the water droplet in a direction normal to the substrate plane. Further modification of the nickel micronails surface with a hydrophilic PAA layer led to a considerable increase in the hydrophilicity.
of the microtexture. As a result, the water droplet readily wetted the surface as if it touched the caps of the nickel micronails.

![Figure 5.11. Static water contact angle as a function of micronails surface functionalization](image)

As discussed previously, the developed methodology of step-by-step, controllable etching of PDMS allowed us to functionalize different segments of the nickel nanowires. We utilized this same technique to functionalize the different segments of micronails. **Scheme 5.3** illustrates the steps for the functionalization. The arrays of PAA-modified nickel micronails were entrapped in the PDMS matrix. Our target was to open the caps of
micronails to functionalize them with a layer of hydrophobic polymer-PS. To reach this goal, we etched 8–9 μm of the PDMS matrix. **Figure 5.12** reveals arrays of nickel micronails entrapped into the PDMS matrix (**image A**), and partially etched silicone matrix with opened micronails caps (**image B**). The analysis of the SEM image showed that we etched 8–9 μm of the silicone matrix. Finally, we etched the remaining PDMS to open the PAA-modified stems of the Ni micronails (**Fig. 5.12, image C**).

**Scheme 5.3.** Representation of the method used for modification of the arrays of Ni micronails: step 1 – template removing; step 2 – PAA deposition; step 3 – entrapment of micronails into the PDMS matrix; step 4 – partial etching of PDMS matrix and deposition of the PS; step 5 – full etching of PDMS matrix
The contact-angle analysis allowed us to estimate the surface screening with the polymer layers. The water contact angle of the nickel micronails embedded into the PDMS matrix was equal to 108.8°. The value corresponded well with the literature reporting water contact-angle values for pure PDMS.\textsuperscript{61,62} \textbf{Figure 5.13} shows the variations of the water contact angles after the PDMS etching and the PGMA and PS layer grafting respectively. The interface of the sample surface had a composite morphology comprised of the surface of the hydrophobic PDMS matrix (77% of the total area) and the surface of hydrophilic micronail caps (23% of the total area) when the PDMS was partially etched. Thus, the value of the water contact angle decreased to 95.0° after the PDMS etching. The decrease in the water contact angle could be attributed to the presence of the hydrophilic PAA layer attached to the exposed caps of the Ni micronails.

\textbf{Figure 5.12.} SEM images of forests of Ni micronails entrapped in the PDMS matrix (A); opened caps of micronails (B); fully opened micronails after all modification steps were completed (C)

The modification of the sample with the PGMA resulted in the homogeneously functionalized surface. Thus, the interface that comprised the surface of the hydrophobic PDMS matrix and hydrophilic micronails caps was uniformly functionalized with the
PGMA and resulted in a decrease in the water contact angle to 73.0°. Due to the polystyrene hydrophobicity, the surface covered with the PS-grafted layer was expected to exhibit high water contact angles. Wang et al. reported values in the range 90.0°–95.0° for the atactic PS. The contact angle increased to 103.0° after surface functionalization with the PS.

![Static water angle analysis before and after functionalization with PGMA and PS polymer layers](image)

**Figure 5.13.** Static water angle analysis before and after functionalization with PGMA and PS polymer layers
Finally, the silicone was etched further to expose the stems modified with the hydrophilic PAA layer prior to embedding the micronails into the PDMS matrix. Figure 5.13 (image C) reveals the fully opened micronails after the silicone etching. The contact-angle analysis of the nickel micronail surfaces with additional functionalization revealed that they demonstrated superhydrophobic properties with an apparent contact angle $> 150.0^\circ$. We could not force the transition from Cassie to Wenzel by pressing the drop downward direction normal to the surface plane as compared to the not functionalized micronails. Thus, additional modification of the micronails surface enhanced the superhydrophobic properties of the nickel micronails.

5.4 Conclusion

We designed an effective method for functionalization of the surface of nickel nanowires/micronails. This method, which combines a step-by-step, controllable etching of the silicone matrix and surface modification by the "grafting to" technique, resulted in the functionalization of the different segments of nickel nanofibers and micronails with different polymers. The hydrophobic PS layer was grafted to the upper segment of the nanofibers/micronails, and the hydrophilic poly acrylic acid layer was grafted to the lower segment of the nanofibers/micronails. The PGMA was used to form the reactive primary layer. The grafted layers of PAA and PS were stable and robust. The versatility of the developed methodology of surface modification opens a number of new possibilities for prospective applications, whose investigations are underway in our laboratory.
5.5 References


CHAPTER SIX
SURFACE MODIFICATION OF MICROPRINTED GOLD ELECTRODES AND 
EFFECT OF ENVIRONMENT ON ELECTRICAL CONDUCTIVITY OF 
GRAFTED POLYMER LAYERS

6.1 Introduction

Polymers possess unique functionalities that can be employed for a number of 
electronic applications, ranging from memory devices to molecular switches\textsuperscript{1-6}. In fact, 
insulating and charge-transporting polymer films are readily used in modern electronic 
systems\textsuperscript{4}. These materials offer an opportunity for molecular design through the synthesis 
and possess a high level of processability, enabling the fabrication of devices that, in 
principle, can be miniaturized to molecular level dimensions. However, as electronic 
devices are scaled down to submicron sizes, it has become critical to obtain uniform 
(pinhole free) polymer films and to guarantee ordering/location of the components in the 
organic functional layers and at the interfaces\textsuperscript{1, 7, 8}. To this end, densely chemically 
grafted polymer layers (polymer brushes) have recently been explored for the fabrication 
of components for electronic devices.

For instance, it was reported that charge-transporting polymer brushes made of 
poly (triphenylamine acrylate) demonstrated an increase of up to 3 orders of magnitude in 
current density normal to the substrate as compared with a spin-coated film\textsuperscript{8}.

Valery Bliznyuk, Yuriy Galabura, Ruslan Burtovyy, Pranay Karagani, Nickolay Lavrik and Igor Luzinov, Electrical conductivity of insulating polymer nanoscale 
Rutenberg et al. found that a poly (norbornene)-grafted polymer layer can be used as the dielectric layer in electronic devices\(^9\). Pinto et al. successfully employed poly (methyl methacrylate) brushes in organic field-effect transistors as gate insulators\(^7\). Devices based on a polyelectrolyte (polyacrylic acid) brush were shown to display repetitive switching between low conductance and high conductance states depending on applied voltage and could, therefore, function as nanoscale memory devices\(^1\). The switching voltage could be controlled by chemical modification of the brushes.

The above outlined utilization of the polymer brushes in the electronic devices was realized in a controlled environment. However, it is well known that the properties and behavior of polymer brushes can be significantly changed depending on external stimuli (pH, humidity, temperature, or the presence of organic molecules)\(^{10-13}\). Therefore, the electrical properties of the brushes can be affected by the environment, where even the presence of solvent vapors or small temperature changes may influence the electrical properties of the grafted nanoscale film.

The effective way to study this behavior is fabrication and utilization of the model electrodes. In fact, if polymers grafted to the surface of model electrodes will change properties in the presence of solvent vapors the conductivity of electrodes will change also. Thus, the response of functionalized model electrodes (change in conductivity) can be decoded and used to interpret the change in electrical properties of grafted polymer films.
The purpose of this part of dissertation is to describe the grafting of thin polymer films onto the microprinted gold electrodes and evaluate the effect of the environment and temperature on their electrical properties.

6.2 Experimental

6.2.1 Grafting of nanoscale polymer films to the surface of model electrodes

Si/SiO₂/Au electrodes chips with lithographically prepared parallel electrodes were used as substrates for grafting thin polymer films (Figure 6.1). The electrodes were fabricated at Oak Ridge National Lab ORNL by Dr. Lavrik. Layers of PGMA, PAA, PS and P2VP were grafted to the substrate surface. Drop (~0.2 ml) of PGMA 0.1 w/v % solution in methyl ethyl ketone (MEK) was placed on a clean substrate and left to dry at a room temperature. Then, PGMA was annealed at 120 °C for 1 hour. Next, the sample was rinsed vigorously 3-4 times with fresh MEK to remove ungrafted polymer. Thin polymer films of PAA, PS and P2VP were synthesized following the procedure and conditions developed on model surfaces (Chapter 4 page 65).

The surface properties of the grafted polymer layers were characterized using contact angle measurements, ellipsometry (thickness measurements on model surfaces) and AFM (morphology and thickness measurements on electrode chips).
Figure 6.1 Top view of the Si/SiO$_2$/Au electrode chip with lithographically prepared parallel electrodes 200 mm in length and with a 1 mm or 0.6 mm gap between them (A) and similar interdigitated electrodes with 3 mm length and a 2 mm gap (B). The optical images are made before the surface modification.
6.2.2 Studying of swelling of nanoscale polymer films grafted to the model surfaces

Swelling studies of the polymer films grafted to the silicon wafers and model surfaces of the gold were conducted. For this purpose, a sealable transparent cuvette was fabricated (Figure 6.2). The cuvette was designed such that two transparent windows were perpendicular to the laser beam and did not alter its polarization state. Firstly, the sample was put into the cuvette and the dry thickness of the film was measured. Next, a small bucket with a solvent was introduced into the cuvette and ellipsometric measurements were conducted for 60 minutes as the film absorbed the solvent. After the acquisition, raw data was fitted using ellipsometer software and Origin 6.1 following the algorithm proposed by Chyasnavichyus14.

![Figure 6.2](image)

**Figure 6.2** Schematic of the glass cuvette for solvent absorption (swelling) measurements using an ellipsometer (left). Example of thickness change of the PS/PGMA film upon exposure to saturated chloroform vapors (right).
6.2.3 Conductivity measurements

Measurements of electrical properties of the grafted polymer films and physical interpretation of their conductivity were conducted by Dr. Bliznyuk group at College of Engineering and Applied Sciences, Western Michigan University. To measure the electrical properties of the films, spring contact electrodes were mechanically attached to the electrode pads and connected to a Keithley 2400 source meter operated using Labview software. The electrical noise level was below 10 pA during these measurements allowing confident detection of >100 pA response. The surface conductivity was determined by applying electrical potential to gold electrodes and then measuring the current passing through a polymer brush on top of an insulating substrate and the electrodes. Sensor response of the samples was studied by placing the samples in a saturated vapor atmosphere of an analyte of interest. For this purpose, 1–2 ml of liquid solvent (water, ethanol, chloroform or toluene) was put into the glass container and 5 min were allowed for equilibration before measurement. I–V curves were collected via stepwise variation of electrical potential applied using the Keithley source. The voltage was first increased from 0 V to +5 V, then decreased from +5 V down to - 5 V, and finally increased to 0 V. I–V curves were also measured in air for several minutes before and after exposure to the analyte vapors to study the reproducibility and recovery of the sample’s response.

Temperature-dependent conductivity measurements were carried out using a programmable oven. The temperature inside the oven was increased from 20 °C to 160 °C in steps (typically 2 or 5 degrees) with stabilization after each step for at least 2 min
before collecting the I–V curves. The total spread of current $I_{\text{max}} - I_{\text{min}}$ (for the maximum variation of the voltage – i.e., for 10 V) has been plotted as a function of the temperature. All measurements were repeated under slow cooling of a sample back to room temperature. The results were found to be reproducible – i.e., upon cooling, the conductivity was reduced, following approximately the same curve as upon heating.

6.3 Results and discussion

6.3.1 Characterization of the grafted polymer layers

To cover a broad range of polymer/environment interactions we have selected polymers with different properties for grafting. In fact, the layers of PAA (hydrophilic/hydrogen bonding/acidic), P2VP (hydrogen bonding/aromatic/basic), PS (hydrophobic/non hydrogen bonding/aromatic) were grafted. These polymers were in “glassy” low mobility state at a room temperature. A “grafting to” approach was employed for deposition of the polymer brush layers on a flat silicon oxide surface using the PGMA anchoring sublayer\textsuperscript{15}. The PGMA layer was previously demonstrated to be an effective macromolecular anchoring layer for grafting polymers onto inorganic and polymeric surfaces\textsuperscript{13, 15-17}.

The PGMA layer is fabricated as a thin internally cross-linked film, covalently bound to the native silicon oxide and gold, using its epoxy functionalities\textsuperscript{15, 17}. When polymer films were deposited by drop casting over the PGMA layer, the epoxy functionalities in the loops and tails sections of the anchoring layer reacted with
complementary groups of polymer films thus enabling the covalent attachment of PAA, PS and P2VP\textsuperscript{15, 18, 19}.

The thickness of the nanoscale anchored layers was also measured by AFM (on a silicon substrate with electrodes) using the border of the film deposited and by ellipsometry on model silicon wafers. The AFM and ellipsometric measurements provided close results. The preparation procedure resulted in the anchored polymer films with a total thickness of 10–20 nm (Table 6.1).

**Table 6.1** Parameters of the polymer layers grafted to the Si/SiO\textsubscript{2}/Au electrodes.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>h, nm</th>
<th>f, mg/m\textsuperscript{2}</th>
<th>δ, chains/nm\textsuperscript{2}</th>
<th>D, nm</th>
<th>Rg, nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>12±2</td>
<td>12.96</td>
<td>0.045</td>
<td>5.4</td>
<td>21.1</td>
</tr>
<tr>
<td>PS</td>
<td>9±1</td>
<td>9.45</td>
<td>0.119</td>
<td>3.3</td>
<td>12.9</td>
</tr>
<tr>
<td>PAA</td>
<td>9±1</td>
<td>10.26</td>
<td>0.062</td>
<td>4.5</td>
<td>22.3</td>
</tr>
<tr>
<td>P2VP</td>
<td>6±1</td>
<td>6.36</td>
<td>0.072</td>
<td>4.2</td>
<td>13.5</td>
</tr>
</tbody>
</table>

The nanoscale films consist of two parts: a crosslinked PGMA anchoring layer and a grafted (PAA, PS, or P2VP) layer. Structural parameters for the grafted layers are presented in Table 6.1. For all polymer films under study, the effective distance between grafting sites, D, is lower than the average radius of gyration, (R\textsubscript{g}) of the macromolecules. Therefore, PS and P2VP end-grafted layers are in the brush regime\textsuperscript{18}. PAA chains, anchored at multiple points, are forming a “Guiselein brush” where, as brush components, constituent parts of the chains located in tails and loops (pseudotails) of the anchored macromolecule are taken\textsuperscript{20}. Imaging using an optical system of AFM (images are not shown) indicated that the resulting films bridged 0.6 mm or 1 mm gaps between parallel gold electrodes with a length of 100 mm (Figure 6.1) or a 2 mm gap.
between an interdigitated electrode pattern (Figure 6.1). It is necessary to point out that the anchoring and grafted layers were attached to the surface of silicon oxide and gold electrode. AFM imaging studies conducted for the model silicon wafers indicated that our grafting procedures resulted in the formation of a complete, uniform, and virtually pinhole-free polymer grafted layer in each case (Figure 6.3). AFM RMS roughness for the grafted layers was on the level of 0.3–0.8 nm, which is much lower than the thickness of the nanoscale films.

![AFM images of PGMA, PAA, PS, and P2VP layers](image)

**Figure 6.3** AFM images of PGMA, PAA, PS, and PVP layers anchored to the substrate surface. Scan size: 1 x 1 μm, vertical scale: 3 nm (PGMA, PS) and 10 nm (PAA, P2VP).

**Figure 6.4** shows the results of water contact angle measurements for the microelectrode-containing samples covered with the grafted layers under study. As expected, based on the chemical structure of the polymer compounds, a hydrophobic layer is formed in the case of PS (contact angle ~ 90 degrees), and a highly hydrophilic layer was observed in the case of PAA (contact angle ~ 0–10 degrees, practically complete wetting). PVP and PGMA are characterized by an intermediate water contact angle. The measurement of the contact angles for the layers anchored to the model
samples showed the same values of the contact angle. Therefore, thickness and water contact angle data demonstrated that similar grafted layers can be attached to both the wafers with electrodes and the model samples.

![Graph showing static contact angle for different polymers](image)

**Figure 6.4** Values of the static contact angle measured after modification of the surface with PGMA, PS, PAA and P2VP layers respectively.

### 6.3.2 Conductivity measurements

#### 6.3.2.1 Effect of solvent vapors

Typical current-voltage curves were recorded in air before the analyte exposure, under analyte exposure, and after the analyte exposure (**Figure 6.5**). First of all, it is necessary to highlight that the polymer layers under ambient conditions practically did not conduct electricity and, therefore they behaved as insulators. Depending on the
polymer layer/analyte combination, moderate to dramatic changes in the system conductivity were observed. In all cases, the effect of organic vapor atmosphere on the electric properties of the polymer films was completely reversible, and all “after exposure” curves coincided with the initial “before the exposure” ones.

**Figure 6.5** Examples of electrical conductivity changes in polymer brush layers under the influence of organic solvent vapors. The PAA polymer brush shows weak response to chloroform vapor (A) but a much stronger response to water vapors (B). For the PS polymer brush the situation is reversed: it shows significant variation of conductivity in a chloroform vapor environment (C) but remains practically insensitive to water vapors (D). The polymer brush P2VP displays strong response to both ethanol (E) and water (F) but I–V curves have different characteristic features: a symmetrical curve is recorded in an ethanol environment while an asymmetrical behavior is observed in a saturated water vapors atmosphere. Red curves (circles) correspond to a pristine polymer film before the exposure to an analyte, blue curves (squares) to the saturated polymer layer (5 min after the exposure to the vapor), and green curves (diamonds) to a completely recovered state after removing the sample into air (5 min after the exposure to air).
Table 6.2 summarizes the conductivity response of the samples to different analytes. The measurements indicated that the grafted nanoscale polymer films displayed significant selectivity and sensitivity to vapors of different organic solvents. More specifically, PGMA and PAA systems displayed high sensitivity to water and ethanol vapors, while hydrophobic non-polar PS film were more sensitive to chloroform and toluene and practically insensitive to water or ethanol exposure. Being a hydrogen bonding polymer, P2VP material showed a high sensitivity and selectivity to ethanol and water.

Table 6.2 Factor of electrical conductivity increase for the grafted polymer layers under exposure to saturated vapors of solvents.

<table>
<thead>
<tr>
<th>Solvent/Polymer</th>
<th>PGMA</th>
<th>PAA</th>
<th>P2VP</th>
<th>PS</th>
</tr>
</thead>
<tbody>
<tr>
<td>Water</td>
<td>2500</td>
<td>50000</td>
<td>500</td>
<td>10</td>
</tr>
<tr>
<td>Ethanol</td>
<td>500</td>
<td>200</td>
<td>1000</td>
<td>50</td>
</tr>
<tr>
<td>Chloroform</td>
<td>70</td>
<td>25</td>
<td>80</td>
<td>250</td>
</tr>
<tr>
<td>Toluene</td>
<td>2</td>
<td>2</td>
<td>5</td>
<td>15</td>
</tr>
</tbody>
</table>

Different shapes of the I–V curves were observed for different polymer film/organic solvent analyte combinations. Several examples of such different shapes can be seen in (Figure 6.5). All I–V curves were characterized by a hysteresis between voltage increase and voltage decrease ramps. The existence of such hysteresis is a typical signature of organic materials with relatively low conductivity. The kinetics of conductivity variation is shown in (Figure 6.6). Figure 6.6 a and b show examples of the variation of the I–V curve shape under exposure to organic solvent vapors while Figure
6.6 c and d display the measured current at a certain bias, depending on the time during cyclic application of chloroform or ethanol vapors. Polymer brushes under study showed a practically instantaneous (30 s) response to the organic vapor exposure.

Figure 6.6 Kinetics of the current response for the polymer brushes. Variation of I–V curves with time for the PAA polymer in a saturated water vapor atmosphere (A); and for the PS polymer in a saturated chloroform vapor atmosphere (B). I–V curves were recorded at 30 second intervals and demonstrate a significant increase of polymer films in-plane conductivity. Vertical arrows show the trend in I–V curves variation with the time of the analyte exposure. Examples of variation of the conductivity versus time under repeated exposure to the analyte vapors are shown in portions (C) and (D): current at biases of +5 V and -5 V for the PS brush exposed to chloroform vapors (C) and for the PAA brush sample exposed to ethanol (+5 V only) (D). The arrows point to the beginning (ON) and the end (OFF) of the exposure cycles.
Saturation of the conductivity was observed after 5–7 min of the exposure. The response time for conductivity during recovery in air was even faster. Typically, the conductivity of the sample dropped back to the original insulating properties within less than 30 seconds after exposing it to air (Figure 6.6 c and d).

6.3.2.2 Understanding of the response of polymer layers. Thermodynamic affinity

To understand solvent-selective response of the polymer layers two factors should be taken into the account. First of all, the thermodynamic affinity between polymer layers and solvents, which can be estimated using Hansen solubility parameters should be considered\(^{21,22}\). The solubility parameter can be defined as\(^{23}\):

\[
\delta_T = \left( \frac{\Delta E}{V} \right)^{0.5} = (\delta_d^2 + \delta_p^2 + \delta_h^2)^{0.5}
\]

where \(\Delta E\) is the cohesive energy, \(V\) is the molar volume of the molecule, \(\delta_d\) is the dispersive interaction from van der Waals forces, \(\delta_p\) is the polar interaction from distribution of electron density within the molecule, \(\delta_h\) is the hydrogen bonding interaction from de-shielded hydrogen atoms semi-bonding with electron rich atoms. A smaller difference between the solubility parameters in polymer/solvent pair points to the higher affinity. The HSPiP software\(^{24}\) has been used (based on Hansen method\(^{21}\) of solubility parameters determination) to estimate the parameters for the polymer and solvents involved in the study (Table 6.3). In Table 6.3, the solvent analytes are arranged in accordance with their affinity to the polymers grafted. For example 1\(^{st}\) and 5\(^{th}\) rows represent a PAA-water pair: the corresponding analyte is the best solvent for the polymer. The analyte located in the neighboring 6\(^{th}\) row show a relatively good
solubility property for the corresponding solvent (PAA-ethanol). Thus, the PS brush (4th row) can swell to the highest extent in toluene (8th row) and in chloroform (7th row) but not significantly in ethanol or water. PGMA (3rd row) swells to the highest extent in chloroform (7th row) but also to some extent in toluene (8th row) and ethanol but not in water. The P2VP (2nd row) brush has a better affinity for ethanol (6th row) but can also adsorb considerable amounts of chloroform (7th row) when exposed to the corresponding vapor.

Table 6.3 Solubility parameters and dipole moments for polymers/solvents under the study.

<table>
<thead>
<tr>
<th>Polymer/Solubility parameter</th>
<th>$\delta_i$ {MPa$^{1/2}$}</th>
<th>$\delta_p$ {MPa$^{1/2}$}</th>
<th>$\delta_h$ {MPa$^{1/2}$}</th>
<th>$\delta_t$ {MPa$^{1/2}$}</th>
<th>Dipole moment {D}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PAA</td>
<td>17.3</td>
<td>12.2</td>
<td>18.6</td>
<td>29.1</td>
<td>0.7</td>
</tr>
<tr>
<td>P2VP</td>
<td>19.1</td>
<td>9.6</td>
<td>9.2</td>
<td>24.3</td>
<td>0.57</td>
</tr>
<tr>
<td>PGMA</td>
<td>16.5</td>
<td>7.6</td>
<td>9.2</td>
<td>19.6</td>
<td>0.77</td>
</tr>
<tr>
<td>PS</td>
<td>19.3</td>
<td>6.4</td>
<td>4.8</td>
<td>22.8</td>
<td>0.1</td>
</tr>
<tr>
<td>Water</td>
<td>12.2</td>
<td>22.8</td>
<td>40.4</td>
<td>47.8</td>
<td>1.85</td>
</tr>
<tr>
<td>Ethanol</td>
<td>12.6</td>
<td>11.2</td>
<td>20</td>
<td>26.1</td>
<td>1.7</td>
</tr>
<tr>
<td>Chloroform</td>
<td>11</td>
<td>13.7</td>
<td>6.3</td>
<td>18.7</td>
<td>1.01</td>
</tr>
<tr>
<td>Toluene</td>
<td>16.4</td>
<td>8</td>
<td>1.6</td>
<td>18.3</td>
<td>0.36</td>
</tr>
</tbody>
</table>

To explore the relationships between polymer-solvent interaction and correspondent change in conductivity we have conducted series of swelling experiments of polymer films grafted to model surfaces. Figure 6.7 represents swelling data of polymer films grafted to the silicon wafers and model surface of the gold. Using data obtained from swelling experiments the polymer-solvent vapor effective interaction
parameter chi (χ) for PGMA cross-linked network and cumulative effective interaction parameter chi (χ) for PGMA/PAA, PGMA/PVP and PGMA/PS pairs has been determined.

The effective interaction parameter (χ) was found using the equation 6.2\(^{25}\).

$$\chi = \frac{-(\ln (1 - \phi_2)) - \phi_2 - (\frac{\rho V_1}{M_c} \phi_2^{1/3})}{\phi_2^{1/3}}$$

(6.2)

Where χ is an effective interaction parameter, \(\phi_2\) is the volume fraction of the polymer in a swollen state, \(\rho\) is the density of the polymer, \(V_1\) is the molar volume of the solvent, and \(M_c\) is the average molecular weight between cross-links.

Figure 6.7 Swelling of the grafted polymer layers under exposure to saturated vapors of solvents. The polymer films used in experiments were: 1-PGMA, 2-PAA, 3-P2VP, 4-PS.
The equation 6.2 provided us with good qualitative approximation used to compare different polymer-solvent pairs. Assuming the same degree of cross-linking for thin and thick PGMA films the already determined value of $M_c$ has been used in calculations\textsuperscript{26}. Figure 6.8 represents interaction parameter chi ($\chi$) values for all studied systems.

**Figure 6.8** Effective interaction parameter ($\chi$) for the layers grafted to the model surfaces. The polymer films used in experiments were: 1-PGMA, 2-PAA, 2-P2VP, 4-PS.

Moreover, the variation in the conductivity for such a polymer-solvent pair is the highest. For example, Table 6.4 and Table 6.5 represent calculated effective interaction parameters and correspondent factors of current increase for hydrophilic PAA layer and hydrophobic PS film respectively. In fact, our results showed that the maximum current response was observed for the vapors with the highest affinity between the polymer brush and vapor molecules (red color represent polymer/best solvent pairs).
Table 6.4 Effective interaction parameter ($\chi$) for PAA polymer film and correspondent change in conductivity.

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>PAA/Water</th>
<th>PAA/Ethanol</th>
<th>PAA/Chloroform</th>
<th>PAA/Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{\text{effective}}$</td>
<td>0.81</td>
<td>1.39</td>
<td>1.34</td>
<td>1.98</td>
</tr>
<tr>
<td>Factor of current increase</td>
<td>50000</td>
<td>200</td>
<td>25</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6.5 Effective interaction parameter ($\chi$) for PS polymer film and correspondent change in conductivity.

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>PS/Water</th>
<th>PS/Ethanol</th>
<th>PS/Chloroform</th>
<th>PS/Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{\text{effective}}$</td>
<td>2.33</td>
<td>1.43</td>
<td>0.68</td>
<td>0.82</td>
</tr>
<tr>
<td>Factor of current increase</td>
<td>10</td>
<td>50</td>
<td>250</td>
<td>15</td>
</tr>
</tbody>
</table>

6.3.2.3 Understanding of the response of polymer layers. Dipole moments

Second factor influencing polymer film conductivity variation, is the dipole moments of the polymer and analyte. We used Polymer-Design Tools™ software (based on the Bicerano method of polymer parameters determination) to estimate the dipole moments for the polymers involved in our study. Dipole moments for the solvents were obtained from literature. Data for the dipole moments are summarized in Table 6.3. As followed from the data shown in Tables 6.2 and 6.3, the PS brush swelled well in both toluene and chloroform, however, variation of its conductivity is significantly higher under chloroform exposure. This can be explained by higher dipole moments (and, therefore, a higher polarizability) of the absorbed organic vapor molecules (chloroform has 1 D molecular dipole against the 0.3 D of the toluene). On the other extreme, the
PAA brush is a highly polar matrix, swollen well in water and ethanol (dipole moments: 1.85 D and 1.7 D, respectively). As a result, variation of the conductivity for PAA was the highest among considered brushes, on the whole, 3–4 orders of magnitude higher than in less hydrosopic brush layers (PS and P2VP).

Therefore, two conditions have to be satisfied for higher polymer brush conductivity response. Firstly, it’s the maximal swelling (affinity) of the brush film and analyte. Secondly, the polar nature of the solvent and a polymer should be taken in a consideration. For example, PAA and PS films demonstrated highest increase in conductivity during interaction with “good” solvents; water and chloroform respectively. On the other hand, P2VP and PGMA films demonstrated highest increase in conductivity after exposure to solvents of “bad” and “moderate” quality (Tables 6.6 and 6.7 respectively). For instance, PGMA film demonstrated highest increase in conductivity after exposure to water vapor (bad solvent). This behavior can be explained by high dipole moments (thus, high polarizability) of PGMA and water (0.77 D and 1.85 D respectively). P2VP exhibited high change in conductivity after exposure to ethanol vapor (solvent of moderate quality). It can be explained by a combination of two factors: moderate swelling (affinity) of P2VP film and high dipole moments of polymer and a solvent (0.57 D and 1.7 D respectively).
Table 6.6 Effective interaction parameter (χ) for PGMA polymer film and correspondent change in conductivity.

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>PGMA/Water</th>
<th>PGMA/Ethanol</th>
<th>PGMA/Chloroform</th>
<th>PGMA/Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{effective}$</td>
<td>2.52</td>
<td>1.21</td>
<td>0.96</td>
<td>1.06</td>
</tr>
<tr>
<td>Factor of current increase</td>
<td>2500</td>
<td>500</td>
<td>70</td>
<td>2</td>
</tr>
</tbody>
</table>

Table 6.7 Effective interaction parameter (χ) for P2VP polymer film and correspondent change in conductivity.

<table>
<thead>
<tr>
<th>System/Parameter</th>
<th>P2VP/Water</th>
<th>P2VP/Ethanol</th>
<th>P2VP/Chloroform</th>
<th>P2VP/Toluene</th>
</tr>
</thead>
<tbody>
<tr>
<td>$X_{effective}$</td>
<td>1.59</td>
<td>1.07</td>
<td>0.84</td>
<td>1.11</td>
</tr>
<tr>
<td>Factor of current increase</td>
<td>500</td>
<td>1000</td>
<td>80</td>
<td>5</td>
</tr>
</tbody>
</table>

Besides this, the solvent-sensitive change in conductivity can also be used for the detection of volatile organic molecules using the polymer nanoscale grafted layers. In fact, rearranged according to the analyte type, conductivity change for the films synthesized in this work clearly indicates that each solvent applied in our study produced a unique response pattern that can be used for analyte identification (Figure 6.9).
Figure 6.9 The factor of electrical increase for the grafted layers under exposure to saturated vapors of solvents. The polymer films used in experiments were: 1-PGMA, 2-PAA, 2-P2VP, 4-PS.

6.3.3. Conductivity measurements. Effect of the temperature

Dependence of electrical properties of thin polymer films on a temperature was evaluated. Figure 6.10 shows the variation of the current at particular polarization with temperature.
Figure 6.10 Examples of I–V curves recorded at different temperatures for the PAA brush sample (A), temperature dependence of the current variation ΔI for a -5 V to +5 V voltage sweep for all polymer brushes under study (B), and semi-logarithmic representation of current variation with temperature in the PS brush sample (C).

An exponential increase of the current has been detected for all samples under the study. For example Figure 6.10 c shows how current passing through the sample modified with PS film has changed as function of the temperature. Two regimes have been observed. They both possessed an exponential increase of the current with
temperature and could be characterized with a different slope (activation energy). The change between the regimes can be associated with a glass transition temperature for polymers constituting the grafted layers. Table 6.8 represents $T_g$ values of the polymer films compared to $T_g$ values of the bulk polymers$^{28,29}$.

Table 6.8 Glass transition temperature of the bulk polymers and corresponding grafted polymer layers.

<table>
<thead>
<tr>
<th>Polymer/Value</th>
<th>$T_g$ (bulk) °C</th>
<th>$T_g$ (film) °C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PGMA</td>
<td>74</td>
<td>70</td>
</tr>
<tr>
<td>PS</td>
<td>100</td>
<td>110</td>
</tr>
<tr>
<td>PAA</td>
<td>106</td>
<td>120</td>
</tr>
<tr>
<td>P2VP</td>
<td>104</td>
<td>110</td>
</tr>
</tbody>
</table>

The data obtained at our research are in a good agreement with reported earlier positive deviations of $T_g$ values for ultrathin grafted polymer films with a high degree of confinement$^{30,31}$. Positive deviation of the $T_g$ values of thin polymer films can be explained by confinement of polymer chains constituting the polymer brush. Thus, the number of possible conformations of the polymer chains grafted to the surface is limited in comparison to the polymer chains in a bulk state.

6.3.4 Conductivity mechanisms of thin polymer films

Possible conductivity mechanisms of thin polymer films have been considered in several review papers$^{32-34}$. So-called residual conductivity of highly insulating polymers (like polyethylene or polystyrene) can arise from impurities acting as a dopant. It is well known that the presence of doping molecules capable to reduce or oxidize
segments of polymer chains can change the electrical conductivity of a polymer material. Dopant molecules can selectively interact with appropriate sites on the polymer chains, introducing electrons or holes in the conduction and valence bands of the polymer matrix. In addition, the dopant molecules can become ionized, thus, contributing to the ionic content of the polymer system. The association with the doping reduction–oxidation processes can also lead to localization of charges as the newborn electrons or holes experience strong Coulombic interaction with corresponding molecular counter ions.

As an alternative scenario, charge carriers (electrons or holes) can be injected into polymer film from electrodes, thus, producing “an electrode doping” of the polymer material. This effect may be especially significant for nanoscale gaps between electrodes or ultrathin films of polymers. Similarly to chemical doping, electrode doping can cause formation of dipoles due to Coulombic interaction of injected carriers with corresponding counter ions or ionized molecules. Such dipoles also act as trapping centers for further injected charge carriers. In electrochemical terms, the localized donor and acceptor states may be considered to exist in oxidized or reduced forms. The polymer matrix surrounding each of these sites will have to reorganize its charge distribution (polarization), or even its conformation, to accommodate the created charged states. In turn, this polarization or chain reorganization will change the energy of a state and will contribute to the trapping of charges within its vicinity. Self-trapping or formation of quasi-particles – polarons is an important factor influencing the localization of charges or charge transfer within a polymer matrix. The overall macroscopic polarization of an
insulating polymer may be negligible. Nevertheless, polar groups present in the polymer chains can give rise to substantial local polarizability\textsuperscript{32}.

Polar impurities can also play an important role in the electrical conductivity of insulating polymers. Earlier reports suggested that a low-level conductivity of insulating polymers can be explained by the presence of Na\textsuperscript{+}, K\textsuperscript{+}, Cl\textsuperscript{-}, or some other ions at levels below 1 ppm\textsuperscript{32}. Even a trace amount of water can be highly significant in this respect. Any polar or ionic impurity will be likely to migrate to the neighborhood of a charged state due to electrophoretic forces introduced by this charge, thus, creating the possibility for ionic current.

Summarizing the above consideration we suggest two of the most probable conductivity mechanisms for the polymer layers studied in this work: polaronic or ionic type conductivity. In the former case, electrical current is associated with the movement of quasiparticles – polarons with different degrees of delocalization and, therefore, different ranges of possible hopping. Charge carrier mobility associated with such a type of conductivity is typically low (in the range of $10^{-6}$ to $10^{-3}$ cm$^2$ V$^{-1}$ s$^{-1}$)\textsuperscript{34}. Ionic conductivity requires ionic groups, which can be ionized under certain pH conditions and can drift through free volume channels in a polymer matrix. Both the density of locally-polarized centers and the available free volume in a polymer brush film will be affected by swelling and deswelling processes in the presence of organic solvent vapors. Under swelling, the density of polar centers may increase or decrease depending on the polarizabilities of the solvent molecules and those of the polymer chains.
In principle, different conductivity mechanisms can be distinguished based on temperature or on electric field dependence of conductivity. The Poole–Frenkel (PF) model is typically a good mathematical description for the mobility of carriers in organic solids. The PF law arises naturally from consideration of trapping–detrapping processes in disordered materials but also holds true for a large number of polymer systems. In accordance with the PF equation, the logarithm of the charge carrier mobility, \( \mu \), is proportional to the square root of the applied electric field \( E \): \( \ln \mu \propto SE^{1/2} \) (with a slope parameter \( S \) depending on temperature following \( \sim \exp(-1/T^2) \) or \( \sim \exp(-1/T) \) – i.e. Arrhenius-type law). Electrical conductivity is proportional to the mobility and concentration of charge carriers and will follow the same power law.

On the contrary, non-Arrhenius type temperature dependence is more likely to be observed in cases of ionic conductivity in solid polyelectrolytes. In fact, DC conductivity of small ions in polymer matrices often follows an empirical Vogel–Tamann–Fulcher (VTF) relation: \( \sigma_{dc} = \sigma_0 T^{-0.5} \exp(-B/(T - T_0)) \) with \( \sigma_0 \) and \( B \) being material dependent constants and \( T_0 \), an ideal glass transition temperature of the polymer matrix originally introduced in the Gibbs–DiMarzio theory as an entropy independent glass transition. Temperature independent conductivity is related to the concentration of charge carriers in the polymer system and \( B \) denotes the activation energy of ion transport associated with the configurational entropy of the polymer chains. Thus, the VTF equation relates the ionic conductivity to the variation of the free volume in the system.
Regarding our research, polymer films with high affinity to solvent vapor firstly adsorbed, and then dissolved solvent molecules. This in turn, led to swelling of the films and to “brush” like conformation of the tethered polymer chains constituting the layer. Such a polymer-solvent systems possessed enhanced mobility of the charges. Therefore, their conductivity was higher in comparison to the original unperturbed state. A different situation arised if the polymer brush films were in contact with organic vapors of low affinity for the constituting polymer chains (non-solvent). In this case, the absorption and, especially, penetration of the analyte molecules into the polymer film were insignificant. Thus, no conformational changes occurred within the polymer film. The thickness and concentration of charge carriers remained the same and no noteworthy conductivity increase was observed. However, depending on the chemical nature of the brush, the situation may also be between these two extremes – i.e., some limited solubility of the polymer chains of brush film is in the analyte of interest. As a result, some degree of swelling of the brush macromolecules was observed, leading to intermediate levels of imposed electrical conductivity. The ionic type of conductivity should also lead to electrochemical processes during application of the external electrical potential. Therefore, different strengths of interactions may be observed under positive and negative bias conditions and the I–V curves became asymmetrical (see an example in Figure 6.5).

Previous studies of the electrical behavior of ultrathin polymer films (including polymer brush samples) were done in a vertical electrodes configuration where the electric current is passed across the film thickness (i.e., with the polymer brush sample
sandwiched between the electrodes)\textsuperscript{1, 4, 39}. In such a configuration, the gap between the electrodes is minute, and even an application of a small potential of 1–5 V can cause a breakdown effect. In many reported instances, such so-called soft breakdown phenomenon is completely reversible in a few nanometer-thick dielectric films. Under the applied polarization potential (several MV m\textsuperscript{-1}), highly conductive channels are formed, which may have conductivity values approaching those of superconductors\textsuperscript{40}. These channels remain in their conductive or “ON” state after removing the external potential and can be “erased” with the application of potential of opposite polarity. Due to nanoscale structural organization of the dielectric film, a perfect heat dissipation control is possible, and the breakdown phenomenon does not diverge into irreversible catastrophic thermodestruction of the polymer sample. In fact, self-limiting action of the breakdown current is typically observed. Reversibility of the effect allows its application to memory devices\textsuperscript{1, 4}.

Several recent reports suggest that the switching voltage can ionize ultrathin brush film, creating a conducting channel of electronic levels aligned with the Fermi level. The conductance is determined by the least probable electron hopping along the chain, resulting in a conductance behavior with characteristic hysteresis features and a threshold voltage (“ON” switching potential). A similar effect was discovered in nanometer-thick inorganic glass dielectrics\textsuperscript{39}. Application of high polarization in combination with ionizable impurities can cause irreversible changes in the film morphology. Zhitenev, with co-workers, have reported on the expansion of a polyionomer brush film thickness caused by ionization of ionic bonds in carboxyl groups\textsuperscript{1}. Due to electrostatic
repulsion of the charged segments, chain elongation and thickening of the brush films have been observed.

In our research the gap between electrodes is significantly larger and the “ON” potential is difficult to reach. On the other hand the top surface area of the film is highly accessible for the environment and therefore can be more easily ionized in the presence of organic vapors or water. Moreover, the overall surface area of the brush film not mechanically confined between the electrodes is higher in such a configuration (which generally increases contribution from the top, more mobile polymer fragments and ions).

6.4 Conclusion

The methodology used for polymer grafting to the model gold surface was successfully applied to graft various polymers to the Si/SiO$_2$/Au surface. Grafted polymer films that are insulators at ambient conditions displayed a significant increase in conductivity depending on environmental conditions. The observed response of grafted polymer films was highly chemically specific.

The conductivity of the polymer films as a function of the temperature had been investigated. Under dry conditions, all grafted polymer layers demonstrated Arrhenius type of temperature behavior of conductivity that is typical for polaronic mechanism in insulating polymers. Under solvent exposure, grafted polymer films showed non-linear current-voltage characteristics. The observed electrical response of the polymer layers was attributed to a mixed polaronic-ionic conductivity mechanism. Such behavior is in tune with the swelling-deswelling conformational changes in the system as a response to
changes in the environment. Interaction with the analyte molecules led to electrochemical potential variation within the brush films and could change both the content of the ionized species and the concentration of polarons within the films. The ionic character of the response was manifested in the characteristic shape of the observed curves (Figure 6.5). We demonstrated that observed effects can be used in a micron-sized conductometric transducing scheme for detection of volatile organic molecules.
6.5 References


30. Tate, R. S.; Fryer, D. S.; Pasqualini, S.; Montague, M. F.; de Pablo, J. J.; Nealey, P. F., Extraordinary elevation of the glass transition temperature of thin polymer films


CHAPTER SEVEN

TEMPERATURE CONTROLLED SHAPE CHANGE OF GRAFTED NANOFOAMS

7.1 Introduction

Controlled mechanical motion at the nanoscale level is an important element of practical nanotechnology\textsuperscript{1-3}. There is convincing experimental evidence that nanoscale actuation can be achieved by forces associated with conformational changes of macromolecular chains. In fact, actuation by densely grafted polymer layers (polymer brushes), which can stretch and collapse as a result of external stimuli, has been recently demonstrated\textsuperscript{1, 4-6}. The level of actuation is determined by the competition between entropic energy related to chain stretching and excluded volume interactions between segments of the grafted macromolecules. Nanoactuation with the grafted polymer layers reported to date is realized when the polymer chains are placed in a solvent. To the best of our knowledge, the actuation potential of grafted polymer layers in the dry state (that is based on conformational changes and going beyond employment of thermal expansion and/or phase-transition phenomena) has not been reported in the scientific literature. To fill this gap in this chapter we described a synthesis of a grafted polymer layers that can provide nanoscale actuation without a solvent. Specifically, we utilized a “grafting to” technique to obtain a 20–200 nm porous grafted polymer film - “nanofoam.”\textsuperscript{7} The grafted nanofoam possessed the behavior of a shape-memory material, which exhibited mechanical action under external stimulus.

Yuval Galaburda, Anna Paola Soliani, James Giammarco, Bogdan Zdyrko and Igor Luzinov, Temperature controlled shape change of grafted nanofoams. Soft Matter 2014, 10, 2567-2573
The concept of shape-memory polymer materials (SMPs) was introduced more than 50 years ago. In general, macromolecules constituting SMPs can be deformed and fixed into a temporary dormant shape under specific conditions of temperature, stress, or environment. The materials are capable of relaxing to their original, stress-free, permanent shape under the influence of external stimuli (such as heat, light, electrical current, magnetic field, presence of chemical or biological compounds in the environment). This relaxation is associated with elastic energy stored in the stretched macromolecules that constitute SMPs when the system is in a “frozen” thermodynamically unstable state. Once relaxed to a stable state, the SMP requires special treatment to return to the temporary frozen state. SMPs can be synthesized as nonporous or porous material. In contrast to nonporous SMPs, porous ones can achieve higher temporary deformations and, therefore, exhibit higher deformations when they recover their permanent shape. The majority of porous SMPs can be synthesized through a variety of methods, such as thermal-induced phase separation, salt or particle leaching, emulsion templating within high internal-phase emulsions, high internal-phase supercritical CO2-emulsion-templating, foaming, decomposition of the thermoliable block of the block copolymers, and freeze drying.

Up to date, significant work has been accomplished in the development of porous shape-memory polymers that provide actuation at the macro- and microscopic scales. However, the nanoscale level of actuation by SMPs has not been
reported. In this chapter we report the synthesis of grafted nanofoams with nanoscale actuation potential upon thermal treatment.

Furthermore, we demonstrated that polymer based shape memory systems can be utilized to create platform for prospective unattended temperature sensing devices. We report synthesis and actuation of grafted PGMA/nanoparticles composite nanofoam. Gold nanoparticles are employed as optically active element of a system\textsuperscript{23, 24}. Fabrication of PGMA/gold nanoparticles composite was possible due to strong chemical interaction between gold and PGMA (Chapter 4 page 65). Upon foaming and then after thermal actuation, the optical response of the system changes due to the nanolevel alteration of internal structure of the PGMA/gold nanoparticles composite. This change in optical properties was monitored by means of UV-vis spectroscopy.

7.2 Experimental

7.2.1 Synthesis, characterization and actuation of PGMA and PS/PGMA nanofoams

Highly polished, single crystal silicon wafers were used as a substrate. The wafers were first cleaned in an ultrasonic bath for 30 min, placed in a hot “piranha” solution (3:1 concentrated sulfuric acid–30% hydrogen peroxide) for 1 h, and then rinsed several times with high purity water. After being rinsed, the substrates were dried under the stream of dry nitrogen in cleanroom 100 conditions.

A PGMA layer was deposited on the surface of the wafers by dip coating (dip-coater Mayer Feintechnik, model D-3400) from a 1.5 w/v % solution in chloroform. The lower and upper limits of the dip coater were set to enable near-complete dipping of the
substrate. The specimens were placed in a vacuum oven at an elevated temperature (120 °C) overnight to facilitate the surface attachment and cross-linking of the PGMA macromolecular layer. The layer was then rinsed with the solvent (three to four times) to remove unattached macromolecules. The typical lateral dimensions of the films under investigation were 1 x 2 cm.

Carboxy-terminated polystyrene (PS) with Mn of 2000 g/mole, PDI = 1.2 was obtained from Polymer Source, Inc. PS was deposited from a 3 w/v % chloroform solution on the wafers previously modified with the PGMA film. To avoid dewetting during the annealing, 30 w/v % by weight of high-molecular weight nonreactive PS (M_n = 170 000 g/mol; Aldrich) was added to the PS solution. Specimens were annealed in an oven under nitrogen at 170 °C overnight to facilitate the reaction between the carboxylic groups of the PS chains and the epoxy groups of the PGMA monomeric units. After the annealing, samples were thoroughly rinsed with chloroform to extract unreacted PS macromolecules.

To create the porous grafted layers, we carried out freeze-dry foaming of the PGMA and PS/PGMA films. Specifically, the films were swollen in a good solvent (chloroform) and cooled to freeze the solvent (−90 °C) with subsequent solvent removal under reduced pressure (100–150 mTorr). Foaming was conducted inside the foaming stage, which consisted of a vacuum chamber where swelling and solvent sublimation take place, and copper temperature-regulated table, which was cooled with liquid nitrogen (Figure 7.1). The table was equipped with a thermocouple that was used to control the temperature of the sample. The collapse of the nanofoams was conducted in an oven
preheated to the necessary temperature. The samples were placed in the oven for 30 minutes at each temperature.

![Image of foaming station](image)

**Figure 7.1.** Foaming station used for synthesis of PGMA, PS/PGMA, and PGMA/gold nanoparticles grafted shape memory nanofoams.

The “nanotomography” approach was utilized to visualize the pores distribution within grafted polymer layers\(^25\). This method is based on a step-by-step air plasma etching of the polymer film with a subsequent step-by-step AFM analysis of the etched surface, after which the morphology inside the film can be revealed. Synthesized PGMA grafted nanofoam and reference grafted PGMA film were analyzed.

Ellipsometry, atomic force microscopy, spectroscopic reflectometry were utilized for analysis and characterization of grafted polymer films and nanofoams.

To characterize the efficiency of the grafted PGMA and PS/PGMA nanofoams the shape recovery ration (\(R_R\)) has been calculated using the following equation:
\[ R_R = \frac{Z_T - Z_D}{Z_I - Z_D} = \frac{\varepsilon_T}{\varepsilon_0} \quad (7.1) \]

\[ \varepsilon_T = \frac{Z_T - Z_I}{Z_I} \quad (7.2) \]

where \( Z_T \) is the variation of the foamed film thickness with temperature, \( Z_I \) is the initial nonfoamed film thickness, \( Z_D \) is the initial thickness of the foamed film, \( \varepsilon_T \) is the variation of the strain with a temperature, and \( \varepsilon_0 \) is the initial strain before recovery at the imposed by foaming film thickness, \( Z_D \).

The nanofoam, as a first approximation, was considered to behave as an extended Gaussian elastic network of cross-linked macromolecules. Thus, the residual conformational stress accumulated by the polymer chains at the nanofoam at room temperature could be estimated by following equation:\(^2^6\):

\[ \sigma = \left( \frac{E}{3} \right) \times \left( \lambda^2 - \frac{1}{\lambda} \right) \quad (7.3) \]

where \( E \) is chain Young’s modulus, \( \lambda = Z_D/Z_I \) is an extension ratio for the macromolecules constituting the nanofoam.

The Young’s modulus of the polymer chains can be approximated by the following equation:

\[ E = \frac{dRT}{M_x} \quad (7.4) \]
where \( d \) is the density of the polymer, \( R \) is the gas constant, \( T \) is the temperature, and \( M_x \) is the molecular weight between cross-links.

The level of cross linking of PGMA film was estimated using the relationship determined for cross-linked poly methyl metacrylate (PMMA) that has a chemical structure close to PGMA\(^{27} \).

\[
\Delta T = 0.78 \times 10^5 \times \rho \tag{7.5}
\]

where \( \Delta T \) is the change in glass transition temperature with cross-linking, and \( \rho \) is the degree of cross-linking defined as a number of the cross-links per gram.

The mole fraction of the cross-linked monomeric units per chain, \( m_c \) was estimated using the following equation:

\[
m_c = \rho \times M_{AV} \tag{7.6}
\]

where \( M_{AV} \) is the average molecular weight for the monomer-cross linker mixture.

### 7.2.2 Synthesis, characterization and actuation of the PGMA/gold nanoparticles composite nanofoam

Glass microscopy slides were used as a substrate. The glasses were first cleaned in an ultrasonic bath for 30 min, placed in a hot “piranha” solution (3:1 concentrated sulfuric acid–30% hydrogen peroxide) for 1 h, and then rinsed several times with high purity water. After being rinsed, the substrates were dried under the stream of dry nitrogen in clean room 100 conditions.

Gold nanoparticles (d=5 nm, nanoComposix) (16 wt% relative to PGMA amount) were dispersed in 1.5 w/v % solution of PGMA. PGMA/gold nanoparticles film was
deposited on the surface of the glasses by dip coating (dip-coater Mayer Feintechnik, model D-3400) from a 1.5 w/v % solution of polymer in chloroform. The lower and upper limits of the dip coater were set to enable near-complete dipping of the substrate. The specimens were placed in a vacuum oven at an elevated temperature (150 °C) for 8 hours to facilitate the surface attachment and cross-linking of the PGMA macromolecular layer. The layer was then rinsed with the solvent (three to four times) to remove unattached macromolecules.

To fabricate the porous PGMA/gold nanoparticles composite film the foaming was conducted following the procedure employed in synthesis of PGMA and PS/PGMA nanofoams.

Atomic Force Microscopy and UV-vis spectroscopy analysis (Shimadzu UV-2501 PC) were used to characterize PGMA/gold nanoparticles composite films before, after foaming and after thermal actuation.

7.3 Results and discussion

7.3.1 Synthesis and characterization of PGMA nanofoam

A schematic for the fabrication and operation of the grafted nanofoam is presented in Figure 7.2. First of all, PGMA layer was deposited by dip coating on a silicon wafer from a solution and annealed at an elevated temperature in a vacuum oven. During the annealing, besides a surface groups-epoxy reaction, a cross-linking reaction between the epoxy groups occurred. In essence, the PGMA layer was fabricated as a thin internally cross-linked film, covalently bound to the native silicon oxide (covering the
silicon surface) using its epoxy group functionalities\textsuperscript{7, 28}. Epoxy groups of PGMA not involved in the reaction with the surface and cross-linking can be used for the grafting of other polymer chains to modify the chemical composition of the nanoscale film. In fact, the polymer was demonstrated to be an effective anchoring layer for grafting polymers to inorganic and polymeric surfaces using the “grafting to” and “grafting from” approaches\textsuperscript{29-32}.

![Diagram of synthesis and operation of the nanofoam](image)

**Figure 7.2.** Schematics of the synthesis and operation of the nanofoam.

The typical thickness of the deposited PGMA layers was on the level of 80–90 nm, as measured by ellipsometry and reflectometry. The size of PGMA chains (end-to-end distance) can be estimated to be \(\sim 21.0\) nm\textsuperscript{28}. Therefore, the thickness of the film is about four times larger than the size of the PGMA macromolecules constituting the film. AFM studies of the PGMA layer revealed that the film was smooth and homogeneous (Figure 7.3 A). The PGMA layer uniformly covered the substrate on the micro- and nanolevels. The layer was virtually featureless with RMS roughness less than 0.5 nm.

To create a porous film foaming of the grafted macromolecular layer was conducted. Specifically, the glassy PGMA film was swollen in liquid chloroform and cooled to keep the solvent frozen. Next, the solvent was sublimated under reduced pressure. From visual inspection it was clear that the transparent PGMA film became
opaque after the solvent sublimation. The loss of transparency indicated scattering of light because of pore formation.

Figure 7.3. AFM topography images of the PGMA film: (A) before foaming; (B) after foaming; (C) after 54 °C; (D) after 75 °C; (E) after 105 °C. Size of the images is 1x1 μm. Vertical scale is 10 nm (A, E) and 50 nm (B, C, D).

Thickness of the PGMA film (measured by ellipsometry and reflectometry) increased from 80.0 ± 3.0 nm to 93.0 ± 1.0 nm, about a 15% increment thickness, after the foaming was completed. AFM imaging showed a dramatic change in morphology of the PGMA film after the foaming (Figure 7.3 B). Specifically, formation of nanoscale pores and a corresponding increase in film roughness was observed. RMS roughness of the PGMA film increased from 0.5 nm to 8.0 nm due to development of the open pores within the layer. The morphology and thickness of the films did not change significantly after 3 months of storage, demonstrating that the nanofoam layer does not undergo relaxation at room temperature.
To confirm that the PGMA grafted nanofoam had pores throughout the film “nanotomography” approach was utilized to analyze the inner structure of the PGMA after the solvent sublimation. For the “nanotomography” experiment, a 91.0 ± 1.0 nm PGMA polymer film was deposited on the silicon wafer. Next, the porous polymer film was fabricated. Ellipsometric measurements indicated that the film had an 18% thickness increase upon the foaming. We used low-power air plasma (at 1 minute intervals) to etch the film. Ellipsometry measurements were used to track the thickness of the etched polymer film after each step. Simultaneously, a reference experiment was conducted with the nonporous (100.0 ± 3.0 nm) PGMA film. Results are presented in Figure 7.4. AFM imaging revealed that, in fact, pores were situated not only on the surface but also throughout the PGMA foamed layer. Imaging of the nonfoamed plasma-etched PGMA film clearly demonstrated that the observed porous structure was not an artifact caused by plasma etching. The size of the interconnected and open pores inside the film was estimated to be between 10.0 and 100.0 nm.

Young's modulus (1.3 MPa) and residual stress (0.2 MPa) for the polymer chains constituting the nanofoam film were calculated using equations (7.3 and 7.4) respectively.

7.3.2 Actuation of the PGMA nanofoam

The total vertical actuation potential of the PGMA nanofoam film is equal to the level of the vertical extension of the film during the solvent sublimation procedure and was on the order of 10.0–15.0 nm.
Figure 7.4. AFM topography images of the porous PGMA film and reference non-porous PGMA film after every step of the plasma etching (upper and lower rows respectively). The size of the images is 1x1 μm and vertical scale is 20 nm.

There are two possible modes of nanofoam operation as a mechanical actuator. The first was realized when nanofoam was brought to a temperature above $T_g$. In this mode the film is supposed to shrink and reach the thickness close to that before the foaming procedure. The $T_g$ for PGMA used in this work was measured by DCS to be 62 °C. However, it is well known that cross-linking of a polymer can significantly increase its $T_g$. Therefore, we determined the glass transition temperature for the bulk PGMA annealed at the conditions used for synthesis of the grafted polymer PGMA film. Indeed, the glass transition temperature for the cross-linked polymer increased to 79 °C. When the nanofoam ($Z_t = 80.0 \pm 3.0$, $Z_D = 93.0 \pm 1.0$ nm) was heated to 105 °C, the film contracted reaching $Z$ (105 °C) of 82.0 ± 3.0 nm. Therefore, maximum $R_R = 0.85$ was
determined for the grafted layer. The foaming-temperature collapse cycle was performed three times for the PGMA samples studied. $Z_D$ and $Z$ (105 °C) were reproducible within 1 nm range. The result indicated that a single nanofoam layer could be used for multiple actuation cycles. The obtained results confirmed that the porous grafted layer demonstrated properties of the shape-memory material.

In the second mode of mechanical actuation, temperature has been increased step-by-step until it rose above $T_g$. In this case mechanical actuation on the level of 1.0–2.0 nm was achieved. Elevation of the temperature caused increase of the modulus. As a result, the elastic polymer network shrunk in order to maintain stress, allowing temperature (entropy)-driven, nanoscale-level, mechanical actuation. The nanofoam layers were kept inside an oven where temperature was increased stepwise (10–20 °C per step) from 25 °C to 105 °C. After each step, the polymer film was evacuated and characterized by ellipsometry and AFM. In fact, we found a possibility of continuous nanoscale actuation with the foamed PGMA film. Specifically, we observed a decrease in thickness at each temperature increment (Figure 7.5). When the sample was brought to room temperature, the nanofoam maintained the thickness achieved during the heating step. No further film contraction was observed until the sample was heated again. Both the thickness and shape-recovery ratio almost linearly depended on temperature, with somewhat higher deviation from linearity in the glass transition region (Figure 7.5 A and B).

AFM analysis revealed changes in the surface morphology of the nanofoam film upon heating (Figure 7.3 B-D). After each heating step RMS roughness decreased and
reached the initial value (<1 nm) at 92 °C (Figure 7.5 C). The obtained results demonstrated that the nanofoam film was capable of producing gradual mechanical actuation on a nanometer scale. The slope of the thickness versus temperature dependence was -0.13 nm °C\(^{-1}\), indicating that in principle actuation of 1 nm per each 7.7 °C is possible.

![Figure 7.5](image)

**Figure 7.5.** Thickness (A), shape recovery ratio (B) and RMS roughness (C) of the PGMA nanofoam as a function of the temperature.

**Figure 7.5 C** showed how RMS roughness of the PGMA nanofoam has changed with the temperature. The data clearly demonstrated that the roughness–temperature relationship (originating from the surface corrugations and open pores) did not coincide with the quasi-linear thickness–temperature dependence (**Figure 7.5 A**). Namely, as temperature increased to 40 °C the roughness decreased from 8 to 6 nm and then stayed virtually constant until the \(T_g\) region was reached. Over the region the nanofoam roughness changed significantly until it reached the initial (before foaming) value. We associate this behavior with pronounced disappearance of the open nanopores above glass transition temperature.
7.3.3 Synthesis and characterization of the PS/PGMA nanofoam

The epoxy functionalities present in the structure of the PGMA grafted layer offer potential to conduct further modification of the layer with grafting of another polymers\textsuperscript{7, 34-36}. Introduction of polymer chains of different nature into the system can provide possibility to tune the thermal response of the nanofoam film. To this end, we modified the PGMA film (84.0 ± 2.0 nm thick) by grafting of carboxy terminated polystyrene (PS). The carboxyl end groups in the PS chains have been shown to be capable of reacting with epoxy groups present in the film\textsuperscript{28}. We selected polystyrene having a low molecular weight (2000 g/mole) to ensure that both the surface and inside of the PGMA film would be modified with the PS macromolecules diffusing inside the PGMA network\textsuperscript{28}. Additionally, the glass transition temperature for the carboxy-terminated PS is 79 °C, which is practically the same as for cross-linked PGMA. Therefore, T\textsubscript{g} for the PGMA film grafted with PS was essentially the same as that for the non-grafted PGMA film.

To obtain the nanofoam grafted with the PS macromolecules, we firstly modified the surface of the silicon wafers with an 84 nm thick PGMA film. The PS layer was then deposited over the PGMA film, and the sample was annealed overnight. AFM imaging revealed that the obtained PS/PGMA film was uniform and smooth with RMS roughness <1 nm (Figure 7.6 A). The amount of PS grafted to the film was 142 mg m\textsuperscript{2} (135.0 nm) as measured by ellipsometry. The grafting density of the PS attached to the PGMA layer was 42.8 chains per nm\textsuperscript{2}. Since the PGMA grafting density in the film was
0.31 chains per nm\(^2\), we estimated that each PGMA macromolecule was grafted with 138 short PS chains with a total molecular weight of 276 000 g/mole, giving a total molecular weight for the PS/PGMA of about 452 000 g/mole.

**Figure 7.6.** AFM topography (A, B, C) and phase (D) images of the PS/PGMA film: (A) before foaming; (B) after foaming; (C) after 92 °C. Scan size is 1x1 μm. Vertical scale: 10 nm (A, C), 50 nm (B), and 6 degrees (D).

The high amount of the grafted macromolecules indicated that both the surface and interior of the film were modified with the anchored PS chains. In fact, we previously demonstrated that to the PGMA layer of lower thickness (where the grafting is limited to the surface layer only) much less carboxy-terminated PS of low molecular weight can be grafted\(^{28}\). Neither topographical nor phase AFM images demonstrated a detectable phase separation in the film (Figure 7.6 A and C). This observation, in conjunction with
significant diffusion of the PS macromolecules into the PGMA film, indicated that at least partial miscibility between the PGMA cross-linked chains and the PS macromolecules exists.

7.3.4 Actuation of the PS/PGMA nanofoam

The grafting of the additional macromolecules inside the anchored network caused stretching of the PGMA macromolecules. Namely, the chain extension was on the level of 2.6 that is significantly higher that the extension of the chains in the PGMA nanofoam. The residual stress (estimated by equation (7.3)) for the cross-linked polymer chains in the film modified with the grafting was estimated to be equal to 2.9 MPa. This value is an order of magnitude higher than the stress in the PGMA nanofoam. However, when we conducted foaming of the PS/PGMA film using the same procedure as for the original PGMA film, we found that modification of the PGMA film (cross-linked and anchored to the surface) did not prevent the formation of the nanofoam. Thickness of the PS/PGMA film increased from 219.0 nm to 252.0 nm as a result of the nanofoam formation. The increase in thickness for the PS/PGMA film upon solvent sublimation was about 15%. In fact, the relative increase in thickness for the film was practically the same as for the PGMA film prior to PS attachment. AFM imaging revealed that the morphology of the PS/PGMA film clearly changed due to pore formation (Figure 7.6 C). RMS roughness of the film increased from 0.5 nm to 4.1 nm after solvent sublimation.
Total vertical actuation potential of the PS/PGMA nanofoam (equal to the level of the vertical extension of the film during the solvent sublimation) was on the order of 30 nm. Therefore, grafting of the PS chains increased the total possible actuation approximately three times. In fact, when the nanofoam was heated to 107 °C, it contracted reaching 222.0 nm. This value corresponds to the maximum shape-recovery ratio of $R_R = 0.91$. After heating, the pores disappeared and RMS roughness decreased, approaching the initial value (<1 nm) (Figure 7.6 D). Therefore, the PS/PGMA porous film also demonstrates properties of a shape-memory material and can be employed for nanoscale mechanical actuation. As for the PGMA samples the foaming-temperature collapse cycle was carried out three times for the PS/PGMA films. $Z_D$ and $Z$ (107 °C) were reproducible within 2.0 nm range. Therefore, the PS/PGMA nanofoams could be used for multiple actuation cycles.

We studied how the thickness of the PS/PGMA nanofoam changed with gradual increase in temperature until it rose above $T_g$ value. To this end, the nanofoam was kept inside an oven where temperature was increased stepwise (10–20 °C per step) from 25 °C to 107 °C. The polymer film was withdrawn from the oven after each heating step and characterized by ellipsometry and AFM. It was observed that decrease in thickness is practically linearly dependent on temperature (Figure 7.7 A). At room temperature the nanofoam maintained the thickness achieved during heating. The shape-recovery ratio also had a close to linear relationship with temperature (Figure 7.7 B). The obtained results demonstrated that the nanofoam film was capable of producing gradual
mechanical actuation at the nanometer scale. The slope of the thickness versus
temperature dependence was $-0.36 \text{ nm °C}^{-1}$ and was significantly higher than the slope ($-0.13 \text{ nm °C}^{-1}$) for the PGMA nanofoam. The obtained results indicated that an actuation of 1.0 nm per 2.8 °C was possible. Therefore, it was evident that by modifying the PGMA nanofoam with grafting of low molecular weight polymers, we could accurately tune an absolute nanoscale mechanical response of the porous polymer film.

![Figure 7.7. Thickness (A) and shape recovery ratio (B) of the PS/PGMA nanofoam as a function of the temperature.](image)

7.3.5 Synthesis and characterization of the PGMA/gold nanoparticles composite nanofoam

PGMA/gold nanoparticles composite film was deposited by dip coating on glass slides from a solution and annealed at an elevated temperature in a vacuum oven. In essence, the PGMA/gold nanoparticles composite film was fabricated as a thin internally cross-linked layer, covalently bound to the native oxide surface (covering the glass
substrate) using its epoxy group functionalities. Then, composite film was vigorously rinsed with a good solvent to extract all unattached polymer. Next, grafted PGMA/gold nanoparticles film was foamed following the procedure described previously (Chapter 7, Section 7.3.1). At a same time reference PGMA film and PGMA nanofoam were synthesized and used as background during UV-vis analysis. AFM technique was utilized to analyze and characterize the thickness and morphology of the grafted PGMA and PGMA/gold nanoparticles systems.

Since, PGMA/gold nanoparticles film was grafted on a glass slides the ellipsometry measurements could not be conducted. We have employed AFM to track the thickness of the composite film. The film has been scratched and thickness was determined by analyzing the scratch profile. The thickness of the PGMA/gold nanoparticles composite film was determined to be 77.0±2.0 nm after annealing and washing with a good solvent. Gold nanoparticles were uniformly distributed and have not been removed from polymer matrix after rinsing. Thus, they were thoroughly embedded into PGMA layer due to the strong PGMA-gold chemical affinity (Chapter 4 page 66). The PGMA/gold nanoparticles composite film uniformly covered the substrate on the micro- and nanolevels. The layer RMS roughness was less than 1 nm (Figure 7.8 image B).

Thickness of the PGMA/gold nanoparticles composite film increased from 77.0±2.0 nm to 97.0±2.0 nm, about a 26 % increment thickness, after the foaming was completed. AFM analysis revealed a dramatic change in morphology of the composite film after foaming (Figure 7.8 image C). More specifically, nanoscale pores formation
and increase in film roughness were observed. In fact, RMS roughness of the PGMA/gold nanoparticles film increased from 1 nm to 6.6 nm after the foaming.

**Figure 7.8.** AFM topography images of PGMA/gold nanoparticles composite film: (A) PGMA reference film; (B) PGMA/gold nanoparticles composite film before foaming; (C) PGMA/gold nanoparticles composite nanofoam; (D) PGMA/gold nanoparticles composite nanofoam after actuation at 60 °C; (E) PGMA/gold nanoparticles composite nanofoam after actuation at 110 °C. Vertical scale: 10 nm (A), 10 nm (B), 50 nm (C and D), and 20 nm (E). Size of images is 1x1 µm.

### 7.3.6 Actuation of the PGMA/gold nanoparticles composite nanofoam

PGMA/gold nanoparticles composite nanofoam has been thermally actuated in a two steps fashion. Firstly, nanofoam was brought to a temperature below $T_g$ (60 °C). Then, after characterization and analysis the system was brought to the temperature above $T_g$ (110 °C) of cross-linked PGMA. Elevation of the temperature caused shrinkage of the PGMA/gold nanoparticles nanofoam. Specifically, we observed a decrease in thickness at each temperature increment (**Figure 7.9 A**). Shape-recovery ratio has reached 0.84 at 110 °C. Both parameters showed linear dependence on temperature (**Figure 7.9 B**). AFM analysis revealed changes in morphology of the PGMA/gold nanoparticles surface upon actuation (**Figure 7.8 image C**). After each heating step RMS roughness decreased and reached 2.3 nm at 110 °C (**Figure 7.9 C**). As compared to PGMA nanofoam RMS roughness value has not reached the initial value (1.0 nm). This
behavior can be explained by higher rigidity of the studied system and higher cross-linking density as compared to homogeneous PGMA nanofoam. Thus, gold nanoparticles acted as the cross-linking element. However, the initial surface morphology and RMS roughness was achieved after washing PGMA/gold nanoparticles system in chloroform. The obtained results demonstrated that PGMA/gold nanoparticles composite nanofoam film can be actuated on a nanometer scale as well. The slope of the thickness versus temperature dependence was -0.2 nm °C\(^{-1}\), indicating that in principle actuation of 1.0 nm per 5 °C is achievable. Thus, by incorporating gold nanoparticles into PGMA matrix we were able to tune an absolute nanoscale mechanical response of the system.

**Figure 7.9.** Thickness (A), shape recovery ratio (B) and RMS roughness (C) of the PGMA/gold nanoparticles composite nanofoam as a function of the temperature.

### 7.3.7 Studying of optical properties of PGMA/gold nanoparticles composite nanofoam upon actuation

It well known that coupled oscillation of electron density and evanescent electromagnetic field that are excited near the surface of gold nanoparticles by incident light of a specific wavelength leads to characteristic absorption and scattering bands
By altering particles size, shape, structure or environment the interaction with light can be tuned and altered. We decided to utilize this phenomenon to fabricate and study preliminary platform for unattended sensing based on PGMA nanofoam as a matrix and gold nanoparticles as an optically active element.

More specifically, we have hypothesized that upon foaming/collapsing (actuation) cycles the optical response of PGMA/gold nanoparticles system should change due to alteration of environment (dense film/nanofoam) and possibly degree of nanoparticles association. In this section we describe our investigation of optical properties of PGMA/gold nanoparticles composite film before, after foaming and after each step of actuation by means of UV-vis spectroscopy. PGMA film and PGMA nanofoam have been synthesized and used as background during UV-vis analysis.

**Figure 7.10** represents changes in optical properties of the PGMA/gold nanoparticles system. Indeed, we have observed spectral blue shift of the surface plasmon resonance (SPR) band from 562 nm to 556 nm as a result of the foaming. Moreover, the increase in scattering at UV wavelength has been detected after the foaming. When composite nanofoam was actuated at 60 °C changes in UV-vis spectrum were not observed. However, when PGMA/gold nanoparticles system was actuated at 110 °C for 30 minutes, red shift from 556 nm to 563 nm has been found. Moreover, the intensity of the scattering band at UV wavelength has dropped significantly (**Figure 7.10 B**). Five measurements were made for PGMA/gold nanoparticles system before foaming, after foaming, and after actuation.
Two factors can contribute to appearance of the spectral shifts in PGMA/gold nanoparticles system. It well known that closely located gold nanoparticles interact via overlapping of evanescence fields\textsuperscript{24}. As a result their plasmonic oscillations become coupled. These interactions (coupling) cause the change in position of surface plasmon resonance band; red shift represents decrease in interparticle distance - agglomeration and blue shift represents increase in interparticle distance - dissociation. Thus the first factor we should consider is possible increase in interparticles distance upon foaming due to expansion of PGMA matrix.

\textbf{Figure 7.10.} Extinction UV-vis spectra of PGMA/gold nanoparticles film (A) before foaming, after foaming and after actuation at 110 °C; (B) Magnification of SPR band before foaming, after foaming and after actuation at 110 °C.

Second factor that can cause shift of SPR band is related to change in nanoparticles dielectric environment upon foaming. Indeed, the sensitivity of noble metals nanoparticles to their environment has been broadly studied\textsuperscript{24, 40-42}. The position of
SPR band depends on a refractive index of the medium around gold nanoparticles. Gold nanoparticles suspended in environments with lower refractive indices demonstrate SPR band at shorter wavelength as compared to dispersions in mediums of higher refractive indices\textsuperscript{43}. Indeed, the refractive index of PGMA matrix has dropped upon foaming due to formation of pores (incorporation of air). Therefore, gold nanoparticles can “feel” this change and “respond” accordingly by changing the position of SPR band (blue shift).

In our investigations to decouple these two factors we have used two different backgrounds during UV-vis measurements. Firstly, PGMA film with a thickness close to PGMA/gold nanoparticles system (~80 nm) was grafted to the glass surface and used as a background for the UV-vis measurements during each step (before foaming, after actuation and actuation). In fact, blue shift of SPR band and increase in intensity at UV wavelength range have been detected (Figure 7.10). However, when PGMA nanofoam was used as a background during UV-vis analysis the change in position of SPR band has not been observed. Moreover, when we conducted UV-vis analysis of PGMA film before and after foaming noticeable change in spectrum was detected.

Figure 7.11 represents UV-vis absorption spectrum of PGMA reference film before and after foaming. In fact, foaming of PGMA film caused change of original UV-vis spectra and increase in intensity at UV wavelength range. Therefore, we can conclude that for described PGMA/gold nanoparticles system the observed shifts of the SPR band originates from change in a medium that occurs during foaming/collapsing cycles and not from change in interparticle distance.
Figure 7.11. Extinction UV-vis spectra of PGMA film before and after foaming.

7.4 Conclusion

We demonstrated that nanoscale level actuation can be, in principle, achieved with grafted polymer nanofoams by forces associated with conformational changes of stretched macromolecular chains. The nanofoams can be fabricated via a two-step procedure. First, the “grafting to” technique was used to obtain a 80–200 nm anchored and cross-linked PGMA film. Second, the film was swollen in a good solvent and freeze dried until the solvent was sublimated. The grafted nanofoams possessed the behavior of a shape-memory material. They exhibited gradual mechanical contraction at the nanometer scale as temperature is increased. Both the thickness and shape-recovery ratio of the nanofoam had a close to linear dependency on temperature. We also
demonstrated that by modifying the PGMA nanofoam with grafting of low molecular weight polymers, we could accurately tune an absolute nanoscale mechanical response of the porous polymer film.

Gold nanoparticles can successfully be incorporated into the PGMA film. Composite PGMA/gold nanoparticles nanofoams can be fabricated via the two-step procedure. The grafted composite nanofoam demonstrated shape memory material behavior. More specifically, it exhibited gradual mechanical contraction at the nanometer scale as a temperature was increased. Also, actuation of the PGMA/gold nanoparticles composite nanofoam resulted in a detectable shift of SPR band. Thus, the fabricated platform provide the opportunity to study and develop unattended temperature sensing devices.
7.5 References


CHAPTER 8
SUMMARY

Our work provided results on the synthesis and characterization of thin polymer nanolayers grafted to metal surfaces (nickel and gold). The developed methods for surface modification were successfully employed in the functionalization of the complex nickel nano/microstructures (nanowires and micronails), microprinted gold electrodes, and gold nanoparticles. The conclusions from our investigations are categorized according to the respective chapters.

8.1 Grafting of nanoscale polymer layers to the model surfaces of nickel and gold

Before surface modification of the Ni nano/microstructures and Au electrodes with thin polymer films grafting on the model, flat surfaces was studied. Thin Ni and Au films were sputtered on silicon wafers and gold slides respectively. Next, the surfaces were cleaned and activated by plasma treatments. The PGMA anchoring layer was formed on the surface by a reaction between the epoxy functionalities and the active groups on the surfaces. PS, PAA, PEG, and P2VP polymer layers were grafted to the model surface via the reactions between epoxy containing anchoring layer and the complementary functionalities of the polymer macromolecules being grafted. Ellipsometry, contact angle measurements, and AFM studies revealed that the polymer grafting was successful.
8.2 Pointed modification of nickel nanowires and micronails

The methodology developed for polymer grafting on the model nickel surface was used to develop a novel method for surface modification of nickel 3D structures: nanowires and micronails. The protocol was based on the step-by-step etching of the silicone matrix and the "grafting to" approach. The method resulted in the synthesis of the hydrophobic polymer layer (PS) on the upper segments of the nanowires/micronails and the hydrophilic polymer film (PAA) on the bottom segments. The PGMA was used as a reactive anchoring layer. The PS- and PAA-grafted films were stable and robust. The SEM, EDS, TEM, and water contact angle measurements proved the successful functionalization of the surfaces of Ni nanowires and micronails.

8.3 Surface modification of microprinted gold electrodes and the effect of environment on the electrical conductivity of grafted polymer layers

The methodology used for grafting the polymers on the model gold surface was used to graft polymer films to the Si/SiO₂/Au surface. The PGMA was used as an anchoring layer. Next, the nanothin films of PAA, PS, and P2VP were grafted. The polymer films behaved as insulators at ambient conditions. Their electrical conductivity drastically changed when solvent vapors were introduced into the environment. The observed response of the polymer films was highly sensitive and specific. Two factors determined this response: polymer/solvent affinity and solvent/polymer dipole moments.

The conductivity of the polymer films as a function of temperature was investigated. An increase in conductivity with temperature was observed. Two regimes
were also identified. The change between regimes was associated with the glass transition temperature of the grafted polymer films. Positive deviations in $T_g$ were observed.

### 8.4 Temperature-controlled shape change of with grafted nanofoams

This section of the work focused on the fabrication and nanoscale mechanical actuation of the grafted nanofoams. The fabrication was conducted using a two-step procedure. First, an 80–200-nm thick PGMA film was grafted to the silicon surface. Second, the polymer film was swollen in a good solvent, and then frozen and freeze-dried. This technique resulted in the synthesis of porous nanothin-grafted polymer film with shape-memory properties. Two modes of actuation were studied. The first mode was realized when the nanofoam was heated to a temperature above $T_g$. The PGMA nanofoam shrunk and reached a thickness close to pre-foaming thickness of the polymer film. In the second mode, the temperature was gradually increased until it rose above $T_g$. In this case, a nanoscale actuation on the level of 1–2 nm was achieved.

The absolute mechanical response of the nanofoam was tuned by grafting low molecular weight PS to already grafted PGMA film, and then foaming the synthesized PS/PGMA system.

The PGMA layer was used as a matrix for incorporating gold nanoparticles. The PGMA/gold nanoparticles-grafted composite nanofoam was fabricated. The step-by-step nanoscale actuation of the synthesized composite nanofoam was conducted. The foaming and actuation of the PGMA/gold nanoparticles system resulted in a change in optical properties that could be detected by UV-vis spectroscopy.
8.5 Publications and presentations


James Townsend, Ruslan Burtovyy, Yuriy Galabura, and Igor Luzinov "Flexible chains of ferromagnetic nanoparticles." ACS Nano, 2014 (web)

Yuriy Galabura, Anna Paola Soliani, Bogdan Zdyrko and Igor Luzinov "Shape memory polymers: grafted nanofoams." American Chemical Society National Meeting, New Orleans, LA, April 2013, oral presentation

Yuriy Galabura, Anton Grigoryev, Sergiy Minko, Konstantin Kornev and Igor Luzinov "Surface modification of Nickel nanofibers via polymer grafting." American Chemical Society National Meeting, New Orleans, LA, April 2013, oral presentation

Nickel nanofibers via polymer grafting." American Chemical Society National Meeting, Anaheim, CA, March 2011, poster presentation

Yuriy Galabura, Anton Grigoryev, Alexandr Tokarev, Ruslan Burтовyy, Bogdan Zdyrko, Sergiy Minko, Konstantin Kornev, and Igor Luzinov "Surface modification of Ni nanofibers." American Chemical Society Meeting, Boston, MA, August 2010, poster presentation