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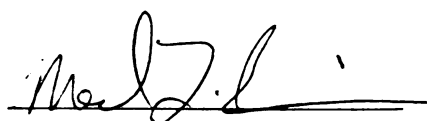
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SYNTHESIS OF ULTRATHIN POLYMER FILMS BY SURFACE-INITIATED RADICAL
POLYMERIZATION FROM GOLD SURFACES

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SKANTH GANESAN

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SYNTHESIS OF ULTRATHIN POLYMER FILMS BY SURFACE-INITIATED
RADICAL POLYMERIZATION FROM GOLD SURFACES

BY

SKANTH GANESAN

AN ABSTRACT OF A THESIS

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ABSTRACT

SYNTHESIS OF ULTRATHIN POLYMER FILMS BY SURFACE-INITIATED RADICAL POLYMERIZATION FROM GOLD SURFACES

By

Skanth Ganesan

This thesis describes a new method for the controlled synthesis of ultrathin polymer films ($<1000 \text{ \AA}$) by grafting from a gold substrate. Such films could eventually be used in sensing, separations, and other application requiring surface modifications. Initial attempts to grow polymer films using initiators attached to alkanethiol monolayers were unsuccessful and yielded coatings that were less than 100 \AA thick. External reflection infrared spectroscopy studies showed that grafting of polymers to alkanethiol monolayers is likely restricted by the instability of these monolayers at high temperature and in the presence of radicals. Problems associated with the stability of SAMs can be overcome with the use of mercaptopropyltrimethoxysilane (MPS) as an adhesion layer for initiator attachment. Attachment of the azo-initiator to a crosslinked MPS layer affords stabilized initiating sites on the surface, allowing successful grafting of polymer films. FTIR spectra and ellipsometry demonstrate the successful grafting of polystyrene films with thicknesses up to 900 \AA . In a second method, attachment of atom transfer radical polymerization initiators to layered polyelectrolyte films also allows grafting of polymer films.

என் பெற்றோர் மற்றும் முன்னோர்களுக்கு சமர்ப்பனம்

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LIST OF ABBREVIATIONS

SAM	Self-Assembled Monolayer
MIP	Molecularly Imprinted Polymer

INTRODUCTION

The control of surface properties is vital to numerous technologies ranging from biotechnology to advanced microelectronics.^{1,2} Attachment of polymeric brushes to substrates is one of the most active areas of research aimed at controlling surface properties. Traditionally, polymeric brushes are prepared from block copolymers where one block is strongly adsorbed to the surface with the other block forming the brush layer.³ However, the brush is generally non-covalently attached to the substrate, and desorption can occur. Additionally, the choice of functional groups in block copolymer structures is limited due to the demands of block copolymer synthesis. To overcome these problems, an increasing amount of interest has been devoted to the covalent attachment of polymer chains to surfaces.³ These tethered polymer chains on surfaces have potential applications in chemical separations, sensing, stabilization of colloidal suspensions, control of wetting and adhesion, corrosion resistance, microelectronics, biocompatibility and fouling resistance.^{1,4}

The most common target in research with polymeric brushes has been the design of surfaces that resist biofouling and protein adsorption. Prevention of protein adsorption is crucial to blood-contacting devices such as dialyzers, oxygenators, and blood containers. When a material surface is brought into contact with blood, adsorption of serum proteins initially takes place, and this subsequently triggers thrombogenesis. Since these unfavorable foreign-body responses can lead to serious clinical problems, various water-soluble polymeric

brushes have been used to create surfaces that resist fouling. The grafted surface is not stable for long periods, but it lasts long enough to accomplish the specific purpose of some devices. Anti-fouling brushes will be more valuable if they can last for longer times in situations such as permanent implantation. Such hydrophilic polymer coatings can be grafted to surfaces by various methods including surface graft polymerization, coupling reactions, and surface segregation.⁵

Another possible application of ultrathin polymer films is the development of chemical sensors. Imprinting of polymers provides one means of introducing selectivity into such systems. One of the major problems with bulk imprinted polymers however, is the longer time required for equilibration with analyte molecules, and hence a long response time. Growth of ultrathin imprinted polymer films may circumvent these problems by reducing diffusion distances. These ultrathin polymer films could show both high selectivity and short response times. Some of the possible uses of molecularly imprinted sensor layers are the detection of polycyclic aromatic hydrocarbons in water,⁶ fiber-optic detection of fluorescently labeled amino acids,⁷ and optochemical sensing.⁸

The main focus of this thesis is development of a method for preparing ultrathin polymer films by thermal initiation at a gold substrate. Such a method might potentially prove useful in synthesizing ultrathin imprinted polymer films if polymerization in solution could be minimized. Gold is a very convenient substrate because initiators can be attached to this surface via Au-thiol bonds.

Gold is also inert towards most organic functional groups and is convenient for electrochemical, ellipsometric, and reflectance FTIR spectroscopy studies.

Two general types of grafting methods are used for covalently attaching polymer chains to surfaces. The “grafting to” technique, which involves reacting end-functionalized polymers with surface sites, leads to thinner films because reactive groups cannot reach the surface after attachment of a few chains. In contrast, the “grafting from” technique, which involves growing polymers from surface-immobilized initiators, leads to thicker polymer films with higher graft densities. Though extensive studies have been performed on polymer grafting from surfaces like silica¹⁰ and carbon black,¹¹ I have found no studies on thermal polymerization from gold surfaces. The purpose of this research is to grow polymer films from gold substrates using surface bound initiators and to define suitable conditions and strategies for this polymerization.

The background for these studies is outlined in chapter 1, and chapter 2 describes experimental techniques and materials used for polymerization. Chapter 3 deals with the stability of self-assembled monolayers under polymerization conditions and the use of a silane layer to stabilize the initiator layer and permit polymerization from this surface. Current work on polymerization on alumina membranes using atom transfer radical polymerization is discussed in chapter 4. Lastly, chapter 5 presents the conclusions of this work.

Chapter 1

BACKGROUND

This chapter first describes previous methods for grafting polymers to surfaces to put the present work in context. Because self-assembled monolayer (SAMs) are attractive for attachment of initiators to gold surfaces, I next include a section on these materials. Finally, I discuss molecular imprinting as this is one of our long-term goals for developing ultrathin films.

1.1 Grafting Techniques

Any method for preparing thin polymer films should ideally fulfill several criteria. First the technique should allow synthesis of films with a wide range of thicknesses. Second the method should be sufficiently versatile to permit growth of films with a large variety of functional groups. Finally, films should be sufficiently robust for a variety of applications. Physisorption of either block-copolymers or polymers containing a short segment that interacts with the surface¹² produces only weakly adsorbed films. In most cases such films are held on the surface by van der Waals forces or hydrogen bonding. These polymer films desorb easily upon exposure to a good solvent and can be displaced by other polymers. To overcome these problems, stronger adhesion between substrate and polymer is required. This can be achieved by covalently binding the polymer to the surface. Two broadly defined methods are commonly used for this purpose: the “Grafting to” and “Grafting from” techniques (Fig 1.1).¹³

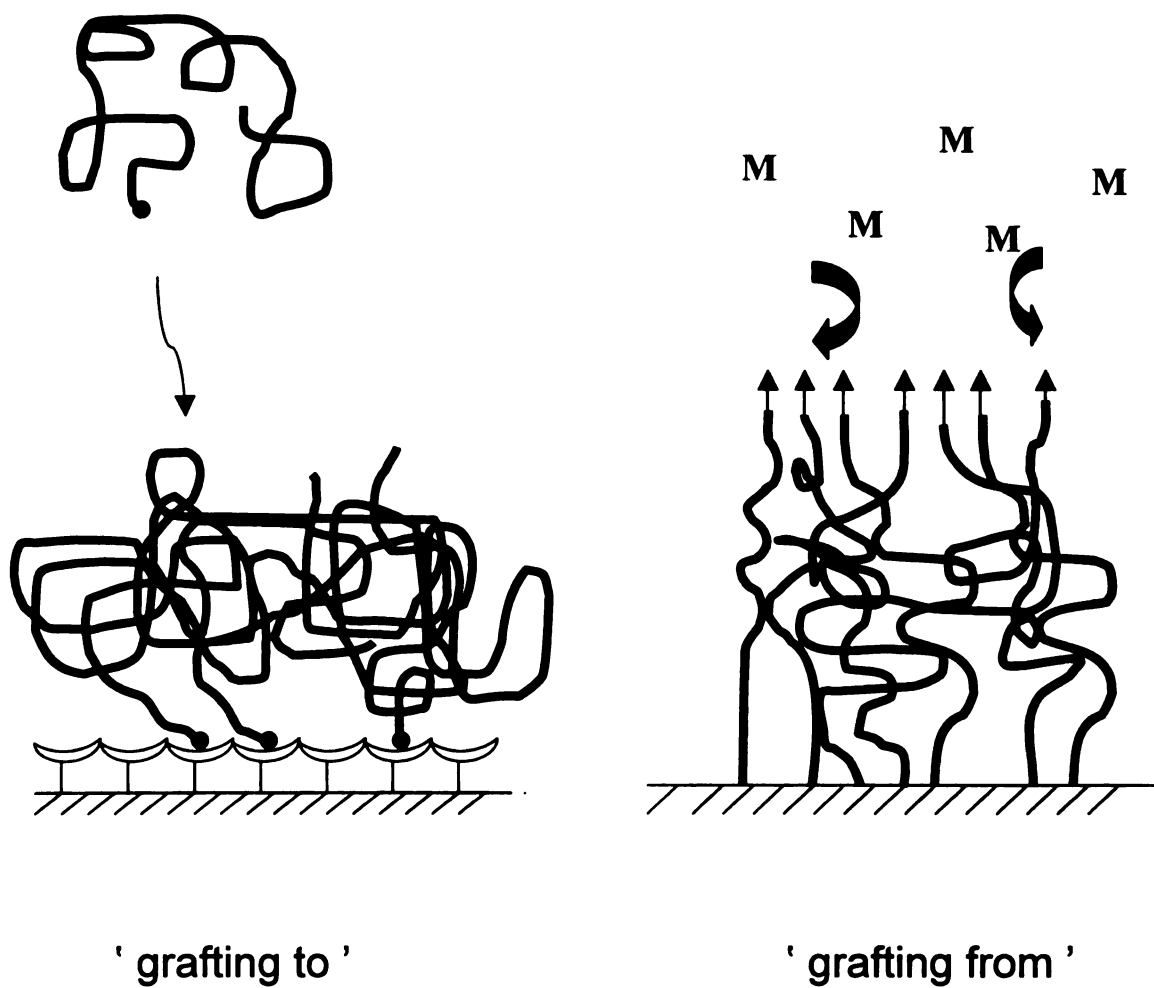


Figure 1.1: Two methods for grafting of polymer films onto solid surfaces

1.1.1 “ Grafting To ” Technique

The “grafting to” method involves the reaction of end-functionalized polymers with appropriate surface sites.^{3,14-18} The reactive sites on the substrate serve as anchors and form bonds with the functional end groups on the polymer. The problem with this technique is that once the surface becomes covered with attached chains, additional chains have to diffuse through the grafted film to reach reactive sites. As the grafting density increases, chains have to increasingly stretch from their random coil confirmation to allow further grafting, and this results in a decrease in the grafting rate.¹⁹ Using this method, only very small amounts of polymer, less than 5 mg/m², can be grafted to the surface. This usually limits film thickness to 10 - 50 Å.

1.1.2 “ Grafting From ” Technique

A more promising approach for the preparation of ultrathin films is the “grafting from” technique. In this strategy, a surface-anchored reactive group is capable of initiating polymerization, and the polymer chain grows from the surface. There is little steric hindrance to film formation as only a small monomer has to reach the growing chain ends during film growth. This increases the number of reaction sites to which the monomer can attach when the substrate is placed in solution. This approach leads to higher grafting densities and film thicknesses than the “grafting to” technique. The polymerization can be carried out with a variety of monomers²⁰ and thicknesses of polymer films can be adjusted over a wide range of values. Although dense polymer brushes can be prepared with this method, there are disadvantages associated with the

technique. Poor immobilization of initiator on the surface can in some instances lead to low densities of initiators and polymers. Side reactions are also possible in the initiator immobilization step, and these can result in undesired structures on the surface.¹³ R  he et al. reported a strategy to overcome this problem with the use of silane monolayers of initiators on silica surfaces.¹³ In the following chapters, we report the grafting of polymers from gold using a similar approach.

1.2 Self-Assembled Monolayers

This section discusses the formation of self-assembled monolayers on gold as these material provide a potentially attractive method for attaching initiators to surfaces. Organic monolayer films can generally be prepared by two distinct methods: the Langmuir-Blodgett technique^{21,22} which involves the transfer of a film assembled at an air-water interface to a solid substrate, and self-assembly, which is based on spontaneous adsorption of dissolved molecules.^{23,24} The Langmuir-Blodgett technique is also adaptable for multilayer construction and allows for the incorporation of a broad range of lipophilic materials in mono or multilayers. The layers are only physically linked to the surface, however, and therefore quite unstable.²⁵

Self-assembly is much more convenient than the Langmuir-Blodgett technique and yield more stable films. In many cases, films form a covalent bond to the substrate. SAMs can be formed using chlorosilanes on silicon, carboxylic acids on metal oxides and organosulfur compounds on a variety of surfaces.²⁶ Organosulfur derivatives coordinate strongly to many transition metal and semiconductor surfaces to form monolayer films.²⁷ This versatility of sulfur-

surface interactions allows preparation of oriented organic monolayer films containing many functional groups of biological and chemical interest. SAMs of alkanethiols on gold are especially well-ordered and consist of densely packed alkanethiolate chains on the surface. These films are easy to prepare and fairly stable. A variety of SAMs on gold are of interest in fields such as corrosion inhibition,²⁸ sensing,²⁹ electrochemistry,³⁰ wetting,²⁵ biofouling,²⁵ and catalysis.²⁵ Thiol or disulfide-containing SAMs are potentially useful systems for depositing polymerization initiations on surfaces, but since Au-thiol bonds can be broken by hot organic solvents,³¹ there are only a few reports describing surface polymerization on gold surfaces. Ulman et al. reported cationic ring-opening polymerization of 2-ethyloxazoline from self-assembled monolayers of initiators on gold, but films were only 100 Å thick.³² Shah et al. reported surface-initiated atom-transfer radical polymerization (ATRP) of various vinyl monomers on gold substrates.³³ Self-assembly of initiators was done at elevated temperature to prevent desorption during polymerization. The use of ATRP also keeps radical concentration low, which may help to stabilize the system. The use of room-temperature for atom-transfer radical polymerization of methyl methacrylate on gold surfaces was reported by Kim et al.³⁴ Niwa et al. described photopolymerization of methacrylic acid using self-assembled monolayer of xanthates.³⁵ However, there are no reports of thermally initiated radical polymerization from gold surfaces. We report the thermal free radical polymerization of styrene using azo-bound initiators attached to a gold surface.

The use of a stabilized monolayer is necessary to make these techniques successful.

1.3 Molecular Imprinting

One of the possible uses of ultrathin polymer films is in sensing applications. This section describes one possible means of incorporating selectivity into ultrathin films. For many years scientists have been trying to exploit and mimic antibody-antigen interactions. Biosensor technology based on these interactions is highly developed and widely applied in the specific detection and measurement of suitable analytes.¹¹ Because antibodies are not available for a large number of applications, a parallel technique for development of synthetic antibodies through “molecular imprinting” has emerged. Molecular imprinting involves polymerization of a monomer-template complex in the presence of excess cross-linking agent as shown in Figure 1.2. Removal of the template through rinsing, hydrolysis, or acidification leaves behind a selective cavity. The concept of using molecularly imprinted polymers (MIPs) for chemical recognition started from Linus Pauling’s template and cast theory³⁶ proposed in the 1940s. Pauling suggested that when antigen is injected into an animal, antigen molecules are captured and held by antibodies. An antibody to this antigen is a molecule with a configuration complementary to that of a portion of the antigen molecule. The antibodies that surround the antigen bond together rendering the antigen ineffective. Pauling expected the antigen to dissociate eventually from

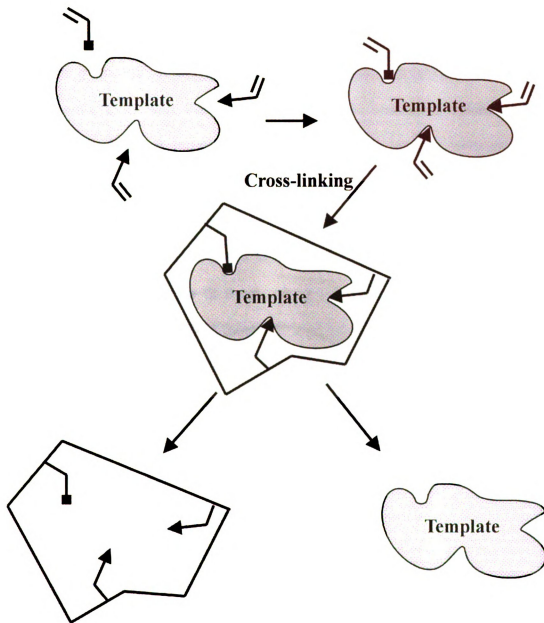


Figure 1.2: Concept of molecular imprinting of polymers (adapted from Wulff,G.; *Angew. Chem. Int. Ed. Engl.*, **1995**, 34, 1812-1832)

the antibody, thus leaving behind a 3-dimensional cavity. When the antigen is re-introduced, it can be trapped again by this antibody structure. Depending on the binding strength of antigen-antibody interactions, the antigen can free itself or permanently bind with the antibody. Molecular imprinting employs a similar concept (Fig 1.2). A template molecule in solution is first allowed to interact reversibly with a suitably functionalized monomer in solution. A Cross-linking agent is present in solution and upon initiation, polymerization occurs around the template. After the removal of the template, polymer with well-defined cavities is left behind. The structure of these cavities is pre-determined by the template molecule. When the template molecule is re-introduced, it binds selectively to the imprinted site. For example molecularly imprinted polyurethanes have been used in detecting polycyclic aromatic hydrocarbons in water.³⁷ The selectivity can be tailored for a distinct analyte by altering the template molecule from anthracene to 1,12- benzoperylene. The use of imprinted ultrathin films should greatly reduce the equilibration time with the analyte molecule, and grafting of films from surfaces should provide a convenient means for synthesizing ultrathin films.

Since the first covalent imprinting of organic polymers by Wulff and coworkers³⁸ in the early 1970s, researchers such as Mosbach³⁹ and Shea⁴⁰ have extended this technique by imprinting polymers using non-covalent interactions. Several advances have been made in this area and now MIPs have been used as stationary phases for chromatography and immunoassays, recognition elements in sensors, and enzyme mimics in catalysis.⁴¹

Chapter 2

EXPERIMENTAL

This chapter first discusses the techniques used for characterizing grafted polymer films. This is followed by a listing of the materials and chemicals used, as well as the synthesis of necessary chemicals.

2.1 Ellipsometry

Ellipsometry is a sensitive technique for determining the thickness and/or refractive index of thin films. The method actually measures the change in polarization of light reflected from a surface. This change in polarization is expressed in psi (ψ) and delta (Δ) values, and these values are related to Fresnel reflection coefficients for p and s polarized light,⁴² as shown in equation 1.

$$\rho = \frac{R_p}{R_s} = \tan(\psi) \exp(i\Delta) \quad (1)$$

In this equation, R_p and R_s are complex Fresnel reflection coefficients for the p and s- directions, respectively, $\tan(\psi)$ represents the relative amplitudes of p and s polarized light, and Δ is the phase difference induced between the two polarizations. Using a model based on Fresnel reflection coefficients, the thickness (t) and refractive index (n) of a film on a surface can be calculated, provided the optical constants of the substrate are known. The s and p polarized light components are perpendicular and parallel, respectively, to the plane of incidence.

A J. A. Woollam Co. M-44 rotating analyzer ellipsometer measured the changes in polarization of reflected light and WVASE32 (Variable Angle Spectroscopic Ellipsometry) software calculated the optical constants of substrates and thicknesses of thin films. In this instrument the white beam of incident light is generated by a Xenon lamp source and strikes the sample with an angle of incidence of 75° . The reflected light passes through a rotating analyzer. In the detector unit, the white light beam is dispersed onto an array of silicon detectors, allowing simultaneous measurement of 44 wavelengths. In our experiment, a refractive index of 1.5 was assumed for all organic films as this value is typical for organic materials. For very thin films, ψ and Δ are relatively insensitive to changes in refractive index, and this value cannot be calculated.

2.2 Infrared Spectroscopy

Reflectance Fourier Transform Infrared (FTIR) spectra were recorded with a Nicolet Magna 560 FTIR spectrometer containing a PIKE grazing angle (angle of incidence of 80°) attachment. This instrument contains a tungsten/ceramic glow bar, a polarizer (p-polarization) and an MCT detector. The instrument was kept in a plexi-glass box continuously purged with dry nitrogen to keep levels of moisture and other contaminants low. The MCT detector was cooled using liquid nitrogen. Spectra were recorded in the range $750\text{--}4000\text{ cm}^{-1}$ using 256 scans and a spectral resolution of 4 cm^{-1} . All spectra were calculated in absorbance units, where absorbance is defined as $[-\log(R/R_0)]$. R and R_0 are the reflected intensities from the film-covered and bare substrate, respectively.⁴³

2.3 Experimental Materials

Gold-coated substrates were prepared by electron beam evaporation of 20 nm of Ti on Si (100) wafers doped with boron, followed by similar deposition of 200 nm of Au on the Ti. Titanium is used to promote adhesion of gold onto Si. In some cases, wafers were sputter-coated with 20 nm of Cr and 200 nm of Au. Gold is used because well-organized monolayers can be readily formed by spontaneous adsorption of organic thiols and disulfides⁴⁴ on this relatively homogeneous surface. Gold is also a convenient electrode for performing electrochemical studies. Aluminium-coated wafers were prepared by sputter-coating 20 nm of aluminium on Si (100) wafers.

3-Mercaptopropyltrimethoxysilane (MPS) was used as received from United Chemical Technologies. 4,4'-Azobis(4-cyanovaleric acid), 11-mercaptoundecanoic acid (MUA), 11-mercaptoundecanol (MUD), 3-aminopropyltrimethoxysilane (APS), 1,3-dicyclohexylcarbodiimide (DCC), ethanol, cystamine, dichloromethane, pyridine, chloroform, poly(allylamine hydrochloride) (PAH) ($M_w=70\ 000$), poly(styrene sulfonate) (PSS) ($M_w=70\ 000$), sodium chloride (NaCl), copper(I) chloride (99.999% purity), copper(II) bromide, 2,2'-dipyridyl (BPY), anhydrous N,N'-dimethylformamide (DMF), 2-bromopropionylbromide (2-BPB), 4,4'-Azobisisobutyronitrile (AIBN), triethylamine and mercaptopropionic acid (MPA) were purchased from Aldrich Chemicals. The silane compounds are moisture sensitive and were opened under nitrogen. Sodium hydroxide pellets and anhydrous sodium sulfate were purchased from Spectrum. $MnCl_2$ was purchased from Mallinckrodt.

Styrene monomer (Aldrich) inhibited with *p*-*tert*butylcatechol was purified by washing with 0.25 M sodium hydroxide and Milli-Q water (Millipore, 18MΩ cm). The monomer was then dried over sodium sulfate and passed through a column of basic alumina (Aldrich, mesh size 80-200). Before the polymerization step, the monomer was distilled under reduced pressure to remove any unwanted styrene polymer that was present in the monomer mixture. Toluene (Aldrich) was first refluxed under a nitrogen atmosphere in the presence of sodium/potassium alloy using benzophenone as indicator until a dark blue colour was obtained and then distilled. Ethylene glycol dimethacrylate (EGDMA) was purchased from Aldrich and purified by passing it through a column of basic alumina and distilling under reduced pressure.

2.4 Synthesis of Trimethoxysilane-Substituted Azo Initiator

The monocarboxylic acid precursor $\text{CH}_3\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{COOH}$, was synthesized according to the method of R  he.^{13,45} 1.11 g of this compound was then coupled with 0.9 g (5 mmol) of 3-aminopropyltrimethoxysilane using 1.24 g (6 mmol) of DCC with pyridine as a catalyst. The synthesis was carried out in 20 mL of anhydrous CH_2Cl_2 at room temperature for 12 hrs. After completion of the reaction, urea byproducts were removed by filtration of the CH_2Cl_2 solution of the product over anhydrous sodium sulfate, and the solvent was evaporated to afford a light-orange solid. The product was used without further purification because of its sensitivity to heat and water. Proton-NMR spectra of the product had multiplet

peaks at 2.18 and 3.2 ppm, corresponding to two methylene groups on either side of the amide bond, confirming the formation of azo-initiator. This synthesis was performed by Dr. Wenxi Huang.

2.5 Preparation and Cleaning of Substrates

Substrates were ozone cleaned using a Boekel UV/O₃ cleaner (Model 135500) for 12-15 minutes and then rinsed with Milli-Q water and dried with nitrogen. Cleaned slides were used to determine the optical constants (n and k) of the particular substrate. These values are necessary to calculate the thickness of the polymer. The FTIR background was also measured with a cleaned slide.

2.6 Formation of MUA and MUD Monolayers on Au Substrates

After cleaning, gold-coated slides were immersed in 2 mM ethanolic solutions of MUA or MUD for 12 hrs (2.0 mg of MUD or 2 mg of MUA in 10 mL EtOH). The slides were then rinsed with EtOH followed by Milli-Q water, and dried under nitrogen.

2.7 Formation of Trimethoxysilane-Substituted Azo-Initiator Monolayers (Fig 2.1 C) on Aluminium Substrates

The aluminium substrates were ozone cleaned for 15 min. The initiator attachment was done in a glove box as the silanes are moisture sensitive. Substrates were immersed in a 0.2 wt % solution of the initiator, $\text{CH}_3\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, in toluene

in the presence of 20 μL of pyridine (base) at 60 $^{\circ}\text{C}$ for 5 min. The slides were then cleaned with toluene and dried under nitrogen.

2.8 Formation of Initiator Monolayers on Various Substrates

Monolayer A (Fig 2.1) was prepared by first attaching a MUD monolayer to the Au surface. The monolayer was coupled with the asymmetric azo-monocarboxylic acid $\text{CH}_3\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{CO}_2\text{H}$, by immersion of the Au substrate in a solution containing 0.1 g of the azo compound and 0.14 g of DCC in 10 mL DMF with 20 μL pyridine as catalyst. After two hours, the substrates were rinsed several times with DMF and dried under nitrogen.

Initiator monolayer B (Fig 2.1) was attached to the gold substrate using the same method, but cystamine was first attached to gold instead of MUD.

2.9 Grafting of Polystyrene onto Gold Substrates

Cleaned gold substrates were immersed in a 2 mM solution of mercaptopropyltrimethoxysilane (MPS) (20 μL in 10 mL methanol) containing 2-3 drops of pyridine as a catalyst for 10 - 12 hrs at room temperature in a glove box (UNILAB 1200, MBraun Inc.). These substrates were then rinsed with methanol. The MPS-coated slides were then immersed in 0.1M HCl overnight to hydrolyze the methoxy groups. The hydroxylated surface crosslinked and stabilized the layer.

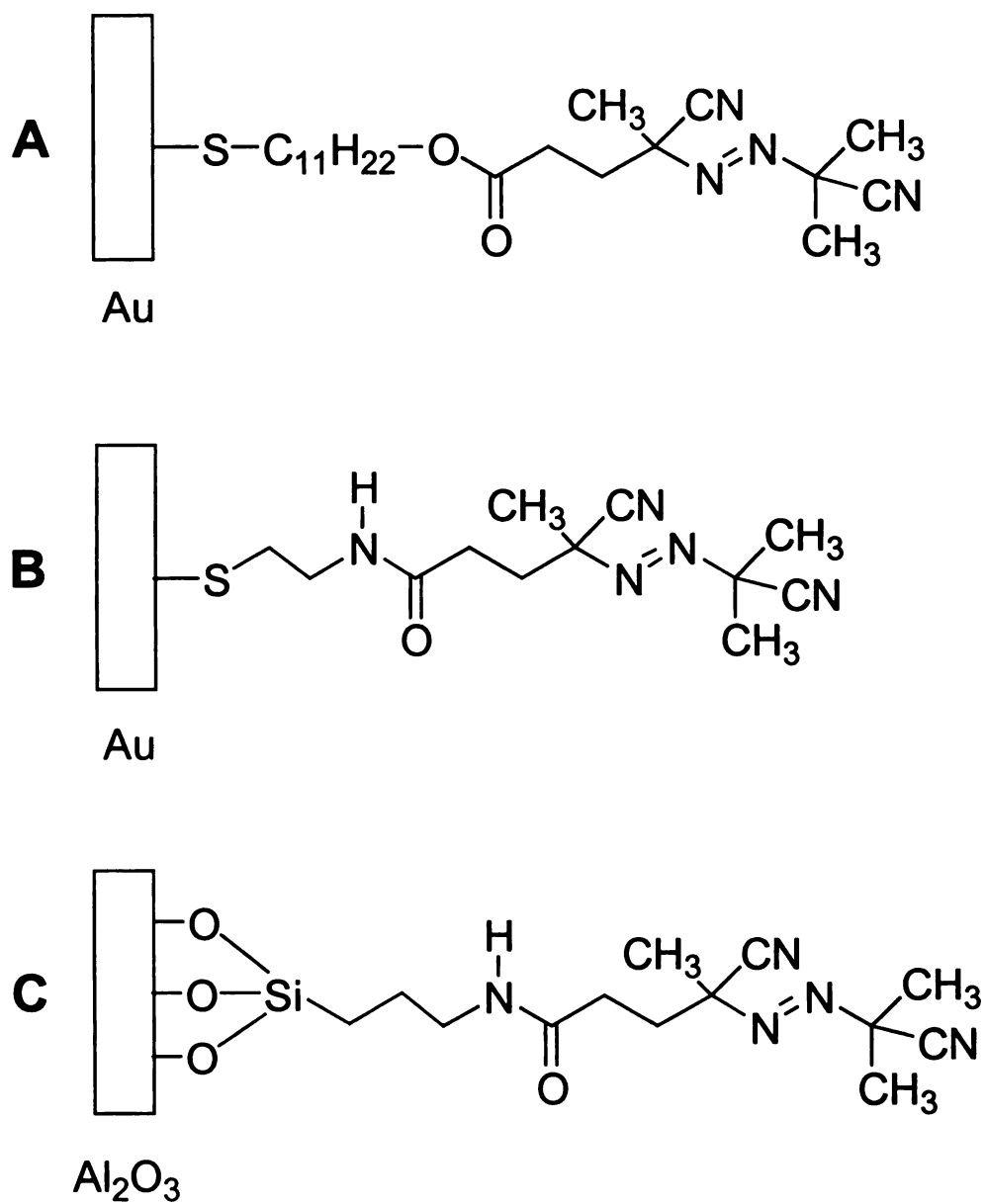


Figure 2.1: Monolayers employed for initiation of polymerization

The modified gold substrate was further treated with a solution containing 150 μL of trimethoxysilane substituted azo initiator, **1** (Fig 2.2), and 20 μL of pyridine in 7 mL of toluene at 60 $^{\circ}\text{C}$ for 5 minutes as shown in fig 2.2. The reactions with silanes were done in a glove box because they are sensitive to moisture and oxygen. The substrate was then washed with toluene 2-3 times and dried under nitrogen.

Monomer solutions containing equal volumes of purified styrene and toluene were degassed using three freeze-pump-thaw cycles. This procedure removed traces of oxygen from the monomer mixture. The mixture was opened in the glove box under nitrogen. A vial containing the initiator-coated gold substrate was filled with the monomer solution until the slide was completely immersed in solution. Polymerization was done in the glove box using an oil bath maintained at 60 $^{\circ}\text{C}$ for different time periods. After the polymerization, the samples were taken outside the glove box and rinsed with toluene several times without allowing the substrate to dry. The substrate was then Soxhlet extracted with CHCl_3 at 60 $^{\circ}$ - 70 $^{\circ}\text{C}$ overnight. Extraction removed physisorbed polymer that formed due to polymerization in solution. Ellipsometry and FTIR spectra were taken at each step of the polymerization process.

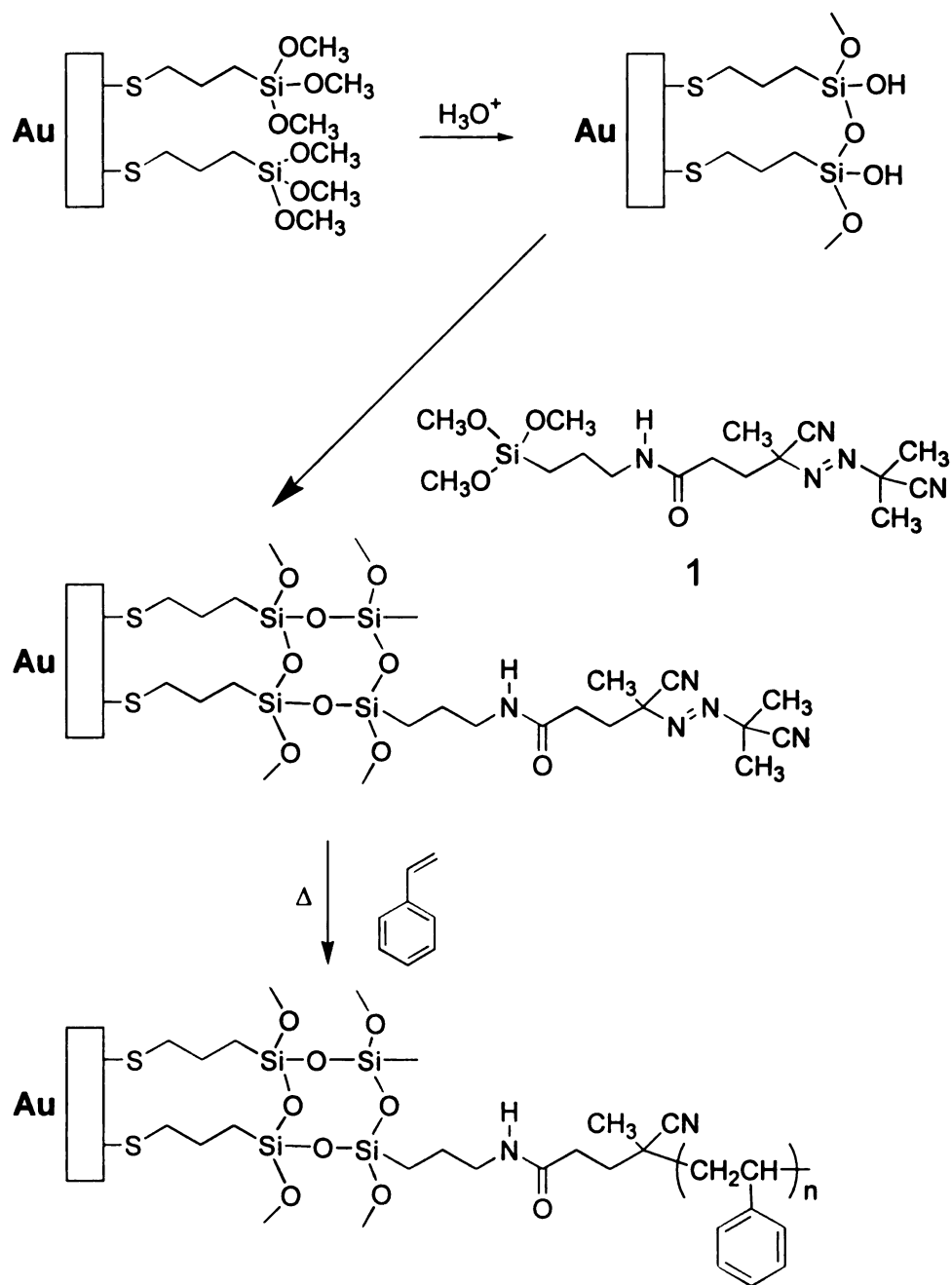


Figure 2.2: Steps involved in grafting polystyrene from a modified gold surface

Chapter 3

POLYMERIZATION OF STYRENE FROM GOLD

Self-assembled monolayers (SAMs) on gold are widely used to vary surface properties. These films have been used for corrosion protection,⁴⁶ control of wetting,^{30,46} lithographic patterning,⁴⁷ and selective adhesion of cells.⁴⁸ SAMs are more stable than traditional Langmuir-Blodgett films⁴⁹ because gold strongly interacts with sulfur.²⁶ This allows formation of monolayers with many types of functional groups. By modifying the functional groups in monolayers, different types of initiators can be attached to the surface.²⁵ However, surface-initiated thermal radical polymerization from SAMs on Au is challenging because of the lability of Au-S bonds and the use of elevated temperatures in polymerization. Strong attachment of initiators to a surface is crucial for surface-initiated polymerization. Initiators tethered to siloxane-based monolayers on oxide surfaces^{44,45,51-56} are covalently bound to the substrate, and these systems allow grafting polymerization to be conducted at high temperatures.

This chapter first examines the stability of SAMs on gold under polymerization conditions and how free radical polymerization from gold is hindered by the stability of alkanethiol monolayers. Subsequently, we demonstrate polymerization from stabilized monolayers on gold.

3.1 Results and Discussion

3.1.1 Stability of SAMs under Polymerization Conditions

Thermal grafting of polymers from gold surfaces requires that the initiator remain attached to the surface during polymerization. To evaluate the stability of alkanethios on gold, MUA monolayers were prepared and exposed to toluene at 60 °C. The absorbances due to the acid carbonyl groups in the monolayers were studied as a function of time of exposure to heated toluene. The MUA reflectance FTIR spectra contained both hydrocarbon peaks at 2925 and 2851 cm^{-1} and a carbonyl stretch at 1724 cm^{-1} (Fig 3.1). However, we relied on the carbonyl peak intensity as a measure of monolayer stability because methylene peaks are subject to increases due to contamination. The normalized integrated absorbance of the carbonyl peak was obtained by dividing by the absorbance of the integrated carbonyl peak before exposure. Figure 3.2 (open squares) shows that the carbonyl absorbance decreases by 40% over the first two hours of exposure to hot toluene and then remains stable for an additional 4 hours of exposure. This is in agreement with data found in the literature,^{26,33} demonstrating that a significant amount of thiol still remains adsorbed under typical polymerization temperatures.

Based on the above result, we expected that polymerization could still be initiated by the remaining derivatized thiols on the surface. To test this possibility, two different monolayers containing azo initiators (Fig 2.1, **A** and **B**) were prepared on gold surfaces. Films of initiator **A** had an ellipsometric thickness of

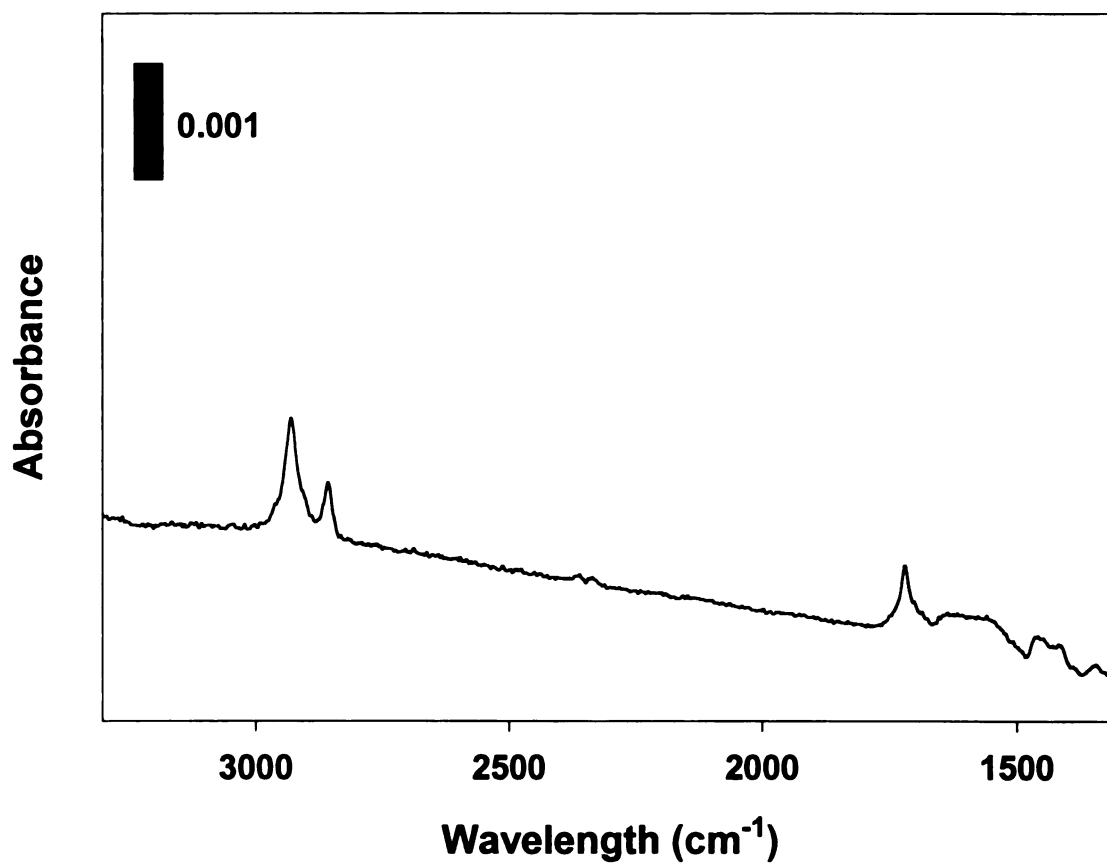


Figure 3.1: Reflectance FTIR spectra of a MUA monolayer showing the crystalline behavior.

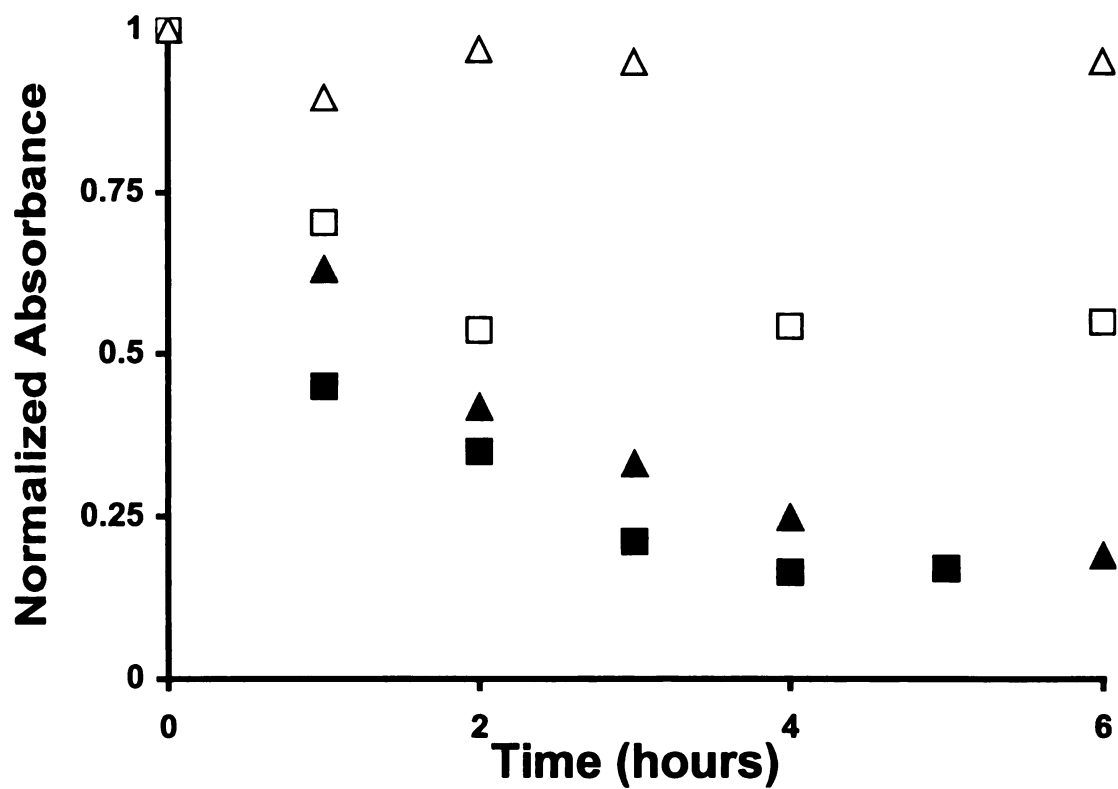


Figure 3.2. Integrated absorbance of the carbonyl peak in reflectance FTIR spectra of MUA monolayers vs time of exposure to toluene at 60 °C (open squares), 6 mM AIBN in toluene at 60 °C (filled squares), toluene at room temperature under UV light (open triangles), and 6 mM AIBN in toluene at room temperature under UV light (filled triangles).

17 ± 2 Å and reflectance FTIR spectra of these films exhibited ester carbonyl peaks around 1737 cm^{-1} . Films of initiator **B** had thicknesses of 14 ± 2 Å and had amide peaks at 1652 and 1548 cm^{-1} . These results confirm that the coupling reactions succeeded and initiators were attached to the surface.

Polymerization was performed by immersing substrates in a 1:1 v/v styrene/toluene mixture at $60\text{ }^{\circ}\text{C}$ for 12 hr. After polymerization, the slides were rinsed with toluene several times and cleaned by Soxhlet extraction. Film thicknesses in the case of both initiators were < 50 Å, and FTIR peaks from polystyrene were not intense. For comparison, we synthesized polystyrene from a silane attached to Al/Al₂O₃ (Fig 2.1, monolayer **C**). The initiator monolayer on alumina had a thickness of 18 ± 2 Å and exhibited amide peaks at 1650 and 1556 cm^{-1} . Polymerization done using the initiator attached to alumina resulted in 400 Å thick films. This showed that for some reason the initiators on gold were rather ineffective. This might be due to quenching of initiator radicals by gold or to desorption of the initiator monolayer.

3.1.2 Stability of SAMs in the Presence of Radicals

We also assessed the stability of SAMs in the presence of radicals. Radicals were generated by either thermal or photo-induced decomposition of AIBN in solution. For the thermal reaction, MUA monolayers on gold were exposed to a hot toluene solution ($60\text{ }^{\circ}\text{C}$) containing 6 mM AIBN. Reflectance FTIR spectra were taken after 1-6 hr of immersion in solution. The intensity of the carbonyl peak in the FTIR spectra revealed that more than 80 % of the MUA

desorbed from the surface after 6 hours (Fig 3.2 filled squares). Experiments done in the absence of AIBN showed that only 40 % of the SAM desorbed from surface (Fig 3.2 open squares). We should note that coverage values based on FTIR spectra are approximate because desorption of SAMs could change the orientation of carbonyl groups in the monolayer.⁵⁷

In a second experiment, MUA SAMs in room temperature toluene solutions were exposed to UV radiation from a mercury lamp. FTIR spectra showed that > 85% of the SAM remained on the surface during 6 hr of UV exposure without AIBN (Fig 3.2 open triangle), but only 20% remained when AIBN was present (Fig 3.2 filled triangles). These results suggest that the radicals may attack the Au-S bond thereby accelerating desorption of thiol bound to surface.

3.1.3 Effect of Thiols on Polymerization

One possible explanation for the lack of polymerization on gold substrates might be that desorbed thiols inhibit radical polymerization. To test this possibility, polymerization on aluminium was done in the presence of either free thiols or SAMs on gold. Reaction conditions were identical to those done with the alumina wafer alone. Thicknesses of polystyrene films on aluminium were $230 \pm 30 \text{ \AA}$ and $310 \pm 30 \text{ \AA}$ when polymerization was performed in the presence of MUD and MUA monolayers, respectively (expts 3, 4 Table 3.1). When compared to polymerization in the absence of SAMs, these values represent a decrease in

Table 3.1: Thickness of surface-grafted polystyrene layers on Al when polymerized in the presence and absence of alkanethiols.^a

Expt	Additives in the Reaction vessel	Thickness of Polystyrene on Alumina (Å)
1	Nothing	410±30
2	Bare Au slide	400±2
3	Mercaptoundecanol in solution (0.25µM in toluene)	250±40
4	Mercaptoundecanol in solution (0.025µM in toluene)	330±20
5	Mercaptoundecanol monolayer on an Au slide	230±30
6	Mercaptoundecanoic acid monolayer on an Au slide	310±30

^a Polymerization was performed for 12 hr at 60 °C, and films were cleaned by Soxhlet extraction.

thickness of 100 - 180 Å. Absorbances in FTIR spectra also decrease when polymerization occurs in the presence of SAMs. In another experiment, trace amounts (0.25 μM or 0.025 μM) of MUD were added to polymerization solutions. In this case, the polystyrene film thicknesses were 250 ± 40 Å and 330 ± 20 Å for solutions containing 0.25 μM and 0.025 μM of MUD, respectively. Film thicknesses were not significantly affected when polymerization was done in the presence of a bare gold slide. The outcome of these experiments, summarized in Table 3.1, suggests that desorbed thiols inhibit radical polymerization from surface.

Figure 3.3, depicts the possible fates of surface bound radicals. When polymerization occurs in solution, there can be radical transfer to solvent or monomer, but neither of these processes terminates polymerization. When polymerizing from a substrate, however, thermal desorption of thiols or transfer of a radical to solvent or a scavenger terminates film growth. In the experiments described in Table 3.1, the ratio of the concentration of monomer to thiol is $10^6 - 10^8$. This is a huge excess of monomer, and we would thus expect negligible transfer of radicals to thiols. However, the experimental values indicate decreases in film thickness of 80-100 Å even when only 0.25 μM or 0.025 μM of MUD solution is present.

One possible explanation for inhibition of polymerization by thiols is that chain-transfer reactions initiate polymerization in solution. This could lead to physisorption of polymer on the surface, thereby blocking monomers from reaching reactive sites. To test this explanation, polymer film thickness was

measured before and after Soxhlet extraction on samples prepared with and without the presence of thiols. We expected that the amount of physisorbed material would be higher for films prepared in the presence of thiols. The ellipsometric thickness of a polymer film prepared in the absence of thiol changed from $440 \pm 30 \text{ \AA}$ to $400 \pm 30 \text{ \AA}$ after Soxhlet extraction. For films prepared in the presence of $0.025 \text{ }\mu\text{M}$ MUD, thickness decreased from $340 \pm 30 \text{ \AA}$ to $300 \pm 30 \text{ \AA}$. These data suggest that the amount of physisorbed material is similar with and without thiols. From our experiments, we clearly see that small concentrations of thiol affect polymerization on aluminium, but the origin of this effect is not yet known.

These studies suggest two possible reasons why we are unable to grow thick polymer films on Au surfaces. First, the alkanethiol monolayers on gold desorb when exposed to high temperatures and radicals. Second, thiols inhibit polymerization. Thus, the stability of SAMs must be ensured before polymerization can be reliably performed. This can be done either by using stabilized SAMs or by carrying out the polymerization at low temperatures using different radical generation techniques.^{34,58} Below I describe thermal radical polymerization from Au surfaces using a cross-linked monolayer containing azo-initiators. The cross-linked surface stabilizes the initiator monolayer.

3.1.4 Preparation of Cross-Linked Azo-Initiator Layers on Gold Surfaces

Mercaptopropyltrimethoxysilanes (MPSs) were used as an adhesion layer for initiator attachment to gold. The mercapto group allows monolayer formation

and terminal silanes can be cross-linked to ensure the stability of the underlying monolayer. Gold substrates were immersed in a 2 mM MPS solution prepared in methanol to form MPS monolayers (Fig 2.2). The reflectance FTIR spectrum of these films contained peaks at 2938 cm^{-1} (overlapping CH_3 and CH_2 bands), 2846 cm^{-1} (CH_2 symmetric stretch) and 1114 cm^{-1} (Si-O-C stretch) (Fig 3.4a). After hydrolysis, methyl peaks disappeared and the intensity of the peak at 1114 cm^{-1} decreased, demonstrating hydrolysis of the MPS layer (Fig 3.4b). During hydrolysis, a three-dimensional poly(siloxane) network formed due to cross-linking of neighboring trimethoxysilane groups. The MPS film thickness was $9 \pm 2\text{ \AA}$, in good agreement with values in the literature.⁵⁹⁻⁶¹ The synthesized azo-initiator, $\text{CH}_3\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, was then attached to the hydroxylated MPS monolayer at $60\text{ }^\circ\text{C}$ (as shown in Fig 2.2). The reflectance FTIR spectrum of this film contained amide peaks at 1652 and 1548 cm^{-1} and the thickness of the layer was $21 \pm 2\text{ \AA}$. The presence of amide peaks confirms that the initiator is attached to the hydrolyzed MPS layer (Fig 3.4c). Surface radical polymerization of styrene from this surface was carried out in a glove box at $60\text{ }^\circ\text{C}$ for 12 hr. The reflectance FTIR spectrum of the polymerized film agrees with standard polystyrene spectra indicating that polymerization was successful, and this sample had a thickness of 400 \AA . Polymerization was carried out for different periods of time using several initiator-coated substrates and the graph of thickness versus polymerization time shows a fairly linear relationship between thickness and reaction time (Fig 3.5). This result

shows that polymerization is reproducible, and the thickness data are in good agreement with the results of R  he et al. on silica surfaces.⁶²

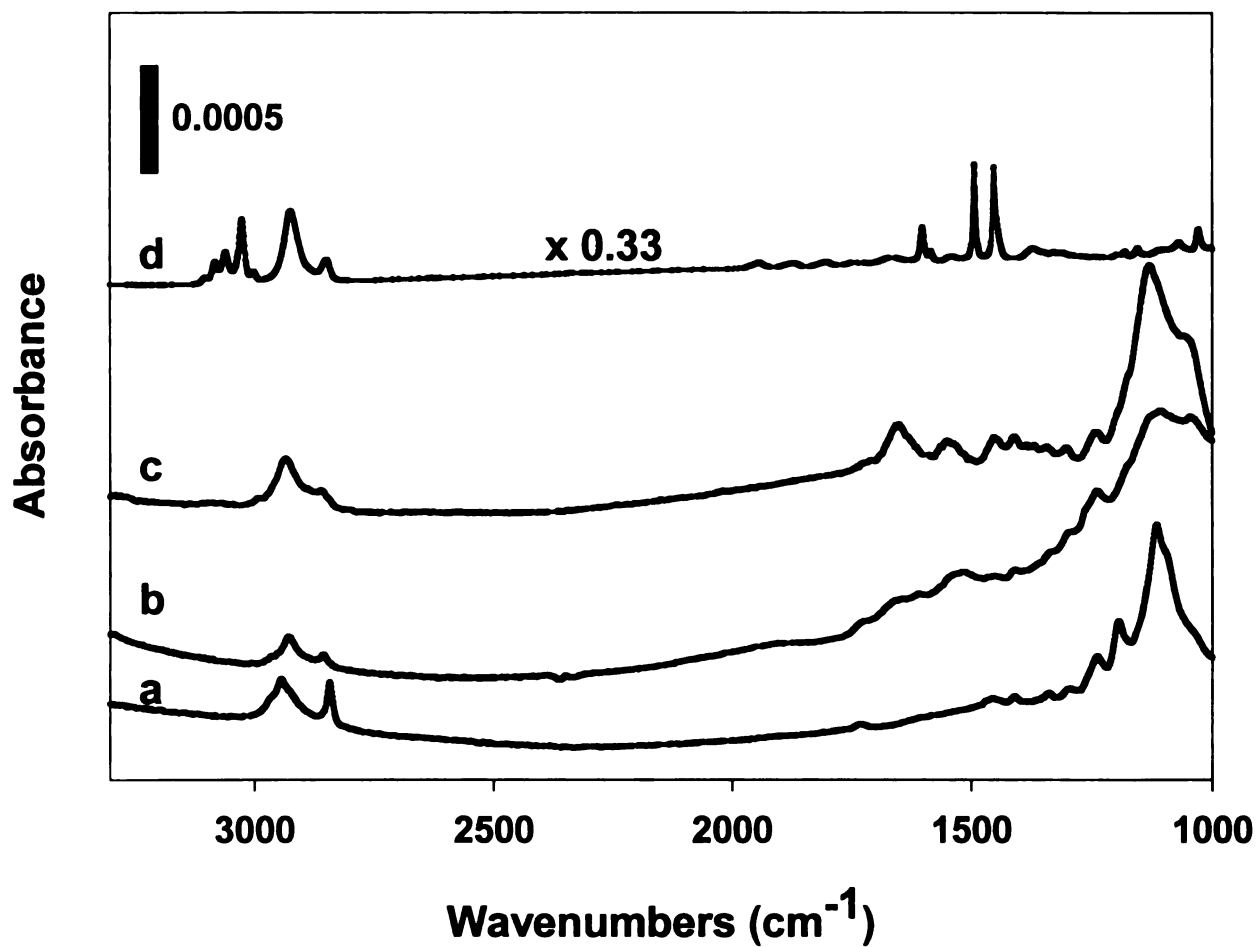


Figure 3.4: Reflectance FTIR spectra of (a) a MPS monolayer, (b) a hydrolyzed MPS monolayer, (c) a hydrolyzed MPS monolayer modified with $\text{CH}_3\text{C}(\text{CH}_3)(\text{CN})\text{N}=\text{NC}(\text{CH}_3)(\text{CN})\text{CH}_2\text{CH}_2\text{CONHCH}_2\text{CH}_2\text{CH}_2\text{Si}(\text{OCH}_3)_3$, an Azo-initiator, and (d) a grafted polystyrene layer.

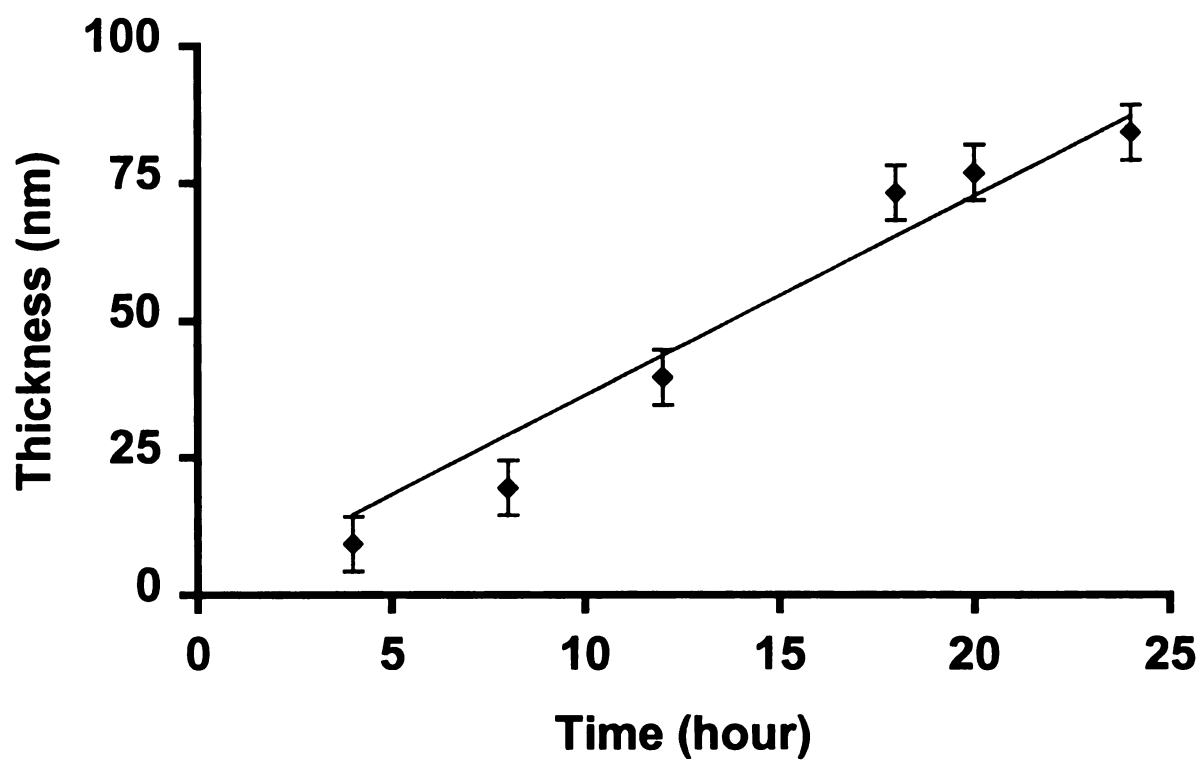


Figure 3.5: Thicknesses of polystyrene films on modified Au surfaces (refer to Fig 2.2 for reaction scheme) as a function of reaction time. Error bars represent the standard deviations of thickness determinations on at least three different samples.

Chapter 4

POLYMERIZATION ON ALUMINA MEMBRANES

The growth of ultrathin polymer films via the alternating adsorption of polyelectrolytes has emerged as a new method of polymer self-assembly.⁶³⁻⁶⁵ This method overcomes problems associated with conventional techniques such as LB assembly, where sample geometry is limited to flat surfaces and preparation requires complicated equipment. In contrast to self assembly, which is usually a slow process and prone to defects, alternating polyelectrolyte deposition is fast and defects are minimal.⁶⁵ This process is capable of producing ultrathin membranes on porous supports. Such composite membranes may find applications in ion separation, food processing, and sensing.⁶⁶ Because they are ultrathin, such membranes allow high flux and can be highly selective. By choosing different layered polyelectrolytes, one can tailor the selectivity of these membranes.

This chapter discusses a hybrid technique of atom transfer radical polymerization (ATRP) at the surface of layered polyelectrolyte membranes. Such a procedure may greatly expand the variety of available ultrathin membranes.

4.1 Experimental

This procedure can be split into three steps: deposition of polyelectrolyte, initiator anchoring, and polymerization as shown in Fig 4.1. The exact procedures for each step are described elsewhere.^{34,66,67}

4.1.1 Deposition of Polyelectrolyte

UV/O₃ cleaned gold-coated substrates were first immersed in a 1.5 mM mercaptopropionic acid (MPA) solution in ethanol for about 30 min. The slides were rinsed with ethanol and dried under N₂. Polyelectrolyte deposition on MPA-coated gold was performed by alternating immersion of the wafer in a PAH solution for 5 min and in a PSS solution for 2 min, with a 1 min water rinse between each immersion. The 0.02 M PAH solution contained 0.5 M NaCl as supporting electrolyte and its pH was adjusted to 4.5 with 0.01 M HCl and 0.005 M NaOH, while the 0.02 M PSS solution contained 0.5 M MnCl₂ and its pH was adjusted to 2.3 with 0.01 M HCl and 0.005 M NaOH. Films were dried with N₂ after depositing all layers. (Polymer molarities are given with respect to the repeating unit.)

4.1.2 Anchoring of Initiator

Initiator was attached to the PAH/PSS films by immersion in 2-bromopropionylbromide (2-BPB) in the presence of triethylamine. The initiator-attachment solution contained 0.432 g of 2-BPB in 10 mL DMF and a solution of base contained 0.242 g of triethylamine in 10 mL DMF. Since the anchoring step

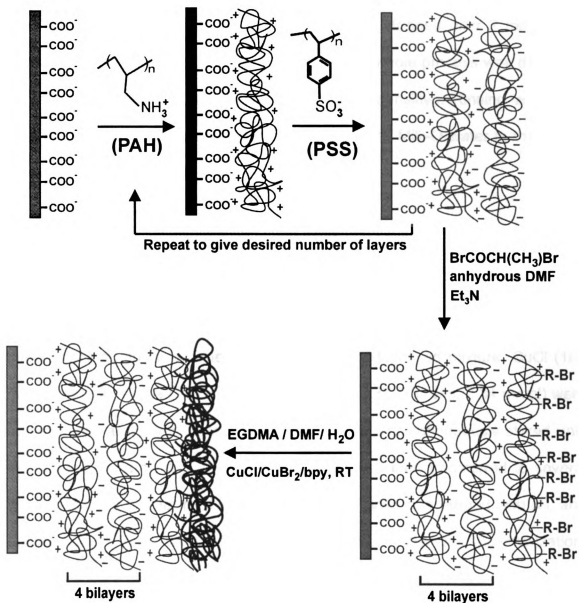


Figure 4.1: Steps involved in grafting poly (EGDMA) from a gold surface coated with a layered polyelectrolyte film.

is exothermic, both solutions were cooled in a freezer to 0 °C before the reaction. The gold slide was first immersed in the solution of base, and then the initiator solution was added all at once. The reaction was stopped after 2 minutes by transferring the slide to a DMF wash solution. The whole process was done in a glove box because the acid bromide is moisture sensitive. Rinsing was done outside the glove box with ethylacetate, ethanol, and Milli-Q water in this order, followed by drying with N₂.

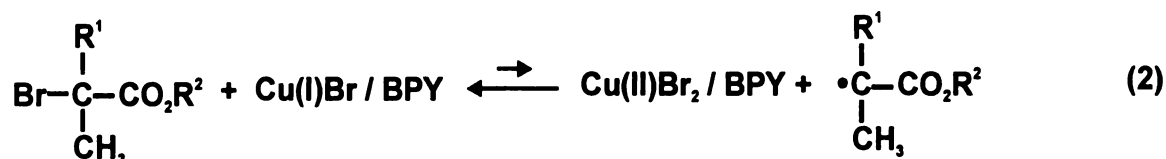
4.1.3 Polymerization Procedure

The monomer mixture contained ethylene glycol dimethacrylate, Milli-Q water, and DMF in a 3:3:8 ratio by volume. The mixture was degassed using three freeze-pump-thaw cycles. To 42 mL of this degassed mixture, CuCl (180 mg, 1.8 mmol), CuBr₂ (120 mg, 0.54 mmol), and BPY (731 mg, 2.34 mmol) were added under a nitrogen atmosphere. The mixture was continuously stirred until the solution became dark brown. This solution was then transferred to several vials containing initiator-modified substrates in a glove bag purged with N₂, and polymerization was done at room temperature. After the polymerization, substrates were rinsed with DMF several times and dried under N₂.

4.2 Results and Discussion

Atom transfer radical polymerization is a living polymerization process. The initiating sites can be activated or deactivated by introduction of Cu (I) (as shown in equation 2). This polymerization can be carried out at room temperature if the

catalysts are sufficiently active, and thus the process can be used with substrates that are sensitive to high temperature. High film thicknesses and negligible reaction in solution make ATRP from a surface an attractive process.^{34,67}



Polymerization was tried initially on gold substrates for characterization purposes. 4.5 bilayers of PAH/PSS were deposited on MPA-coated gold (PAH as the top layer). The ellipsometric thickness of the film was $165 \pm 10 \text{ \AA}$. The FTIR spectra of these films had strong peaks at 1219 and 1177 cm^{-1} characteristic of sulfonate groups and several peaks characteristic of NH_3^+ and phenyl groups (Fig 4.2a). The initiator was then anchored to the surface via the formation of an amide bond. FTIR spectra of the initiator-containing films looked similar to those of PAH/PSS except for a small increase in the peak intensity in the amide region, between 1650 - 1560 cm^{-1} (Fig 4.2b). Polymerization from this surface was carried out for 24 hrs at room temperature, and the film thickness increased from 170 \AA to 1100 \AA . Strong carbonyl peaks at 1735 cm^{-1} in the reflectance FTIR spectrum confirmed the formation of poly(EGDMA) on the surface (Fig 4.2c). C=C stretching from unpolymerized vinyl groups was also seen at 1637 cm^{-1} . Comparison of normalized IR absorbances of vinyl groups in pure monomer and poly (EGDMA), suggest approximately 50 % crosslinking.

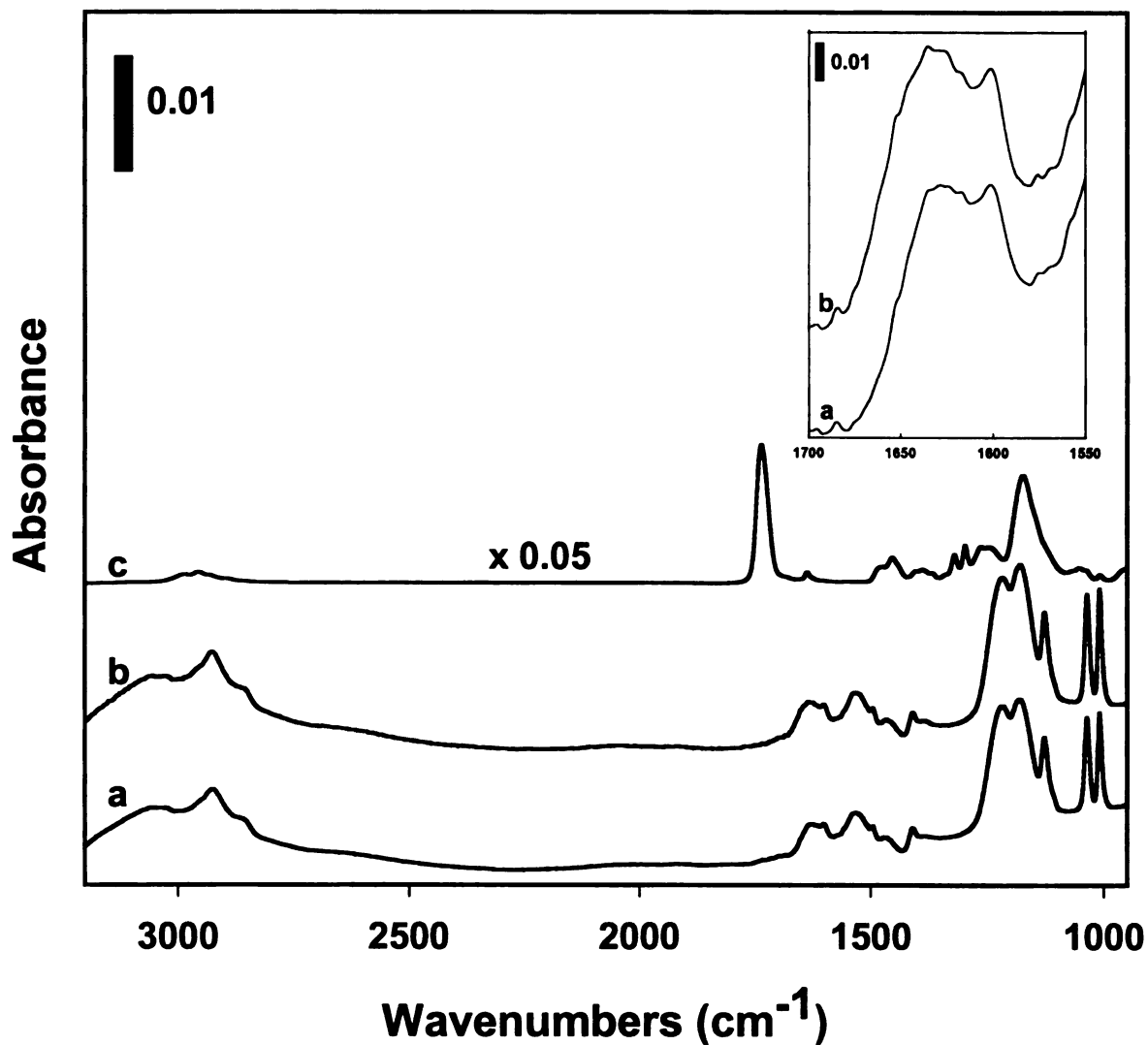


Figure 4.2: Reflectance FTIR spectra of (a) a 4.5-bilayer PAH/PSS film, (b) a 4.5-bilayer PAH/PSS film reacted with initiator, and (c) a grafted poly(EGDMA) film on a 4.5-bilayer PAH/PSS film on gold. The inset shows the amide peaks before and after the initiator attachment.

After the successful grafting of poly(EGDMA) on polyelectrolyte films on gold, the procedure was tried on porous alumina supports (Whatman Anodisc 0.02 μm membrane filters). PSS was deposited first on a UV/O₃ cleaned membrane because of the positive charge on alumina membranes at pH < 8, and then 4.5 bilayers of PAH/PSS were deposited. Deposition of the polyelectrolyte films was restricted to the skin side of the membrane with the use of a holder. Initiator attachment and polymerization were done without a holder. To ensure the reliability of the synthetic procedure, a similar procedure was done on a gold substrate using the same batch of solutions. FESEM (Field Emission Scanning Electron Microscopy) studies show polymer formation on the membranes, but we are not yet able to conclude whether these films can cover underlying pores. In the future, gas permeability and ion-transport studies will give more information about the flux and selectivity of these polymer-coated membranes. The results were promising as ATRP provides a way to graft poly(EGDMA) on polyelectrolyte films on porous supports. By varying the concentration of copper catalyst and the reaction time, cross-linked films of varying thickness can be synthesized at room temperature. This process opens up a new way to prepare cross-linked films. Unlike other methods for preparing cross-linked films, this technique minimizes polymerization in solution. The low temperature process is also compatible with substrates that are unstable at elevated temperature, e.g. Au-thiolates.

Chapter 5

CONCLUSIONS

A short review of previous grafting methods was initially discussed. Because of concerns that the instability of alkanethiol SAMs might affect polymer growth from gold surfaces, we studied the stability of SAMs under thermal polymerization conditions. These studies showed that SAMs are somewhat thermally unstable, but are also attacked by radicals. Other results showed that polymerization is inhibited by the instability of SAMs on gold.

The ability to thermally grow polymers from gold is dependent on establishing a stable initiation system on the surface. The problems associated with the stability of underlying SAMs can be overcome by using mercaptopropyltrimethoxysilane to form an adhesion layer for initiator attachment. The presence of the cross-linked polysiloxane base layer stabilizes the initiator-containing surface to polymerization conditions. When the modified initiator-containing layer is used for radical polymerization of styrene, polystyrene films with thickness ranging from 100 to 900 Å can be obtained.

We conclude that the use of a cross-linked initiator layer provides a simple platform for thermal polymerization. ATRP at room temperature also provides a convenient method to graft high density cross-linked polymers on polyelectrolyte film supports.

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