This is to certify that the

thesis entitled

SYNTHESIS AND CHARACTERIZATION OF ULTRATHIN POLY(STYRENE)
FILMS GRAFTED FROM HYPERBRANCHED POLY(ACRYLIC ACID)

presented by

Anika A. Odukale

has been accepted towards fulfillment
of the requirements for

MS degree in Chemistry

Major professor

Date 08/26/99

O-7639

MSU is an Affirmative Action/Equal Opportunity Institution

SYNTHESIS AND CHARACTERIZATION OF ULTRATHIN POLY(STYRENE) FILMS GRAFTED FROM HYPERBRANCHED POLY(ACRYLIC ACID)

By

Anika A. Odukale

A THESIS

Submitted to
Michigan State University
in partial fulfillment of the requirements
for the degree of

MASTER OF SCIENCE

Department of Chemistry

1999

ABSTRACT

SYNTHESIS AND CHARACTERIZATION OF ULTRATHIN POLY(STYRENE) FILMS GRAFTED FROM HYPERBRANCHED POLY(ACRLYLIC ACID)

By

Anika Assata Odukale

Imprinting of polymer films can produce recognition sites whose selectivity rivals that of natural antibodies. One challenge in applying imprinted polymers for chemical detection is that they equilibrate with analyte molecules very slowly. This project reports on the development of ultrathin polymer films (<100 nm) which are “grafted from” a gold substrate and could be used for imprinting to make a highly selective sensor. The minimal thickness of these films should allow rapid response time to analyte molecules. Using polystyrene as a model system, we address whether the polymer can be successfully grafted from a gold substrate and what conditions are required for this grafting. FTIR and ellipsometry show that styrene polymers cannot be thermally grown from a substrate using a monolayer of thiol-initiator compound, due to the instability of the thiol-gold bonds. However, results indicate that polymerization from a gold substrate is possible utilizing azo-initiators linked to poly(acrylic acid) films.

To Eddie Lloyd Jr. and Constance Fabunmi

ACKNOWLEDGMENTS

First and foremost I would like to thank GOD, whose blessings upon me have been infinite during the course of my graduate studies.

Dr. Merlin Bruening, my advisor, for providing the resources and opportunity to expand on my scientific knowledge, and for seeing me through the completion of this degree.

I would like to acknowledge my Committee: Dr. Crouch, Dr. Hunt and Dr. Rathke, for taking the time to answer all of my “little questions” and being understanding. I am extremely grateful to Dr. Crouch and Dr. Hunt for all of their wisdom, guidance and support. Both have truly altered the course of my life by supplying insight and inspiration in more areas than they will ever know.

Special appreciation is extended to my family, especially my mother, Jabari, who is truly the most beautiful woman I will ever have the pleasure to know, and the best “little bro” a sister could have, Kao. Thank you for always being in my corner, regardless of the situation. And to my extended family, Shalia Lindsey, Christal Spence, T. M. Portis and Dionne Townsend, who could always feel my spirit across the miles.

I am extremely grateful to my best friend, Jesse Edwards III, for the constant support, advice and comfort.

I would finally like to thank Michigan State University and NSF MRSEC for funding provided for this project.

TABLE OF CONTENTS

CHAPTER 4

CHAPTER 5

CHAPTER 6

LIST OF TABLES

LIST OF FIGURES

LIST OF ABBREVIATIONS

SAM	Self-Assembled Monolayer
MIP	Molecular Imprinted Polymer
PTBA	α,ω-diaminopoly(tert-butylacrylate)
T	10-Hour thermal half-life of initiator
Å	Angstrom

INTRODUCTION

The ability to distinguish among molecules in solutions is central to many areas of research and plays a vital role in important technologies ranging from biotechnology to materials science.[1] One example of a particularly exciting area of chemical recognition involves monitoring levels of drugs in the blood stream using "plastic" rather than natural antibodies.[2] This new technology will be especially valuable if it can be used in the development of real-time sensors that are capable of highly selective chemical recognition.

"Plastic antibodies" are based on the use of imprinted polymers, which serve as a medium for molecular recognition. Basic characteristics of a functional imprinted polymer are stiff structure, good accessibility of binding sites, mechanical and thermal stability, and the ability to distinguish between molecules, even enantiomers.[3] In order to minimize diffusion distances and reduce response times of imprinted materials, we are focusing on synthesizing ultrathin films that are <100 nm thick. Ultrathin polymers are what will likely enable imprinted sensors to have fast response times.

The main focus of this thesis is to develop a stable system in which an ultrathin polymer film can be thermally grafted from a gold substrate. An imprinted polymer film of this type can eventually be used in conjunction with a piezoelectric detector to develop a real-time sensor. The reason for developing a model system on gold is that, upon modification of polymer type and other process parameters, it can be applied to the evolution of many different ultrathin polymer substrate systems. Gold is a convenient substrate for electrochemical as well as piezoelectric detection.

The "grafting from" technique, which involves growing polymers from surface-bound initiators, leads to higher graft densities and stronger adhesion of the polymer film to the substrate than does adsorption or end group attachment.[4] Though extensive studies have been performed on the development of stable systems for "grafting from" highly scattered particles such as carbon black [5] and substrates like silica,[6] I have found no prior studies of thermal grafting on gold surfaces. The purpose of this research is to define the parameters necessary for this polymerization.

A good deal of interest has been directed towards the field of terminally grafted polymers on substrates because of the significant role that they play in surface modification and stability.[7] Extensive studies show that one way to successfully achieve stable formation of grafted polymers is by means of grafting them from covalently bound radical polymerization initiators.[8] The background of these studies is outlined in Chapter 1, and Chapter 2 describes experimental techniques and materials used for polymerization. Development of a stable, initiator-containing film on gold is the subject of Chapter 3.

The effect that temperature has on the optimization of polymers grafted from surfaces is analyzed in Chapter 4. Conclusions are made involving the stability of 1PAA and 2PAA substrates with and without initiators, and their response to temperature in Chapter 5. Lastly, future projects are discussed in Chapter 6.

Chapter 1

BACKGROUND

For many years scientist have been interested in molecular recognition and the ability to mimic natural binding phenomena. The ability to synthesize a system that mimics processes found in living organisms has great scientific appeal. One way to achieve such a system is via the use of highly stable, ultrathin, imprinted polymer films that possess selective binding properties because of recognition sites within the polymer matrix.[9]

This chapter presents important previous work that has led to the conceptualization of this project. The ultimate reason for making these ultrathin polymer films is their ability to be molecularly imprinted. First, I review progress in molecular imprinting. I then review the use of self-assembled monolayers (SAMs) which form the basis for our polymer grafting system. Finally, I discuss previous work in grafting polymers from surfaces, and the type of initiators used in this process.

1.1 Molecular Imprinting

The concept of using molecular imprinted polymers (MIPs) for chemical recognition originated from Linus Pauling's template-and-cast theory.[10] In the early 1940's, Pauling speculated that when an antigen is introduced into a blood system, it is recognized as a foreign object. The system creates antibodies that surround the antigen and form a rigid structure, thus holding the antigen in place and rendering it ineffective. He described possible bonding that allows the antibodies to encase the antigen in a 3-dimensional configuration, and proposed that the antigen can eventually dissociate from the antibody structure, thus leaving behind a well-defined antigen-binding cavity. When the antigen is re-introduced to the system, it can be selectively recognized and re-trapped by the same antibody structure. Though Pauling's theory was not correct for antibodies, his idea eventually found fulfillment in the synthesis of molecular imprints.

The challenge in molecular imprinting has been to determine which materials are best suited for a molecular cast for desired template molecules and subsequent release of the template for future recognition. Many researchers began to address this challenge in the 1970's. Gunter Wulff and his group were among these, and in 1972 Wulff's group was the first to report the imprinting of cross-linked organic polymers as a method to synthesize molecular recognition sites.[3]

Over the past 20 years there have been many advances in the development of MIPs, as their practical applications have far-reaching appeal.[11] These include non-covalent imprinting and catalysis using imprinted polymers. Progression in the field has continued through the work of many researchers like Mosbach and Shea. Collectively, these groups have come up with a basic reaction scheme for developing highly selective, imprinted polymers.

The overall concept is very simple, as shown in Figure 1.1.[2] A template molecule is introduced into a solution containing functionalized monomer, and functional groups of the monomer bind to reactive sites on the template molecule. A cross-linking agent is added to the solution and polymerization occurs around the template molecule. When the template is removed, a well-defined cavity remains in the rigid cross-linked polymer. Once re-introduced to the polymer, the template molecule is capable of selectively binding to the site and thus is "recognized ".

1.2 Self-Assembled Monolayers

When a gold substrate is placed in a solution of long-chain thiols, the thiols adsorb at the surface and self-organize as the system approaches equilibrium.[12,13] The resulting surface film is described as a SAM (Figure 1.2). SAMs are fairly stable, highly ordered and can be prepared with constituents containing a range of chain composition and terminal end groups.[14] These features make SAMs very popular in terms of their applications to corrosion studies [15], biotechnology [16] and electrochemical based sensors.[17]

Previously, Langmuir-Blodgett films [18,19] were extensively used for the formation of monolayers on substrates. Though they are capable of forming multilayers, as well as monolayers, they are only physically adsorbed to substrates, and therefore are very unstable.[20] Because SAMs are covalently attached to the surface and highly stable, much of the focus of monolayer formation has turned to SAMs.[21]

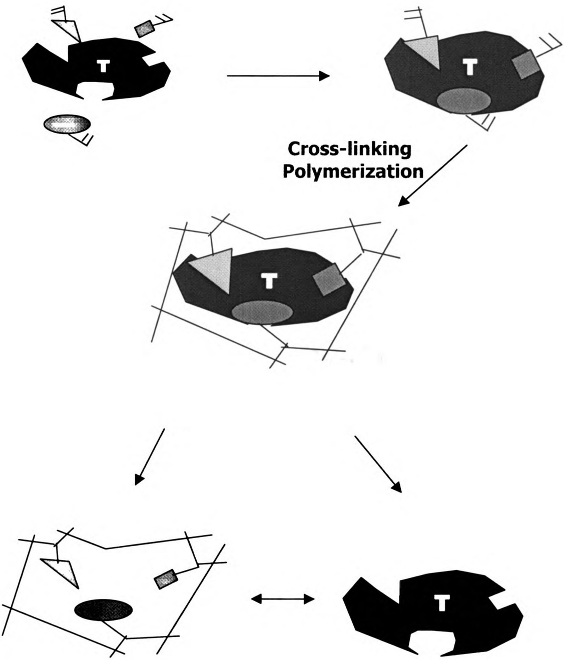


Figure 1.1 Concept of molecular imprinting of polymers.

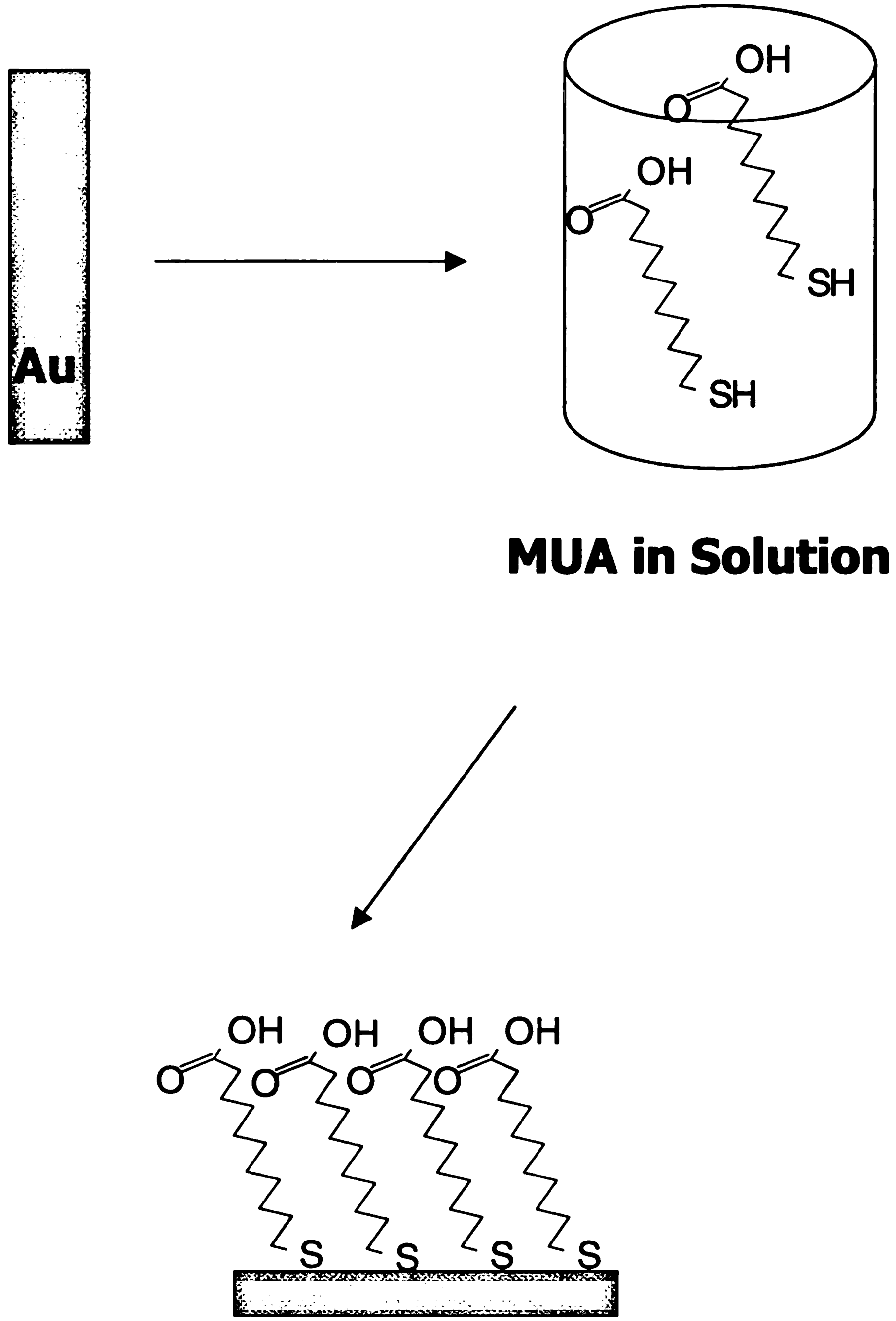


Figure 1.2 Adsorption of an MUA SAM on an Au substrate.

SAMs are ideal systems for making initiation sites on surfaces. Alkanethiol SAMs have been extensively studied over that past 15 years due to their highly stable and ordered formation on gold. This is mainly due to the powerful adsorption of sulfur to metals.[22] Because the end of this chain can be functionally modified, an alkanethiol can be suitable for attaching a wide array of chemicals to its terminal group.

1.3 Grafting Technique

Once it was established that one of the major components of this research would be the formation of ultrathin polymer films on substrates, we had to address which method would be best suited for grafting a dense polymer film from a SAM. Two methods were considered for this purpose: the "grafting to" and "grafting from" technique.

1.3.1 "Grafting To" technique

Grafting polymers to substrates can be done in a variety of ways, which all include either physical or covalent attachment to surface sites.[23] Block-copolymers, or polymer chains, can contain functional end groups that attach to the substrate when it is placed in the solution. The reactive surface sites on the substrate behave as anchors and attach to the functional end groups on the polymer, thus attaching the polymer "to" the surface.[24] One discouraging factor associated with grafting block-copolymers is that less than 5mg/m^2 of polymer can be immobilized on the substrate surface, which may not be a dense enough layer to secure a sufficient amount of template molecules for detection.[25] The main disadvantage of this technique is that most polymerization occurs in solution, and attachment to the surface can not be well controlled.

1.3.2 “Grafting From” technique

A more feasible approach for grafting polymers to substrates is through the “grafting from” technique. In this case, initiators are attached directly to the surface and polymer chains grow from the substrate. This increases the amount of possible reaction sites that the cross-linking agent, monomer and template molecules, which are mixed in solution, can attach to when the substrate is placed in this solution. As the polymer begins to form from a number of sites, it is attached to the surface at many different places. Advantages are that this system can be used with many types of monomers, and more of the polymer should be immobilized on the surface.[26] Control over the number of initiators on the surface should also yield control over the film thickness and density.

1.4 Initiator

In developing films for sensing applications, it is necessary to be able to control immobilized film thickness. In the “grafting from” technique, temperature [27], duration of polymerization, and altering the type [28] and amount of initiator on the surface affect polymer thickness. The amount of initiator should influence the number of attachment sites and hence the film thickness.[29] The type of initiator is important because the amount of film decreases as the rate of decomposition of initiator decreases.[30] Because they decompose at relatively low temperatures (40-90°C), azo-initiators [31] with a low 10-hour thermal half-life [25] have received a good deal of attention for radical polymerization of vinyl monomers.

SAMs of initiators can be prepared through immersing gold slides, which already have a MUA SAM, in an azo-initiator solution. These immobilized initiator "chains" can be thermally activated and the polymer can subsequently be covalently attached, or "grafted from" [32,33] the substrate.

Chapter 2

EXPERIMENTAL

The techniques used to characterize the polymer are first discussed. Then the materials and chemicals used are presented. Finally, syntheses of chemicals are explained.

2.1 Ellipsometry

Optical ellipsometry is a highly sensitive technique that measures the change in polarization in light reflected from a sample. Using a model based on the Fresnel Equations,[34] the thickness and refractive index of thin films can be calculated from the polarization measurement. The change in polarization upon reflection is measured in terms of psi (Ψ) and delta (Δ), which represent the amplitude ratios and phase difference of p and s polarized light.[35] The p and s components have electric field vectors parallel and normal to the plane of incidence, respectively.

Measurements of Ψ and Δ are very sensitive to the thickness of thin films. As the thickness and/or roughness of surface films increase, sensitivity and accuracy of measurements decrease due to deviation from ideal behavior.

A J. A. Wollam Co. ellipsometer was used to measure changes in polarization upon reflection and the WinVASE (variable angle spectroscopic ellipsometry) software calculated the optical constants of substrates and layer thickness (t) of thin films on surfaces.[35] The beam comes through an optical fiber from a xenon lamp source and reflects from the surface at a 75° angle. A diffraction grating allows simultaneous polarization measurements at 44 different wavelengths. The assumed index of refraction used for organic films was 1.5. We had to assume a refractive index for these films because Ψ and Δ are not very sensitive to refractive indices of ultrathin films. The absorption coefficient (k) is presumed to be zero because these polymers do not absorb visible light.

2.2 Infrared Spectroscopy

FTIR-ERS (external reflection spectroscopy) measures the infrared absorption at a reflective substrate using a single reflection mode. A Nicolet FTIR spectrometer, MAGNA-IR 560 model, was used in conjunction with an external reflection attachment to measure infrared spectra. Spectra were taken in a dry nitrogen environment, which was achieved through the design of a plexi-glass glovebox, along with standard sample compartment purging. Measurements were taken using 128 scans and a spectral resolution of 4 cm^{-1} using p-polarized light. The ideal incident angle of ≈87°, [36] which provides maximum absorbance, is difficult to work with so an 80° angle of incidence was used. The FTIR contained an Ever-Glo source and MCT detector. All spectra are recorded as absorbance, which is defined in this instance as $-\log(R/R_o)$ where R is the reflectivity of the monolayer on gold and R_o is the reflectivity of a bare Au substrate.[37]

2.3 Experimental Materials

Gold substrates were prepared by evaporating 200 nm of gold on silicon wafers. The (100) Si wafers are doped with boron, have diameters of 100+/-0.5 mm, thickness' of 380-580 μm and resistivities of 1-20 ohm/cm. Prior to evaporation of Au, 20 nm of Ti was deposited to promote adhesion. Gold substrates are used for attaching polymers because they will eventually allow electrochemical characterization of films. In addition, their chemically homogenous surfaces are easy to clean, practically contaminant free, and suitable for forming well-organized monolayers of organic thiols and disulfides through spontaneous adsorption.[38]

The 11-Bromoundecanoic acid, 4-(Dimethylamino)-pyridine (DMAP), sodium hydroxide, hexanes, dimethylformamide, 4-methylmorpholine, ethyl acetate, tetrahydrofuran (THF), chloroform, ethanol (EtOH), methanol, styrene inhibited with a 4-*tert*-butylcatechol, and ethyl chloroformate were all purchased from Aldrich Chemical Company. Sodium sulfate, triethylamine ($N(Et)_3$), and p-toluenesulfonic acid were purchased from Spectrum. Hydrochloric acid came from Columbus Chemical Industries, thiourea from Mallinkrodt, N, N-dimethylformamide (DMF) from Fisher Chemical, and VA-086 initiator (2,2'-azobis[2-methyl 1-N-(2-hydroxyethyl)propionamide]) was purchased from Wako Chemicals. Further purification was required for styrene and toluene only.

Styrene (100 mL) was purified by first extracting the inhibitor in 50 mL sodium hydroxide, followed by washing with three 50 mL portions of Millipore water. The extracted portion was dried over sodium sulfate and run through a silica or alumina gel column. Nitrogen was blown over the collected solution until it was clear (approximately 24 hours). Toluene was degassed with the same nitrogen purging method.

2.4 Synthesized Chemicals

The 11-mercaptoundecanoic acid (MUA) was synthesized in the following fashion: A mixture of 49.74 g (0.18 mol) 11-bromoundecanoic acid, 14.84 g thiourea (0.19 mol), and 165 mL of methanol was refluxed for 4 hours under nitrogen. The solution was slightly heated with an oil bath and 63 mL of 8 M sodium hydroxide was added dropwise, while stirring. The solution was allowed to reflux for 3 hours. The thick precipitate was acidified to a pH of 3 with concentrated hydrochloric acid and washed with hexanes. There were two phases: an aqueous top layer and a thick, semi-solid bottom. The aqueous portion was collected and dried over sodium sulfate. The solution was concentrated to a precipitate via rotovap, then pump dried. Recrystallization of the precipitate in hexanes gave a product that was pure by ^1H NMR, and confirmed by mass spectrometry. ^1H NMR ($CDCl_3$) δ 2.49 (q, 2H), 2.33 (t, 2H), 1.57 (m, 4H), 1.3 (s, 1H), 1.25 (m, 12H).

Group members synthesized the H_2NR-(PTBA)-RNH_2, referred to simply as PTBA, according to a literature procedure.[39] PTBA= poly(*tert*-butylacrylate), and R= $(CH_2)_2NHCO(CH_2)_2C(CN)\,CH_3$.

Chapter 3

POLYMERIZATION OF STYRENE

Spontaneous adsorption of long chain alkanethiols for the formation of SAM's on gold is a widely used strategy for developing interfaces with tailored properties.[40] This includes modification of wetting [41, 42] and bioadhesion, and introduction of functional groups.[43] In addition to being more stable than traditional Langmuir-Blodgett films,[44] SAM's composed of long-chain thiols [45] where n>10 (n-CH_2), could play a multifunctional role in the stabilization of polymers grafted from gold substrates. First, the structure of the SAM is very uniform and dense on the substrate,[42] thus serving as a stable base for further derivatization. Secondly, functionalized terminal groups of SAM's can present reactive sites for attachment of a large number of initiators to the surface.[20] 11-Mecrapto undecanioc acid is a useful thiol for surface modification for two reasons. One is that the 10 methyl groups provide stability,[46] but do not render the molecule insoluble. Another is that the carboxylic acid group at the tail end of the MUA provides a reactive functional group. This carboxylic acid group does not hinder the coordination of the thiol to the Au substrate, but is what ultimately determines the surface properties of the spontaneously adsorbed monolayer.

Grafting of hyperbranched poly (acrylic acid) (PAA) to MUA SAMs provides a way to further stabilize the SAM on the Au substrate. The increase in film thickness, as well as cross-linking, can induce stabilization that is desired before grafting from the substrate. The hyperbranched PAA contains many -COOH groups that can be utilized for further surface modification.[47]

This chapter examines the process of forming styrene films on gold substrates. This involves evaluating the stability of the MUA SAM, studying stabilization due to derivatized PAA layers, proving that azo-initiators induce polymerization from the surface and establishing temperature ranges for optimal polymerization.

3.1 Experimental

Gold substrates were placed in a Boekel ozone cleaner, model 135500, for 15 minutes and then immersed in Millipore water for 20 minutes. Using ellipsometric measurements, n and k values were calculated for the bare substrate. These are required in the model used to determine film thickness.

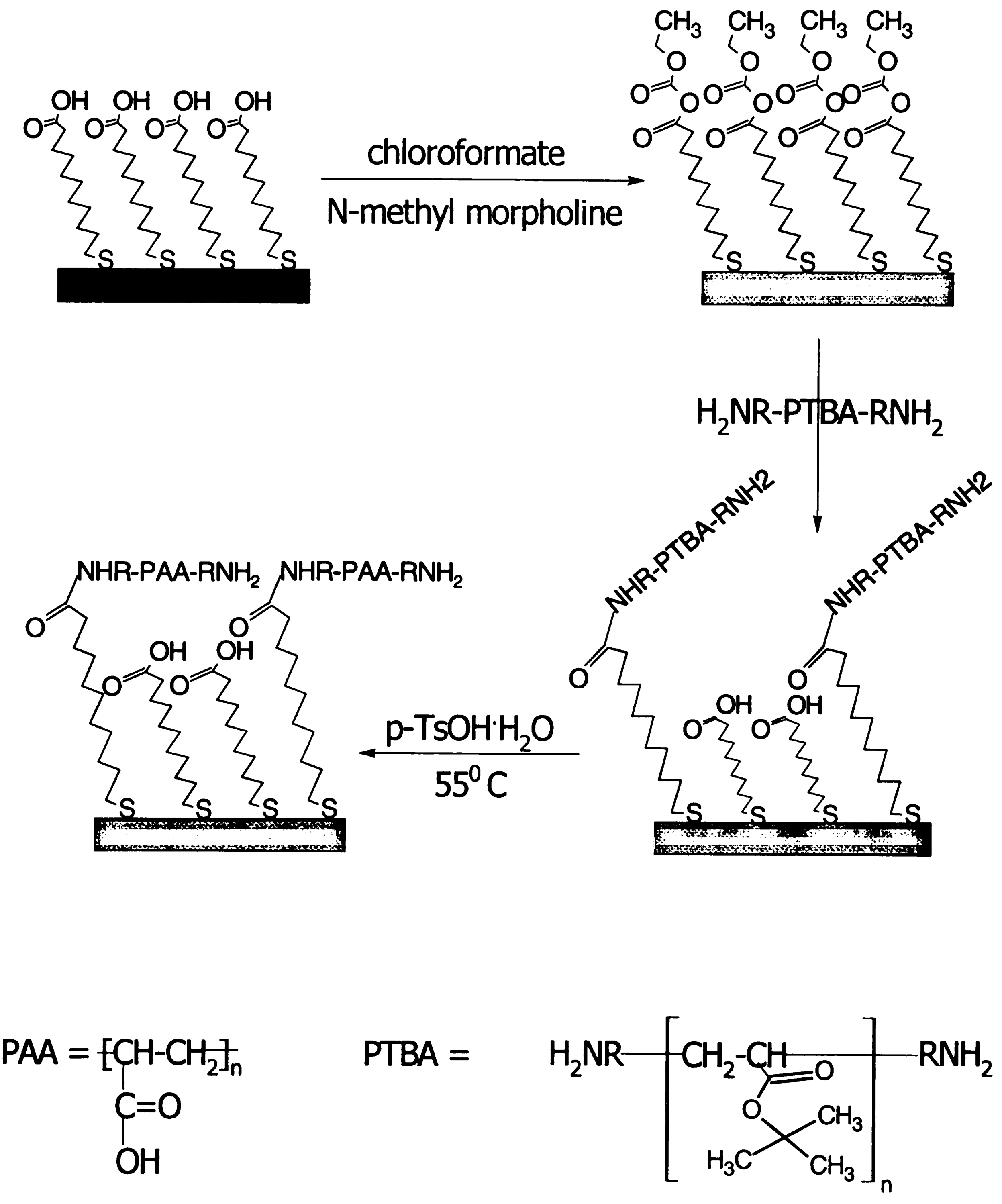
The substrate was placed in a solution containing 0.001 M MUA in EtOH for 30 minutes, rinsed with EtOH followed by Millipore water and dried with a N_2 stream. The MUA SAM was activated in a solution containing 10 mL dry DMF, 80 μL 4-methylmorpholine and 100 μL ethyl chloroformate for 10 minutes, rinsed with ethyl acetate and dried with N_2. This created a mixed anhydride intermediate. To graft PTBA films to this substrate, the activated monolayer was submerged in a solution containing 200 mg PTBA in 4 mL DMF for one hour, rinsed with EtOH and dried with N_2. This film was hydrolyzed by immersing the substrate in benzene saturated with *p*-Toluenesulfonic acid monohydrate at 55°C, for one hour. The slide was removed, rinsed with EtOH and dried with N_2

to yield one monolayer of PAA (1PAA). This process is illustrated in Figure 3.1. To graft a 2PAA film, activation of the –COOH groups of 1PAA, followed by reaction with PTBA and hydrolysis were repeated.

To attach the initiator to a film, the PAA-grafted substrate was activated as previously described, and placed in a solution containing 10 mL DMF, 70 µL $N(Et)_3$, 28 mg DMAP (0.25 mmol) and 124 mg VA-086 initiator (0.43 mmol) for one hour, removed and dried with N_2.

For polymerization, the substrate was placed in a vial and sealed with a septum. The vial was evacuated via suction and filled with N_2. This process was repeated three times. Equal volumes of degassed toluene and styrene were cannula transferred to the vial. The vial was placed in an oil bath at 80-82°C for a period of 24 hours. The substrate was removed, rinsed with toluene and subsequently chloroform, and dried with N_2. Ellipsometric and IR measurements of the substrate were taken after each surface modification.

All data was generated from a pool of 82 samples which were polymerized as either bare gold, 1PAA, 1PAA + initiator, 2PAA, or 2PAA + initiator derivatized substrates.



$R = (CH_2)_2NHCO(CH_2)_2C(CN)CH_3$

Figure 3.1 Formation of 1PAA layer on an Au substrate.

3.2 Results

3.2.1 Grafting PAA to Surfaces

The development of PAA-derivatized substrates was followed at each step using ellipsometry and FTIR-ERS. After the substrate was cleaned it was used as a background spectrum. Once the MUA monolayer was adsorbed on the surface, measurements were taken that verify a surface change. The average ellipsometric thickness of the MUA monolayer was 10 ± 5 Å, and IR showed peaks at approximately 2900-3000 cm^{-1} and 1718 cm^{-1}, which represented the hydrocarbon and carboxylic acid groups, respectively (Figure 3.2). Once the surface was activated, the measured thickness usually varied by ± 2 Å from the MUA monolayer. IR, as seen in Figure 3.2, showed a change in the lower region, which had peaks at approximately 1825 and 1760, cm^{-1}. This indicates the presence of a mixed anhydride. Upon grafting PTBA, ellipsometric measurements varied depending on the age of the PTBA solution from 39 ± 4 Å if new to 78 ± 5 Å for solutions that were approximately 2-3 weeks old. However, IR peaks occur at the same wavenumber, no matter how much PTBA is on the surface. Figure 3.3 shows that there was a noticeable increase in the number and intensity of peaks in the hydrocarbon region, 2900-3000 cm^{-1}, due to the addition of the *tert*-butyl groups and an ester peak at 1730 cm^{-1}. Once hydrolyzed, the average thickness of the PAA monomer was 41 ± 15 Å. The IR peak at 2979 cm^{-1} decreased after hydrolysis due to the removal of *tert*-butyl

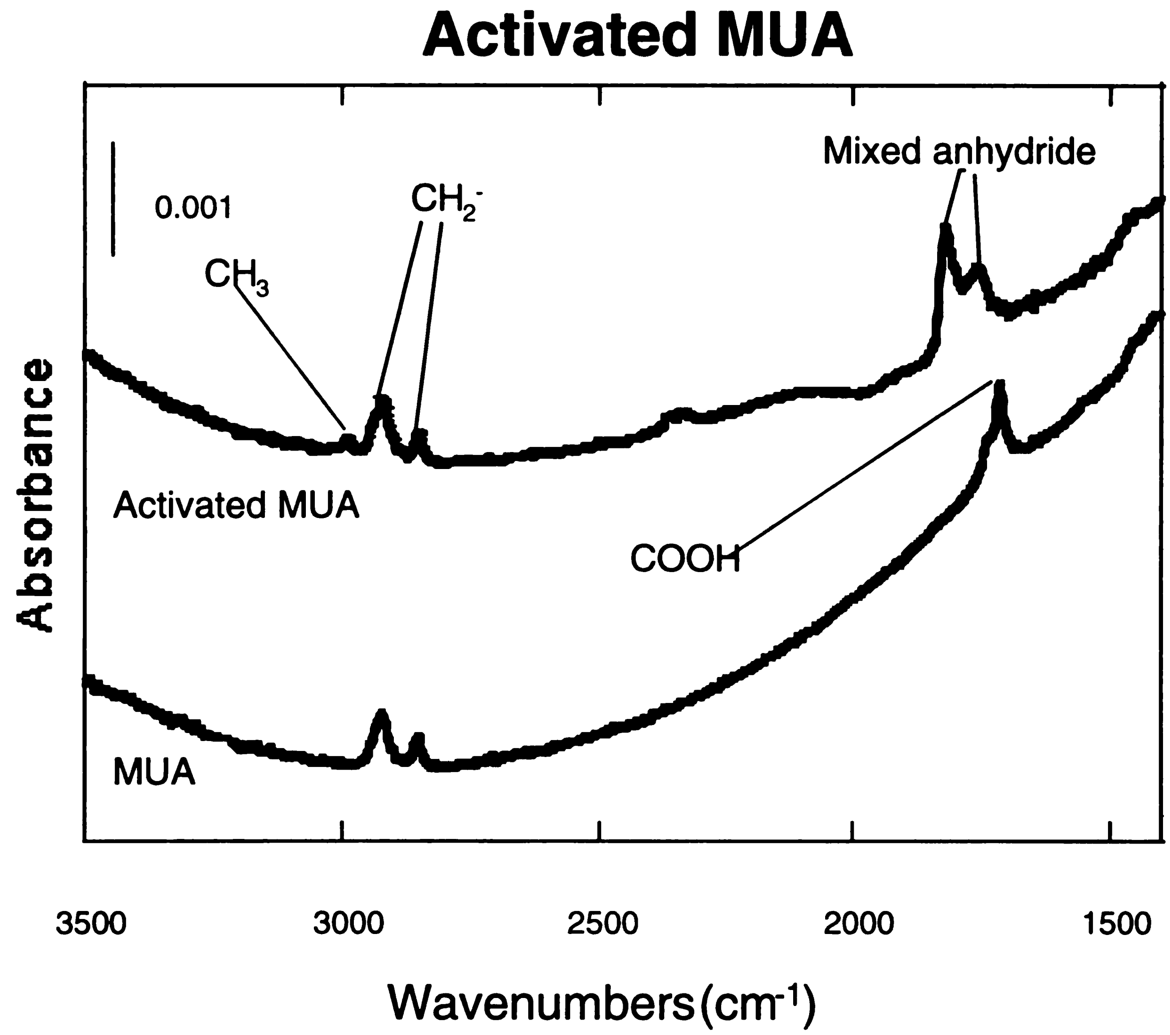


Figure 3.2 FTIR-ERS spectra of a MUA monolayer on Au Before (bottom) and after (top) activation to form a mixed anhydride.

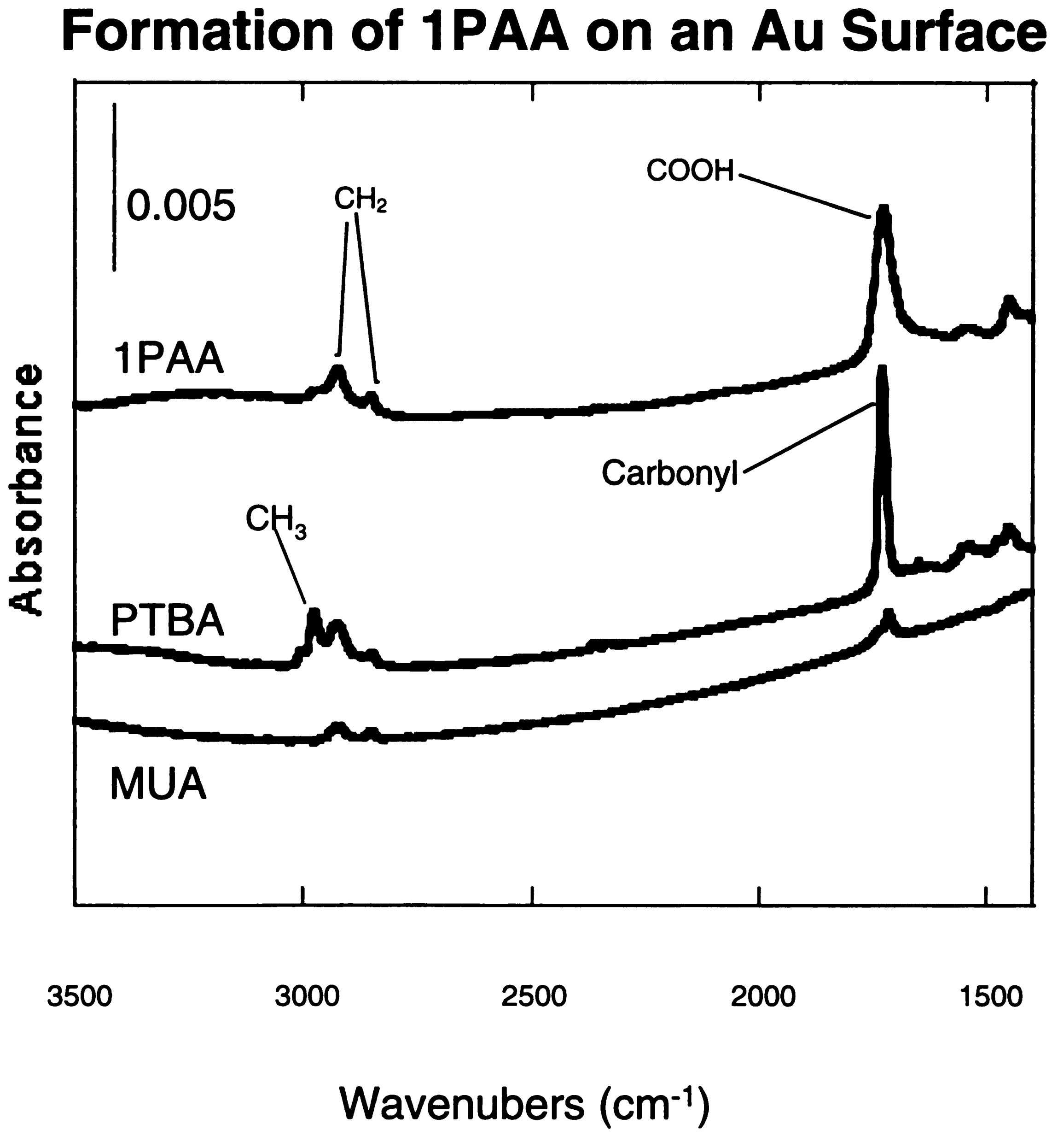


Figure 3.3 FTIR-ERS spectra of MUA(bottom), PTBA(middle), and PAA(top) films on an Au surface.

groups, and the peak around 1730 cm^{-1} became broad, representing the PAA acid carbonyl.

3.2.2 Attempt to use Initiator-Derivatized MUA SAMs for "Grafting From" Polymerization

Initial focus was placed on determining whether a MUA SAM was sufficiently stable for thermal grafting of polystyrene. In order to do this, substrates that were coated with a MUA monolayer, and a MUA monolayer derivatized with initiator, were placed in vials and processed for polymerization, as described earlier. Figure 3.4 shows the FTIR spectrum of polystyrene on a gold substrate. Peaks in this IR will be sought in IR spectra of surfaces used for grafting to determine if there is polymer on the surface. Ellipsometric data of MUA and MUA-initiator films show a 0-5 Å change in thickness after exposure to the styrene/toluene solution at 80°C for 24 hours. This is most likely due to physisorption. These results suggest that there is no significant difference between the MUA and MUA-initiator samples with respect to their ability to initiate polymerization. Thus, polymerizations from MUA surfaces do not work, most likely due to the thermal instability of the Au-S surface bond. In this case, the MUA cleaves from the Au surface upon heating and well before polymerization can occur. The MUA is presumably floating in the polymer solution mixture and does not re-assemble at the surface in any significant amount. The removal of MUA from the surface is confirmed by the disappearance of carbonyl peaks in the IR spectra of these films after exposure to polymerization conditions (Figure 3.5).

3.2.3 Using hyperbranched PAA Monolayers for Surface Stabilization

To increase the stability of our surface films, PAA was grafted to MUA. Subsequently, initiators were attached to the PAA film. Thermal grafting of polymers from these substrates should require the initiator to be present to promote polymerization. This hypothesis was tested through comparing polymerization from substrates covered with MUA, 1PAA, and 2PAA both with and without attaching initiator molecules to the film. The introduction of the 2 layer PAA system, or 2PAA, evolved from consideration as to whether grafting from a thicker PAA-derivatized system would lead to an even thicker polymer film.

Figure 3.6 suggests that when no initiator is grafted to the surface of a 1PAA or 2PAA substrate, exposure to styrene does not result in formation of a significant polystyrene film. In fact, there is not a significant change between bare surfaces and the PAA substrates without initiators, when exposed to heated monomer. The average change in thickness of the film on the surface after exposure to styrene at 76-86°C for 24 hours, was <60 Å in most cases, and generally <30 Å. These changes in thickness suggest that some autopolymerization occurs in solution and polymer physisorbs on the surface, which is difficult to control. Still, as will be seen, the presence of initiators on the

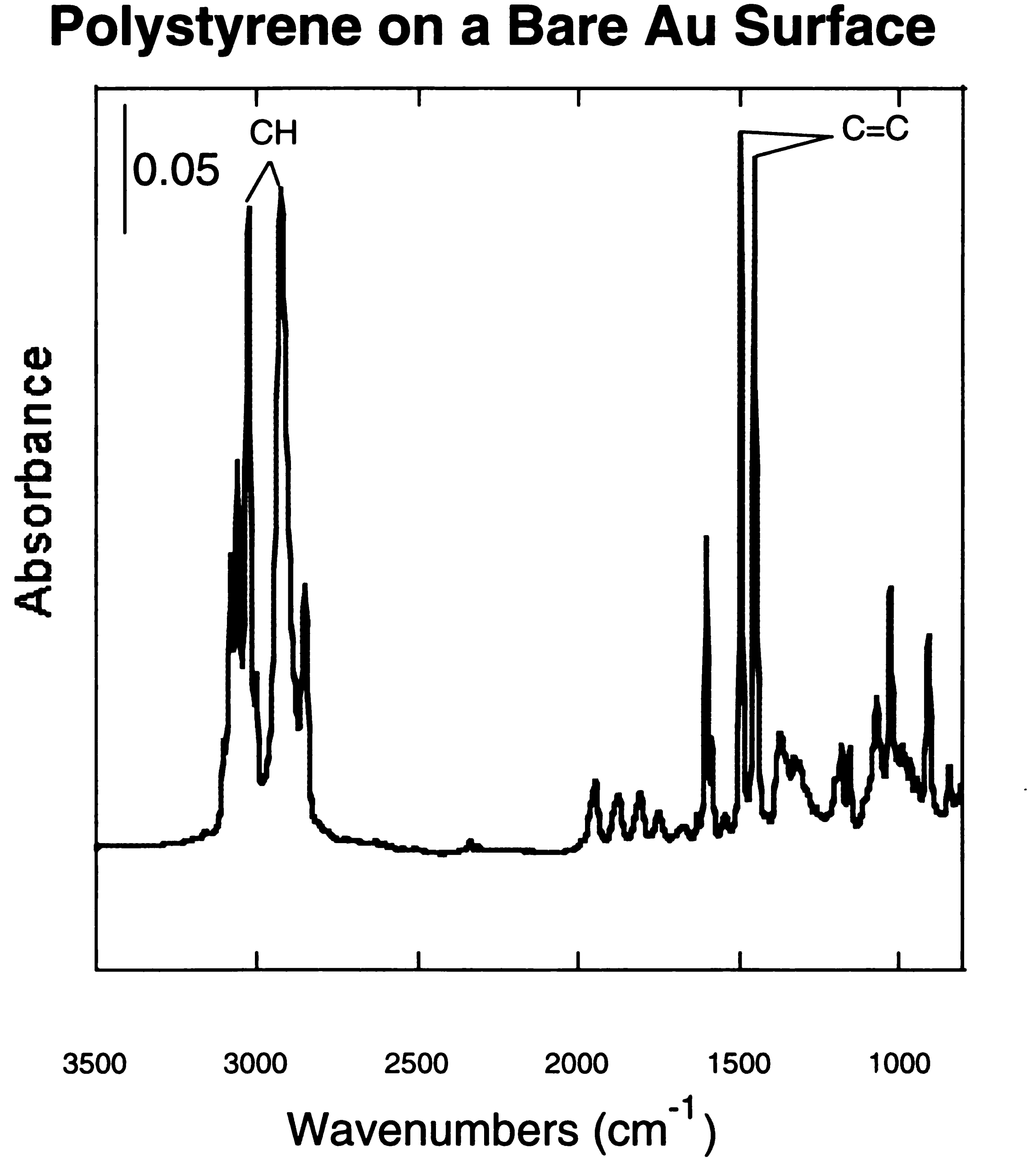


Figure 3.4 FTIR-ERS of polystyrene precipitated on an Au substrate.

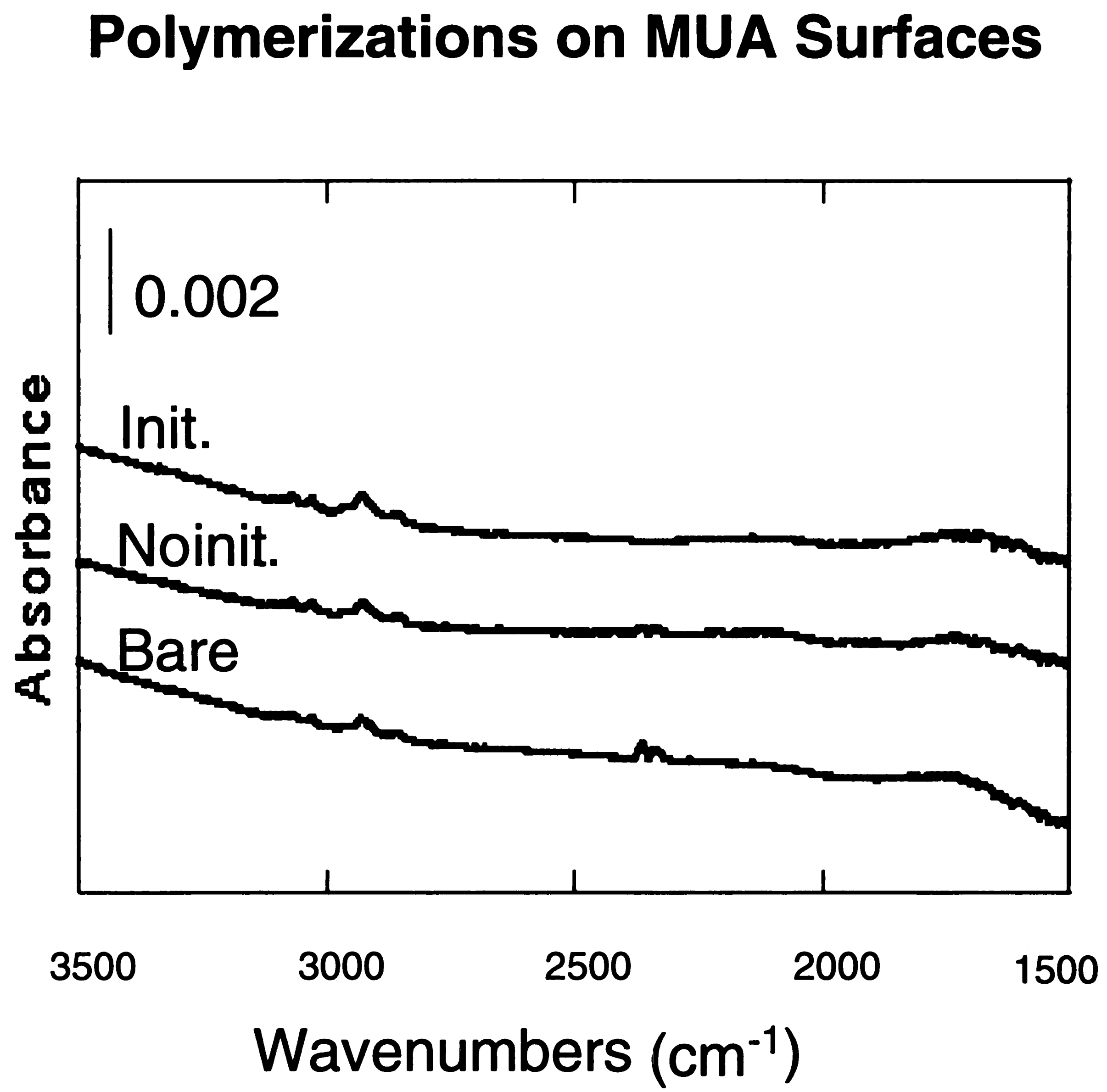


Figure 3.5 FTIR spectra of bare gold, MUA without initiator and MUA with initiator on Au surface, after exposure to styrene/toluene for 24 hours at 80-82°C.

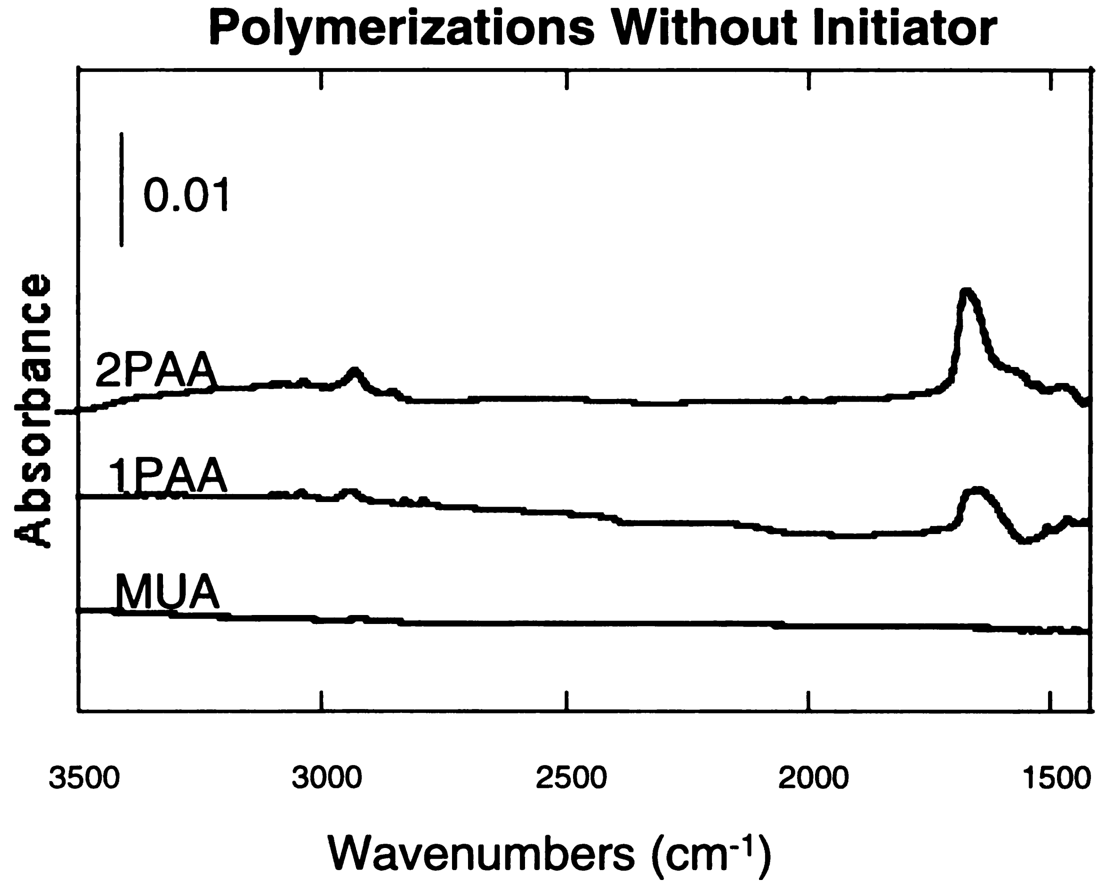


Figure 3.6 FTIR spectra of MUA, 1PAA and 2PAA samples without initiator on an Au surface after exposing to styrene for 24 hours at 80-82°C.

surface results in thicker films. Therefore, the data seems to show that no polymerization occurs on these control surfaces.

FTIR spectra of films exposed to heated monomer when initiators are covalently attached to surface films are shown in Figure 3.7. Both IR and ellipsometry indicate a noticeable increase in the amount of the polystyrene on the surface of the PAA-initiator derivatized substrates. In each temperature range, the use of 2PAA-initiated surfaces appeared to have immobilized polymer films that were slightly thicker than those formed on the 1PAA-initiated surfaces.

One distinct difference between 1PAA and 2PAA polymerizations using the initiator is that the control samples for the 2PAA experiments (those without initiator) were more consistent and easier to keep below the desired thickness of approximately 10% of the thickness of the polymer film of the initiated sample. Thus the 2PAA samples are more definitive in showing the role of initiators. For example, one set of experimental data has an increase in the 2PAA-initiator sample of 441 Å while the non-initiator 2PAA sample increased by 38 Å (see table 4.2). In the same trial, the 1PAA-initiator sample resulted in a 90 Å thickness increase while the non-initiator sample changed by 56 Å (Table 4.1). The variability of thickness increases with 1PAA-initiator and 2PAA-initiator films does not allow us to make definite conclusions as to which film can best initiate polymerization. However, the 2PAA data definitely show that the initiator did increase the amount of polystyrene on the surface. Unfortunately, precise control over the thickness of the polystyrene was not established.

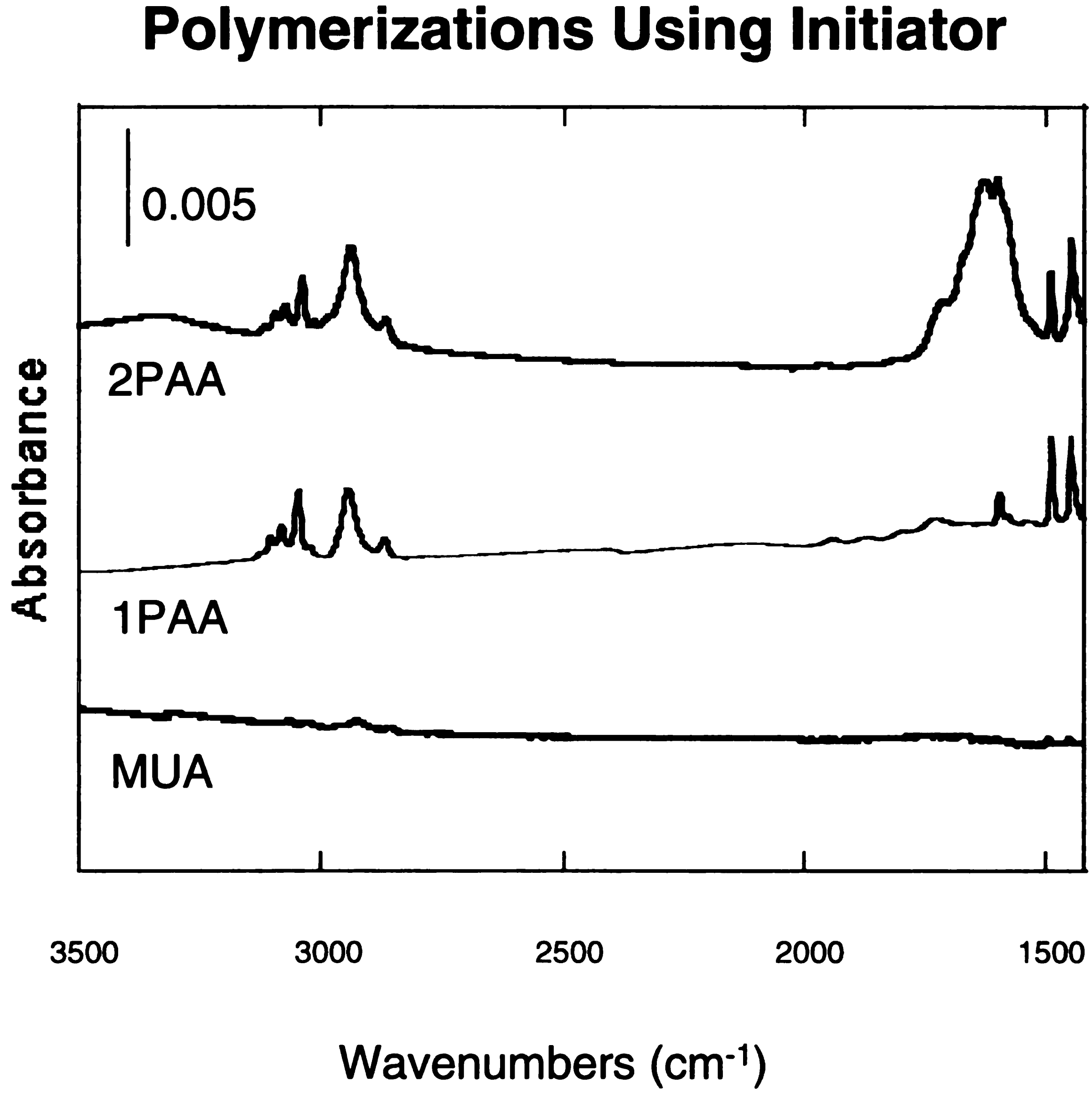


Figure 3.7 FTIR spectra of MUA, 1PAA and 2PAA substrates derivatized with initiator and exposed to styrene/toluene for 24 hours at 80-82°C.

Chapter 4

TEMPERATURE CONTROL STUDIES

The amount of polymer grafted from substrates can be greatly modified by changing experimental variables such as the type of initiator used or type of monomer. However, one of the most sensitive parameters that can affect polymerization is the temperature at which the process takes place. Unfortunately, there is limited information available for choosing temperatures that maximize polymerization at surfaces. Because of this, temperature effects were evaluated in an effort to generalize temperature ranges for polymerizations using different initiators and polymers.

Ultimately, demonstration of grafting from surface bound initiators requires that control surfaces without initiators remain clean under polymerization conditions. In this study the desired thickness of physisorbed polymers on a control sample is <10% of that on the initiator-derivatized film. For example, if the poly(styrene) layer thickness on a 1PAA-initiated sample is 300 Å and 150 Å on the non-initiated 1PAA sample, the trial was not a clear success. If there is a large amount of physisorbed polymer on control films, the amount of polymer that is actually grafted from surface-bound initiators cannot be determined.

4.1 Experimental

The temperature at which polymers begin to "graft from" surfaces depends on the half-life of the initiator used. Research performed using a wide range of initiators in solution has shown that the extent of grafting is optimized when polymerization reactions occur around the temperature, ***T***, that yields a 10-hour thermal half-life of initiators, and that as the ***T*** for the initiator decreased, to a certain point, the amount of polymer grafted from the surface increased.[30]

The Wako-Azo VA-086, which has a rather high ***T*** of 86°C, was employed for this study. Testing was done on 1PAA and 2PAA grafted monolayer systems, both with and without the Wako-Azo initiator, where styrene was polymerized over a series of temperature ranges. This method was used as a means to identify temperatures where physisorption becomes a problem, and temperatures where polymerization from the surface occurs.

4.2 Results

The polymerization system that was analyzed used the Wako-Azo VA-086 initiator with poly(styrene) on PAA derivatized substrates. Table 1 summarizes the series of polymerizations that were performed over a temperature range of ±10°C from the ***T***, 86°C, of the initiator. Unfortunately, oil bath temperature fluctuations were rather large. The best way to transform the data into meaningful information is to focus on the extent of polymerization of samples using the initiator, in comparison to their control samples.

When trials were performed in the range of 76-83°C, virtually no polymer was on the surface, with or without initiator. The very small amount of change in thickness can be attributed in part to physisorption. Even though part of the polymerization process should happen in the 80-82°C range, the lower temperatures during much of the time apparently terminate the entire polymerization.

On the other end of the scale, physisorption on control samples increased at temperature ranges from 81-86°C. Consistent temperatures above 80°C also increase the amount of polymer on initiator-containing surfaces. This is particularly notable for 2PAA samples at 81-86°C. In this case, the initiator definitely causes polymerization, as seen in Table 4.2. However, the magnitude of grafting at higher temperatures, such as 86°C, is still partly a result of physisorption.

Substrate Type	Set Point Temp. (⁰C)	Temp. Range (⁰C)	Thickness (Å)
Bare	76	≈ 76-83	8±5
1PAA	76	≈ 76-83	30±20
1PAA + initiator	76	≈ 76-83	42±10
Bare	80	≈ 80-82	5±3
1PAA	80	≈ 80-82	18±6
1PAA + initiator	80	≈ 80-82	123±30
Bare	83	≈ 80-85	7±5
1PAA	83	≈ 80-85	44±10
1PAA + initiator	83	≈ 80-85	81±13
Bare	86	≈ 81-86	17±11
1PAA	86	≈ 81-86	56±15
1PAA + initiator	86	≈ 81-86	90±40

Table 4.1 Poly(styrene) layer thickness of 1PAA derivatized samples over a range of various temperatures. Reported values are averages of three samples.

Substrate Type	Set Point Temp. (⁰C)	Temp. Range (⁰C)	Thickness (Å)
Bare	76	≈ 76-83	8±5
2PAA	76	≈ 76-83	15±7
2PAA + initiator	76	≈ 76-83	36±10
Bare	80	≈ 80-82	5±3
2PAA	80	≈ 80-82	23±14
2PAA + initiator	80	≈ 80-82	134±27
Bare	83	≈ 80-85	7±5
2PAA	83	≈ 80-85	14±5
2PAA + initiator	83	≈ 80-85	125±15
Bare	86	≈ 81-86	17±11
2PAA	86	≈ 81-86	58±20
2PAA + initiator	86	≈ 81-86	441±220

Table 4.2 Poly(styrene) layer thickness of 2PAA derivatized samples over a range of various temperatures. Reported values are averages of three samples.

Chapter 5

CONCLUSIONS

This research first studied the development of thermally grafted ultrathin polymer films from gold substrates where a short historical background of the process was presented. Through this we developed a method in which styrene could be grafted from a gold substrate using a MUA/PAA film derivatized with an azo-initiator. Due to the limited temperature range over which polymerization occurred, reproducibility was relatively poor.

We have found that the ability to polymerize is dependent on establishing a stable surface system. The MUA formed a highly ordered SAM on the gold substrates. However, this surface is not sufficiently stable at the conditions required to initiate polymerization.

We then determined that one way to enhance the surface stability for the MUA SAM was through grafting of PAA. Next, we reported that initiators were required for grafting polystyrene from Au surfaces. An azo-initiator was suitable for this purpose.

Finally, we concluded that temperature had a significant effect on the thickness of the polymer layer grafted to the substrate. Polymerization began to occur at the T of the initiator. There is a limited range in which polymerization can be successful. When temperatures were too low there was no significant polymerization, and physisorption of the polymer was uncontrollable at high temperatures.

The results for development of this system were promising, as they are applicable to making an ultrathin polymer that can be molecularly imprinted. Ultimately, combining a piezoelectric detector with this imprinted film will increase the likelihood of developing of a real-time chemical sensor.

Chapter 6

FUTURE PROJECTS

Future studies should move from model polymers to imprinted systems on piezoelectric transducers. However, current studies on establishing a system in which an ultrathin polymer film can be grafted from a substrate have led to many new concepts that deserve consideration and open the door into different areas of future investigation that will expand the scope of this research. These topics include improving the current technique and its reproducibility, applying this technique to other polymers and decreasing the reaction time.

6.1 Improving Current Technique and Reproducibility

The "model" system developed in this study gave good results for polymerization, but control of consistency and reproducibility could not be established. This may be possible in future studies by altering several process parameters such as purity of chemicals used, the amount of oxygen present while preparing the substrates, using an initiator with a low T, limiting the amount of light on the reaction vials, and having the temperature confined to a 2°C range. We anticipate that efforts made to master these parameters will lead to increased experimental control.

6.1.1 Chemical Purification

Many research groups report that one of the essentials for grafting polymers to substrates is the use of chemicals purified by the freeze-thaw method.[24] Our studies show that, under our polymerization system, using chemicals purified in this way stopped polymerization, as shown in table 6.1. However, polymerizations are achieved when the chemicals are purified by N_2 purging. This may have been a result of the apparatus in which polymerization occurred more than the use of the pure chemical, which will be discussed in the next section. Since it was reasonable to assume that impurities may interfere with polymerization, we conclude that the use of pure chemicals for future polymerizations can help to graft thicker polymers with better control samples.

6.1.2 Oxygen

Too much oxygen may terminate polymerization, or the extent of the process, at the surface. In previous studies, polymerizations were carried out in vials which had freeze-thawed polymer solutions, which is where the use of purified chemicals may have been so important. In our studies, we used vials that were pumped with the aspirator and filled with N_2, which may have limited polymerization. Performing the polymerizations in a glove box, in which the contents are under nitrogen only, is a fairly easy way to reduce oxygen during polymerization.

Substrate Type	Reaction Temp. (°C)	Styrene Type	Thickness (Å)
Bare	≈76-83	Freeze-thaw	6
1PAA	≈76-83	Freeze-thaw	9
1PAA + initiator	≈76-83	Freeze-thaw	4
2PAA	≈76-83	Freeze-thaw	15
2PAA + initiator	≈76-83	Freeze-thaw	26
Bare	≈76-83	N_2 purging	8±5
1PAA	≈76-83	N_2 purging	30±20
1PAA + initiator	≈76-83	N_2 purging	42±10
2PAA	≈76-83	N_2 purging	15±7
2PAA + initiator	≈76-83	N_2 purging	36±10
Bare	≈80	Freeze-thaw	12
1PAA	≈80	Freeze-thaw	11
1PAA + initiator	≈80	Freeze-thaw	4
2PAA	≈80	Freeze-thaw	4
2PAA + initiator	≈80	Freeze-thaw	19
Bare	≈80-82	N_2 purging	5±3
1PAA	≈80-82	N_2 purging	18±6
1PAA + initiator	≈80-82	N_2 purging	123±30
2PAA	≈80-82	N_2 purging	23±14
2PAA + initiator	≈80-82	N_2 purging	134±27

Table 6.1 Polymerizations of samples using styrene that was freeze-thawed in comparison to samples polymerized with styrene purified through extraction. Values with standard deviations are averages of three samples.

6.1.3 Using Low-Temperature Initiators

An initiator with a ***T*** that is below 75°C may be a significant factor in the thermal grafting of ultrathin polymers to these substrates. We believe that at or below this temperature there is enough heat to initiate polymerization, but not enough to create a significant amount of physisorption on the surfaces. In an effort to test this hypothesis, a chloro-terminated initiator, $(C_6HClNO)_2$, with an estimated ***T*** of 69°C was synthesized by a group member, Dr. Wenxi Huang.

6.1.4 Exposure to Light

Styrene is a photosensitive monomer, and prolonged exposure to light may initiate polymerization and increase physisorption. Limiting the amount of light in the environment, as polymerizations are performed, may help keep control samples clean.

6.1.5 Controlled Temperature

Our studies have implied that the establishment of a constant reaction temperature is beneficial to polymerization. A controlled environment may be achieved through an apparatus set up in an area where airflow disturbance is minimal, perhaps in a glove box.

6.2 Application of Current Technique to Other Polymers

One of the major goals in designing this experiment was to develop a model system for the immobilization of a broad range of vinyl monomers such as methyl methacrylate and methacrylic acid. Polymerization may be accomplished for these different polymers in a similar manner to polystyrene.

6.3 Decreasing Reaction Times

Reaction methods that require less time for polymerization to occur should be investigated. One technique that can be used for this purpose is photopolymerization. This technique involves UV light [48, 49, 50, 51] and can happen over a period of a few minutes. One group of initiators that appear to have promising attributed for this purpose are xanthates,[50] due to their capability to attach exactly one bound polymer chain for each initiator. Varying the pH in which they are formed can also control the xanthate monolayers.

BIBLIOGRAPHY

Bibliography

1)Husseman, M., Malmstrom, M., McNamara, M., Mate, M., Mecerreyes, D., Benoit, D., Hedrick, J., Mansky, P., Huang, E., Russell, T., Hawker, C. *Macromolecules* **1999**, *32*, 1424-1431.

2)Flam, F. *Research News* **1994**, *263*, 1221-1222.

3)Wulff, G. *Angew. Chem. Int. Ed. Engl* **1995**, *34*, 1812-1832.

4)Habicht, J., Schmidt, M., Ruhe, J., Johannsmann, D. *Langmuir* **1999**, *15*, 2460-2465.

5)Tsubokawa, N., Handa, S. *J.M.S.-Pure Appl. Chem.* **1993**, *A30*, 277-286.

6)Zhang, J., Cui, C., Lim, T., Kang, E., Neoh, K., Lim, S., Tan, K. *Chem. Mater.* **1999**, *11*, 1061-1068.

7)Marchand-Brynaert, J., Deldime, M., Dupont, I., Dewez, J., Schneider, Y. *J. Colliod and Interface Science* **1995**, *173*, 236-244.

8)Huang, X., Wirth, M. *Macromolecules* **1999**, *32*, 1694-1696.

9)Kriz, D., Ramstrom, O., Svensson, A., Mosbach, K. *Anal. Chem.* **1995**, *67*, 2142-2144.

10)Pauling, L. *J. Am. Chem. Soc* **1940**, *62*, 2643-2657.

11)Jenkins, A., Manuel Uy, O., Murray, G. *Anal. Chem.* **1999**, *71*, 373-378.

12)Karpovich, D., Blanchard, G. *Langmuir* **1994**, *10*, 3315-3322.

13)Ulman, A. *Chem. Rev.* **1996**, *96*, 1533-1554.

14)Karpovich, D., Blanchard, G. *Langmuir* **1997**, *13*, 4031-4037.

15)Crispin, X., Lazzaroni, R., Geskin, V., Baute, N., Dubois, P., Jerome, R., Bredas, J. *J. Am. Chem. Soc.* **1999**, *121*, 176-187.

16)Sun, L., Crooks, R., Ricco, A. *Langmuir* **1993**, *9*, 1775-1780.

17)Nuzzo, R., Allara, D. *J. Am. Chem. Soc.* **1983**, *105*, 4481-4483.

18)Knoll, W., Philpott, M., Golden, W. *J. Chem. Phys.* **1982**, *77*, 219-225.

19)Rabolt, J. F., Burns, F.,C., Schlotter, N., E., Swalen *J. Chem. Phys.* **1983**, *78*, 946-952.

20)Motesharei, K., Myles, C. *J. Am. Chem. Soc.* **1998**, *120*, 7328-7336.

21)Finklea, H., Robinson, L., Blackburn, A., Richter, B. *Langmuir* **1986**, *2*, 239-244.

22)Troughton, E., Bain, C., Whitesides, G., Nuzzo, R., Allara, D., Porter, M. *Langmuir* **1988**, *4*, 365-385.

23)Prucker, O., Ruhe, J. *Mat. Res. Soc. Symp. Proc.* **1993**, *304*, 167-172.

24)Velten, U., Shelden, R., Caseri, W., Suter, U. *Macromolecules* **1999**, *32*, 3590-3597.

25)Prucker, O., Ruhe, J. *Macromolecules* **1998**, *31*, 592-601.

26)Jordan, R., Ulman, A., Kang, J., Rafailovich, M., Sokolov, J. *J. Am. Chem. Soc.* **1999**, *121*, 1016-1022.

27)Domack, A., . Procker, O., Ruhe, J., Johannsmann, D. *Phys. Rev, E* **1997**, *56*, 681-689.

28)Prucker, O., Ruhe, J. *Langmuir* **1998**, *14*, 6893-6898.

29)Xia, J., Gaynor, S., Matyjaszewski, K. *Macromolecules* **1998**, *31*, 5958-5959.

30)Prucker, O., Ruhe, J. *Macromolecules* **1998**, *31*, 602-613.

31)Zhao, B., Brittain, W. *J. Am. Chem. Soc.* **1999**, *121*, 3557-3558.

32)Biesalski, M., Ruhe, J. *Macromolecules* **1999**, *32*, 2309-2316.

33)Tovar, G., Paul, S., Knoll, W., Prucker, O., Ruhe, J. *Supramolecular Science* **1995**, *2*, 89-98.

34)Blanchard, G. *CEM 835 Lab Manual, Chapter 23 excerpt*, 1998.

35)Woollam Co, J., A. *Manual* **1997**, 5-59.

36)Greenler, R. *J. of Chem. Physics* **1966**, *44*, 310-315.

37)Porter, M., Bright, T., Allara, D., Chidsey, C. *J. Am. Chem. Soc.* **1987**, *109*, 3559-3568.

38)Niwa, M., Mori, T., Higashi, N. *Macromolecules* **1993**, *26*, 1936-1940.

39)Bruening, M., Zhou, Y., Aguilar, G., Agee, R., Bergbreiter, D., Crooks, R. *Langmuir* **1997**, *13*, 770-778.

40)Knoll, W., Matsuzawa, M., Offenhausser, A., Ruhe, J. *Israel J. of Chem.* **1996**, *36*, 357-369.

41)Husemann, M., Mecerreyes, D., Hawker, C., Hedrick, J., Shah, R., Abbott, N. *Angew. Chem. Int. Ed.* **1999**, *38*, 647-649.

42)Bain, C., Whitesides, G. *Science* **1988**, *240*, 62-63.

43)Ingall, M., Honeyman, C., Mercure, J., Bianconi, P., Kunz, R. *J. Am. Chem. Soc.* **1999**, *121*, 3607-3613.

44)Prucker, O., Schimmel, M., Tovar, G., Knoll, W., Ruhe, J. *Adv. Mater.* **1998**, *10*, 1073-1077.

45)Bain, C., Troughton, B., Tao, Y., Evall, J., Whitesides, G., Nuzzo, R. *J. Am. Chem. Soc.* **1989**, *111*, 321.

46)Finklea, H., Avery, S., Lynch, M. *Langmuir* **1987**, *3*, 409-413.

47)Zhou, Y., Bruenung, M., Bergbreiter, D., Crooks, R., Wells, M. *J. Am. Chem. Soc.* **1996**, *118*, 3773-3774.

48)Kubota, H., Yamaguchi, T., Tanaka, T. *Polymer Degradation and Stability* **1993**, *40*, 369-373.

49)Wolfe, D., Oldenburg, S., Westcott, S., Jackson, J., Paley, M., Halas, N. *Langmuir* **1999**, *15*, 2745-2748.

50)Niwa, M., Date, M., Higashi, N. *Macromolecules* **1996**, *29*, 3681-3685.

51)Niwa, M., Mori, T., Nigashi, N. *J. Mat. Chem.* **1992**, *2*.