Chemical Vapor Deposition of Antimicrobial Polymer Coatings

by

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ABSTRACT

There is large and growing interest in making a wide variety of materials and surfaces antimicrobial. Initiated chemical vapor deposition (iCVD), a solventless low-temperature process, is used to form thin films of polymers on fragile substrates. To improve research efficiency, a new combinatorial iCVD system was fabricated and used to efficiently determine the deposition kinetics for two new polymeric thin films, poly(diethylaminoethylacrylate) (PDEAEA) and poly(dimethylaminomethylstyrene) (PDMAMS), both candidates for antimicrobial coatings. Fourier transform infrared (FTIR) spectroscopy shows that functional groups are retained in iCVD of PDMAMS and PDEAEA, whereas essentially all fine chemical structure of the material is destroyed in plasma-enhanced CVD. It was found that the combinatorial system in all cases provided agreement, within experimental certainty, with results of blanket iCVD depositions, thus validating the use of the combinatorial system for future iCVD studies.

Finished nylon fabric was subsequently coated with PDMAMS by iCVD with no affect on the color or feel of the fabric. Coatings PDMAMS of up to 540 µg/cm² were deposited on fabric. A coating of 40 µg/cm² of fabric was found to be very effective against gram-negative E. coli, with over a 99.9999%, or 6 log, reduction in viable bacteria in one hour. A coating of 120 µg/cm² was most effective against the gram-positive B. subtilis. Further tests confirmed that the iCVD polymer did not leach off the fabric.

Type-II photoinitiation was utilized to perform vapor phase deposition of covalently-bound polymer coatings of the polymer PDMAMS. The durability was improved so that 80 wt% of the fabric coating was retained after extended antimicrobial testing and three rounds of ultrasonication. The coating was effective, killing 99.9% of E. coli in one hour. The gCVD process was then further explored using the less-UV-sensitive monomer DEAEA for deposition onto spun cast PMMA thin films. Durable films up to 54 nm thick retained 94% of their thickness after 10 rounds of ultrasonication. Gel Permeation Chromatography (GPC) and Variable Angle Spectroscopic Ellipsometry (VASE) swelling cell measurements gave estimated ranges of 72-156 kDa for the molecular weight and 0.1-0.24 chains/nm² for the graft density.

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Chapter One

Introduction
1.1 Combinatorial Initiated Chemical Vapor Deposition

The process of chemical vapor deposition has many parameters. The time-consuming process of exploring this large parameter space is exemplified by recent work in our lab completed by Jessie Mao on poly(glycidyl methacrylate). The precursor ratios and filament temperature were varied systematically. The resulting growth rate and molecular weight were examined, both of which are critical for the intended application, patternable resist materials. The results of the work are presented in Figure 1-1. This CVD process exploration is somewhat tedious and time consuming, but critical for the optimization of each deposition chemistry attempted. In this case, the work required about one semester. For the standard system, much effort must be expended to ensure the
other experimental conditions are held very near constant to ensure repeatability, which can be difficult over four month’s worth of experiments while the equipment is shared with one or two other researchers. While the precursor ratios probably cannot be systematically varied combinatorially (at least in a parallel sample growth scheme), the filament temperatures can. It is theoretically possible to vary all the temperatures simultaneously, thus depositing the groups of samples indicated by the dotted lines in one deposition experiment. The application of combinatorial techniques can also reduce experiment-to-experiment variation, as fewer experiments results in less variability. The time saved could effectively be used to examine more of the parameter space, such as the effect of pressure and substrate temperature, or move on to application work if the optimization goals have been satisfied.

The application of combinatorial techniques to materials discovery has lagged behind its use in other fields, such as pharmaceuticals, but work in the area is increasing as evidenced by the establishment of NIST’s Combinatorial Methods Center in January 2002 as part of the polymers division. There are many examples of the ways the combinatorial experimentation concept has been successfully applied, but only a small sample will be presented here, after a short general description of combinatorial research strategies.

There are three essential components that must be in place for large scale combinatorial methods to succeed. The materials to be tested should be rapidly produced, either individually in parallel or as part of a continuous gradient. The capability for rapid, preferably parallel, testing of the properties of interest should be in place. Finally, an efficient database system is needed for recording the data gained and
making it readily available to interested parties. Having one or two of these components while disregarding the third simply shifts the discovery bottleneck around while only marginally increasing the pace of discovery. Setting up a new combinatorial discovery system with all three components is very expensive, well out of the reach of most small scale research labs. However, while because of this limitation combinatorial methods are currently applied mainly in industrial settings, they hold promise for individual research groups as well. Often, in a small research lab setting, synthesis of samples covering a range of variables is the bottleneck, and speeding this step of the process can provide large gains, without necessarily having to upgrade testing equipment and data handling as well. This will be shown after a short review of the history of combinatorial materials experimentation and current combinatorial materials discovery strategies.

Hanak\(^9\) was one of the first to propose and synthesize a combinatorial library in 1970. He used a system for sputtering binary and ternary targets to produce compositional gradient thin film libraries, and subsequently tested each substrate along its compositional axis for the desired property, electrical resistance. The strategy of using the line-of-site property of physical deposition processes for the production of compositional gradient libraries has since become common\(^{10-12}\). The low availability of automation and computer equipment hindered the further development of Hanak’s ideas for some time. Also, co-sputtering is realistically limited by the number of elements and spread of composition that can be simultaneously tested.

The limitations of Hanak’s sputtering technique eventually gave rise to solution techniques\(^{10-12}\) in which an essentially unlimited number of elements or polymeric components can be combined. The use of micropipetting robots means that large
numbers of samples can be synthesized in parallel. A possible issue with these methods is that often the final product will not be synthesized in a similar fashion, and the synthetic method can have a large bearing on the final properties, particularly in the case of catalysis research. While the automatic synthesis of libraries using solution techniques is fascinating, the proposed work will be fundamentally different, and so these techniques will not be examined further here.

More closely related to this work are recent attempts to effectively combine combinatorial methods with chemical vapor deposition (CVD) thin film synthetic techniques. This is desirable because CVD is widely used in various industries, and as mentioned above, it is best to use the same synthetic technique in materials research as that which will be used to make the final product. However, there are issues inherent in using CVD to produce combinatorial sample libraries in parallel. Since CVD generally is not a line-of-site deposition process, it will be difficult to produce compositional gradient films by CVD (although one example below does just that). Many of the important factors in CVD processing, such as precursor flows and pressure, can not be varied in parallel without multiple reaction chambers, an expensive prospect.

There have been three strategies employed to apply combinatorial techniques to research on CD systems: sequential deposition of discreet samples through a physical mask \cite{1,13-15}, compositional spreads \cite{5,6} using a method somewhat analogous to the above outlined PVD technique, and varying substrate conditions \cite{2,3,16}.

Physical masking techniques have been used to deposit discreet samples sequentially on one substrate \cite{1,13-15}, (Figure 1-2a) saving the time required for loading and unloading the substrate. In particular the authors are interested in amorphous silicon,
which is highly sensitive to the deposition conditions. An advantage of this technique is that several processing conditions can be tested on one substrate, for instance, steadily increasing the pressure for each sample, which would be difficult otherwise.

Additionally, a moving shutter (Figure 1-2b) has been used in conjunction with the mask to produce a series of film thickness gradient samples at varying deposition conditions. This provides a ready method for examining the affect of film thickness on final properties. The authors also point out the usefulness of the physical masking system for testing the films in a device-like system. The moving shutter can be used to deposit films of varying thickness at different deposition conditions, and then overlay, on the other axis, another ten films. In this way many “devices” of multiple layers can be rapidly produced and film performance can be tested in a more directly in a device-like setting.

![Image: Schematic of a system for deposition of thickness gradient films.](image)

Figure 1-2. Images from Wang  
(a) Library of 16 discreet samples deposited serially using a mask, each spot at different conditions.  
(b) Schematic of a system for deposition of thickness gradient films. Each strip is deposited at different conditions.

Similar work on combinatorial deposition of amorphous silicon thin film transistors  is included but not described for brevity.

The deposition kinetics and fluid dynamics of CVD have been utilized to make ternary metal oxide compositional spread films for study as high k dielectric materials.
By placing the inlet for the reactants directly over the heated substrate, the deposition is highly non-uniform in a circular pattern around the inlet (See Figure 1-3a for a schematic of the reactor). Spacing three separate inlets, each with a separate precursor, results in a ternary compositional spread, as measured by XPS, an example of which is shown in Figure 1-3b, with confirmation by RBS. The film thickness is also highly non-uniform using this method. In this case, the parameter of interest, effective dielectric constant, is automatically corrected for the different thicknesses at each point. However, the variation in growth rate across the substrate is not an ideal situation for testing other properties, such as adhesion, roughness or conformality. They were able to map the dielectric constant in the same manner the composition was mapped, and therefore find the best composition. The best compositions found by the combinatorial method were then deposited, tested, and confirmed as a single uniform film. This combinatorial
method is similar in technique to the ternary sputtering strategy described above, in the sense that physical spacing determines film composition.

Carbon nanotube (CNT) growth is highly dependent on the substrate catalyst utilized. While technically catalyst research, the work here uses a combinatorial surface treatment scheme with CVD\(^2\) for testing the catalyst, and so is of interest here. Figure 1-4 shows the combinatorial placement of catalyst material along one axis and concentration of an additive along another. The SEM shows clearly which combination of factors gives the desired growth characteristics. The authors also employ a useful strategy wherein a series of combinatorial libraries are fabricated, first a wide parameter discovery library, followed by more focused libraries to pinpoint the optimal catalyst composition.

![Figure 1-4. Image from Cassell et al. 2 Combinatorial testing of carbon nanotube growth catalysts, simultaneously testing both surface directing agent (SDA) concentration and catalyst composition.](image)

Finally, in the work with the most relevance to the proposed work, individually programmed microhotplates are used to vary the deposition temperature systematically\(^3\).
The microstructure of deposited titanium dioxide was examined over a wide range of deposition temperatures. In addition, the temperature programming and rapid heating/cooling of such devices meant the authors could ramp or pulse the devices between two temperatures and examine how this affected the microstructure. This work is similar to the proposed in the sense that the deposition temperature is the key variable, and that the molecular and microstructure structure will be key properties, as described below. SEM images of the microstructure obtained at a range of temperatures are shown in Figure 1-5. The obvious drawbacks to the technique include the somewhat arduous fabrication of the microhotplates and limitations on the substrate materials. An advantage is that the microhotplates with such films on top are investigated for sensing applications, and, as before, it is always an advantage to fabricate the films in the same manner as the hoped-for final application.

Figure 1-5. Images from Semancik et al.\textsuperscript{3}. TiO\textsubscript{2} films simultaneously grown by CVD on an array of microhotplates, each image is of a film grown at the indicated temperature.

The value of applying the combinatorial work to monomers which have not previously been deposited by iCVD is to quickly identify the successful process window for deposition and the associated kinetics. In this paper, the results of the combinatorial depositions will be compared to the results of traditional blanket iCVD films to verify if the same chemical structure, growth rate, and other film properties are obtained.
1.2 Antimicrobial Technologies

There is large and growing interest in making a wide variety of materials and surfaces antimicrobial. Textiles and other materials present in a hospital setting have been shown to be sufficient bacterial supports\textsuperscript{17} raising the possibility that these materials could be responsible for disease transfer among hospital populations, a common occurrence.\textsuperscript{18,19} Thus, it may be possible to reduce infection rates by adding antimicrobial agents to textiles and other surfaces. There has been and continues to be a considerable amount of research into making fabrics antimicrobial to address this and other issues.\textsuperscript{20-29} For instance, self-sterilizing fabrics are also under study for biowarfare protection.\textsuperscript{29} In addition to fabrics, antimicrobial surfaces are of interest for medical devices\textsuperscript{30-39} particularly to combat the insidious problem of biofilm formation,\textsuperscript{40} and for reduction of biofouling in water handling systems,\textsuperscript{41,42} among other areas.

A wide range of antimicrobial agents have been added to surfaces: antiseptics and antibiotics including chlorhexidine, rifampin and monocyline and others,\textsuperscript{30-33,35-37,41,43,44} silver/silver ions/silver compounds,\textsuperscript{20,27,28,31,34,36,45} hydantoin (also known as halamine) compounds,\textsuperscript{21,26,29,46,47} furanone compounds,\textsuperscript{38,39,48} and quaternary ammonium\textsuperscript{22-25,28,42,49-55} or phosphonium polymers\textsuperscript{28,56}. There have been a smaller number of non-permanently cationic antimicrobial polymeric materials prepared for use on surfaces, generally incorporating benzoic acid derivatives\textsuperscript{57,58}. While a large number of other antimicrobial agents have been prepared for use in solution, these are beyond the scope of this work, except Gellman et al\textsuperscript{59} in which the polymer described within has been used here to provide antimicrobial protection to surfaces.
The various agents are most often physically applied to the surface,20,27,30,45 physically impregnated into the bulk of the material,31,33,35,36,44 or physically incorporated into a coating that is then applied to the surface for release.32,34 In all these approaches the antimicrobial agent leaches from the surface, leading to two key problems: a limited time of effectiveness and environmental, health and safety concerns, such as the promotion of drug resistant microbes. Non-leaching antimicrobial surfaces have been created by covalently grafting an antimicrobial polymer to the surface,21-26,28,29,42,46,47,49-53 including atom transfer radical polymerization of an antimicrobial polymer directly from an initiating surface,55 and covalent attachment of an agent to a polymer chain.38,39,41,43,58 In the later case any attachment scheme must not obscure the active moiety of the molecule.

Antiseptics and antibiotics have generally been employed for medical applications.30-33,35-37 Central venous catheters have been both impregnated with chlorhexidine and a silver compound31 and coated with rifampin/minocycline on the exterior and intraluminal surfaces30,60 to successfully reduce the rate of catheter-related blood stream infections. Each case uses two active agents in an attempt to reduce the promotion of resistant bacteria. These approaches have been successfully commercialized and are now recommended for use in certain situations,37 and have lead to significant reductions in mortality and healthcare costs in some hospitals.31,60 There are concerns about the emergence of drug resistant bacteria,61 (although this is still under study for the specific case of impregnated catheters33) and cases of anaphylactic shock reaction to chlorhexidine impregnated catheters have been reported.62 Some in the medical profession are uneasy about employing a leaching strategy in medical devices
wherein active agents are released into a compromised patient. In such cases, native and beneficial bacteria populations (i.e. E. coli in the intestines) may be reduced, allowing pathogenic species to gain a foothold in the patient, among other side effects. In addition to central venous catheters, the use of antibiotics has also been explored in such various devices as a coating on wires and pins, impregnated in endotracheal tubes, and slow release from periodontal implants. In addition to medical devices, antibiotics have been covalently bound to a polymer backbone for use in a biosensor and water systems. In theory, covalently bound antibiotics would never be released, and so should not promote resistant bacteria. However, it is not yet clear what affect, if any, covalently bound antibiotics may have on the promotion of drug resistant bacteria.

The new antimicrobial polymer coatings under study here are non-leaching. Thus, they would not have a diminished effectiveness over time, greatly reduced incidence of systemic side effects, and, most significantly, it is currently thought that bacteria probably will not develop resistance to antimicrobial polymers although this needs to be shown for the new polymers under study here.

Silver, silver ions, and silver compounds have been used for a somewhat more varied range of applications. Medical devices impregnated with both an antibiotic and a silver compound were discussed above. In addition, urinary catheters with a silver alloy/hydrogel coating have also been examined. Various vapor deposition methods have been employed to coat fabric and polymer/metal surfaces with silver. No matter how the silver component is incorporated it can only work as a leaching agent because it only kills the cells after being taken up by the bacterium. Hence, any system utilizing silver will have a diminished effectiveness over time. The length of
effectiveness can be increased by incorporating more silver, but at some point this becomes untenable. In addition, patient sensitivity to silver compounds and coatings has been reported.\textsuperscript{63-65} In one case the patient showed no allergic reaction to topical application of silver ions yet had a strong adverse reaction to internal use of a device coated with silver.\textsuperscript{65} Finally, some researchers have found bacterial populations that have developed resistance to silver, similar antibiotic resistance.\textsuperscript{66,67}

Various hydantoin compounds have been successfully incorporated as polymer pendant groups or grafted to fabrics to impart antimicrobial action. Sun et al. have created a variety of hydantoin moieties and both incorporated them into polymer beads\textsuperscript{47} for water purification applications and grafted them onto various textiles\textsuperscript{21,26} to provide enhanced protection against bacteria. Worley et al. also created polymer beads with hydantoin pendant groups for water purification.\textsuperscript{46} The hydantoin moieties are essentially storage compounds for chlorine, which is released to the bacterium to kill it. In addition, the amine-halogen bond is photosensitive.\textsuperscript{29}

Furanones\textsuperscript{38,39} have been incorporated into a polymer matrix and covalently bound to the surface of catheters. These compounds stop the growth of biofilms, a major route to bacterial toxicity attributed to biomaterials,\textsuperscript{40} by interrupting cell to cell communication.\textsuperscript{48} The coating reduced bacterial adhesion to the coated catheters and reduced level of infection at the implant site in an animal model trial.\textsuperscript{38}

Numerous quaternary ammonium, and to a lesser extent phosphonium, compounds and polymers have been shown to be effective antimicrobial agents. All these polymers are permanently cationic. This work will mainly be concerned with quaternary ammonium polymers used on solid surfaces. Klibanov et al. covalently bound
quaternary amine polymers, for instance poly(4-vinyl-N-alklypyridinium bromide) and N-alkyl-poly(ethyleneimine), to nonporous substrates and textiles by various methods for a range of potential applications. Polyquaternary amines have also been grafted to water filtration membranes for use in biofouling applications grown by atom transfer radical polymerization from a fabric surface and condensation of siloxyl compounds with an attached quaternary amine moiety. Several other quaternary ammonium and phosphonium polymers are described in a recent review.

A few antimicrobial polymers that do not contain quaternary amine or phosphine moieties have been synthesized. These have incorporated pendant groups of benzoic acid derivatives attached to a polymer backbone or benzoic acid in the backbone of a polyimide coating. In the former case the goal was to make a bulk antimicrobial polymer for use in biomedical applications instead of a surface coating. The later case has the most relevance to this work as the polyimide coating was formed by a solventless vapor deposition process, as were the polymers examined in this work. However, the process developed by Irikura et al. requires that the substrate withstand high temperatures, ~200°C. The process developed for the current work is capable of coating fragile heat-sensitive substrates as the substrate will be near room temperature at all times.

Gellman et al. developed an antimicrobial polymer that is not permanently cationic, in contrast to the quaternary ammonium polymers described above. Instead, the amino moiety has a conjugate acid of pKa of ~9, and so the nitrogen atom is protonated to a significant extent at physiological conditions, resulting in a cationic polymer. However, the antimicrobial testing was carried out in solution and it was not
apparent the same antimicrobial properties would hold true for the polymer applied to a
surface. This study examines a polymer formed from the same monomer, but instead
using an all-dry vapor deposition process.

Hot-filament CVD (HFCVD) has been used to deposit diamond\textsuperscript{68}, amorphous
silicon\textsuperscript{69}, and polymer thin films\textsuperscript{70}. Initiated chemical vapor deposition (iCVD) is a
subset of HFCVD in which a free radical initiator species is used to decrease the filament
temperature and substantially enhance the deposition rate\textsuperscript{4,71-74}. The iCVD method has
been previously used to deposit a range of functional polymers, including
poly(tetrafluorethylene)\textsuperscript{71}, poly(fluorocarbonsiloxane)\textsuperscript{72}, and a variety of methacrylate
polymers including poly(methyl methacrylate)\textsuperscript{73}, poly(hydroxyethyl methacrylate)\textsuperscript{75},
poly(glycidyl methacrylate)\textsuperscript{4}, poly(perfluoralkylethyl methacrylate)\textsuperscript{74}. Deposition from
the vapor phase results in conformal coatings and requires no solvent use, advantages for
coating complex and/or solvent-sensitive substrates. ICVD of coatings onto medical
devices completely avoids the use of solvents, the entrainment of which has been
identified as a leading cause of medical device failures [Bhat-Biomaterials]. Though this
work used fabric as a convenient deposition substrate, the coating could be easily
extended to medical devices.

1.3 Grafting Chemical Vapor Deposition

Type-II photoinitiators are widely-used for grafting polymer chains to surfaces.\textsuperscript{76-79} They work by abstracting labile hydrogen atoms from other molecules to create
radicals. Benzophenone (BP) is one of such initiators and is able to abstract hydrogen
atoms when excited photochemically. As shown in Fig. 1-6, BP, under UV irradiation, is
excited to a singlet state ($S_1$) and then converted to a triplet state ($T_1$) by intersystem crossing (ISC). ISC progresses efficiently for BP due to the closeness of the energy levels of the $S_1$ and the $T_1$ states and occurs within a fraction of a second. The resulting $T_1$ state is long-lived, so there is ample time for the molecule to collide with and abstract a hydrogen atom from a donor molecule. This abstraction event leads to the production of two radicals, the benzohydrophenone radical and the donor radical, denoted $R\cdot$ in Fig. 1-6. While both of these radicals can initiate polymerization, the donor radical is more efficient because it is less sterically hindered. In addition, the benzohydrophenone radical is less reactive because of the stabilizing effect of the two phenyl rings.

Figure 1-6. Hydrogen abstraction by benzophenone through photochemical excitation

Grafting occurs when the donor molecule is part of a surface. When a hydrogen atom is abstracted from the surface, the resulting radical can initiate polymerization, leading to a covalently-attached polymer chain. Many chains will be grafted when a number of hydrogen atoms are abstracted from the surface. This grafting of chains onto the surface effectively creates a polymer film that is chemically bonded to the underlying material. Although grafted, the polymer layer has similar properties as a non-grafted thin film of the same material. At the same time, the chemical bonding between the two layers of materials offers many advantages. First, the grafted layer is resistant to abrasion. A covalent bond would have to be broken for a chain to be removed from the surface. Second, the grafted polymer is stable against virtually any solvent, provided that
the solvent does not dissolve the underlying layer or cause bond-breaking reaction(s).
This stability allows the surface to be used in solvents that would otherwise dissolve the bulk polymer.

Grafting using BP has been investigated by a number of researchers. The methods can be divided into three main categories shown in Table 1. The most prominent is the all-solution-phase technique—both BP and the monomer are dissolved in a solution in which the surface to be grafted is immersed. This can also be performed by dipping the substrate in solutions of each material sequentially. On the other hand, a BP-pretreated surface can be exposed to vaporized monomer to effect grafting. This pretreatment can be wet or dry. In the wet case, BP is dissolved in a solution (typically acetone) and cast onto the surface to be grafted. The surface is then dried to remove the solvent, leaving behind BP. The all-dry method exposes the to-be-grafted surface to BP vapor, and the surface uptakes BP during the exposure. Although different, these three categories use the same Type-II behavior of BP under UV irradiation—it abstracts labile hydrogen atoms from the surface to create chain-initiating radicals.

<table>
<thead>
<tr>
<th>Technique</th>
<th>Benzophenone delivery</th>
<th>Monomer delivery</th>
</tr>
</thead>
<tbody>
<tr>
<td>Wet</td>
<td>Solution-phase</td>
<td>Solution-phase</td>
</tr>
<tr>
<td>Semi-dry</td>
<td>Solution-phase</td>
<td>Vapor-phase</td>
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<tr>
<td>All-dry</td>
<td>Vapor-phase</td>
<td>Vapor-phase</td>
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As with thin-film deposition, dry techniques such as chemical vapor deposition (CVD) are becoming increasingly prevalent due to their environmental benefits. The success of all-dry CVD has been demonstrated by methods such as plasma-enhanced CVD (PECVD), hot-filament CVD (HFCVD), and initiated CVD (iCVD). A wide variety of polymeric and organosilicon materials have been made using these methods. iCVD, unlike PECVD and HFCVD, uses initiators to accelerate film growth and allow control of molecular weight and morphology, yet linear, well-defined chemical structures are produced. CVD is able to produce films of nanoscale thickness with macroscale uniformity on complex geometries. The dryness of the process avoids the wetting and surface-tension effects associated with wet techniques, so surfaces with nano- or microscale topography can be coated uniformly. The added benefits of grafting motivate the investigation of an iCVD-like grafting process. The envisioned scheme combines the benefits of iCVD and grafting by exposing surfaces to vapors of a Type-II photoinitiator, such as BP, and a monomer in a continuous or a semi-batch manner. Although all-dry vapor-phase photografting has been examined, there have been few if any reports of one-step CVD-like grafting processes. The goal of this portion of the thesis is to use an existing CVD chamber to perform solventless grafting, hereby referred to as grafting CVD (gCVD).

1.4 Scope of Thesis

Chapter Two reports a combinatorial approach to iCVD. A five fold increase in research efficiency has been realized by simultaneously depositing films at five filament temperatures. The system was validated for use with both an acrylic and styrenic
monomer by comparing chemical structure, growth rates, and molecular weights with films deposited at the same conditions in a conventional reactor.

**Chapter Three** describes the use of the styrenic polymer characterized in Chapter Two for antimicrobial coating of finished textile substrates. The coatings were highly effective, killing about 6 log of both gram-negative and gram-positive bacteria.

**Chapter Four** examines a new method for covalently bonding polymer films deposited from the vapor phase known as grafting CVD, or gCVD. The new technique was used to deposit more durable antimicrobial coatings.

Appendices A, B, and C describe three additional projects, unrelated to antimicrobial coatings, which are through the proof-of-concept stage and show promise for future work. These are iCVD of organic high-κ dielectric films, grafted superhydrophilic coatings and microfluidic channel coating.

Chapter Two through Four are structured as journal articles, and can thus be read as a self-contained work containing an abstract, introduction, experimental details, results and discussion, and relevant references. The Thesis concludes with a summary of work and suggestions for future work. Finally, the authors would like to thank the Institute for Soldier Nanotechnologies for funding.

### 1.5 References


Chapter Two

Combinatorial Initiated Chemical Vapor Deposition for Polymeric Thin Films*

*Originally published as Martin, T. P. and Gleason, K. K., Chemical Vapor Deposition, 2006, 12, 685-691
2.1 Abstract

A new combinatorial initiated chemical vapor deposition (iCVD) system was fabricated and used to efficiently determine the deposition kinetics for two new polymeric thin films, poly(diethylaminoethylacrylate) (PDEAEA) and poly(dimethylaminomethylstyrene) (PDMAMS). The results of combinatorial depositions were compared to blanket iCVD depositions at identical conditions using the appropriate vinyl monomer with tert-amylperoxide as the initiator. Fourier transform infrared spectroscopy (FTIR) reveals similar chemical structure in blanket and combinatorial films. FTIR also show that functional groups are retained in iCVD of PDMAMS, whereas essentially all fine chemical structure of the material is destroyed in plasma-enhanced CVD. The maximum observed growth rate of PDEAEA and PDMAMS was 43 and 11 nm/min respectively. The activation energy of growth with respect to, filament temperature \((E_{a,filament})\) was 88.4±1.6 kJ/mol for PDEAEA and 42.0±1.7 kJ/mol for PDMAMS. Activation energies for growth with respect to substrate temperature \((E_{a,substrate})\) were -59.5±2.7 kJ/mol for PDEAEA and -82.7±2.6 kJ/mol for PDMAMS, with the negative values consistent with adsorption limited kinetics. The molecular weight of PDEAEA films ranged from 1 to 182 kDa as a function of substrate temperature. It was found that the combinatorial system in all cases provided agreement, within experimental certainty, with results of blanket iCVD depositions, thus validating the use of the combinatorial system for future iCVD studies.
2.2 Introduction

Hanak\(^1\) was one of the first to propose and synthesize a combinatorial materials library in 1970. A system for sputtering binary and ternary targets was used to produce compositional gradient thin film libraries, and the strategy of using the line-of-site property of physical vapor deposition (PVD) processes for the production of compositional gradient libraries has since become common.\(^2-4\) Since that time, techniques for rapidly examining large numbers of discreet compositions have become widely used,\(^2-4\) for instance in the study of catalyst materials.\(^5\) However, in these combinatorial studies, the synthesis method differs substantially from that employed in manufacture. A closer match between research and potential production processes is desired.

Several strategies have been applied to CVD research. Sequential deposition of discreet samples through a physical mask/manipulation of the substrate\(^6-10\) provides some gain in research efficiency. Parallel depositions provide larger gains in research efficiency and have been reported for compositional spreads using a method analogous to Hanak's PVD technique.\(^11-13\) Parallel depositions have also been reported where substrate temperature has been discreetly\(^14-16\) or continuously\(^17\) varied, and for varying gas-phase reactant concentrations.\(^18\)

Hot-filament CVD (HFCVD) has been used to deposit diamond,\(^19\) amorphous silicon,\(^20\) and polymer thin films.\(^21\) Initiated chemical vapor deposition (iCVD) is a subset of HFCVD in which a free radical initiator species is used to decrease the filament temperature and substantially enhance the deposition rate.\(^22-26\) The iCVD method has been previously used to deposit a range of functional polymers, including
poly(tetrafluorethylene),\textsuperscript{22} poly(fluorocarbonsiloxane),\textsuperscript{23} and a variety of methacrylate polymers including poly(methyl methacrylate),\textsuperscript{24} poly(hydroxyethyl methacrylate),\textsuperscript{27} poly(glycidyl methacrylate),\textsuperscript{25} and poly(perfluoralkylethyl methacrylate).\textsuperscript{26} Deposition from the vapor phase results in conformal coatings and requires no solvent use, advantages for coating complex and/or solvent-sensitive substrates and for biomedical applications.

Antimicrobial polymers have received recent attention for their potential in providing a permanently active surface with the promise of possibly avoiding the development of resistant bacteria strains.\textsuperscript{28} The majority of the work in the area has involved traditional wet chemical synthesis of permanently-cationic quaternary ammonium or phosphonium groups. However, Gelman et al.\textsuperscript{29} have shown strong antimicrobial activity of a polymer containing a tertiary amino group with a conjugate acid having a high $pK_a$. The deposition of similar polymers using a new combinatorial iCVD system will be the focus of the current paper. Subsequent publications will present results of antimicrobial testing of the iCVD polymeric thin films.

The two monomers used in the current work, diethylaminoethyl acrylate (DEAE) and dimethylaminomethyl styrene (DMAMS), both contain tertiary amino groups with conjugate acids of high $pK_a$ (estimated at near 8.0 and 8.5 respectively) and hence are potential candidates to deposit antimicrobial coatings. The first monomer, an acrylate, is anticipated to have some similarities in process to previously reported iCVD methacrylates. Deposition of the second monomer holds additional interest, since to the authors’ knowledge iCVD deposition of a styrenic monomer has not previously been reported. Behbahani and Inoue\textsuperscript{30} may have been the first to form thin film coatings of a
polystyrene from the gas phase. They first applied a free radical initiator to the substrate surface from solution, then simultaneously raised the temperature of the substrate and exposed it to styrene vapor. Subsequent work using very similar methods has achieved higher growth rates. In the current work, both the initiator and monomer are delivered through the gas phase.

The value of applying the combinatorial work to monomers which have not previously been deposited by iCVD is to quickly identify the successful process window for deposition and the associated kinetics. In this paper, the results of the combinatorial depositions will be compared to the results of traditional blanket iCVD films to verify if the same chemical structure, growth rate, and other film properties are obtained.

2.3 Experimental

Blanket iCVD depositions occurred in a custom built low pressure reactor (Sharon Vacuum) with a radius of 12 cm and height of 3.3 cm, and a top consisting of a quartz plate, which allowed laser interferometry and visual inspection of the system. A filament array provided the thermal energy for reaction and consisted of 0.5 mm diameter tungsten wire (Goodfellow) resistively heated with a DC power source (Sorensen DHP 300-10) to the desired temperature within the range from 473-604 K. The filaments were spaced 20 mm apart and suspended 12 mm above the substrate surface. Further details are available. The filament temperature was measured with a type K thermocouple (Omega Engineering) attached to a filament in the center of the array directly over the substrate. 100 mm diameter, 0.5 mm thick FTIR transparent silicon wafers were used as the substrate for all depositions. The substrate temperature was controlled to 303-338 K.
Figure 2-1. Chemical reactants for combinatorial iCVD: a. DMAMS monomer (para- isomer shown, both ortho- and para- isomers utilized) b. DEAEA monomer c. TAP initiator

Figure 2-2. Schematic of combinatorial initiated chemical vapor deposition system. Partial top-down view showing gas inlet and distribution using a perforated baffle plate. Filament temperature zones are shown, and each filament is marked with the corresponding temperature.
by backside cooling of the stage with a recirculating chiller/heater (Neslab CFT-33). At constant pressure, the substrate temperature is a function of chiller setting and filament temperature; the substrate temperature was calibrated and confirmed to be constant across the wafer under real combinatorial or blanket deposition using a silicon wafer embedded with a grid of nine thermocouples (Thermodynamic Sensors). The pressure was maintained at 200 mTorr using a throttling butterfly valve (MKS Instruments 253B).

Combinatorial iCVD experiments were carried out in the same vacuum chamber using the same filament spacing and height. (See Figure 2-2 for schematic). A separate DC power supply (Sorensen 30-10) was used to control the temperature of each filament section. The same filaments and power settings were used for all combinatorial depositions. The five filament sections were at 473K, 493K, 518K, 562K and 604K, with the lowest temperature nearest the reactor inlet and the highest near the outlet. The hottest and coldest filament sections are extended past the ends of the substrate to provide pre-heating and post-heating zones, as shown in Figure 2-2. The pre-heat zone stops the monomer from condensing prior to reaching the substrate, which is placed in the center of the reactor. The post-heat zone avoids a rapid temperature decrease, and thus deposition rate decrease, at the trailing edge of the substrate. The substrate temperature was controlled and calibrated in the same manner as described for blanket depositions. Note that no temperature gradient was measured in the silicon substrate, despite the filament temperature gradient. This observation is constant with the high thermal conductivity of the silicon wafer (148 W/m/K).

The monomer (dimethylaminomethyl)styrene (DMAMS), consisting of 50/50 ortho- and para- isomers, was purchased from MP-Dajac Laboratories at 95% purity and
vacuum purified before use to remove volatile organic contaminants. The monomer
diethylaminoethy)acrylate (DEAEA) was purchased from Aldrich at 95% purity and
vacuum purified at room temperature in the same manner before use. The initiator di-
tert-amylperoxide (TAP) was purchased from Aldrich and used without further
purification. Figure 2-1 shows the chemical structure of the three reactants. DMAMS
and DEAEA were vaporized at 343K and 333K respectively and were metered through a
mass flow controller (MKS 1153). The flow rate of the monomer was 2.4 SCCM. TAP
was vaporized at room temperature and metered through a mass flow controller (MKS
1479A) at a rate of 0.6 SCCM. The monomer and initiator streams were joined before
entering the reactor.

Variable angle ellipsometric spectroscopy (VASE, M-2000, J. A. Woollam) was
employed as a non-destructive manner of determining film thickness, refractive index,
and absorbance. The VASE system was equipped with focusing optics to reduce the spot
size of the measurement to approx 0.5mm x 2mm. The exact spot size is dependent on
the measurement angle. The focusing optics were necessary to avoid “crosstalk” between
different regions on the combinatorial gradient films. A xenon light source was used at
225 wavelengths between 315-800 nm. A Cauchy-Urbach isotropic model for index of
refraction (n) and extinction coefficient (k) was used to fit the ellipsometric angles Δ and
Ψ. WVASE32 software from JA Woollam was used to perform regressions to the
ellipsometric data. The model consisted of four layers: air/Cauchy-Urbach/1.7 nm native
SiO₂/Si substrate. For all film characterization, ellipsometric data was taken at three
angles, 65°, 70°, and 75°, at the center of the wafer and regressed to determine n and k.
The angle was then set at 70° and ellipsometric data was taken across the whole wafer.
using an automated mapping stage in conjunction with VASE Manager software, both from JA Woollam. The material properties determined at the center point were used as initial guess values to rapidly fit the thickness, index of refraction and extinction coefficient at each of up to 73 points across the wafer. The minimum thickness is observed for the region of the wafer near the gas inlet of the reactor, as this is the lowest $T_F$ region, and increases up to a maximum thickness directly under the highest $T_F$ region.

For combinatorial depositions, growth rates were determined by averaging the thickness directly under the length of the filament at the temperature of interest. The error bars include the non-uniformity in thickness under the filament of interest as well as the error in measuring the thickness. The growth rate reported for blanket depositions is the average rate across the entire wafer, and the error bars contain information about the non-uniformity across the wafer as well as the measurement error.

Fourier transform infrared spectroscopy (FTIR) was performed on Nicolet Nexus 870 ESP was used in transmission mode with a DTGS detector. The use of infrared-transparent silicon wafers allowed the direct transmission mode examination of the films while on the substrate, and thus is non-destructive. All spectra were baseline corrected and normalized to film thickness as measured by VASE. For structure comparison, a poly(DMAMS) commercial polymer was purchased from MP-Dajac.

PDEAEA films were dissolved in tetrahydrofuran (THF) for GPC measurements. Combinatorial library wafers were split into five sections prior to dissolution. Each section was centered on the corresponding filament and 20 mm wide at the center point. The GPC system was comprised of a Waters 1515 isocratic high-performance liquid chromatography (HPLC) pump, a Waters 2414 refractive index detector, and two
Styragel® HR 4 7.8 x 300 mm columns. Poly(methyl methacrylate) (PMMA) standards (Polymer Laboratories) dissolved in THF were used for calibration at 35°C.

Pulsed plasma deposition of DMAMS occurred in a separate reactor described previously. The same substrate, monomer vaporization temperature, monomer flow rate, and reactor pressure were used as for the iCVD depositions described above. The peak power was set at 100 W. A square wave pulse generator was used to modulate the plasma corresponding to on times of 10 ms and off times of 90 ms for a 10% duty cycle. These are the same parameters previously used for the successful pulsed plasma CVD deposition of poly(methyl methacrylate).

2.4 Results and Discussion

2.4.1 Acrylate monomer: diethylaminoethyl acrylate (DEEA EA)

Figure 2-3 compares the FTIR spectra of DEEA EA monomer with those of the blanket and combinatorially deposited iCVD polymer films deposited at the same conditions: T_r=604 K and T_s=303 K. The vinyl peaks at 810, 985, 1410 and 1635 cm⁻¹ are present only in the spectrum of the monomer, confirming the vinyl polymerization of DEEA EA. Additionally, the peaks assigned to the carbonyl (1735 cm⁻¹) and tertiary amino (2700-2850 cm⁻¹) present in all the spectra confirming the retention of pendent groups during the polymerization. The spectrum of the combinatorial iCVD film is essentially identical to that of the iCVD film deposited in the blanket system.

Figure 2-4 shows deposition rate for iCVD PDEEA EA deposition in the combinatorial system at three substrate temperatures, requiring three experiments. These represent a total of fifteen data points, which would have required fifteen separate experiments in the blanket system. Thus, the new combinatorial iCVD system resulted in
Figure 2-3. FTIR spectra of a) DEAEA monomer with b) blanket-deposited PDEAEA and c) combinatorially-deposited PDEAEA films prepared at the same conditions (T_{filament} = 604 K, T_{substrate} = 303 K).

Figure 2-4. Combinatorial and blanket growth rate chart for PDEAEA. Temperature of the substrate indicated by symbols: 321 K (▲), 312 K (●), and 303 K (■) combinatorial data; all five points at each substrate temperature were obtained simultaneously. Data for blanket deposition at 303 K (○) also shown. Lines indicate the slope for the three lower filament temperatures, which were used to determine the apparent activation energies shown in Table 2-1; solid lines represent combinatorial data and the dotted line is for two blanket depositions. The slopes for the three combinatorial depositions match within experimental certainty with the slope for the blanket depositions, though the absolute deposition rate is 20% lower at the fastest set of conditions.
a five-fold increase in research efficiency. For comparison, data from five blanket depositions performed at a substrate temperature of 303 K are also shown in Fig 2-4. It is observed that the polymer deposition rate increases as the filament temperature increases. In addition, deposition rate increases as substrate temperature decreases. The highest deposition rate is thus found using the highest filament temperature, 604 K, and lowest substrate temperature, 303 K. These conditions provided a rate of 43 nm/min and 53 nm/min in the combinatorial and the blanket systems respectively. The lines on the chart are linear best fits to 1/(filament temperature) with natural log(deposition rate) to the three data points at filament temperatures of 473 K, 493 K and 518 K. In this range the deposition rate is observed to increase linearly with filament temperature on a log scale, as presented in Figure 2-3. The deposition rate continues to increase at filament temperatures of 562 K and 604 K, but the increase is less than the trend suggested by the three lower filament temperatures.

The primary motivation for the data presented in this paper is to allow comparison of the blanket and combinatorial deposition schemes. Thus, only two mechanistic hypotheses regarding the observed kinetics will be described here, leaving more detailed considerations to a future publication. First, the observed increase in deposition rate with increasing filament temperature is likely the result of increased decomposition of the initiator TAP into radical species on or near the filament resulting in increased flux of these initiating radicals to the substrate surface. Thus, at a given substrate temperature, the growth rate is most likely limited by the flux of initiating radicals to the surface. Second, decreasing substrate temperature is observed to increase growth rate. This is consistent with the hypothesis of additional adsorption of the monomer species as the
surface temperature is reduced. Thus, this may indicate that, at a set filament
temperature, the growth rate is limited by the adsorption of monomer.

The reasons for the relatively small increase in growth rate at filament
temperatures of 562 K and 604 K are not clear. It is possible that the well-known mass-
transfer-limited regime is approached when the concentration of generated radicals
become high at these highest temperatures. Or that there is a lower efficiency of
utilization of the radicals formed at the filaments from decomposition of the initiator
TAP. Finally, a large percentage of the TAP may be decomposed at 518 K, and further
increases in filament temperature may only slightly increase the radical formation rate.
Because of the different behavior of the rates at the highest two temperatures, only the
lower three temperatures will be considered to evaluate apparent activation energy with
respect to the filament.

As in previous iCVD work, two assumptions are made so that the deposition
rate is related to the overall reaction rate constant. The first is that the reaction is zeroth
order in initiator concentration. The second is that the monomer concentration in the
reactor gas phase is constant in space and time. These assumptions allow us to determine
apparent activation energy of growth rate using the slopes determined from an Arrhenius-
style plot (Fig. 2-4). The average apparent activation energy in filament temperature,
abbreviated $E_{a,filaments}$, are 89.5 ± 1.6 and 90.4±1.6 kJ/mol for the combinatorial and
blanket systems, respectively (Table 2-1). Similarly, the average apparent activation
energy in substrate temperature, $E_{a,substrate}$, is determined to be -58.0±2.7 for the
combinatorial system and -64.5±2.7 kJ/mol for the blanket deposition system (Table 2-1).
These are negative because the deposition rate increases as substrate temperature
Table 2-1. Apparent activation energy in filament ($E_{a,\text{filament}}$) and substrate ($E_{a,\text{substrate}}$) temperature for deposition of PDEAEA. Data for both combinatorial and blanket depositions are shown. a. $E_{a,\text{filament}}$ found at three substrate temperatures ($T_{\text{Sub}}$) using the combinatorial system are slightly lower than that found using the blanket system at one substrate temperature. b. $E_{a,\text{substrate}}$ determined at five filament temperatures are slightly lower than that determined by using the blanket system at one filament temperature.

decreases. Therefore, it is found that the results of the combinatorial system are valid for kinetic studies to determine activation energies for iCVD depositions of acrylates; data for deposition of a styrenic polymer is presented below.

The deposited PDEAEA films are highly soluble in THF, indicating that few, if any, crosslinks are formed by the iCVD process. Wafers examined by VASE after soaking in THF all had <1 nm film thickness remaining, so essentially all film is dissolving into THF. There were no visual signs of material suspended in solution. Therefore, there are no indications that only a portion of the films were soluble. The GPC determined number average molecular weight, $M_n$, of the PDEAEA films (Table 2-2) depends strongly on substrate temperature but shows little sensitivity to changes in
Table 2-2. Gel permeation chromatography was performed to determine the molecular weight of the deposited PDEAEA, and PDI is shown in parenthesis. It has been previously shown by Chan et al. that molecular weight is linearly proportional to the surface concentration, which is a function of the substrate temperature. The uncertainty is estimated from experimental and measurement error. It is clear that the combinatorial system provides the same information as if every point was deposited separately using the blanket deposition system.

Films deposited at a substrate temperature of 303 K had an average $M_n$ of 182 ± 11 kDa for the combinatorial films and 189 ± 11 kDa for the blanket films. These molecular weights dropped sharply to near 1 kDa at higher substrate temperatures. Thus, it is likely that a wide range of molecular weights can be achieved by closely controlling the substrate temperature, which is desirable for tailoring of film properties for specific applications.

Both the growth kinetics and film characterization support the similarity between the combinatorial and blanket depositions of PDEAEA. The combinatorial and blanket FTIR spectra show excellent agreement, indicating the chemical structure of the material deposited by the two systems is nearly identical. The combinatorial growth rate averaged
14% lower than the blanket rate for all depositions at the same filament and substrate temperatures, and was 20% lower at the maximum deposition rate conditions of $T_{\text{filament}} = 604 \, \text{K}$ and $T_{\text{substrate}} = 303 \, \text{K}$. However, as can be seen in Figure 2-4, there is significant overlap of error bars, and it can be shown that the combinatorial point is well within the 95% confidence interval of expected deposition rates for the blanket rate point based on the estimate experimental and measurement error. Similarly, the calculated $E_{a,\text{filament}}$ values agree to within 0.9 kJ/mol, or within 1%, and the $E_{a,\text{substrate}}$ values are 6.4 kJ/mol apart, or within 10%. Both systems deposit polymers with high solubility in water and a range of organic solvents, indicating linear or nearly linear material. Finally, GPC results show that the deposited polymers from the combinatorial and blanket processes have essentially the same molecular weight, agreeing to within 6 kDa, or 3%, well within the estimated error of 11 kDa for depositions at $T_{\text{substrate}} = 303 \, \text{K}$. Together, these results show that the combinatorial system provides good agreement with the blanket system for deposition of PDEAEA.

### 2.4.2 Styrenic Monomer: dimethylaminomethyl styrene (DMAMS)

Figure 2-5 compares the FTIR spectra of DMAMS monomer with those of the blanket and combinatorially deposited iCVD polymer films, where both films have been deposited at the same conditions: $T_f = 604 \, \text{K}$ and $T_s = 320 \, \text{K}$. The spectrum for a conventionally polymerized commercial polymer is shown for comparison. Also included is the FTIR spectrum of a pulsed-plasma polymerized film from the DMAMS monomer. The spectra are very complex as the monomer consists of both the ortho- and para- isomers of DMAMS. The peaks chiefly attributed to the vinyl moiety at 900, 1030, 1360 and 1510 cm$^{-1}$ are significantly reduced in the conventional polymer and the two
Figure 2-5. FTIR spectra of a) DMAMS monomer with b) commercially available PDMAMS c) blanket-deposited PDMAMS and d) combinatorially-deposited PDMAMS films prepared at the same conditions ($T_{\text{filament}} = 604 \text{ K}$, $T_{\text{substrate}} = 320 \text{ K}$). e) A film deposited by pulsed-plasma enhanced CVD from DMAMS monomer.

thin film polymer spectra. It is clear the two iCVD polymer films are very similar in structure to each other, as well as the conventionally prepared polymer. The one exception is the peak at $1700 \text{ cm}^{-1}$, attributed to carbonyl moieties resulting from the reaction of unterminated radical chain ends in the film with atmospheric oxygen upon opening the reactor. Also, the peak at $2700 \text{ cm}^{-1}$, attributed to the tertiary amino-methyl C-H moieties, is slightly reduced in the two iCVD films relative to the conventional polymer. Additionally, the deposited polymer films were not soluble in water or any
organic solvents representing the entire range of solubility parameters. This indicates some degree of crosslinking present in the iCVD films. These few differences from the conventionally prepared polymer suggest side reactions in addition to the iCVD vinyl polymerization. However, it is important to note that the two iCVD spectra, combinatorial and blanket, are essentially identical. By comparison, the pulsed-plasma polymerized film has lost essentially all fine structure, indicating the fragility of this monomer. In this case, the iCVD method provides a vapor deposited film likely unattainable by plasma-enhanced CVD techniques.

Figure 2-6 shows the deposition rate for iCVD PDMAMS deposition in the combinatorial system at substrate temperatures of 320 K, 329 K and 338 K. For comparison, data from three blanket depositions performed at a substrate temperature of 320 K are also shown in Fig 2-6. The polymer deposition rate increases as the filament temperature increases and as substrate temperature decreases, as observed for deposition of the acrylate monomer described above. The highest deposition rate is thus found at the highest filament temperature of 604 K and lowest substrate temperature of 320 K. At these conditions, the combinatorial and the blanket systems provided a rate of 10.6 nm/min and 11.7 nm/min, respectively. The lines on the chart are linear best fits to $1/(\text{filament temperature})$ with natural log($\text{deposition rate}$) to the three data points at filament temperatures of 473 K, 493 K and 518 K. In this range the deposition rate is observed to increase linearly with filament temperature on a log scale, as presented in Figure 2-6. The deposition rate continues to increase at filament temperatures of 562 K and 604 K, but as with the acrylate deposition, the increase is less than the trend suggested by the three lower filament temperatures.
Figure 2-6. Combinatorial and blanket growth rate chart for PDMAMS. Temperature of the substrate indicated by symbols: 320 K (△), 329 K (●), and 338 K (■) combinatorial data; all five points at each substrate temperature were obtained simultaneously. Data for blanket deposition at 320 K (○) also shown. Lines indicate the slope for the three lower filament temperatures, which were used to determine the apparent activation energies shown in Table 3; solid lines represent combinatorial data and the dotted line is for two blanket depositions.

The same assumptions employed for Fig. 2-4, allow determination of the overall apparent activation energy in filament temperature, presented in Table 2-3. It is found that the deposition rate is again slightly lower using the combinatorial system than using the blanket system. However, as found for deposition of the acrylate, $E_{a,\text{filament}}$ found using the combinatorial and blanket systems to deposit PDMAMS, 40.2 ± 1.7 kJ/mol and 39.7 ± 1.7 kJ/mol respectively, match closely. Similarly, $E_{a,\text{substrate}}$, is determined to be -80.3 ± 2.6 kJ/mol for the combinatorial system and -82.7 ± 2.6 kJ/mol for the blanket deposition system. As above, it is found that the results of the combinatorial system are valid for kinetic studies to determine activation energies for iCVD depositions of styrenic polymers.
<table>
<thead>
<tr>
<th>$T_{Sub}$</th>
<th>$E_{a,filament}$</th>
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<tbody>
<tr>
<td>Blanket</td>
<td>320 K</td>
</tr>
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<td></td>
<td>39.7 ± 1.7 kJ/mol</td>
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<td>Combinatorial</td>
<td>320 K</td>
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<tr>
<td></td>
<td>40.2 ± 1.7 kJ/mol</td>
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<tr>
<td>Combinatorial</td>
<td>329 K</td>
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<tr>
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<td>43.7 ± 1.7 kJ/mol</td>
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<tr>
<td>Combinatorial</td>
<td>338 K</td>
</tr>
<tr>
<td></td>
<td>42.0 ± 1.7 kJ/mol</td>
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<table>
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<th>$T_{Fil}$</th>
<th>$E_{a,substrate}$</th>
</tr>
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<tr>
<td></td>
<td>-82.7 ± 2.6 kJ/mol</td>
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<tr>
<td>Combinatorial</td>
<td>604 K</td>
</tr>
<tr>
<td></td>
<td>-80.3 ± 2.6 kJ/mol</td>
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<tr>
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<td>473 K</td>
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<tr>
<td></td>
<td>-85.7 ± 2.6 kJ/mol</td>
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</table>

Table 2-3. Apparent activation energy in filament ($E_{a,filament}$) and substrate ($E_{a,substrate}$) temperature for deposition of PDMAMS. Data for both combinatorial and blanket depositions are shown. a. $E_{a,filament}$ found at three substrate temperatures ($T_{Sub}$) using the combinatorial system are slightly higher than that found using the blanket system at one substrate temperature. b. $E_{a,substrate}$ determined at five filament temperatures are generally slightly higher than that determined by using the blanket system at one filament temperature.

The above results show that the combinatorial system results are similar to results of blanket depositions of PDMAMS. The combinatorial and blanket FTIR spectra show excellent agreement, indicating the chemical structure of the material deposited by the two systems is nearly identical. The combinatorial growth rate averaged 4% lower than the blanket rate for all depositions at the same filament and substrate temperatures, and was 9% lower at the maximum deposition rate conditions of $T_{filament} = 604$ K and $T_{substrate} = 303$ K. However, as can be seen in Figure 2-6, there is significant overlap of error bars, and it can be shown that the combinatorial point is well within the 95% confidence interval of expected deposition rates for the blanket rate point based on the estimate.
experimental and measurement error of ± 1.2 nm/min. Similarly, the calculated $E_{a,\text{filament}}$ values agree to within 0.5 kJ/mol, or within 2%, and the $E_{a,\text{substrate}}$ values are 2.4 kJ/mol apart, or within 4%. Together, these results show that the combinatorial system provides good agreement with the blanket system for deposition of PDMAMS.

2.5 Conclusion

A new combinatorial iCVD system has been fabricated and used to study the deposition of two new iCVD thin films, poly(diethylaminoethylacrylate) and poly(dimethylaminomethylstyrene). Substrate temperature has been decoupled from filament temperature and found constant across the wafer despite a gradient in filament temperature. The results of combinatorial depositions were compared to those obtained by traditional iCVD depositions at the same deposition conditions, and in all cases the results matched within experimental uncertainty. Results were compared for FTIR structure characterization, growth rate, overall apparent activation energies of growth, molecular weight. It was found that the combinatorial system in all cases provided agreed, within experimental certainty, with results of blanket iCVD depositions, thus validating the use of the combinatorial system for further iCVD studies. This work extends previous combinatorial CVD work to the new technique of iCVD, and the new system could be used for combinatorial HFCVD (also known as Hot-Wire CVD) studies as well. While only one deposition variable, filament temperature, has been combinatorially varied, a five-fold increase in research efficiency is realized. Also, the same system could be used to intentionally deposit films with a thickness gradient, once it has been confirmed filament temperature does not affect the film composition for the
particular material being studied. This could be used to study varying thickness of these films in electronic devices. Future work will detail application testing of the two new materials deposited here, as well as kinetic studies of the deposition of new iCVD materials.

2.6 References

Chapter Three

Initiated Chemical Vapor Deposition of Antimicrobial Polymer Coatings*

*Originally published as Martin, T. P.; Kooi, S. E.; Chang, S. H.; Sedrank, K. L.; and Gleason, K. K., Biomaterials, 2007, 28, 909-915
3.1 Abstract

The vapor phase deposition of polymeric antimicrobial coatings is reported. Initiated chemical vapor deposition (iCVD), a solventless low-temperature process, is used to form thin films of polymers on fragile substrates. For this work, finished nylon fabric is coated by iCVD with no affect on the color or feel of the fabric. Infrared characterization confirms the polymer structure. Coatings of poly(dimethylaminomethyl styrene) of up to 540 µg/cm² were deposited on the fabric. The antimicrobial properties were tested using standard method ASTM E2149-01. A coating of 40 µg/cm² of fabric was found to be very effective against gram-negative E. coli, with over a 99.99%, or 4 log, kill in just two minutes continuing to over a 99.9999%, or 6 log, reduction in viable bacteria in 60 minutes. A coating of 120 µg/cm² was most effective against the gram-positive B. subtilis. Further tests confirmed that the iCVD polymer did not leach off the fabric.
3.2 Introduction

The range of applications for antimicrobial surfaces has spawned a number of different synthetic strategies. When applied to textiles, the resultant self-sterilizing fabrics have the potential possible benefits of reduced disease transfer among hospital populations, biowarfare protection and other applications.

A wide range of antimicrobial agents have been added to textiles: silver based, hydantoin compounds, and quaternary ammonium or phosphonium polymers. Most often, these agents are physically associated with the material, and the antimicrobial agent leaches from the surface, leading to two key problems: a limited time of effectiveness and environmental, health and safety concerns.

Non-leaching antimicrobial treatments have been created by covalently grafting antimicrobial polymers onto textile surfaces, by various means including atom transfer radical polymerization of an antimicrobial polymer directly from an initiating surface, and covalent attachment of an agent to a polymer chain.

Surface treatments have been successfully developed for hydantoin compounds. The hydantoin moieties are essentially storage compounds for chlorine, which is released to the bacterium to kill it. Thus, hydantoin has a limited effective life before it must be reactivated with bleach.

Numerous quaternary ammonium, and to a lesser extent phosphonium, compounds and polymers have been shown to be effective antimicrobial agents. These polymers are amphiphilic with permanent cationic charge. The mechanism of action has been described as similar to that of antimicrobial peptides. Significantly, it is
currently thought that bacteria probably will not develop resistance to antimicrobial polymers. Klibanov et al. covalently bound quaternary amine polymers, to nonporous substrates and textiles and several other quaternary ammonium and phosphonium polymers are described in a review.

Gellman et al. successfully synthesized the polymer, poly(dimethylaminomethylstyrene) (PDMAMS) and demonstrated antimicrobial properties in solution. The current work explores the ability of PDMAMS polymer to maintain its antimicrobial properties when applied to a surface by initiated Chemical Vapor Deposition (iCVD). This surface treatment involves the introduction of monomer vapor above the surface through the vapor phase and the formation of a polymeric film directly on a cooled substrate (generally 20° to 50°C). Thus, the iCVD method differs from the vapor deposition method reported by Irikura et al of antimicrobial polyimide coatings, which requires that the substrate withstand high temperatures of near 200°C and thus cannot be used on heat sensitive substrates including most textile materials. The iCVD process developed for the current work is capable of coating fragile heat-sensitive substrates as the substrate temperature will be near room temperature at all times.

A key feature of iCVD is the introduction a free radical initiator species which is thermally cracked over a heated filament to induce vapor phase monomers to deposit coatings at high rates. Deposition from the vapor phase results in conformal coatings and requires no solvent use, advantages for coating complex and/or solvent-sensitive substrates. CVD is a conformal process, meaning the coating closely follows the contours of the substrate surface. Thus porous textiles can be coated without blocking the pores of the material. Dyes used in coloring textiles are sensitive to organic solvents,
so it is difficult to coat finished textiles without affecting the look of the fabric, a problem avoided by using iCVD. Also, sufficient hydrophobicity has been identified as a key factor in the efficacy of the antimicrobial cationic polymers.\textsuperscript{19,20} The low solubility in water that results makes it difficult to apply these polymeric coatings from aqueous solution, thus the coating may most easily be applied by the iCVD method. Another approach involves increasing the aqueous solubility while maintaining the antimicrobial efficacy.\textsuperscript{27}

Previously, the authors reported\textsuperscript{28} the ability to deposit coatings from the same DMAMS monomer used by Gellman et al.\textsuperscript{20} Structural characterization of these iCVD films grown on silicon wafers revealed retention of the active amine pendant groups with some degree of crosslinking resulting in zero solubility in water. Examination of various iCVD processing parameters permits optimization and tuning of the deposition rate, molecular weight, and film properties. However, antimicrobial testing was not performed as part of the previous study.

In this work, iCVD coatings are deposited onto porous textile substrates and antimicrobial testing is performed. While the previous work confirmed that the functional groups believed responsible for antimicrobial activity were preserved during the iCVD synthesis, the actual measurement of performance is needed to confirm the efficacy of these materials.

\subsection{Experimental}

\textit{iCVD Materials and Methods}
Optimization of the iCVD deposition of poly(dimethylaminomethylstyrene) (PDMAMS) has been previously described. Depositions occurred in a custom built low pressure reactor (Sharon Vacuum) with a radius of 12 cm and height of 3.3 cm. The top was a quartz plate which allowed laser interferometry and visual inspection of the system. A filament array provided the thermal energy for reaction and consisted of 0.5 mm diameter tungsten wire (Goodfellow) resistively heated with a DC power source (Sorensen DHP 300-10) to the 331 K. The filaments were spaced 20 mm apart and suspended 12 mm above the substrate surface. The filament temperature was measured with a type K thermocouple (Omega Engineering) attached to a filament in the center of the array directly over the substrate. The stage temperature was controlled to 316 K by backside cooling with a recirculating chiller/heater (Neslab CFT-33). The pressure was maintained at 200 mTorr using a throttling butterfly valve (MKS Instruments 253B).

Substrate fabric consisted of the nylon shell of the Army Poncho Liner (#8405-00-889-3683, Tech. Products Mfg. Corp.), which has a dyed woodland camouflage pattern, a basis weight of approximately 5.3 mg/cm², and average fiber diameter of approximately 15-18 μm. Squares of this fabric, 4 cm x 4 cm, were weighed (Mettler Toledo XS205) pre- and post-coating to determine the amount of PDMAMS coating added. The deposition was carried out for 12-60 min on the first side, then the substrate was turned and coated for the same time on the second side, for a total time of 24-120 minutes. Time was the only deposition parameter varied to achieve different coating weights.

The chemical species utilized are shown in Figure 3-1. The monomer (dimethylaminomethyl)styrene (DMAMS), consisting of 50/50 ortho- and para-isomers,
Figure 3-1. Chemical reactants for combinatorial iCVD: a. DMAMS monomer (para- isomer shown, both ortho- and para- isomers utilized) b. TAP initiator

was purchased from MP-Dajac Laboratories at 95% purity and vacuum purified before use to remove volatile organic contaminants. Monomer liquid was placed in the precursor delivery system at room temperature and all valves and the flow controller were full open while the vacuum pump was running; monomer was considered sufficiently pure when there was no further flow of material through the MFC. The initiator di-tert-amylperoxide (TAP) was purchased from Aldrich and used without further purification. DMAMS was vaporized at 343 K and metered through a mass flow controller (MKS 1153) at a flow rate of 2.0 SCCM. TAP was vaporized at room temperature and metered through a mass flow controller (MKS 1479A) at a rate of 0.6 SCCM. The monomer and initiator streams were joined before entering the reactor. The deposition was carried out for 20-27 min on the first side, then the substrate was and coated for the same time on the second side. Time was the only deposition parameter varied to achieve different coating weights. Using these parameters, ~5% of the monomer is converted to polymer in the reactor, and ~27% of the polymer formed coated the fabric substrates. The top and walls of the reactor were heated to avoid film growth in these areas and reduce cleaning effort.
Fourier transform infrared spectroscopy (FTIR) was performed on Nicolet Nexus 870 ESP was used in transmission mode with a DTGS detector. The use of infrared-transparent silicon wafers allowed the direct transmission mode examination of the films while on the substrate, and thus is non-destructive. All spectra were baseline corrected and normalized to film thickness as measured by variable angle spectroscopic ellipsometry (VASE). For structure comparison, poly(DMAMS) commercial polymer was purchased from MP-Dajac.

Fabric Coating Characterization

Scanning electron microscopy (SEM) was performed on a JEOL JSM-6060 for Figure 3-4a. A thin layer of gold was sputtered prior to imaging to avoid charging. The focused ion beam (FIB) fiber cross section was prepared in a JEOL JEM-9310FIB. To avoid charging, a thin layer of gold:palladium was sputtered over the coated fabric. An amorphous carbon film was deposited in the FIB over the area of interest by decomposition of a hydrocarbon vapor by the ion beam prior to milling. This served as a protective coating to ensure the Gallium ion beam did not degrade the antimicrobial coating. The Gallium ion beam was then used to mill through the carbon layer, polymer coating and nylon fiber. After milling, the resulting cross section was imaged in a FEI/Philips XL30 FEG ESEM for Figure 3-4b.

Antimicrobial Testing
Escherichia coli (ATCC 29425) and Bacillus subtilis (ATCC 6633) were purchased from American Type Culture Collection. Antimicrobial properties were assayed according to ASTM E2149-01. Briefly, the microbe of interest was cultured overnight and diluted in phosphate buffer solution (PBS) to approximately $10^6$/ml. Coated and control swatches of fabric were shaken with this solution in an orbital mixer at 200 rpm for the desired period of time. Initial and final coated or control bacterial concentrations were found using the serial dilution/plate count method. All results in Figure 3-5 were for tests performed for 60 minutes; results in Figure 3-7 are for tests performed for the indicated period of time. Error bars are estimated at half an order of magnitude based on the serial dilution/plate count method.

Two tests were performed to ensure the antimicrobial polymer was not leaching from the fabric. First, a standard zone of inhibition test was performed. A fabric swatch coated with 120 $\mu$g/cm$^2$ PDMAMS (three times the minimum effective coating against E. coli) was placed on an agar plate seeded with a confluent layer of E. coli and the zone of inhibition was determined. The second test was performed on the bacteria/PBS solution at the end of performing the fabric shake test, as recommended in ASTM E219. A well was bored into agar plates seeded with a confluent layer of E. coli. 200 $\mu$l of the post-test bacteria/PBS was placed in the well and the plate was incubated overnight.

3.4 Results and Discussion

Fabric Coating
Figure 3-2 shows the addition of polymer to the fabric is non-linear in early deposition times, prior to about 70 minutes. After this time the increase in mass appears linear in time. This may be due to an induction time effect. In this case the induction time may be long due to the large surface area of fabric relative to flat substrates. Some of the spread in deposited polymer mass may be due to different levels of thermal contact with the cooling stage in the vacuum reactor. Previous work has shown an increase in substrate temperature decreases the deposition rate of iCVD PDMAMS. Fabric portions with slightly less contact with the cooling stage will be slightly hotter due to radiation from the filaments, and so the growth rate would be expected to be lower.

The chemical structure of the deposited polymer was confirmed by FTIR analysis, shown in Figure 3-3, performed on films deposited on silicon wafer substrates simultaneously with the fabric. The spectra are very complex as the monomer consists of both the ortho- and para- isomers of DMAMS. The peaks chiefly attributed to the vinyl moiety at 900, 1030, 1360, 1510, 1630 and 3085 cm$^{-1}$ are significantly reduced in the conventional polymer and iCVD polymer spectrum. It is clear the iCVD polymer film is very similar in structure to the conventionally prepared polymer. The one exception is the peak at 1700 cm$^{-1}$, attributed to carbonyl moieties resulting from the reaction of unterminated radical chain ends in the film with atmospheric oxygen upon opening the reactor. Also, the peak at 2700 cm$^{-1}$, attributed to the tertiary amino-methyl C-H moieties, is slightly reduced in the two iCVD films relative to the conventional polymer.

Qualitatively, there was no change in the look or feel of the fabric for any of the depositions performed. Figure 3-4 shows SEM micrographs of nylon fabric coated by iCVD PDMAMS. Fig. 3-4a confirms the conformal nature of the iCVD process results.
Figure 3-2. Polymer mass added to the fabric is not linear in deposition time. The mass increases slowly at early times and then increases rapidly after about 50 minutes. At least two depositions were performed at each time and error bars represent the standard error.

Figure 3-3. FTIR spectra of DMAMS monomer (a), commercial PDMAMS reference (b), and iCVD PDMAMS (c). The deposited polymer spectrum is consistent with that of the conventionally prepared commercial polymer reference. Peaks associated with the monomer are marked (*).
Figure 3-4. Scanning electron microscopy images of nylon fabric conformally coated with PDMAMS. 

a. Coating weight of 86 µg/cm², showing the coating forms conformally around each fiber. Scale bar indicates 10 µm. The coating does not form bridges and does not coalesce, so pores between the fibers remain open.

b. Coated fiber cross-section performed with a focused ion beam (FIB). Coating weight of 204 µg/cm², corresponding to a thickness of ~195 nm. Scale bar indicates 1 µm. Coating is in the area demarcated by arrows. The nylon fiber is inside the curve, and a layer of carbon deposited for FIB purposes lays on top of the coating (see experimental details).
in coatings that do not occlude the pores. Small particles visible are dust either on the fabric before coating, in which case the edges of the particles appear smooth, or after coating, in which case the particle edges appear sharper. The coated fabric was cross-sectioned using a focused ion beam (FIB), as shown in Figure 3-4b, to determine the relationship between added mass and coating thickness. It was found that, for this particular substrate material, 204 µg/cm² of fabric corresponds to 195 nm of coating thickness on the fiber surface. This is consistent with the fiber diameter of 17 µm, fabric specific mass of 5.3 mg/cm², nylon density of 1.15 g/cm³ and film density of 1 g/cm³, which provides a calculated thickness of 188 nm on the fiber for the coating mass of 204 µg/cm².

Antimicrobial Testing

Figure 3-5 shows results of ASTM E2149-01 antimicrobial testing a range of coating thicknesses against two microbes, E. coli and B. subtilis, for 60 minutes. Results for uncoated control tests are also shown on the chart at a coating weight of zero. For both species, the control fabric slightly reduced the concentration of viable bacteria. This is due to bacteria absorbing to the fabric surface, and though the bacteria are not killed the concentration of bacteria suspended in solution is reduced. The reduction in colony forming units per ml is expressed as “Log Reduction” on the left axis and “% Reduction” on the right axis.

Results of testing against E. coli, which is gram negative, show a step change in efficacy at 40 µg/cm². At lower specific coating weights, the coating does not
reduce the viable bacteria concentration significantly more than the control fabric, at

most about a 1 log, or 90%, reduction. At and above 40 µg/cm², a reduction greater than 6 log is observed, or >99.9999% reduction. The step change could possibly result from non-contiguous film coverage at lower coating weights, and complete fiber coverage is achieved at 40 µg/cm².

By contrast, the efficacy against B. subtilis shows linear behavior (on this log plot), with about a 3 log kill at a weight of 40 µg/cm² increasing to over a 6 log kill at 120 µg/cm². It is not clear why a breakthrough curve in efficacy is not observed for this species, though the differing efficacy curves may be related to the different Gram status. The thicker cell wall of the Gram positive B. subtilis may retard the action of polymer
chains that are anchored to a surface so that a thicker layer is required. Also, it is possible that breakthrough curve behavior is present, but for some reason (i.e. thicker cell wall) it has been broadened to the point wherein it appears linear over the tested range of coating weights.

The “breakthrough curve” behavior observed against E. coli is similar to that observed in minimum inhibitory concentration (MIC) testing of antimicrobial agents in solution, in which no affect is observed below the agent MIC, and essentially no viable bacteria observed above the MIC. However, there are three pieces of evidence that indicate in the present case the antimicrobial polymer is not simply dissolving into the test solution to kill the bacteria. First, the deposition procedure for PDMAMS results in crosslinking, and solubility testing found no measurable solubility in water. The second and third items are presented in Figure 3-6. The first image, 6a, shows a standard zone of inhibition test performed on a sample of the dyed nylon fabric coated with 120 μg/cm² of PDMAMS, three times the minimum effective thickness against E. coli. It is placed on an agar plate seeded with a confluent film of E. coli and incubated overnight. No growth is observed on or beneath the fabric, and no zone of inhibition is observed around the fabric, indicating the antimicrobial polymer is not diffusing off the fabric to kill bacteria. Figure 3-6b shows a test performed on the supernatant from the antimicrobial test (the same solution that is spread to determine viable bacteria concentration). A well is bored in an agar plate seeded with E. coli and the supernatant is placed in the well. No zone of inhibition is observed around the well, indicating there is not sufficient antimicrobial agent in the test solution to kill bacteria. Taken together, this evidence indicates the antimicrobial polymer coating is not leaching from the surface.
Figure 3-6. Leaching tests. a. As deposited coating on nylon fabric is placed on a confluent film of E. coli. There is no zone of inhibition (ZOI), indicating the active agent is not diffusing off the fabric to kill bacteria away from the edge. Sample shown has coating of 120 μg/cm², three times the minimum effective coating against E. coli of 40 μg/cm². b. A 1 cm well is bored into an agar plate seeded with a confluent film of E. coli. 200 μL of supernatant from the antimicrobial test is placed in the well. After incubation overnight no ZOI is present around the well, indicating there is not sufficient antimicrobial polymer in the solution to kill the bacteria.
Finally, a series of tests were performed at different contact times against E. coli to determine how quickly the coating kills the bacteria. The results are shown in Figure 3-7. The minimum effective coating thickness against E. coli found in Figure 3-5, 40 μg/cm², was shaken with E. coli in PBS for 2, 5, 15 and 60 minutes. It was found that approximately 99.99%, or 4 log, of the bacteria were killed in two minutes, and the efficacy increased to greater than a 6 log kill in 60 minutes.

3.5 Conclusion

An antimicrobial polymer coating has been applied to fabric by iCVD. The technique is an all-dry method of forming thin, conformal films of polymers on a wide range of substrates. Functional groups of fragile monomers are preserved, in this case
allowing the rapid, one step, low temperature synthesis of an active antimicrobial polymer coating. Dyed nylon fabric has been coated with no apparent change in the fabric’s color or feel. The coating was found to be and 99.9999% effective against both gram-negative E. coli and gram-positive B. subtilis after 60 minutes. Further testing showed the coating is 99.99% effective against E. coli after just 2 minutes. Two leaching tests were performed, and neither test indicated the antimicrobial polymer dissolves off the fabric to kill bacteria in solution. iCVD antimicrobial coatings are of interest for a wide range of applications. The complete lack of any solvent and the low temperature of the substrate make the process particularly ideal for coating fragile materials. In this case, finished nylon fabric, which is sensitive to organic solvents, was easily coated. The technique could also be easily extended to medical devices, where the use of solvents in applying a coating could be an issue. The coating is also non-leaching, reducing possible problems with its use in the body. Future work will extend iCVD of antimicrobial polymers to new substrates, including those used in medical devices.

3.6 References

Chapter Four
Solventless Surface Photoinitiated Polymerization: Grafting Chemical Vapor Deposition (gCVD)

*To be submitted to Macromolecules
4.1 Abstract

Vapor phase deposition and characterization of covalently-bound polymer coatings using Type-II surface photoinitiation of the monomers (dimethylamino)methyl styrene (DMAMS) and (diethylamino)ethyl acrylate (DEAEA) are reported. Grafting chemical vapor deposition (gCVD), a solventless, low-temperature process, was first used for coating finished nylon fabric with a previously-characterized antimicrobial polymer, PDMAMS. The durability was improved so that 80 wt% of the coating was retained after extended antimicrobial testing and three rounds of ultrasonication. The coating was effective, killing 99.9% of E. coli in one hour by ASTM E2149. The gCVD process was then further explored using the less-UV-sensitive monomer DEAEA for deposition onto spun cast PMMA thin films. The structure of the grafted coatings was confirmed with Fourier Transform Infrared (FTIR) spectroscopy. Durable films up to 54 nm thick retained 94% of their thickness after 10 rounds of ultrasonication. Optimization of conditions allowed for the deposition of nearly linear polymer chains. Gel Permeation Chromatography (GPC) and Variable Angle Spectroscopic Ellipsometry (VASE) swelling cell measurements gave estimated ranges of 72-156 kDa for the molecular weight and 0.1-0.24 chains/nm$^2$ for the graft density.

4.2 Introduction

Type-II photoinitiators are widely-used for grafting polymer chains to surfaces.$^{1-4}$ The essential feature of Type II initiation involves abstracting a labile hydrogen atom to
create a radical. Grafting results when a hydrogen atom is abstracted from a surface and
the resulting radical initiates polymerization, leading to a covalently-attached polymer
chain. The reader is referred to a previous work for a more detailed mechanistic
discussion.\(^5\) Multiple surface-grafted of chains result in a polymer film that is chemically
bonded to the underlying material. The chemical bonding between the polymer film and
the substrate offers many advantages. First, the grafted layer is resistant to abrasion since
a covalent bond would have to be broken for a chain to be removed from the surface.
Second, the grafted polymer is stable against virtually any solvent, provided that the
solvent does not dissolve the underlying layer or cause bond-breaking reactions. This
stability allows the surface to be used in solvents that would otherwise dissolve the bulk
polymer.

Benzophenone (BP) is a Type II initiator which can be excited photochemically
with UV irradiation at 254 nm. Grafting using BP has been investigated by a number of
researchers.\(^1-4\) The methods can be divided into three main categories. The most
prominent is the all-solution-phase technique—both BP and the monomer are dissolved
in a solution in which the surface to be grafted is immersed, or the substrate is
sequentially exposed to solutions of each.\(^6,7\) Alternatively, a BP-pretreated surfaces have
been exposed to vaporized monomer to effect grafting. This pretreatment can be wet or
dry. In the wet case, BP is dissolved in a solution (typically acetone) and cast onto the
surface to be grafted. The surface is then dried to remove the solution, leaving behind
BP.\(^8\) The all-dry method exposes the to-be-grafted surface to BP vapor, and the surface
uptakes BP during the exposure.\(^9-11\) Although different, these three categories use the
same Type-II behavior of BP under UV irradiation resulting in abstraction of labile hydrogen atoms from the surface to create chain-initiating radicals.

As with thin-film deposition, dry techniques such as chemical vapor deposition (CVD) are becoming increasingly prevalent due to their environmental benefits. The success of all-dry CVD has been demonstrated by methods such as plasma-enhanced CVD (PECVD), hot-filament CVD (HFCVD), and initiated CVD (iCVD). A wide variety of polymeric and organosilicon materials have been made using these methods. CVD is able to produce films of nanoscale thickness with macroscale uniformity on complex geometries. All dry processing avoids the wetting and surface-tension effects associated with solution-based coating techniques, so surfaces with nano- or microscale topography can be coated uniformly. The added benefits of grafting motivate the investigation of an iCVD-like grafting process. The envisioned scheme combines the benefits of iCVD and grafting by exposing surfaces to vapors of a Type-II photoinitiator, BP. All-dry vapor-phase photografting has been demonstrated, but lack characterization for key features such as molecular weight and graft density. The goal of this work is to use an existing CVD chamber to perform and extensively characterize films produced by solventless grafting, hereby referred to as grafting CVD (gCVD), onto both flat and textile polymer substrates.

Antimicrobial polymer coatings were previously deposited on fabric by initiated CVD (iCVD) from the monomer DMAMS. Grafting CVD (gCVD) is examined to improve the durability of these coatings. However, DMAMS is not an ideal monomer for general optimization of the gCVD process as it is susceptible to UV irradiation and the deposited polymer is not soluble for Gel Permeation Chromatography (GPC) analysis. It
is likely that any of the various vinyl monomers used for iCVD\textsuperscript{18-20, 24, 25} could be used to deposit grafted layers by gCVD for the creation of desirable surface characteristics. The vinyl monomer DEAEA was chosen for general gCVD optimization because it contains a tertiary amino functional group and so retains some chemical similarity to the functional monomer DMAMS. Also, DEAEA was convenient for two reasons. First, DEAEA experiences negligible degradation under UV exposure, allowing the monomer to retain its structure for subsequent polymerization. Second, DEAEA and its polymer are soluble in water and tetrahydrofuran, facilitating durability characterization, GPC, and swelling. Therefore, molecular weight and graft density of gCVD PDEAEA films can be experimentally determined.

4.3 Experimental Details

Depositions were carried out in a custom built low pressure reactor (Sharon Vacuum) with a radius of 12 cm and height of 3.3 cm. The top was a quartz plate which allowed laser interferometry and visual inspection of the system. Further details are available.\textsuperscript{26} A shortwave UV light source (UVG-54, UVP) provided the energy to initiate the reaction. The lamp-to-substrate standoff was 12.5 cm, providing 60 ± 10 μW/cm\textsuperscript{2} of 254 nm wavelength irradiation at the growth surface.

The chemical species utilized are shown in Figure 1. The monomer 4-(N,N-dimethylamino)methyl styrene (DMAMS), consisting of 50/50 ortho- and para-isomers (MP-Dajac Laboratories) was vacuum purified before use, vaporized at 346 ± 2 K, and metered at 2.0 ± 0.1 sccm through a mass flow controller (MKS 1153). The monomer 2-(diethylamino)ethyl acrylate (DEAEA) (Aldrich) was vacuum purified before use,
Figure 4-1. Chemical reactants for grafting CVD: a) Monomer: (dimethylamino)methyl styrene (DMAMS), b) Type II Photoinitiator: Benzophenone (BP), c) Monomer: (2-diethylamino)ethyl acrylate (DEAEA)

vaporized at 351 ± 2 K, and metered at 1.0 ± 0.1 sccm through a mass flow controller (MKS 1153). For gCVD experiments, the initiator benzophenone (BP) (Aldrich) was vacuum purified before use and vaporized at 395 ± 2 K.

The gCVD process consisted of three phases with the duration of each indicated: initiator application ($t_{BP}$, 0-60 min), UV pretreatment ($t_{UV}$, 5-30 min), and UV exposure with monomer flow ($t_M$, 15-60 min, where “M” is either DMAMS or DEAEA). During the first two phases, the pressure was maintained at the system base pressure of 3 mTorr. In the third phase, the monomer pressure was maintained at the specified pressure in the range 75-225 mTorr using a throttling butterfly valve (MKS Instruments 253B). The stage temperature, $T_s$, was controlled to a specified value within the range 303-318 K using a recirculating chiller/heater (Thermo RTE740). Table 1 lists all sample conditions. All depositions were performed in triplicate.

For deposition of grafted antimicrobial polymer coating, gCVD DMAMS, substrate fabric consisted of the nylon shell of the Army Poncho Liner (#8405-00-889-3683, Tech. Products Mfg. Corp.), which has a dyed woodland camouflage pattern, a basis weight of approximately 5.3 mg/cm², and average fiber diameter of approximately 15-18 μm. Squares of this fabric, 4 cm x 4 cm, were weighed (Mettler Toledo XS205)
<table>
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<tr>
<th>Sample</th>
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<th>Substrate</th>
<th>( t_{BP} )</th>
<th>( t_{UV} )</th>
<th>( t_{M} )</th>
<th>( T_{Stage} )</th>
<th>( P_{M} )</th>
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<td>DMAMS</td>
<td>Fabric</td>
<td>40 *</td>
<td>5 *</td>
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<td>303</td>
<td>75</td>
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</tr>
<tr>
<td>S2</td>
<td>DMAMS</td>
<td>Si wafer</td>
<td>2 x 40*</td>
<td>2 x 5*</td>
<td>2 x 15*</td>
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</tr>
<tr>
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<td>DEAEA</td>
<td>PMMA</td>
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<td>5</td>
<td>15</td>
<td>308</td>
<td>75</td>
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</tr>
<tr>
<td>BP3</td>
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<td>PMMA</td>
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<td>5</td>
<td>15</td>
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<td>75</td>
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</tr>
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</tr>
<tr>
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</tr>
<tr>
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</tr>
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</tr>
<tr>
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<td>PMMA</td>
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<td>5</td>
<td>45</td>
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</tr>
<tr>
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<td>PMMA</td>
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<td>5</td>
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</tr>
<tr>
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</tr>
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<td>Fig. 6d</td>
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<tr>
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<td>PMMA</td>
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<td>5</td>
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<td>318</td>
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<tr>
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<td>PMMA</td>
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<td>30</td>
<td>15</td>
<td>308</td>
<td>75</td>
<td>Table 2</td>
</tr>
</tbody>
</table>

*: Each side of the fabric substrate is coated with these deposition parameters.
+: The silicon wafer underwent two rounds of deposition on the same side.
#: These four designators denote the same set of three samples at these conditions, but for clarity they are listed under each grouping in which they appear in Figure 6.
pre- and post-coating to determine the amount of coating added. The monomer was DMAMS, of which iCVD-deposited coatings were previously optimized and shown to be antimicrobial. The stage was maintained at 303 K and the pressure was 75 mtorr. The fabric was coated on each side. For each side, the time of each deposition phase was: $t_{BP} = 40$ min, $t_{UV} = 5$ min, and $t_{M} = 15$ min (denoted Si in Table 1). Simultaneous deposition on silicon wafers allowed FTIR characterization (sample S2). For comparison, non-grafted iCVD depositions of PDMAMS were performed as previously described. Briefly, DMAMS and tert-amylperoxide (TAP) were fed to the reactor at 2.0 and 0.6 sccm respectively, at 200 mtorr, and a tungsten filament (Goodfellow) resistively heated to 604 K provided the energy to initiate the reaction. Total coating weight was $131 \pm 6$ mg/cm$^2$ for samples made using both gCVD and iCVD. Durability testing in phosphate buffered saline (PBS) was performed by orbital mixing at 200 rpm for 24 hrs followed by three rounds of ultrasonication for 10 minutes each.

Both silicon wafers and PMMA (GPC standard, MW = 18 kDa, polydispersity = 1.04, Scientific Polymer Products) films spun cast to ~25 nm thickness on silicon wafer were used as substrates for the gCVD DEAEA runs. It is well known that UV-initiated grafting results in some non-grafted homopolymer. Deposited coatings were rinsed in 37% HCl for 10 minutes to remove non-grafted material, as it was found that a rinse in deionized (DI) water was insufficient to remove all non-grafted material. The acid rinsing results in more extensive protonation of the basic tertiary amino group than occurs in DI water, thereby solubilizing and removing essentially all non-grafted material. Bare silicon wafers provide a non-graftable surface control; all material was removed.
from these substrates in the rinse step. Four series of samples are denoted as BP1-BP5, M1-M4, P1-P4, and T1-T4 are fully described in Table 1.

A longer UV pretreatment time of $t_{UV} = 30$ min was subsequently used for swelling and GPC experiments (samples denoted MW in Table 1). This resulted in the BP initiator producing a higher degree of tethering to the spun cast PMMA layer and thus reducing the amount of free BP available to cause crosslinking of the deposited polymer chains.

Fourier transform infrared spectroscopy (FTIR) was performed on Nicolet Nexus 870 ESP was used in transmission mode with a liquid nitrogen cooled HgCdTe detector. All spectra were baseline corrected and normalized to film thickness as measured by variable angle spectroscopic ellipsometry (VASE). For structural comparison, PDMAMS commercial polymer was purchased from MP-Dajac. Scanning electron microscopy (SEM) was performed on a JEOL JSM-6060. A thin layer of gold was sputtered prior to imaging to avoid charging.

Variable angle ellipsometric spectroscopy (VASE, M-2000, J. A. Woollam) was employed as a non-destructive manner of determining film thickness, refractive index, and absorbance. A Cauchy-Urbach isotropic model for index of refraction ($n$) and extinction coefficient ($k$) was used to fit the ellipsometric angles $\Delta$ and $\Psi$. $^{27}$ WVASE32 software from J. A. Woollam was used to perform regressions to the ellipsometric data. A liquid cell (J. A. Woollam) was used in conjunction with VASE to swell grafted polymer layers. $^{24}$ Films were swelled in water controlled at pH 7.0 with phosphate buffer at room temperature. Ellipsometric data was taken at 75° before and after swelling and fit.
to a Cauchy-Urbach model. Data was taken every 15 seconds until films had attained equilibrium and stopped swelling. Generally, this took less than one minute.

Grafted films with underlying PMMA layers were dissolved in tetrahydrofuran (THF) for GPC measurements and compared to a calibration using six PMMA GPC standards representing 1800 – 2 kDa. The narrow peak due to the underlying PMMA that was not grafted to deposited polymer was clear at 18 kDa, with another peak clearly visible at shorter elution time due to the higher molecular weight PDEAEA-grafted-PMMA. The number average molecular weight of grafted PDEAEA was estimated by subtracting the PMMA $M_n$ from the $M_n$ of the larger-$M_n$ peak. The GPC system consisted of a Waters 1515 isocratic high-performance liquid chromatography (HPLC) pump, a Waters 2414 differential refractive index detector detecting at 880 nm, and two Styrage® HR 4 7.8 × 300 mm columns. Poly(methyl methacrylate) (PMMA) standards (Polymer Laboratories) dissolved in THF were used for calibration at 35°C.

Escherichia coli (ATCC 29425) were purchased from American Type Culture Collection and antimicrobial properties were assayed according to ASTM E2149-01. Briefly, the microbe was cultured overnight and diluted in phosphate buffer solution (PBS) to approximately $10^6$/ml. Coated and control swatches of fabric were shaken with this solution in an orbital mixer at 200 rpm for one hour. Initial and final coated or control bacterial concentrations were found using the serial dilution/plate count method.

4.4 Results and Discussion

First, the ability of grafting CVD to improve the durability of vapor deposited polymer coatings over non-grafted iCVD coatings was examined. The iCVD PDMAMS
coatings applied to 16 cm² squares of nylon fabric retained 25 ± 3% of their mass (for those starting at ~131 µg/cm²) after the PBS durability test described above. Although iCVD coating is insoluble in PBS, the testing causes the coating to delaminate. By contrast gCVD PDMAMS coatings retained 80 ± 3% after the same treatment. Indeed, the SEM characterization of gCVD PDMAMS coated fibers (Fig. 2) shows that the coating remains intact on visible portions of the fibers. It is likely the bulk of the mass loss is from the back sides of fibers and fiber intersections where the UV irradiation is partially or completely shadow masked. As shown by the FTIR comparison in Figure 3, gCVD PDMAMS has the same major chemical functional groups as the commercial standard and the iCVD film. However, the sensitivity of the styrenic monomer at 254 nm resulted in a loss of some of the tertiary-amino functional group, indicated by the marked peaks at 2700-2850 cm⁻¹. The coating was tested for antimicrobial efficacy to ensure the material was active despite losing some of the cationic group. The material was effective, killing approximately 99.9%, or 3-log, of E. coli in one hour, continuing to a 4-log kill in 24 hrs. However, this is not quite as effective as the original iCVD PDMAMS coating, which killed over 6-log of E. coli in one hour. Further work is required to find a coating process that will be durable and effective as a fabric coating, perhaps by using less-UV sensitive monomers.

To this end, an acrylate monomer with similar tertiary amino function group, DEAEA, was chosen to perform further exploration of gCVD deposition parameters. Initial tests confirmed that grafting did result when the gCVD process employed this monomer. Figure 4 shows the results of durability testing of gCVD and iCVD PDEAEA films in water. In 4a, it is apparent that the water soluble iCVD polymer is essentially
Figure 4-2. SEM image of gCVD-PDMAMS coated nylon fibers after severe durability testing of 24 hrs swirling at 200 rpm in an orbital shaker in PBS followed by 3 rounds of ultrasonication in DI water. It is clear that the coating remains chiefly intact. (Sample S1)

Figure 4-3. FTIR spectra of a) commercial standard PDMAMS, b) iCVD PDMAMS, and c) gCVD PDMAMS. Peaks attributed to the tertiary amino group at 2700-2850 cm$^{-1}$ are marked. (Sample S2)
Figure 4-4. Durability testing of poly(DEAEA) deposited on spun cast PMMA. 
a) Poly(DEAEA) deposited by iCVD, with no grafting or crosslinking; 5% of film is retained after one wash. b) Poly(DEAEA) deposited by gCVD; 94% of the film is retained after ten wash rounds. (Sample P2)

completely removed by just one wash. For the tested samples, consisting of sample P2 in triplicate, an average of $54 \pm 13$ nm of grafted material remained, and $94 \pm 1\%$ of the film thickness was retained after 10 wash rounds (Figure 4b). Thus the main goal of improving film durability by gCVD is attained.

The chemical structure of the deposited PDEAEA was confirmed by FTIR analysis, shown in Figure 5. The FTIR spectrum of a representative gCVD PDEAEA
polymer film (P2, Table 1) is shown with those of the iCVD film and DEAEA monomer. The spectrum of the gCVD film appears noisier than the others due to its relative thinness of 72 nm. The vinyl peaks, denoted by asterisks at 810, 985, 1410 and 1635 cm\(^{-1}\) are present only in the spectrum of the monomer, confirming the vinyl polymerization of DEAEA. Additionally, the peaks assigned to the carbonyl (1735 cm\(^{-1}\)) and tertiary amino moieties (2700-2850 cm\(^{-1}\)) are present in all the spectra confirming the retention of these pendent groups during the polymerization. Despite the noisiness of the gCVD spectrum, it is clear the spectrum substantially matches that of the iCVD polymer film.

The dependence of grafted thickness on process parameters is shown in Figure 6. First, in Fig. 6a, only the duration of the photoinitiator benzophenone (BP) flow is varied
Figure 4-6. gCVD process optimization. Four deposition variables are explored a) Initiator time (samples BP1 - BP4), b) Monomer time (samples M1 - M4), c) Monomer pressure (samples P1 - P4), and d) Stage temperature (samples T1 - T4).

(samples BP1-BP5). The control is tBP=0, in which case no growth is expected because of the absence of initiator. However, some film did grow but the thickness was just 2 nm. The observation of any film formation indicates that the UV radiation alone reacts with the DEAEA monomer, but the very thin nature of the deposited layer indicates DEAEA is only slightly sensitive to irradiation at 254 nm. It is expected that the thin film formed has simply been highly crosslinked by the UV radiation and so cannot be washed away. However, film formed in this manner would not be expected to retain any function similar to the linear polymer due to the high degree of crosslinking. Introducing the BP
prior to adding the monomer (Fig 6a) results in film thicknesses of 6 nm or greater, confirming that the presence of the Type II initiator promotes the deposition process.

Figure 6b shows the results of varying the monomer flow time, $t_M$. In an ideal vacuum polymerization process, the polymerization would be living and thus the grafted layer thickness would increase linearly with $t_M$. In this case, however, while an increase in thickness is observed upon increasing $t_M$ from 15 to 30 min, further increases in the duration of the monomer flow period does not increase the grafted layer thickness. The maximum thickness attained by varying monomer flow time is ~25 nm. This indicates the growing chain radicals have all been terminated after 30 min. The growing chains could have terminated through radical combination, disproportionation, or through reaction with contaminants in the vacuum chamber.

Monomer partial pressure has been previously shown by our group to be a critical variable in iCVD, a vapor polymerization process.\textsuperscript{29-31} The concentration of monomer at the surface is described by a Burnauer-Emmett-Teller (BET) adsorption isotherm\textsuperscript{31, 32}, wherein the surface concentration increases monotonically with the ratio of gas phase pressures $P_m/P_{m,\text{sat}}$, which is the partial pressure of the monomer divided by the monomer’s saturation vapor pressure evaluated at the substrate temperature. In this case, the vapor pressure of the monomer is not well known, so the appropriate pressure-substrate temperature combination could not be chosen a priori. Figure 6c shows the results of varying the monomer pressure for the gCVD process. This variable is observed to have a much larger affect that the initiator or monomer flow times. An increase in pressure from 75 mtorr to 125 mtorr increased the grafted film thickness from 8 nm to 54 nm. However, further increasing the pressure is detrimental, as the film formed at 225
mto is 34 nm thick after removing non-grafted material. This is likely because the monomer pressure is approaching or is above saturation, and indeed liquid monomer is observed in parts of the reactor, though not on the samples. Such a high concentration of monomer at the surface results in mainly homopolymerization of non-grafted material as the monomer/initiator ratio increases.

A similar trend is observed when the stage temperature is varied. In this case, however, the surface concentration of both monomer and initiator are affected. The result is a wide range of grafted thicknesses, from zero (at 318 K) to 29 nm (at 303 K). Figure 6d shows the plot of this data. Lowering \( T_s \) increases the deposited thickness as would be expected for an absorption-limited process. The discussion above regarding the BET isotherm also applies in this situation. Reducing the \( T_s \) decreases \( P_{m,\text{sat}} \), thereby increasing the monomer concentration at the surface and the coating thickness.

Finally, the length of the grafted polymer chains and the density at which they attach to the surface are determined (Table 2, sample MW). The grafted polymer layers were not soluble in THF or other solvents at the short \( t_{\text{UV}} \) of 5 min, even though they would delaminate from the silicon wafer as the underlying PMMA layer dissolved. However, by increasing \( t_{\text{UV}} \) to 30 min the entire film, PMMA and grafted layer, was completely soluble when ultrasonicated in THF. The reason for this is twofold: the increased UV time tethers more of the BP to the PMMA layer, and more of the untethered BP is pumped out of the reactor. Both mechanisms reduce the amount of BP available to cause crosslinking. GPC and VASE can be used independently to determine the molecular weight, as described by equations 1 and 2 (from Milner et al.\textsuperscript{33} and Jordan et al.\textsuperscript{34}).
\[ M_{n,\text{GPC}} = M_{n,\text{peak}} - M_{n,\text{PMMA}} \]  

(1)

\[ M_{n,\text{VASE}} = \frac{1.074(h_{\text{swollen}})^{3/2}}{[h_{\text{dry}}(\text{Å}^2)]^{1/2}} MW_m \]  

(2)

where \( M_{n,\text{GPC}} \) is the grafted chain number average molecular weight determined by GPC, \( M_{n,\text{peak}} \) is the number average molecular weight of the early elution time peak, \( M_{n,\text{PMMA}} \) is the number average molecular weight of the spun cast PMMA layer (= 18 kDa), \( M_{n,\text{VASE}} \) is the grafted chain number average molecular weight determined by VASE with a swelling cell, \( h_{\text{swollen}} \) is the thickness of the swollen grafted layer in Å, \( h_{\text{dry}} \) is the thickness of the dry grafted layer in Å, and \( MW_m \) is the molecular weight of the monomer (= 171 for DEAEA). The polymerization method under study may not result solely in linear chains despite the longer UV pretreatment time; some degree of crosslinking may be expected. In this case, GPC will provide the maximum linear chain length, as any branching and/or crosslinking will result in shorter elution times. Conversely, VASE will provide the minimum chain length, as crosslinked chains will swell to a lesser extent. Therefore, the two methods will bracket the ‘true’ value for hypothetical linear chains. The graft density implied by each method is then found using equation 3(from Feng et al.\textsuperscript{35}), where GPC and VASE will indicate the minimum and maximum graft density, respectively.

\[ \sigma = \frac{h_{\text{dry}}\rho N_A}{M_n} \]  

(3)

where \( \sigma \) is the graft density, \( \rho \) is the polymer bulk density (assumed equal to 1 g/ml), \( N_A \) is Avogadro’s number, and \( M_n \) is the number average molecular weight as determined by GPC or VASE. Table 1 contains the results of characterization by the two methods. There is indeed a spread in values, indicating that some degree of branching/crosslinking
## Table 4-2. Molecular weight and graft density found using GPC and VASE swelling cell. GPC provides the maximum MW and minimum graft density, whereas VASE swelling cell data provides the minimum MW and maximum graft density. Thus the two methods bracket the ‘true’ value. (Sample MW)

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<td>Mn (kDa)</td>
<td>175 ± 6</td>
<td>72 ± 1</td>
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<tr>
<td>Graft Density</td>
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is present. Dry films were 28±1 nm and swelled films were 35±1 nm thick. GPC results show a molecular weight of 175 kDa whereas VASE-swelling results indicate 72 kDa, with the calculated respective graft densities of 0.10±0.01 and 0.24±.01 chains/nm². The graft density implied by this range is comparable to that achieved by ATRP.34,35 The results show that accurate molecular weight and graft density characterization of UV photografted chains should include both GPC and VASE swelling methods.

### 4.5 Conclusion

Covalently-bound polymer coatings have been applied to flat and textile substrates by gCVD, an all dry technique amenable to polymerization of monomers which lack solubility in desirable solvents. The method is also low temperature, making it ideal for grafting to fragile polymeric substrates. Durable, effective antimicrobial coatings were applied to fabric by gCVD. Further gCVD parameter exploration was performed to expand the process to the full roster of monomers useful for iCVD. Durable layers up to 54 nm thick were formed in 60 minutes on flat substrates by gCVD. Molecular weight could be determined by GPC and swelling tests and was found to be in
the range 72-175 kDa, indicating some branching and/or crosslinking occurred. From this, the graft density was found to be in the range of 0.1 to 0.24 chains/nm², similar to that generally achieved by other grafting techniques. It is anticipated that gCVD can be extended to create polymers using monomers for which the iCVD method has already been demonstrated. This would result in durable hydrogels, superhydrophobic, and functionalizable surfaces.

4.6 References


Chapter Five

Conclusions and Future Work
6.1 Conclusions

This thesis has described the deposition of antimicrobial polymer coatings by chemical vapor deposition. Proper monomer choice allowed for the one step coating of finished textile and other substrates. A new combinatorial iCVD system improved research efficiency five fold, so optimization of the new material proceeded rapidly. The material studied here was the first styrenic polymer deposited by iCVD, thereby broadening the pool of monomers available for future iCVD applications. The coatings were shown to be highly effective antimicrobial coatings, but not durable. So, a new methodology for depositing durable coatings was implemented. More effort is required to achieve truly durable antimicrobial coatings effective over the long term, but the work in this thesis has significantly advanced the field. In addition, three side projects advanced CVD for use in thin film transistors, microfluidics and grafted superhydrophilic coatings.

6.1.1 Combinatorial Initiated Chemical Vapor Deposition

A new combinatorial iCVD system has been fabricated and used to study the deposition of two new iCVD thin films, one of which poly(dimethylaminomethylstyrene) is the first successfully iCVD-deposited styrenic polymer. The material was subsequently studied for use as an antimicrobial coating and high-κ dielectric. Substrate temperature has been decoupled from filament temperature, allowing the affect of each to be independently studied. The results of combinatorial depositions matched, within experimental uncertainty, those obtained by traditional iCVD depositions at the same deposition conditions. Results were compared for FTIR structure characterization,
growth rate, overall apparent activation energies of growth, and molecular weight. Thus the use of the combinatorial system for further iCVD studies was validated. This work extends previous combinatorial CVD work to the new technique of iCVD, and the new system could be used for combinatorial HFCVD (also known as Hot-Wire CVD) studies as well. While only one deposition variable, filament temperature, has been combinatorially varied, a five-fold increase in research efficiency is realized. Also, the same system could be used to intentionally deposit films with a thickness gradient, once it has been confirmed filament temperature does not affect the film composition for the particular material being studied.

6.1.2 Antimicrobial Coatings

Initiated CVD coatings of PDMAMS were applied to fabric. The active tertiary amino functional group of this fragile monomer is largely preserved by the iCVD technique. Thus the rapid, one step, low temperature synthesis of an active antimicrobial polymer coating is achieved. Dyed nylon fabric has been coated with no apparent change in the fabric’s color or feel at effective coating weights. The coating was found to be 99.9999% effective against both gram-negative E. coli and gram-positive B. subtilis after 60 minutes. Two leaching tests were performed, and neither test indicated the antimicrobial polymer dissolves off the fabric to kill bacteria in solution. iCVD antimicrobial coatings are of interest for a wide range of applications. The complete lack of any solvent and the low temperature of the substrate make the process particularly ideal for coating fragile materials. In this case, finished nylon fabric, which is sensitive to organic solvents, was easily coated. The technique could also be easily extended to
medical devices, where the use of solvents in applying a coating could be an issue. The coating is also non-leaching, reducing possible problems with its use in the body.

6.1.3 Grafted Antimicrobial Coatings

Grafting CVD (gCVD) has been used to apply covalently bound polymer coatings to flat and textile substrates. The fragile substrates can easily be coated because the technique is solventless and low temperature. Durable layers up to 54 nm thick were formed on spun cast polymer substrates by gCVD, and the structure confirmed by FTIR. Molecular weight could be independently found using GPC and swelling tests and was found to be in the range 72-175 kDa. The range of values indicates some branching and/or crosslinking occurred. The graft density was found to be in the range of 0.1 to 0.24 chains/nm², similar to that generally achieved by other grafting techniques. Durable, effective antimicrobial coatings were then applied to fabric by gCVD, though the coatings were slightly less effective than iCVD coatings. It is hoped that gCVD can be extended to other polymer applications, such as for durable hydrogels or superhydrophobic materials.

6.2 Future Work

Work still remains to be done to make durable antimicrobial coatings that are effective over several test/wash cycles. It is not clear at this point why the coating, of which about 80% is retained, does not continue to kill after one round of testing and ultrasonication. It does, however, kill after ultrasonication if it is performed prior to the antimicrobial test. Therefore, it is possible that the surface is somehow deactivated by
the high bacterial concentrations used in testing the coating. It was thought that ultrasonication would remove any biological detritus spoiling the surface, but this may not be the case. In any case, it is not clear that ASTM E2149 is the appropriate test for coatings on medical devices or textiles. Neither real-world application will involve the concentrations of microbes called for in that test procedure. There may not be an \textit{in vitro} test that can sufficiently replicate the \textit{in vivo} conditions for medical devices. So, further testing of the coating for use on medical devices should probably include some animal model testing. Permanent antimicrobial textiles will be a difficult research problem, but one that is probably more appropriately performed at the industrial level, as any solution will need to be integrated into commodity textile manufacturing, difficult to replicate at the lab bench level.

There are other areas of opportunity for continued work in iCVD and gCVD as well. First, lower temperature initiators for iCVD would reduce the heating load on the substrate, and may be very helpful in coating low-heat-conducting substrates, such as fabrics, or ones that make only slight thermal contact with the cooling stage. Second, continuing projects in gCVD should explore the possibility of creating more linear grafted chains. This may prove important for expanding applications for gCVD. At the same time, it would be advantageous to increase the graft density that can be achieved with gCVD so that it is more competitive with solution phase techniques such as ATRP. Finally, the living nature of gCVD should be explored. It was apparent in Chapter 4 that gCVD as practiced here has some living nature, as the graft thickness increased up to 30 minutes of monomer time, but no attempt was made to explore this further. A living, or
near to it, polymerization may hold promise for increasing the molecular weight and decreasing the polydispersity of the grafted chains.

In summary, the work in this thesis significantly advanced the use of CVD to make polymer coatings for antimicrobial coatings and other applications.
Appendix A

Organic High-κ Dielectric
Introduction

Organic field effect transistors (OTFT) are an area of intense research interest due to the possibility of greatly reduced cost compared to inorganic TFTs with comparable performance.\(^1\) This project envisions replacing cast, stamped or monolayer assembly of the dielectric layer in these devices. The CVD of polymers under study in the Gleason lab offer advantages over spin casting, namely that the device does not need to be removed from vacuum, thus the overall process remains cleaner, and reduced environmental and health concerns due to lack of solvent use. In addition, depositing films directly from the gas phase offers the possibility of controlled crosslinking, thereby providing a layer that could not be spun cast due to lack of any solubility. The dielectric layer should have sub-nanometer level RMS roughness, a high effective dielectric constant at least over 3.0, and provide a low leakage current. Recent work has successfully used styrenic polymers as a high-\(\kappa\) dielectric layer.\(^1,2\) Therefore, the properties of PDMAMS films, examined for Chapter Two, were found to match those required for use as a high-\(\kappa\) dielectric layer for OTFTs.

Experimental

Blanket and combinatorial iCVD depositions of PDMAMS occurred in the custom built vacuum reactor in room 66-259 at MIT as described in Chapter Two. The data presented here was originally part of Chapter Two, but was removed to improve clarity of that work. Thus, both dielectric data for both combinatorial and blanket depositions correlate with the FTIR spectra, film growth rates and other information provided in that Chapter. PDMAMS films were also deposited on gold substrates for
device fabrication in the Bulovic lab at MIT, but unfortunately high particulate concentration in the iCVD reactor resulted in device failure. A newly-fabricated add-on to the UHV system in the Bulovic laboratory will allow clean transfer between metal sputtering and iCVD polymer film deposition steps in the future, thus greatly improving the chances for successful device fabrication.

In addition, films of a second styrenic polymer, poly(4-vinylpyridine) were also examined. Depositions occurred in the same reactor. The monomer, 4-vinylpyridine (4-VP), was purchased from Aldrich, vaporized at 343 K, and metered at 2.4 sccm through an MKS 1153 mass flow controller. The initiator di-tert-butylperoxide (TBP), was purchased from Aldrich, vaporized at room temperature, and metered at 0.6 sccm through a MKS MFC. Reactor pressure was 200 mtorr, filament temperature was 493K, and substrate temperature was 320K. The film was deposited for 300 minutes and had a thickness of 137.1 nm. This was the only film tested for dielectric constant, though films were successfully deposited using $T_f = 453-533$ K and $T_s = 300-325$ K as well. (Note: It may be possible to get higher growth rates using the initiator TAP instead). Structure was confirmed with FTIR spectroscopy (not shown).

Electrical measurements to determine dielectric constants were performed using a mercury probe instrument from Materials Development Corporation (MDC). A 1 MHz frequency was used. Dielectric constant was determined in reference to a SiO$_2$ film of dielectric constant 3.9, thickness 107.5 nm, and capacitance of 130 pF:

$$\kappa_{film} = \kappa_{ref} \frac{t_{film}}{t_{ref}} \frac{C_{film}}{C_{ref}}$$

(1)
where $\kappa_{\text{film}}$, $t_{\text{film}}$, and $C_{\text{film}}$ are the deposited film dielectric constant, thickness and capacitance, and $k_{\text{ref}}$, $t_{\text{ref}}$ and $C_{\text{ref}}$ are the reference SiO$_2$ dielectric constant, thickness and capacitance, respectively.

**Results**

Dielectric constant data for the combinatorial and blanket films is shown in Figure 5-1. Data is shown for a range of filament temperatures and at a substrate temperature of 320 K only. In all cases the combinatorial films showed a higher dielectric constant at the same conditions. However, the same trend is observed for films deposited in both systems. The dielectric constant is lowest, near 4.0 for the combinatorial film and 2.9 for the blanket film, at the lowest $T_f$ of 473 K. The combinatorial system shows an increase to 5.0 at 562 K, then a slight decrease to 4.8 at the highest $T_f$ of 604 K. The blanket system shows an increase to a dielectric constant of 4.6 at $T_f = 604$ K. Despite slight differences in the measured dielectric constants for the films formed in the two deposition systems, both sets of films show the same trend.

Figure 5-2 shows the trend in dielectric constant for varying substrate temperature ($T_s$), for films deposited at a $T_f$ of 604 K. The blanket films show a maximum dielectric constant of 4.6 at the lowest $T_s$ of 320 K, whereas the combinatorial films showed a maximum dielectric constant of 5.2 at $T_s$ of 329 K. Both sets of films show the same trend to lower dielectric constant at the highest substrate temperature, though the values vary somewhat. The relatively high dielectric constants found here shows promise for the use of iCVD PDMAMS as a dielectric in thin film transistor devices.
Figure A-1 Dielectric constants for PDMAMS films deposited at the indicated filament temperature. All films were deposited at $T_f = 320$ K. Large variation in measurement at low temperature is likely due to the films being very thin.

Figure A-2 Dielectric constants for PDMAMS films deposited at the indicated substrate temperature. All films were deposited at $T_r = 604$ K.
Films of poly(4-vinylpyridine) were also examined for use as a high-κ dielectric material at one set of deposition conditions. The dielectric constant was found to be 5.2 ± 0.3, indicating this may also be a promising material for this application. One issue may be that P(4-VP) films are completely soluble in THF, indicating that self-crosslinking is not occurring, which is desirable for the application. It may prove necessary to use a divinyl crosslinker, such as divinylbenzene, to achieve the desired film properties. Further work is required as the deposition of this material was not examined in as much detail as PDMAMS deposition.

**Conclusion**

PDMAMS films, already characterized for use as an antimicrobial coating, was examined as a high-κ dielectric material for thin film transistor (TFT) applications. Dielectric constants as high as 5.0 were measured on silicon. Depositions on gold substrates for TFT device formation also showed initial promise.

Appendix B

Grafted Superhydrophilic Scleral Lens Coatings
Introduction

The general work in grafting described in Chapter Four lead to other applications of gCVD. The group has made superhydrophilic hydrogel layers by crosslinking polymers that are highly soluble in water,\textsuperscript{1,2} and achieved advancing contact angle as low as 37° and receding angle as low as 11°. In theory, grafted linear chains of the same materials could be even more hydrophilic by eliminating the use of the crosslinking agent, which is generally more hydrophobic than the monomer. At the same time, an ideal application for this technology presented itself when the Boston Foundation for Sight (www.bostonsight.org) contact fellow researchers at MIT for help with a fouling problem on their scleral lenses\textsuperscript{3}, which have been very successful in treating severe dry eye due to a multitude of disorders. The lens helps injured corneas to heal by continually holding a pool of water over the cornea. For most patients, this was a life-altering prosthetic, and they went from being unable to leave their house, in some cases, to now being able to drive and work again. One issue that arose as more patients were fitted with these lenses is that the outer surface of the lens, in contact with the atmosphere, in some cases becomes dried out. As it becomes drier, mucus and proteins adsorb to the surface. This becomes exceedingly uncomfortable for the patient and the lens must be removed and cleaned. In the worst cases, the patient must remove the lens after less than an hour of wearing and clean them, which is a 20 minute process. Therefore, reducing fouling of the outer surface of the lens is a very real quality of life issue that may affect as many as 200 people in the Boston area alone.
Experimental

The experimental details for gCVD were described in detail in Chapter Four. The experimental setup changed slightly from that used in that Chapter. In brief, an improvement in the feed system allows benzophenone (BP) to be vaporized at 368 K instead of 393 K. The needle valve was removed and total tubing distance to the reactor was shortened to affect this change. The monomer vinylpyrrolidone (VP) was vaporized at 343 K and metered at 2.0 sccm through a needle valve. A handhelp UV lamp (UVGL-54, UVP) provided UV irradiation at a distance of 11.4 cm above the substrate. The chiller was set at 303 K. Deposition time parameters were $t_{BP} = 30$ min, $t_{UV} = 10$ min, and $t_{M} = 60$ min. These conditions still need to be optimized.

Currently, substrates consist of films of poly(V3D3) deposited on silicon wafers by William O’Shaugnessy of the Gleason group at MIT. These are meant as a flat surrogate for the scleral lens, which is made of a proprietary polymer blend that consists of siloxane backbone with fluorinated pendant groups as well as poly(acrylic acid) to improve hydrophilicity. The lenses are curved, making characterization difficult, so currently the deposition parameters are being optimized with regard to contact angle on poly(V3D3) films instead.

The scleral lens coating must last a long time under fairly harsh conditions. While worn on the eye, blinking will aid in clearing debris from the surface, but will also constantly shear the coating. They are cleaned at least daily by thorough finger rubbing with saline and stored nightly in hydrogen peroxide to avoid infection. To at least partially simulate this, coating durability is tested by storing PVP-coated poly(V3D3) films in both saline and hydrogen peroxide.
Results

The initial grafting work presented in Chapter Four laid the groundwork for other applications requiring a durable polymer coating. As in that work, there are three stages to the deposition: Initiator application, UV pretreatment, and monomer flow with UV irradiation. Very preliminary results are promising. The coating retained ~74% of its thickness after soaking in hydrogen peroxide for seven days. However, in a demonstration of the complexity of the problem, just 60% was retained after soaking in saline for seven days. This may not necessarily be an issue as long as sufficient coating is permanently grafted to improve the hydrophilicity.

Contact angle results are similarly promising but need improvement. In general, all films, on both bare silicon and poly(V3D3) film substrates, and having been soaked in either saline or hydrogen peroxide, had advancing contact angles of near 70 degrees. This is far too high, and ideally this value can be made closer to 30 degrees by optimizing deposition conditions. The receding angle was much better, at near 20 degrees. Ideally, this value can be made closer to 10 degrees. It is interesting that the hysteresis is so large. This may indicate that some of the high advancing contact angle can be attributed to surface roughness and not the intrinsic surface energy. Or it is possible the polymer chains are highly mobile and can quickly reorganize to present the hydrophilic moieties once the surface is wetted. It is probably necessary to reduce both values so that the lens remains wetted even in patients with very few tears supplied to the surface. Then hopefully the eyelid can clear absorbed debris, such as mucus and proteins, from the lens surface easily by blinking.
Previous work, in Chapter Four, discussed how the grafted polymer chains can be made less crosslinked by reducing the amount of benzophenone added to the surface and increasing the UV pretreatment time. These will be the next steps in attempting to reduce contact angles. This will be followed by coating the scleral lens itself and testing durability and surface energy on this real-world substrate.

Conclusion

This work considered using grafted superhydrophilic coatings on scleral lenses. Poly(vinylpyrrolidone) was grafted to flat substrates of poly(V3D3), which is similar in chemical structure to the proprietary polymer used by BostonSight to make the scleral lenses. Initial tests showed an advancing water contact angle of about 68 degrees and receding angle of about 20 degrees. It is not clear why there is such a large hysteresis, but it is not desirable and should be reduced before attempting to coat lenses for use in patients.

Appendix C

Microfluidic Channel Coating
Introduction

Microfluidic devices made of poly(dimethylsiloxane) (PDMS) are widely used and studied for the relative ease of fabrication, use and low cost. However, the inherent intermediate hydrophobicity of PDMS devices is a major drawback to their use in long-term applications. Proteins and other solutes will absorb to the hydrophobic walls and eventually the device can no longer be used. At the same time, it would be advantageous for various applications to be able to add a desired functionality to the channel walls. This may include, for instance, superhydrophobic or hydrophilic walls, changing the wall pKa to avoid electro-osmotic problems, and adding functional molecules such as enzymes, peptides, or sensing molecules. At the same time, previous microfluidic channel coatings are either short-lived or have precluded binding to close the channel (as the plasma excitation currently employed to do so would destroy the coating). CVD is well suited to coat within microchannels because it can coat them conformally by avoiding the surface tension affects of liquid phase coatings. Preliminary results for a platform using iCVD coating that allows all four walls of the channel (three of PDMS and one of glass) to be coated, a binding step that closes the channel, and a functionalization step to make the channel hydrophilic are described.

Experimental

ICVD depositions occurred in the custom built vacuum reactor in room 66-259 at MIT as described in Chapters Two and Three and will not be described in detail here. The monomer glycidyl methacrylate (GMA) was purchased from Fluka, vaporized at 345 K, and metered at 2.0 sccm through an MKS 1153 MFC. The initiator di-tert-
butylperoxide (TBP), was purchased from Aldrich, vaporized at room temperature, and metered at 0.6 sccm through a MKS MFC. Glass microscopy slides and microfluidic devices made of poly(dimethylsiloxane) were provided by Ylva Olsson of the research lab of Klavs Jensen at MIT. The temperature of the slide and PDMS surfaces were not determined, but are expected to be higher than the chiller temperature and likely are different from each other. The microfluidic device channels were straight, 3 mm wide, 0.5 mm deep and 4 cm long. Generally, two PDMS section and two glass slides were coated simultaneously, with a small piece of silicon to use for real-time deposition monitoring with laser interferometry. The substrates were placed in the reactor and the pressure was reduced to close to base pressure to remove gaseous contaminants from the PDMS. Chiller temperature was set at 303 K. The system was pumped down for 1 hr or until gas bubbles visible between the stage and PDMS had disappeared. After this, the GMA was flowed into the reactor up to a pressure of 2 torr, at which point the chamber exhaust valve was closed and the flow of monomer stopped. The reactor was left in this condition for 1 hr to “pre-soak” the PDMS with monomer. At this point the deposition was begun. Reactor pressure was reduced to 400 mtorr with monomer flowing at 2.0 sccm for 10 minutes prior to starting TBP flow to remove all oxygen that may have leaked into the system while the chamber exhaust valve was closed. After this TBP flow at 0.6 sccm was begun and 0.5 mm tungsten filaments were heated to 353 K. Deposition time varied 60-120 minutes. After coating the substrates were pumped at full vacuum until the reactor pressure had attained 8 mtorr to remove most of the GMA monomer that had soaked into the PDMS but had not polymerized.
The coating thickness was determined as follows. A small piece of PDMS with channels was pumped under full vacuum for 1 hr to remove most gaseous contaminants, at which time it was weighed. After coating, the piece was pumped at full vacuum for ~30 hrs to remove all monomer from the PDMS and then weighed again. The overall average growth rate was determined by dividing the total added mass by the surface area of the PDMS section.

The device channels were closed after coating both surfaces by the following procedure. The PGMA-coated glass slide was uniformly covered with ethanol and placed on the vacuum reactor stage. The PGMA-coated PDMS device was placed channel-down on the glass slide, the vacuum reactor closed and slowly pumped down to reduced pressure. (The pressure should be reduced slowly as rapidly decreasing the pressure results in rapid vaporization of the ethanol and the PDMS section may move, potentially destroying the iCVD coating.) Generally, at least 1 hr of pumping was required to remove any visible ethanol and all gas bubbles visible between the slide and PDMS. When this was achieved, a handheld UV lamp (UVLG-54, UVP) was placed 11.4 cm above the stage surface directly over the substrates to provide 60 μW/cm² intensity of 254 nm wavelength irradiation. The substrates were irradiated for 8-10 minutes under vacuum.

UV susceptibility of the PGMA coating was tested by irradiating PGMA films on silicon wafer for 4-20 minutes at the same conditions described above. The chemical structure of the film was examined with FTIR at each time point.
After closing the channels, it was attempted to functionalize the PGMA coating that is on the four walls of the channel. The functionalization has yet to be confirmed and work continues in the area.

Results

The coating procedure results in PGMA films on both the glass slide and PDMS substrates. The overall average growth rate on PDMS was determined as outlined above and found to match, within about 10%, to the rate indicated by laser interferometry in real-time, over at least one hour of deposition. The growth rate was found to be approximately 1 μm/hr. The coating thickness used for subsequent experiments was about 2 μm on PDMS. The coating thickness on glass was not determined, but is expected to be close to that found on the silicon wafer and PDMS, both of which were ~2 μm. Therefore, the polymer layer binding the two substrates was about 4 μm thick and the coating inside the channel walls was about 2 μm thick. This thickness has not been optimized, though it was found that a thickness of ~280 nm on each surface was insufficient for binding.

The above outlined binding procedure was successful in producing closed microfluidic channels that held up to 2 bar of water pressure at a flow rate of 10 ml/min without leaking for at least 10 hrs. The ethanol swells but does not dissolve the PGMA coating, allowing the polymer coating on the two substrates to intercalate when they come in contact. Essentially all the solvent is removed in the vacuum step to ensure good surface contact. The glycidyl group is UV sensitive and some portion of these rings open to affect crosslinking of the polymer coating within and between the polymer layers.
However, the solvent to use for the binding step has not been optimized and better solvents may very well be found.

Films of PGMA on silicon wafers were exposed to the same level of UV irradiation for 4-20 min. FTIR was used to examine the chemical structure of the films at each time point. The peaks attributed to the glycidyl group are narrow and well-resolved at 907, 848 and 760 cm$^{-1}$. No amount of UV irradiation examined had any affect on these peak intensities. However, the glass and PDMS substrates or the ethanol treatment may somehow alter the UV sensitivity, so these limited experiments should be re-examined.

**Conclusion**

Microfluidics were coated with poly(glycidylmethacrylate) for the third side project. Generally, coating PDMS microfluidics with functional polymer films has proven difficult because they could not then be bonded to glass slides to close the channels. For this work, both the glass and PDMS surfaces were coated with PGMA. It was found that the two materials could be then bonded by using the UV-sensitive property of the glycidyl side group. Initial tests show that the devices bonded in this manner could hold up to about 2 bar of water pressure before leaking, compared to about 5 bar for the conventionally-plasma-bonded devices. However, 2 bar should be a sufficient pressure ceiling for most applications. Preliminary tests showed that significant amounts of the active glycidyl groups survive the UV bonding step, so there should still be enough available to functionalize. Work to this end is continuing in the Jensen group.