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SYNTHESIS AND ANALYSIS OF NANO-THIN POLYMER FILMS FOR SEPARATION APPLICATIONS

Azadeh Samadi-dezfouli
Clemson University, asamadi@clemson.edu

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SYNTHESIS AND ANALYSIS OF NANO-THIN POLYMER FILMS FOR
SEPARATION APPLICATIONS

A Dissertation
Presented to
the Graduate School of
Clemson University

In Partial Fulfillment
of the Requirements for the Degree
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by
Azadeh Samadi
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Accepted by:
Dr. Scott Husson, Committee Chair
Dr. Douglas Hirt
Dr. Christopher Kitchens
Dr. Igor Luzinov
ABSTRACT

This dissertation focuses on the fabrication of uniform polymer nanolayers using surface-initiated polymerization. The kinetics of low temperature surface-initiated atom transfer radical polymerization (ATRP) is discussed in detail. The work is then extended to the surface modification of polymeric membranes to tune the physical and chemical properties of the membranes for gas separations. I discuss how atom transfer radical polymerization might be advantageous compared to some of the techniques that have been proposed in the literature for preparing polymeric membranes for CO₂ separation.

The first part of this dissertation describes the synthesis of polystyrene (PS) nanolayers by surface-initiated ATRP at low temperatures. Relative to prior work, thick PS brushes were grown from initiator-functionalized layers of poly(glycidyl methacrylate) on silicon, and layer thickness evolution was measured by ellipsometry. Constant growth rates provided indirect evidence that the polymerizations were controlled. A detailed kinetic study was done for surface-initiated ATRP of styrene at 60 °C. An unexpected shift was observed in the reaction order (from first to zero order) with respect to the monomer concentration. A reaction mechanism is proposed for this change in rate order.

The second part of the dissertation focuses on the growth of uniform poly(ionic liquid) (PIL) nanolayers using surface-initiated ATRP. Surface-tethered polymer brushes with variable layer thicknesses were fabricated from silicon substrates and growth kinetics of the nanolayers were characterized.
The methodology that was developed in the silicon substrate work was then extended to modification of commercially available regenerate cellulose membranes for CO₂ separation studies. I report a solution to the leaking problem of supported ionic liquid membranes that have been used at the lab scale for CO₂ separation and also address the need for high selectivity, high flux membranes for CO₂ capture. Using surface-initiated ATRP to graft PIL nanolayers from the surfaces of commercial membrane supports is advantageous because the PIL nanolayer is attached to the membrane surface covalently. Therefore, there is no concern for leakage from the support. Relative to PIL membranes prepared by solvent casting, the composite membranes that I prepared offer an ultrathin selective layer, with uniform coverage ensured by the ATRP process. A nanothin selective layer offers advantages in terms of improving the CO₂ flux through the membrane.

Pure-component CO₂ and N₂ permeabilities were measured for unmodified and modified membranes. Covering the outer surface of the membrane with PGMA seems to improve the membrane integrity during permeation measurements, but has resulted in low permeability membranes, likely due to pore clogging.
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CHAPTER ONE
INTRODUCTION

This dissertation focuses on the fabrication of uniform polymer nanolayers using surface-initiated polymerization. I write in detail about the kinetics of low temperature surface-initiated atom transfer radical polymerization. The work is then extended to the surface modification of polymeric membranes to tune the physical and chemical properties of the membranes for gas separations. I discuss techniques that have been used to prepare polymeric membranes for CO₂ separation and how atom transfer radical polymerization might be advantageous compared to some of the techniques that have been proposed in the literature.

1.1 Polymer Nanolayer Synthesis

The structure and properties of a surface can be modified by tethering polymer chains to it. Here I focus on systems where the polymer chains are tethered covalently, recognizing that physisorption of polymers to an interface can have similar impacts on surface properties. If the distance between the polymer chains that are attached to a surface or interface is less than twice the radius of gyration of the chains in solution, then the polymer chain assembly is referred to as a “polymer brush”. Chains extend away from the surface forming a brush-like structure. Polymer brushes show new behavior and properties compared to the flexible polymer chains in solution as a result of confinement to the surface. In general, polymer brushes can be formed by grafting to or grafting from techniques. In the covalent “grafting to” technique, the polymer molecules with reactive
ends are attached to a desirable substrate that carries reactive groups as well. In the “grafting from” technique, monomers are polymerized from an initiator-functionalized substrate [Auroy et al., 1992; Zhao and Brittain, 2000]. The “grafting from” approach has the advantage of producing end-tethered polymer brushes with higher chain grafting density. In late stages of the “grafting to” process, the polymer chains must diffuse through the existing polymer film in order to reach the reactive sites on the substrate. This diffusion problem becomes more pronounced as the thickness of the attached polymer layer increases. An advantage of the “grafting to” technique is that the structure and chemical properties of the polymer chains can be studied rigorously prior to deposition. However, the “grafting from” approach allows more synthesis flexibility (e.g., crosslinked networks) [Auroy et al., 1992; Zhao and Brittain, 2000]. My work uses surface-initiated (i.e., grafting from) polymerization.

Because of their potential widespread applications, polymer brushes grown from flat substrates have been studied extensively. The main focus has been on exploring the proper conditions for controlling film thickness, functionality, and properties such as tribology, wettability, conductivity, and adhesion. To characterize these polymer films, techniques such as Attenuated Total Reflectance (ATR) FTIR Spectroscopy, ellipsometry, contact angle goniometry, X-ray Photoelectron Spectroscopy (XPS), Neutron Reflectivity, and Atomic Force Microscopy (AFM) have been used extensively.

Different types of surface-initiated polymerization have been used to prepare polymer nanolayers, including free radical polymerization [Prucker and Ruhe, 1998], photopolymerization [Luo et al., 2002; KizIllel et al., 2006], anionic polymerization
[Bywater, 1994; Jordan et al., 1999; Sakellariou et al., 2008], cationic polymerization [Jordan and Ulman, 1998; Matyjaszewski and Sigwalt, 1994], nitroxide-mediated radical polymerization [Li and Brittain, 1998], reversible addition-fragmentation chain-transfer radical polymerization [Baum and Brittain, 2002], and atom transfer radical polymerization (ATRP) [Matyjaszewski and Xia, 2001; Jeyaprakash et al., 2002; Li et al., 2004; Liu et al., 2006; Bao et al., 2006].

Conventional free radical polymerization has been used to grow polymer chains covalently attached from a surface with high grafting densities [Prucker and Ruhe, 1998]. However, controlled polymerization methods like ATRP have grown in popularity. Since ATRP yields well-defined polymers, it has allowed researchers to prepare a wide variety of uniform polymer brushes [Ejaz et al., 1998; Husseman, 1999; Zhao and Brittain, 2000]. Using ATRP, a number of research groups have conducted studies in which the polymer brush composition, degree of polymerization, and grafting density have been changed to modify surface properties [Ejaz et al., 1998; Husseman, 1999; Matyjaszewski, 1999; Wu et al., 2007]. ATRP has been used to modify a wide variety of surfaces such as silicon wafers [Ejaz et al., 1998; Liu et al., 2004; Samadi et al., 2005], flat gold surfaces [Huang et al., 2002; Kim et al., 2002; Li et al., 2006], silica particles, membranes [Sun et al., 2005; Singh et al., 2005; Singh et al., 2008], and so on. I was interested in surface-initiated ATRP specifically because it allows growth of uniform polymer chains with control over polymer layer thickness and grafting density.
1.2 ATRP Mechanism

ATRP is a type of controlled radical polymerization. Controlled polymerization in ATRP is achieved by establishing a dynamic equilibrium between the propagating and dormant species with transition metal-ligand complexes acting as a reversible halogen atom transfer reagent. Scheme 1 shows the general mechanism of ATRP. Copper in its +1 oxidation state is a transition metal that is used commonly in ATRP. Most often, an alkyl halide is used as an initiator in ATRP. The activation step involves carbon-halogen bond breaking to generate a carbon radical species and transfer of the halogen atom to yield a new metal-ligand deactivator complex with the Cu in the +2 oxidation state. The radical that is formed adds monomer units via free radical attack before it is deactivated by this metal complex to reform the dormant species [Kamigaito et al., 2004; Matyjaszewski and Xia, 2001]. As a result of this dynamic equilibrium, the concentration of the propagating species is lowered greatly relative to conventional radical polymerization methods, and the contribution of termination to the overall reaction is suppressed. It has been suggested that for a good degree of control, a sufficient concentration of deactivator species must be present in the polymerization medium [Matyjaszewski and Xia, 2001]. Excess deactivator (typically Cu^{II}Cl₂ or Cu^{II}Br₂) can be added at the beginning of the polymerization reaction to push the reaction towards the dormant species and to maintain low concentration of free radicals [Matyjaszewski et al., 2005]. Termination by coupling or disproportionation of transient radicals is a natural process. Otsu et al. [Otsu et al., 1982] were the first to suggest that the effect of this reaction could be minimized if the growing polymer chains would permanently undergo a
reversible dissociation at the end group into a transient propagating radical and a persistent radical, which does not add to the monomer. If the equilibrium constant of the reversible dissociation is sufficiently small, then there will be a low radical concentration and, as a result, only a low incidence of termination [Otsu et al., 1982]. As mentioned previously, ATRP involves “dormant” chain molecules terminated by a halogen atom. This halogen atom is transferred reversibly to a metal complex in a lower oxidation state, and, thereby, propagating radicals are formed together with the complex in its oxidized form. In this scheme, the oxidized form of the complex takes the role of the persistent species, i.e., it does not self-terminate and propagate [Fischer, 1999]. The lack of termination reactions enables a controlled polymerization with a narrow molecular weight distribution because chains grow at the same rate. Controlled surface-initiated ATRP from flat surfaces is, however, a challenge. The very low concentration of initiating groups on the surface leads to a very low concentration of the deactivator (via halogen atom transfer to the transition metal catalyst) in solution. The deactivator concentration is generally too low to reversibly cap the propagating radicals, resulting in increased levels of early termination. Addition of radical-deactivating complexes at the beginning of the reaction resulted in a continuous increase in brush film thickness for ATRP of styrene and methyl acrylate [Matyjaszewski, 1999]. This strategy of a priori addition of deactivator to the reaction formulation is now standard practice for surface-initiated ATRP.

Various monomers such as styrenes [Kwak and Matyjaszewski, 2008; Qiu and Matyjaszewski, 1997], (meth)acrylates [Kwak and Matyjaszewski, 2008; Mori and
Müller, 2003], dienes, acrylamides [Jiang et al., 2008; Neugebauer and Matyjaszewski, 2003], and acrylonitriles have been polymerized successfully using ATRP [Matyjaszewski and Xia, 2001].

Scheme 1. General mechanism of ATRP.

The free radical that is formed via Scheme 1 can propagate with a vinyl monomer (with a rate constant, $k_p$), terminate as it typically does in conventional free radical polymerization by a coupling reaction or disproportionation ($k_t$), or deactivate by atom transfer from the catalyst deactivator. In ATRP, the equilibrium constant ($K = k_{act}/k_{deact}$) is shifted highly towards the dormant species as the activation rate constant ($k_{act}$) is much lower ($\sim 10^{-7}$ times) than the deactivation rate constant [Matyjaszewski et al., 1997; Ohno et al., 1998].

A wide variety of catalysts have been used for ATRP, but complexes of Cu have been found to be the most efficient catalysts in the ATRP of a wide variety of monomers. The dynamic equilibrium between the dormant species and propagating radicals can be adjusted for a given system by modifying the complexing ligand of the catalyst.
[Matyjaszewski and Xia, 2001]. The main role of the ligand in ATRP is to solubilize the transition-metal salt in the (typically) organic media and to adjust the redox potential of the metal center for appropriate reactivity. There are several guidelines for an efficient ATRP catalyst. Firstly, fast and quantitative initiation ensures that all of the polymer chains start to grow simultaneously. Secondly, the equilibrium between the alkyl halide and the transition metal is strongly shifted toward the dormant species. Thirdly, fast deactivation of the active radical by halogen transfer ensures that all of the polymer chains are growing at approximately the same rate. Fourthly, relatively fast activation of the dormant polymer chains provides a reasonable polymerization rate. Some of the nitrogen-based ligands that are used commonly in conjunction with Cu ATRP catalysts are derivatives of bidentate bipyridine (bpy) [Wang and Matyjaszewski, 1995], tetratentate tris[2-aminoethyl]amine (TREN) [Xia et al., 1998], tetraazacyclotetradecane (CYCLAM) [Konáč et al., 2002], and \(N,N,N',N''\)pentamethyldiethylenetriamine (PMDETA) [Teare et al., 2005].

1.3 Kinetics of ATRP

In ATRP, kinetics and control depend on both the activator and the deactivator forms of the catalyst. The polymerization rate increases as the initiator concentration is increased and is dependent on the ratio of activator to deactivator concentration according to the following equation:

\[
R_p = -d[M]/dt = \frac{k_p [M]P^*}{k_p M_{ATRP} [RX](\frac{[Mt^n/L]}{[Mt^{n+1}X/L]})}
\]  

(1.1)
As shown in **Equation 1.1**, the rate of polymerization is first order in monomer, and first order with respect to initiator and activator. However, the overall kinetics may be more complex due to the formation of the $\text{M}^{n+1}\text{X}$ species via the persistent radical effect (PRE). Different factors such as the solubility of the activator and deactivator, their possible interactions, and variations of their structures and reactivities with respect to composition of the polymerization solution can affect the actual polymerization kinetics [Qiu et al., 2001]. According to **Equation 1.1**, the rate of polymerization is governed by the ratio of the concentrations of the activator to deactivator, and that the absolute amount of metal catalyst in the reaction mixture can be decreased without affecting the rate of polymerization. The synthesis of polymers with low polydispersities, however, requires a sufficient concentration of the deactivator in the polymerization solution [Matyjaszewski et al., 2005]. When the contribution of chain breaking reactions is small and initiation is complete, the polydispersity index (PDI) in ATRP is defined by the following equation:

$$\text{PDI} = 1 + \left( \frac{\left( k_p \left[ R\text{X} \right]_o \right)}{\left( k_d \left[ X - \text{Cu}^{II} \right] \right)} \right) \left( \frac{2}{p} - 1 \right)$$

**Equation 1.2**

As shown in **Equation 1.2**, PDI decreases with increases in conversion, $p$, the deactivation rate constant, and also the concentration of the deactivator (in this case for a copper based catalyst). It increases with increases in the propagation rate constant and the concentration of the initiator. The PDI is low when the deactivator is very reactive (e.g., Cu(II) complexed by 2,2′-bipyridine or pentamethyldiethylenetriamine) and monomer addition is slow (e.g., styrene-based versus acrylate-based).
Kim et al. [2003] studied the kinetics of surface-initiated ATRP of methyl acrylate from Au surfaces. In these studies, the monomer concentration was held constant at 2 M, and the Cu(I) concentration was varied over a wide range from 40 mM to $2.5 \times 10^{-4}$ mM, and the Cu(II) concentration was kept at 30 mol % relative to Cu(I). These results showed that uncontrolled growth can be obtained even in the presence of the deactivator if the overall Cu(I) concentration is too high. Therefore, as shown by Xia and Wirth [2002] for the ATRP of acrylamides from silicon wafers, controlled growth also can be achieved by dilution of the catalyst.

One obstacle to direct characterization of the molecular weight and PDI of polymer chains grown from flat surfaces is the low mass of the tethered polymers. Baker and coworkers [Kim et al., 2000], however, characterized poly(methyl methacrylate) chains grown from high surface area Au wafers, and determined PDI values of 1.3–1.5, indicating that controlled growth was achieved by the addition of Cu(II) at the beginning of the polymerization reaction. In my work, I focused on surface-initiated ATRP of styrene from flat substrates at low temperatures. I also studied the kinetics of this reaction and proposed a mechanism for the unusual observed behavior in this system. Finally, that work was extended to the surface modification of polymeric membranes by ATRP for CO$_2$ separation.

1.4 Background on CO$_2$ Separation

In 2008, global CO$_2$ emissions from the burning of fossil fuels were 20 percent above the value reported in 2000. The rate of increase of CO$_2$ emission between 2000 and
2006 was twice the rate of increase during the 1990s. Carbon dioxide emissions have been growing steadily for 200 years, since fossil fuel burning began on a large scale at the start of the Industrial Revolution. But the growth in emissions is now accelerating despite unambiguous evidence that CO₂ is warming the planet and disrupting ecosystems around the globe [Moore, 2008]. Fossil fuel burning is not the only source of carbon dioxide emissions. Currently, roughly 2 gigatons of carbon are released every year as forests are logged for timber or burned to provide agricultural land. Carbon dioxide is accumulating continuously in the atmosphere. The CO₂ concentration increased from 280 ppm at the beginning of the Industrial Revolution to 384 ppm in 2007. This increase in CO₂ concentration already has increased the global average temperature by 0.8 degrees Celsius [Moore, 2008]. Records indicate that there is more CO₂ in the atmosphere than there has ever been in the past 650,000 years. Half of the CO₂ released to the atmosphere is removed by CO₂ sinks such as the ocean and the plants, and the other half remains in the atmosphere. As CO₂ emissions increase and the planet warms, however, studies suggest that these sinks will begin to saturate and will be unable to continue taking up the same share of emissions. Carbon dioxide is less soluble in a warmer ocean, for example, and warmer soils tend to hold less carbon. So, as temperatures rise, a smaller proportion of CO₂ emissions will be taken up by land and ocean sinks. This warming already has resulted in more heat waves, longer and more intense droughts, and stronger hurricanes around the globe [Moore, 2008].

Some of the most reliable methods for reducing CO₂ emissions are decreasing fuel consumption; switching to lower carbon content fuels such as natural gas instead of
coal; improving the natural sinks for CO₂, which uptake CO₂ from the atmosphere; and finally switching to renewable energy sources such as biomass, which have lower CO₂ emissions.

Here I outline some of the technologies that currently are being used for CO₂ capture.

1. Chemical absorption is the most commonly used method for separation of CO₂ from exhaust gases when CO₂ concentration is low (5–15 % by volume) in a gas stream at atmospheric pressure. There are two steps involved in a chemical absorption process: absorption of CO₂ by chemical solvents at a low temperature (40–65 °C) and the use of low-grade heat to recover CO₂ from the chemical solvents (a.k.a. regeneration). The drawback of this technique is that the regeneration process is highly energy intensive. Amine solvents (e.g., monoethanol amine, MEA) have been used commonly for this purpose. Sterically hindered amines, which show better absorption and desorption properties than MEA, recently have become of interest, as they can reduce energy requirements by as much as 40%.

2. Physical adsorption is another technology commonly used for CO₂ separation. In this technique, the solid adsorbent (such as activated carbon or zeolite) is brought in contact with the gas stream. The adsorbent is regenerated to release the CO₂. In pressure-swing adsorption (a.k.a., PSA), the gas mixture flows through a packed bed of adsorbent at elevated pressure until the adsorption of the desired gas approaches equilibrium conditions at the bed exit. The bed is then regenerated by
stopping the feed mixture and reducing the pressure. In temperature-swing adsorption (a.k.a., TSA), adsorption is done at low temperature, and the adsorbent is regenerated by raising its temperature. These techniques are not practical for large-scale separation of CO₂ from flue gas as the CO₂ capacity and selectivity of the available adsorbents are low.

3. Another technique that normally is used for high CO₂ concentrations (~90% by volume) is cryogenic fractionation, in which the gas stream is compressed and cooled to a temperature low enough to allow separation by distillation. The drawback of this technique is the high energy usage that is required for refrigeration. Low concentration streams would need an initial concentration step prior to cryogenic fractionation.

4. Membranes, which are porous or semi-porous structures, through which some chemical species permeate more easily than others, also are used for CO₂ separation. As discussed in the next section, differences in physical or chemical interactions between gases and a membrane material cause one component to pass through the membrane faster than another.

1.5 Membranes for Gas Separation

The progress in the field of gas separation by membranes has been very fast. Membrane systems have emerged as desirable separation platforms because of their environmentally benign nature, process flexibility, low energy usage, and low capital investment. Over the years, membrane technologies have been developed for CO₂
capture, driven largely by demand for natural gas purification. Natural gas is a combustible mixture of hydrocarbon gases. While natural gas is formed primarily of methane (~70% by volume or more), it also can include ethane, propane, butane and pentane, as well as ~10% CO₂ by volume. So there is significant interest in CO₂/CH₄ separation in addition to CO₂ recovery from flue gas, where CO₂/N₂ separation is the interest.

Researchers are working continuously to produce membranes with improved separation factors and high fluxes. Both the permeability coefficient and selectivity of the more rapidly transporting gas molecule should be as large as possible for a polymeric membrane to be considered for gas separation. Therefore, new materials and new processing techniques are being developed to produce thinner, defect-free membranes with controllable porosity [Xu et al., 1997; Chung et al., 1995; Koros and Mahajan 2000; Bara et al., 2007; Bara et al., 2008; Bara et al., 2008]. Currently, there are not a wide variety of polymeric membranes that show both large values of permeability and selectivity. There have been structural modifications to the membranes that have led to improved permeabilities, but normally there is a corresponding loss in permselectivity, which is the ratio of permeabilities [Kusakabe et al., 1996; Koros et al., 1991; Bara et al., 2008]. In the area of gas separation membranes, Robeson [Robeson, 1991; Robeson, 2008] presented a very simple approach for comparing membranes made from different materials and different manufacturers. The permselectivity, which is equal to the ratio of the permeability of the more permeable gas to that of the less permeable gas, was plotted as a function of the permeability of the more permeable gas on a log–log scale. Data for a
large number of different membranes were all clustered below a critical line, or upper bound, which is often referred to in the gas separations community as the “line of death” since there are few membranes that provide a combination of selectivity and permeability above this limit. The goal in my work is to surface modify commercially available membranes in a manner that results in high selectivity and permeability (close to the “line of death”).

Chemical and thermal resistance, sorption capacity, and good mechanical strength are among the most important criteria for selecting polymeric membranes for gas separation applications. The polymer should interact more favorably with one of the mixture components in order for the separation to be effective. It is well established that chemical structure coupled with the physical properties of a membrane influence the permeability and selectivity. Chemical structure of the membrane is only one of the determining factors for assessing membrane performance properties. The physical structure, which includes the mechanical state of the matter such as density and mobility, has a strong influence on the gas separation capability of a membrane [Kurdi and Kumar, 2005; Li et al., 2006].

Many physical structures exist for membranes. Among these are microporous, nanoporous, dense, asymmetric, and composite supports. Membranes normally are classified according to the pore size or the size of the molecules that they are used to separate. Particulate filters are membranes with pore sizes of 5000 nm or greater. Microfiltration membranes have pore sizes in the range of 100–5000 nm and can be used for separating suspended particles like blood cells. Ultrafiltration membranes with pores
sizes in the range of 2–100 nm can be used to clarify protein solutions. Nanofiltration membranes with a pore diameter of less than 10 Å can separate small molecules like dissociated acids. Reverse osmosis (RO) membranes have pore diameters of a few Angstrom [Kesting, 1990], and are used in water treatment (e.g., desalination).

For gas separation, the selectivity and permeability of the membrane material determines the efficiency of the gas separation process. Porosity is an important membrane characteristic. A micro- or macroporous membrane is similar to a conventional filter in terms of its structure and function, so only molecules (or molecular aggregates) that are very different in size can be separated by microporous membranes. Porous membranes generally show high flux but low (no) selectivity for gas separation. Non-porous or dense membranes, however, provide high selectivity for separation of gas mixtures, but the rate of gas transport is normally low. An important characteristic of non-porous, dense membranes is that even small molecules can be separated if they have different solubilities in the membrane.

Membranes that are used typically in laboratory scale set-ups for gas separation applications are homogeneous and symmetric because they are easy to cast. However, for these membranes to be commercially viable, they are converted to asymmetric or composite forms. Asymmetric or composite membranes provide a barrier with a thin effective separation layer, which enables high permeability, with an underlying structure that maintains the desirable mechanical strength. Asymmetric membranes consist of a thin dense layer on top of a porous support layer of the same material. Composite membranes, however, consist of a thin dense skin layer coated on the top of a porous
support layer. The thin coated layer and the support layer are made from two different types of material. Using composite membranes minimizes the membrane cost by reducing the quantity of the expensive high-performance material used.

### 1.6 Membrane Modification to Improve Separation Characteristics

Cross-linking, grafting, and blending are three methods that are used to improve the separation characteristics of membranes. The sorption of CO₂ into polymers results in swelling and changes in the mechanical and physical properties of those polymers. The most important effect is the reduction of the glass-transition temperature ($T_g$), often simply called plasticization. Plasticization results in accelerating the permeation of the other gases through the membrane, and, as a consequence, the polymer membrane loses its selectivity [Alessi et al., 2003]. Therefore, a polymer is normally cross-linked in order to decrease the degree of plasticization of the polymer and, as a result, to maintain high selectivity.

Three different types of cross-linking are available: direct chemical reaction, radiation-induced reaction, and physical cross-linking [Pandey and Chauhan, 2001], often done by curing the membranes at high temperatures. A good example of chemical cross-linking is modification of polyimide membranes using 3,5-diaminobenzoic acid (DABA) as the cross-linking agent. DABA contains two carboxylic acid groups that can be used to crosslink the polymer chains with ethylene glycol and aluminum acetylacetonate. Excessive cross-linking should be avoided, as it makes the membrane brittle and, as a result, the membrane cannot be used for high-pressure applications [Wind et al., 2006].
Benzophenone-based polyarylate and polyimide membranes can be cross-linked by UV radiation. The benzophenone dicarboxylic acid (BnzDCA) structural unit contains a chromophore (carbonyl between aromatic rings) which is useful for UV crosslinking of these homopolyarylates [McCaig and Paul, 1999]. A significant improvement in selectivity can be observed depending on the duration of radiation, but the permeability normally is reduced as a result of densification and reduced mobility of the polymer chains after crosslinking. Irradiation is not considered a desirable technique for commercial use as the degree of crosslinking is not normally reproducible [McCaig and Paul, 1999; Wright and Paul, 1997].

Also, a good example of physical cross-linking is the work of Bos et al. [1998] who used elevated temperature to crosslink an existing polyimide Matrimid 5218 membrane to avoid CO$_2$ plasticization.

Grafting is another modification method in which oligomeric chains are attached as side chain branches to the main polymer chain. Grafting normally is done by chemical reaction or by irradiation. If the oligomeric chains contain groups that can react with another group in the polymer, then grafting by chemical reaction can take place. Grafting by irradiation normally is used for insoluble polymer membranes. Polymers with good chemical resistance can be made into films by melt extrusion followed by modification using irradiation. As an example, grafting thin-films on high flux microporous polyetherimide support yielded composite membranes with significantly improved permeability [Fritsch et al., 1993].
Finally, in blending, two polymers are mixed together without being covalently bonded. Homogeneous and heterogeneous blends may be prepared. The two polymers are miscible in homogeneous blends and partially to fully immiscible in heterogeneous blends. Heterogeneous blends do not possess sufficient mechanical strength when formed into thin membranes. Homogeneous blends have shown reduced CO₂ plasticization and improved selectivity for CO₂/CH₄ separation.

### 1.7 Gas Transport Mechanism Through Polymeric Membranes

The transport of gases through a dense polymeric membrane is described by a solution-diffusion mechanism. In the solution-diffusion mechanism, the permeant molecules dissolve in the polymeric membrane and then diffuse through the membrane as a result of a chemical potential gradient across the membrane. A separation is achieved between different permeating species as a result of differences in permeability coefficients and the chemical potential driving forces. The solution-diffusion mechanism consists of three steps: (1) the absorption or adsorption on the upstream side of the membrane, (2) diffusion of the absorbed molecule through the membrane, (3) desorption of the molecule on the downstream side of the membrane. The solution-diffusion mechanism is driven by a difference in the thermodynamic activities existing at the upstream and downstream sides of the membrane, as well as the interaction between the permeating molecule and the molecules that constitute the membrane material.
The gradient in chemical potential is the driving force for the movement of the permeant across the membrane. The chemical potential gradient across the membrane is expressed as a concentration gradient, as the solution-diffusion model assumes a uniform pressure within a membrane [Wijmans and Baker, 1995]. Therefore, the flux, \( J_i \), of a component, \( i \), through a flat sheet membrane is described by the following equation [Prausnitz et al., 1999]:

\[
J_i = -D_i \frac{dc_i^M}{dx}
\]

(1.3)

where \( dc_i^M/dx \) is the gradient in molar concentration of component \( i \), \( D_i \) is the diffusion coefficient (with units \( m^2 s^{-1} \) with \( J_i \) in \( mol m^{-2} s^{-1} \)), and \( x \) is the length coordinate perpendicular to the top layer of the membrane with thickness \( l \).

Therefore, to determine the driving forces for various species, we need the chemical potential for each species at state conditions of the feed and the permeate. In gas separation, a gas mixture at a certain pressure is applied to the feed side of the membrane, while the permeate gas is removed from the downstream side of the membrane at a lower pressure. The chemical potentials on both sides of the gas/membrane interface should be set equal [Prausnitz et al., 1999]. By doing so, the following equations are obtained:

\[
\mu_i^G = \mu_i^M
\]

(1.4)

**Equation 1.4** can be re-written in terms of measureables:

\[
\mu_i^{\ast G} + RT \ln \left( \phi_i P_i \right) = \mu_i^{\ast M} + RT \ln \left( \gamma_i^{c^M} c_i^M \right)
\]

(1.5)
where $\mu_i^{G}$ is the standard-state (1 bar) chemical potential of the pure gas, $\varphi_i$ is the fugacity coefficient, $P_i$ is the partial pressure, $\mu_i^{M}$ is the standard state chemical potential for the membrane phase, $c_i^M$ is the concentration (mol/m$^3$) of component $i$, and $\gamma_i^{c,M}$ is the activity coefficient linking concentration with activity. **Equation 1.5** can be re-written as:

$$\gamma_i^{c,M}c_i^M = P_i \varphi_i \exp \left( \frac{\mu_i^{G} - \mu_i^{M}}{RT} \right)$$

(1.6)

where the gas solubility coefficient of component $i$ is:

$$S_i^G = \frac{\varphi_i}{\gamma_i^{c,M}} \exp \left( \frac{\mu_i^{G} - \mu_i^{M}}{RT} \right)$$

(1.7)

Therefore,

$$c_i^M = S_i^G P_i$$

(1.8)

Integrating **Equation 1.3** over the thickness of the membrane gives:

$$J_i = -\frac{D_i (c_i^M - c_i)}{l}$$

(1.9)

where $c_i^M$ and $c_i$ are the concentrations in the membrane boundaries at the feed side and permeate side, respectively. **Equation 1.9** is valid only if $D_i$ is independent of concentration.

Combining **Equations 1.8 and 1.9** gives,

$$J_i = D_i S_i (p_i - p_{ip}) = \mu_i (p_i - p_{ip})$$

(1.10)
where $P_i$ is the product of diffusion and sorption coefficients, called the permeability coefficient [Wijmans and Baker, 1995]. $p_{if}$ and $p_{ip}$ are the partial pressures of component $i$ in the pressurized feed side and the permeate side, respectively. At low pressure, where the fugacity coefficients are equal to one, the solubility coefficient defined by Equation 1.7 is constant on the feed and permeate sides [Prausnitz et al., 1999].

Now that I have discussed different modification techniques for improving membrane properties for gas separation and also discussed the gas transport mechanism through polymeric membranes, I will shift focus to widely studied organic salts that have been used for CO$_2$ separation.

### 1.8 Ionic Liquids and CO$_2$ Separation

Ionic liquids are chemically inert and nonvolatile organic salts that have melting temperatures lower than 100 °C [Huddleston and Rogers, 1998]. They remain fluid at low temperatures mainly because of the large size and asymmetry of the cation, coupled with resonance-stabilized anions. Ionic liquids have gained significant attention in recent years as a result of their high conductivity, excellent chemical stability, nonflammability, and negligible volatility [Wasserscheid and Keim, 2000]. Of particular interest to my work, it has been shown that CO$_2$ has much higher solubility in imidazolium-based ionic liquids than other gases such as methane or nitrogen [Bates et al., 2002; Cadena et al., 2004]. Also noteworthy is that polymeric forms of ionic liquids have high stability and exceptional CO$_2$ absorption ability [Tang et al., 2005]. Tang et al. [2005] showed that
solid polymerized ionic liquids adsorb and absorb CO₂ with a higher capacity and at a much faster absorption rate than room temperature ionic liquids.

Several approaches have been used to study the properties of room temperature ionic liquids (RTILs) for gas separation applications. Some studies have focused on measuring the solubility of CO₂ relative to CH₄ and N₂ over a range of pressures. The drawback of separation through pressure swing absorption [Baltus et al., 2005] is that the volume of the RTIL solvent required is proportional to the volume of the gas to be processed and inversely proportional to the concentration of CO₂ in the feed stream. Therefore, there is normally a large volume of RTIL required to separate large volume of low concentration CO₂ from the flue gas streams. RTIL cost prohibits this technique for large-scale commercial usage.

Scovazzo et al. [2004] have used supported ionic liquid membranes (SILMs) as an alternative platform for CO₂ separation in order to avoid using a large volume of RTIL. SILMs typically are prepared by “wetting” a porous polymer support with the desirable RTIL [Scovazzo et al., 2004]. The volume of the gas that is being separated is directly proportional to the membrane surface area and feed pressure. Data that are available in the literature indicate that some SILMs exhibit ideal CO₂ permeability approaching 1000 barrers and ideal CO₂/N₂ separation factors reaching 60 or higher [Camper et al., 2006; Scovazzo et al., 2004]. Looking at Robeson plots and comparing these data to those reported for polymeric membranes, it is clear that SILMs are highly competitive with polymeric membranes [Robeson, 2008].
SILMs, however, have their own drawbacks since the RTILs are held within the polymeric matrix via weak capillary forces. The lack of strong interactions between the ionic liquid and the support allows for high gas permeability through the liquid phase, but results in a lack of stability for the SILM configuration. When the transmembrane pressure difference is greater than a few atmospheres, the RTIL is squeezed out of the support [Scovazzo et al., 2004].

Another approach to functional RTILs for gas separations is to incorporate polymerizable groups for the formation of solid poly(RTILs). Poly(RTILs) have been used as powders in CO₂ uptake experiments, and they have shown affinity for CO₂ [Blasig et al., 2007; Hu et al., 2006; Tang et al., 2005; Tang et al., 2005]. Hu et al. [2006] showed that poly(RTIL)-co-poly(ethylene glycol) (PEG) exhibited enhanced CO₂ solubility and selectivity. Copolymers of poly(RTIL)s with PEG fared better than neat poly(RTILs) in terms of permeability and selectivity [Hu et al., 2006], but the PEG component of these films was much larger than the poly(RTIL) component, so the influence of the poly(RTIL) component was not completely clear. These reports, however, confirm that poly(RTILs) are mechanically weak (brittle) and require a crosslinker or copolymerization for effective testing as flat thin membranes [Bara et al., 2007; Hu et al., 2006; Tang et al., 2005; Tang et al., 2005].

Research is being conducted to improve the mechanical stability of poly(RTILs). Addition of a crosslinker can serve this purpose, but RTIL monomers have been synthesized to be self-crosslinking, eliminating the need to introduce a secondary, and chemically different, cross-linkable species [Bara et al., 2008; Nakajima and Ohno,
Bara et al. showed that these types of membranes exhibited low permeabilities. The ideal separation selectivities, however, were similar to poly(RTILs) that were not crosslinked. They concluded that these crosslinked poly(RTIL) membranes are not desirable for high-throughput gas separation, but they may be of interest in barrier applications where permeation of gases is not desirable [Bara et al., 2008].

Poly(RTIL)s also have been formed into thin films and studied as gas separation membranes [Bara et al. 2007; Bara et al. 2008; Bara et al. 2008]. There is still a need to improve the permeability of these materials. This group currently is focusing on creating composites that incorporate fluid or “free” (i.e. non-polymerizable) RTILs into the poly(RTIL) matrices. They believe that the presence of “free” ions could provide more rapid gas permeability (i.e. increasing diffusivity) while maintaining selectivity. In one study, they made composite gas separation membranes by photopolymerization of an RTIL monomer in the presence of 20 mol% nonpolymerizable RTILs with various anions. The composite membranes contained polymer-bound cations, “free” cations, and “free” anions. The permeabilities of gases increased by 2-5 times compared to poly(RTIL)s with no “free” RTIL [Bara et al., 2008]. However, poly(RTIL)-RTIL composite membranes exhibited lower ideal selectivities compared to an analogous polymer without a “free” RTIL component. Nevertheless, selectivities were still higher than what can be achieved in most SILMs. However, poly(RTIL)-RTIL composites were approximately an order of magnitude less permeable than some SILMs [Bara et al., 2008]. No phase separation was observed between poly(RTIL) and RTIL under the low applied pressure (~ 2 atm) studied. It is hypothesized that the ionic interactions will most
likely hold the “free” RTIL within the polymer matrix such that applied pressure alone will not be able to separate the RTIL from the poly(RTIL). This group has yet to quantify the conditions required for “free” RTIL to escape the membrane.

ATRP grafting is new to the membrane modification community, and the focus of my surface modification work with membranes was to graft PIL nanolayers from commercially available membranes to produce CO₂-philic thin-film composite membranes. The advantage of this technique is that it allows the formation of nanothin selective PIL layers that could be useful in improving gas flux through the membranes.

1.9 Outline of the Dissertation

Chapter Two provides basic information about the analytical equipments and techniques for their use. Chapter Three describes the graft polymerization of polystyrene by atom transfer radical polymerization at 50 °C, 60 °C, and 75 °C. Thick polystyrene brushes were grown from initiator-functionalized poly(glycidyl methacrylate) layers on silicon, and constant growth rates provide indirect evidence that the polymerizations were controlled.

Chapters Three and Four present my work in describing the kinetics of surface-initiated polymerization of styrene by atom transfer radical polymerization at 60 °C using the CuBr/PMDETA catalyst/ligand system. In Chapter Three, I show that surface-initiated ATRP of styrene at low temperature avoids problems with thermal self-polymerization and side reactions, thereby retaining control. In Chapter Four, a wide
range of monomer concentration is studied in order to determine the reaction order with respect to the monomer concentration. In anisole, the polymerization rate was first order with respect to monomer concentration up to a monomer concentration of approximately 3.5–4.3 M and, unexpectedly, it became zero order for higher monomer concentrations. I present a mechanism for this behavior.

Chapter Five describes a methodology to use surface-initiated ATRP to covalently graft poly(ionic liquids) nanolayers from the surfaces of commercially available regenerated cellulose membranes. Because the PIL is attached to the pore surface covalently, there is no concern for leakage from the support. The composite membranes are tested as CO₂-selective separation agents.

Chapter Six presents the conclusions of my studies and recommendations for future studies.
1.10 References


Homopolymers and Block Copolymers from Silicon Surfaces in the Absence of Untethered Sacrificial Initiator. Macromolecules 32(26): 8716-8724.


CHAPTER TWO

ANALYTICAL TECHNIQUES

The purpose of this chapter is to provide basic information about the analytical equipment and techniques for their use. The specific details for measurements will be presented in each of the chapters.

2.1 Atomic Force Microscopy (AFM)

The poly(styrene) brushes grown from flat silicon substrates were imaged in air using AFM to examine surface uniformity. Data were collected using a Digital Instrument NanoScope in the tapping mode. The topography and phase images were both captured using a scanning rate of 1.0 Hz. Surface roughnesses were determined using the NanoScope Software Version 5.12 RMS roughness calculation.

2.2 Attenuated Total Reflectance (ATR) FTIR Spectroscopy

A Thermo Nicolet Magna 550 single-bounce ATR-FTIR spectrometer equipped with a Thermo-Spectra-Tech Foundation Series diamond crystal with Deuterated Triglycine Sulfate (DTGS) detector was used to confirm the successful grafting of PIL nanolayers from regenerated cellulose membranes. The number of scans was 32.
2.3 Scanning Electron Microscopy

A Hitachi Field Emission Scanning Electron Microscopy (FE-SEM 4800) was used to study the morphologies of the membrane surfaces before and after surface modification. Membranes were cut into small pieces with a razor, and they were attached to aluminum stubs with a carbon tape. They were then coated with a layer of platinum a few nanometers thick. Magnifications from 2000 to 4000 were used.

2.4 Static Contact Angle Goniometry

The surface hydrophilicity of the grafted polymer brushes was evaluated by static water contact angles via the sessile drop technique using a Kruss DSA10 goniometer equipped with a digital photo-analyzer. An average contact angle was computed from measurements on at least 3 drops. Reported values represent this average with error given by the standard deviation. Water drops of 0.5 μL were used and allowed to equilibrate for exactly 30 seconds before each measurement.

2.5 X-ray Photoelectron Spectroscopy (XPS)

XPS data were collected using a Kratos Axis Ultra photoelectron spectrometer with Al Kα radiation (15 kV, 225 W). All spectra were collected at an electron takeoff angle of 90° to the sample surface. Survey scans were recorded over the 0-1200 eV
binding energy range using a pass energy of 80 eV. High-resolution spectra of the C 1s, O 1s, and N 1s core levels also were recorded. Spectral analysis was done using casaXPS software, and all binding energies were referenced to the C 1s binding energy of 285 eV.

### 2.6 Ellipsometry

A Beaglehole Instruments Picometer™ Ellipsometer (He-Ne laser, \( \lambda = 632.8 \) nm) was used to measure layer thicknesses. The angle of incidence of the laser was varied from 80° to 35°, and the ellipsometric angles \( \psi \) and \( \Delta \) as a function of incident angle were fitted using a Cauchy model (Igor Pro software) to determine layer thickness. Thickness was measured at a minimum of three locations on each sample in ambient air.
CHAPTER THREE
LOW TEMPERATURE GROWTH OF THICK POLYSTYRENE BRUSHES VIA SURFACE-INITIATED ATRP

3.1 Introduction

Atom transfer radical polymerization (ATRP) of styrene previously has been done at temperatures near or above the $T_g$ for PS [Matyjaszewski et al., 1997; Matyjaszewski and Xia, 2001]. Under these conditions, thermal self-polymerization of styrene occurs readily [Walling et al., 1946], resulting in consumption of monomer and, in the case of surface-initiated polymerization, cessation of layer growth. Polymerization at lower temperatures would be advantageous for a variety of reasons. For example, the process would be compatible with substrates such as self-assembled monolayers on gold that degrade at elevated temperatures. Additionally, thermal polymerization, thermal crosslinking, chain transfer, and other side reactions occur less readily at lower temperatures [Matyjaszewski and Xia, 2001; Ramakrishnan et al., 2002]. Better molecular weight control also is obtained at lower temperatures, likely due to a lower contribution of the thermal self-initiation [Ramakrishnan et al., 2002].

This fundamental work on the preparation of well-defined PS nanolayers on model substrates can be extended to applied studies, such as synthesis of membranes for separation applications. Most polymeric membranes are temperature-sensitive and would deteriorate at elevated temperatures; therefore, the polymerization conditions developed in this chapter would be compatible with membranes as well. I note that ATRP reaction
conditions are also flexible in the sense that one can change solvents as required to maintain membrane integrity. Holmberg et al. [Holmberg et al., 2002] investigated the ATRP of styrene from poly(vinylidene fluoride)-graft-poly(vinylbenzyl chloride) membranes at elevated temperatures (100–130 °C). These membranes were designed for fuel-cell applications. By conducting the polymerization at lower temperatures and, as a result, avoiding thermal self-polymerization of monomer in solution, one could attain more control over the polymerization process and achieve more uniform modification of the membrane surface. In another study, Cowan and Ritchie [Cowan and Ritchie, 2007] modified existing polyethersulfone ultrafiltration membranes for enhanced filtration of whey proteins. In that work, PS was grown in the membrane pores by cationic polymerization. The PS grafts were then sulfonated using sulfuric acid. Functionalization of the membrane in this manner decreases average effective membrane pore size and, hence, molecular weight cutoff. It also improves rejection of negatively charged proteins due to charge repulsion [Cowan and Ritchie, 2007]. Thus, the modification had two effects here: to change the membrane surface chemistry and also to change its porosity. Those modified membranes were used to examine the transmission/rejection of charged whey protein in solution. ATRP would perhaps be a more desirable technique for this application as it allows facile control of chain molecular weight ($M_n$) [Matyjaszewski and Xia, 2001], which allows one to have more control over changes in the average effective membrane pore size. Our group has used ATRP successfully to simultaneously change the surface functionality, pore size, and pore size distribution [Singh et al., 2005; Singh et al., 2008; Bhut et al., 2008].
In this chapter, I describe the low temperature (50–75 °C), surface-initiated growth of PS from an initiator-functionalized primary layer of poly(glycidyl methacrylate) (PGMA) on silicon using ATRP. Deposition of the anchoring PGMA layer on the surface and attachment of the initiator to the PGMA-modified surface allows regulation of the initiator surface density. The PGMA layer provides a larger number of α-bromoester surface initiator sites compared to self-assembled monolayers [Jones et al., 2002] and has yielded high graft density PS brushes by ATRP at 110 °C [Liu et al., 2004]. Another advantage of using PGMA is that its epoxy groups are reactive towards different functional groups such as carboxyl, hydroxyl, amino, and anhydride. Thus, PGMA could be used to amplify the number of surface reactive groups by reaction with chain ends on membranes made from materials such as nylon, polyethersulfone, and polyethylene terephthalate. It also makes possible modification of relatively inert membranes such as PVDF membranes for separation applications [Singh et al., 2005]. In the work by Singh et al., PVDF membrane, which is non-reactive, was plasma treated, and PGMA was anchored to a small number of reactive sites formed by plasma treatment to provide lots of surface epoxy groups. Here again, PGMA allowed amplification of the number of initiator groups on the membrane surface.

ATRP was used to prepare PS brushes because it has been shown to produce homogeneous, uniform polymer films compared to conventional radical polymerization methods [Huang et al., 1998]. Li et al. [Li et al., 2004] showed that ATRP produces a smoother topography by comparing surface roughness values to those reported for conventional radical polymerization. Surface-initiated polymer growth also leads to
higher graft densities relative to “grafting to” approaches [Zhao and Brittain, 2000; Jordan et al., 1999]. Graft density also can be varied independently from layer thickness, which is not possible with “grafting to” methods. These features are advantageous because of the potential application of graft-polymerized membranes for separation applications. Surface modification is very important for tailoring membrane performance. However, one of the major problems faced previously in graft polymerization from membranes was the marked decline in the membrane permeability after modification due to pore blocking by the grafted polymer [Freger et al., 2002]. Surface-initiated ATRP is advantageous for preparing separation media using base membrane supports because it can controllably adjust the average effective membrane pore diameter, and pore-size distribution, while simultaneously building in required chemical functionality to improve the overall performance.

3.2 Experiments

3.2.1 Materials

Chemicals were used as received unless noted otherwise; they were aluminum oxide (~150 mesh, Aldrich), copper (I) bromide (Cu(I)Br, 99.999%, Aldrich), toluene (Certified A.C.S., Fisher), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%, Alfa Aesar), methyl ethyl ketone (MEK, 98%, Baker), glycidyl methacrylate (97%, Aldrich), 2,2-azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich), and 2-bromo-2-methylpropionic acid (BPA, 98%, Acros). Styrene (≥ 99%, Aldrich) was dehibited by passing it through a column of Al₂O₃.
Silicon wafers (Silicon Quest International) with a crystal orientation of <1-0-0> were used as substrates. Prior to use, the silicon substrates were cleaned in deionized water using an Aquasonic ultrasonic bath for 30 minutes. Subsequently, they were treated with piranha solution (a 3:1 mixture by volume of concentrated sulfuric acid (95–98%, EMD) and hydrogen peroxide (30%, VWR)) for 1 hour, then rinsed thoroughly with HPLC water and then dried in a stream of nitrogen. Note: Piranha solution reacts violently with organic compounds and must be used with caution. Gloves, goggles, and face shields are needed for protection.

3.2.2 Functionalization of Silicon with PGMA and ATRP Initiator Groups

The PGMA was prepared and characterized by members of Dr. Igor Luzinov’s group at Clemson University. The PGMA was prepared by radical polymerization of glycidyl methacrylate in MEK at 60 °C using AIBN as an initiator. Glycidyl methacrylate was purified using an aluminum oxide column. The polymer obtained was purified by multiple precipitations from the MEK solution by diethyl ether. Gel permeation chromatography (GPC) using PS standards showed that $M_n = 24,000$ g/mol and a polydispersity index of 1.7.

PGMA was deposited on the silicon surface by dip coating from a 0.1 wt.% PGMA solution in MEK (dip coater Mayer Fientechnik D-3400). Details of the dip coating procedure were presented by Liu et al. [Liu et al., 2004] in a previous publication. The PGMA-coated silicon surfaces were annealed at 110 °C for 30 minutes under vacuum generated by a water aspirator to react some of the epoxy groups with hydroxyl
groups on the silicon wafer. To add ATRP initiator groups, the PGMA-functionalized surfaces were placed into a 100 mL Schlenk tube with 1-2 g of BPA. The Schlenk tube was evacuated to 1 mmHg and placed in an oven at 110 °C for 18 h, which has been shown to provide enough time to reach equilibrium for this system [Liu et al., 2004]. Reaction of vapor-phase BPA with the remaining epoxide groups of PGMA produced tethered α-bromoester groups capable to initiate ATRP. After treatment, the surfaces were soaked in MEK for 10 minutes and rinsed with MEK three times. This completely defined protocol was used throughout these studies, though it should be noted that lower temperatures and longer reaction times can be used for annealing and initiator grafting on temperature-sensitive substrates. However, it also should be noted that the maximum areal initiator density at 30 °C was around 10 molecules/nm²; while at 90 °C it reached 28 molecules/nm² [Liu et al., 2004].

3.2.3 Surface-initiated Polymerization of Styrene

Polymerization of styrene from the PGMA-coated silicon substrates was carried out using pure styrene (8.6 M). The catalyst comprised Cu(I)Br and ligand, PMDETA, with a molar ratio of 1:1 and a catalyst concentration of 86 mM. The catalyst solution was prepared separately from the monomer solution, and then the two were added. All solutions had to be stirred for about 10 minutes to form a homogeneous catalyst complex. The monomer was deoxygenated using at least three freeze-pump-thaw cycles. Freeze-pump-thaw cycle is a process in which the solution is frozen using liquid nitrogen, and then vacuum is pulled to remove the vapor in the head space. Once the liquid starts
melting, the vacuum line is closed and complete melting is allowed. The degassing process is repeated 3-4 times for each polymerization experiment. To avoid catalyst oxidation, polymerization was carried out inside an oxygen-free glovebox (MBraun UNIlab). Temperature was controlled by placing the polymerization solution in a constant-temperature glass bead bath (ISOTEMP 145D, Fisher). The temperatures that were studied were 50 °C, 60 °C, and 75 °C. The polymerization solution was brought to the desired temperatures first, and then the silicon wafers were added to start the polymerization. After removal from the polymerization solution, the PS-grafted silicon wafers were washed in toluene using an ultrasonic bath for 30 minutes, rinsed with toluene, and dried in a stream of nitrogen. This cleaning procedure has been shown to effectively remove any physisorbed PS [Liu et al., 2004].

Different surfaces were removed from the polymerization solution at regular time intervals in order to study the polymerization kinetics (i.e., nanolayer thickness versus time). Polymer layers were characterized by multi-angle, phase-modulated ellipsometry, contact angle, and AFM methods.

3.2.4 Characterization

Ellipsometry

Ellipsometry measurements were done using the general methodology described in Chapter Two. A refractive index of 1.590 was used for PS, 1.525 for PGMA, and 1.500 for BPA. Dry layer thickness was measured at a minimum of three locations on each sample in ambient air.
To determine the solvent-swollen layer thicknesses, samples were placed inside a specially designed cylindrical glass cell with a diameter of 2.5 cm and a volume of 25 cm$^3$. It has one open end that is sealed during measurements with a screw cap. There is a flow inlet for solution introduction and an outlet for solution removal. A Teflon platform with a mechanical fastener holds the substrate in the center of the cell. In this glass cell, the PS brushes were brought into contact with toluene (good solvent) and allowed to respond (swell) for approximately 15 minutes before the ellipsometric measurements were made of the swollen layer thickness. After this period of time, no further increase in layer thickness occurs; the ellipsometric signals were constant. The layer refractive index was allowed to vary in these measurements.

**Water Contact Angle**

Static water contact angles were measured for polystyrene layers using a KRÜSS Contact Angle Meter. The sessile drop method was used with HPLC grade water. At least three sample spots were taken on each surface. The contact angle was determined using the Young-Laplace fitting method.

**Atomic Force Microscopy (AFM)**

The PS brushes grown from flat silicon substrates were imaged in air using AFM to examine surface uniformity. Data were collected using a Digital Instrument NanoScope in the tapping mode. The topography and phase images were both captured
using a scanning rate of 1.0 Hz. Surface roughnesses were determined using the NanoScope Software Version 5.12 RMS roughness calculation.

3.3 Results and Discussion

The dip-coating procedures resulted in 5.5 ± 0.2 nm-thick anchoring PGMA films, and the initiator density was approximated to be 8 ± 1 initiator molecules/nm² from the results of Liu et al. [Liu et al., 2004]. This site density is higher than the approximately 3 initiator molecules/nm² that typically result from self-assembled monolayers of ATRP initiators [Jones et al., 2002].

As mentioned previously, ATRP of styrene has been only reported for high temperatures (typically 110–130 °C), and significant thermal self-polymerization of styrene is inevitable even at temperatures as low as 90 °C [Ramakrishnan et al., 2002]. Under these temperature conditions, the polymerization solution becomes highly viscous, and diffusion of monomer molecules to the propagation sites becomes restricted. Therefore, at longer polymerization times (i.e., high conversions), layer growth slows and essentially stops. Indeed, previous studies on graft ATRP of styrene at these temperatures report non-constant growth rates that slow markedly after polymerization times of about 10 h, and, after that time, only small increases in brush layer thickness were observed with increasing polymerization time [Jeyaprakash et al., 2002; Liu et al., 2004].

To assess the degree of thermal polymerization as a function of temperature, I used the data of Walling et al. [Walling et al., 1946], who measured the rate of thermal polymerization of styrene at 127.3 °C. As shown in Figure 3.1, the monomer
concentration was plotted as a function of time. An equation relating the monomer consumption to reaction time was regressed from this plot. By taking the derivative of this equation \( [M] = 0.04 t^2 - 1.19 t + 8.6 \) with respect to time, the rate of monomer consumption (polymerization) was obtained as a function of monomer concentration \(-r_m = k[M]^\alpha\). Figure 3.2 shows a plot of \( \ln(\text{rate of monomer consumption}) \) versus \( \ln(\text{monomer concentration}) \). The slope of this plot gives the apparent reaction order of 0.5. The intercept is equal to the natural log of the rate constant; the rate constant for thermal polymerization was calculated to be 0.4 \( \text{mol}^{0.5} \text{L}^{-0.5} \text{hr} \). This rate constant and the activation energy of 19 kcal/mol provided by Chu et al. [Chu et al., 1981] were used in the Arrhenius equation \( (k = Ae^{-Ea/RT}) \) to estimate the rate constants of thermal polymerization of styrene for my experimental conditions. They are \( 1.4 \times 10^{-3} \text{mol}^{0.5} \text{L}^{-0.5} \text{hr} \) at 50 °C, \( 3.2 \times 10^{-3} \text{mol}^{0.5} \text{L}^{-0.5} \text{hr} \) at 60 °C, and \( 1.1 \times 10^{-2} \text{mol}^{0.5} \text{L}^{-0.5} \text{hr} \) at 75 °C.

As seen in Figure 3.1, at 127.3 °C and similarly high temperatures typically used for ATRP of styrene, the monomer concentration drops significantly in the first 10 hours due to thermal polymerization but remains nearly constant at the lower temperatures used in this work. With low conversions at these lower temperatures, polymer growth should not be limited by mass transfer of monomer to propagation sites, and I hypothesized that this would result in continuous polymer growth for long polymerization times.
Figure 3.1. Monomer concentration versus time in the thermal polymerization of styrene. Closed symbols represent experimental data at 127.3 °C, which have been adapted with permission from Walling et al., Copyright (1946) American Chemical Society. Curves represent my predictions of monomer concentration versus time at different temperatures.
Figure 3.2. Relationship between the rate of monomer consumption and monomer concentration in the thermal polymerization of styrene. Symbols represent experimental data at 127.3 °C, which have been adapted with permission from Walling et al., Copyright (1946) American Chemical Society.
Another factor that may contribute to the nonlinear growth observed at higher temperatures is termination by chain transfer and bimolecular termination. Chain-transfer processes increase the overall rate of termination, thereby decreasing the degree of polymerization [Fried, 1995]. The number-average degree of polymerization is a function of the chain-transfer coefficient (as shown in Equation 3.1), which is a ratio of chain-transfer rate constant \( (k_{tr}) \) to propagation rate constant \( (k_p) \).

\[
\frac{1}{X_n} = \frac{1}{(X_n)_o} + C \left( \frac{[SH]}{[M]} \right)
\]  

(3.1)

where \( (X_n)_o \) is the degree of polymerization in the absence of chain transfer and \( C = k_{tr}/k_p \) is the chain-transfer coefficient. \([SH]\) and \([M]\) represent the concentrations of chain transfer agent and monomer, respectively.

Both \( k_p \) and \( k_{tr} \) show a strong Arrhenius dependence on temperature [Fried, 1995], and termination by chain-transfer becomes more pronounced at higher temperatures [Matyjaszewski et al., 1997]. In their study of graft polymerization of PS, Jeyaprakash et al. [Jeyaprakash et al., 2002] attributed a decreased growth rate after approximately 10 h to an increasing loss of active chain ends. This conclusion is consistent with increased chain-transfer and bimolecular termination events at higher temperatures.

In this work, a kinetic study was done to understand the surface-initiated growth rate behavior of styrene at lower temperatures in order to provide strategies that minimize self-initiation of this monomer and to achieve better control over graft layer thickness (i.e., graft molecular weight). Figure 3.3 shows that dry layer thicknesses varied linearly
with time to produce thick PS brushes at three different temperatures. To the best of my knowledge, these are the thickest (dry layer) PS brushes grown by ATRP at such low temperatures. The error bars in Figure 3.3 represent the standard deviations between two replicates. For each surface, at least three ellipsometric measurements were taken at different locations to examine uniformity of thickness. In all cases, the difference among the same-surface thickness measurements was < 3%, demonstrating that the polymer films were macroscopically uniform. As seen in Figure 3.3, the growth rate was constant even without the addition of Cu(II) or sacrificial initiator. This supports my hypothesis that continuous polymer growth could be achieved for long polymerization times at lower temperatures by minimizing mass transfer limitations and side reactions such as chain transfer.

As seen in Figure 3.3, the rate of polymerization increases with increasing temperature. Figure 3.4 shows the Arrhenius plot obtained from these data. From the slope, an apparent activation energy of 11 ± 3 kcal mol⁻¹ was calculated for the surface-initiated ATRP, which agrees well with the value reported for the homogeneous dNbpy/CuBr ATRP system (11.9 kcal mol⁻¹) [Matyjaszewski et al., 1997].

Atomic force microscopy was used to examine the nanoscale surface topography of the PS brushes. Each scan covered a 1 μm × 1 μm lateral area. Root mean square (RMS) roughnesses, which give a reasonable measure of surface roughness on the nanometer scale, were ≤ 1.4 nm, and, for every surface, the RMS roughness was ≤ 3% of the measured (average) ellipsometric thickness.
Figure 3.3. Growth of surface-initiated polystyrene at 50–75 °C from PGMA-modified silicon surfaces with α-bromoester initiator. The catalyst was 86 mM Cu(I)Br/PMDETA. The concentration of styrene was 8.6 M.
Figure 3.4. Arrhenius plot for the PMDETA/CuBr ATRP of styrene. The catalyst was 86 mM Cu(I)Br/PMDETA. The concentration of styrene was 8.6 M.
The RMS roughness ($R_{\text{MS}} = \sqrt{\frac{\sum_{i=1}^{N} (Z_i - Z_{\text{ave}})^2}{N}}$) is the standard deviation of the Z values within a given area. $Z_{\text{ave}}$ is the average Z value within the given area, $Z_i$ is the current value, and N is the number of points within a given area. Water contact angles of polymer brushes were determined to be $90^\circ \pm 3^\circ$ at room temperature, which is consistent with previous wetting experiments with water on PS brushes [Jordan et al., 1999]. Taken together, the AFM and contact angle results suggest that the PS brushes were smooth, uniform, and dense.

In situ ellipsometric swelling measurements were conducted to estimate the degree of polymerization, N, and the grafting density, $\sigma$, of the tethered chains. Equation 3.2 was used to estimate N. This equation was originally proposed by Jordan et al. [Jordan et al., 1999] and is based on the analytically-determined swollen brush thickness resulting from the self-consistent mean field (SCF) analysis of a grafted polymer brush presented by Milner et al. [Milner, 1988; Milner et al., 1988];

$$N = \frac{[1.074(h_{\text{swollen}}^*)^{3/2}]/[(h_{\text{dry}}(\text{Å}))^{1/2}]}{\text{(3.2)}}$$

It should be noted that the swollen heights, $h_{\text{swollen}}^*$, predicted by the SCF theory result from a parabolic segment density profile. However, the heights obtained from ellipsometry, $h_{\text{ellip}}^{\text{box}}$, result from fitting the ellipsometric data using a step-like segment density profile (“box-like” model). As noted by Milner et al. [Milner et al., 1988] and shown in Appendix A, the ratio of the parabolic $h_{\text{swollen}}^*$ to the step-function equilibrium height is $4/3$: $h_{\text{swollen}}^* = (4/3) \cdot h_{\text{ellip}}^{\text{box}}$. Therefore, all my measured swollen heights, $h_{\text{ellip}}^{\text{box}}$,
Figure 3.5. AFM phase and topographical images (1 μm × 1 μm lateral area) showing the morphology of the surfaces. RMS roughness values are 0.3 nm for the initiator-functionalized PGMA layer (a) and 0.6 nm for the grafted PS layer with 18.5 nm thickness (b).
were multiplied by 4/3 for my calculation of N.

By doing this adjustment, I replace one idealized profile (box) with another, albeit more representative, profile (parabolic) and implement consistently the result of the SCF model [Milner, 1988; Milner et al., 1988].

Table 3.1 summarizes the measured thicknesses and calculated degrees of polymerization for three surfaces that cover a wide range of initial dry layer thicknesses, $h_{dry}$. The first two samples listed in Table 3.1 were prepared by polymerization at 60 °C for two different times, and the third sample was prepared by polymerization at 75 °C.

For these brush layers, $\sigma$, was calculated from Equation 3.3, and the distance between grafting sites, D, was estimated by Equation 3.4.

$$\sigma = \frac{\rho_o h_{dry} N_{Av}}{m_o N}$$ \hspace{1cm} (3.3)

$$D = \left(\frac{4}{\pi \sigma}\right)^{1/2}$$ \hspace{1cm} (3.4)

In Equation 3.3, $m_o$ is the monomer molecular weight, and $N_{Av}$ is Avogadro’s number. As is done typically for polymer brush systems, Equation 3.3 assumes that the dried layers collapse to their bulk density, $\rho_o$, and Equation 3.4 assumes that each brush chain occupies a cylindrical volume with its base coincident with the grafting surface [Luzinov and Tsukruk, 2002]. Alternatively, one could assume a hexagonal volume element that accounts for packing volume fully. In that case, the factor of $4/\pi$ is replaced with $2/\sqrt{3}$. In Equation 3.3, the thickness of the underlying PGMA was subtracted in determining $h_{dry}$.

To confirm that dense PS brushes were formed, the distance between grafting
sites, $D$, was compared with the expected radius of gyration, $R_g$, of the corresponding PS chain in the good solvent, toluene. The dimensions of the polymer chains in a good solvent were considered here since $R_g$ is being compared to the $D$ calculated from $N$, which was based on measurements in the swollen state. Equation 3.5 applies to PS in a good solvent [Parsonage et al., 1991; Zhao and Brittain, 2000].

$$R_g (\text{Å}) = 1.86 \cdot N^{0.595}$$ (3.5)

The brush regime is characterized by $D < 2R_g$ [Kilbey et al., 2001]. As Table 3.1 shows, my calculated $D$ values are significantly less than $2R_g$ in all cases, confirming that the PS layer has adopted the characteristic stretched configuration ascribed to polymer brushes of high grafting densities. By way of comparison, my reported grafting densities are considerably higher than those reported for poly(4-vinylpyridine) brushes grafted from a planar surface by free radical chain polymerization [Biesalski and Ruhe, 2002]. However, my reported grafting densities were lower than those reported for PS brushes grafted from gold substrates by surface-initiated anionic polymerization by means of self-assembled monolayers [Jordan et al., 1999]. As indicated before, PGMA should lead to higher graft densities than SAM layers. The initiator density that results from anchoring the initiator molecules to the PGMA layer should be greater than the one that results from anchoring the initiator to the SAM layer. But in my case it appears that a high percentage of initiator sites either 1) did not generate a chain because they were not approached by the relatively large catalyst complex to form radicals or 2) generated a chain that terminated by bimolecular radical coupling early in the reaction. However, in their case of surface-initiated anionic polymerization, the polymerization was probably more
controlled, resulting in a higher initiator efficiency.

An interesting consequence of these high graft densities is that the layers swell only modestly when immersed in a good solvent. Biesalski and Rühe showed that the degree of swelling decreases significantly with increasing graft density. In my case, because of high graft densities, the chains are already stretched in the dry state, and immersing them in a good solvent does not induce a significant change in height. From Table 3.1, Sample 1 had a lower graft density than Samples 2 and 3, and its swelling ratio \( \frac{h_{\text{ellip}}}{h_{\text{dry}}} \) was significantly higher. Samples 2 and 3 had graft densities that were equal within experimental uncertainties, and their swelling ratios were also equal within the limits of uncertainty. Thus, swelling ratio correlated to graft density in this study as well.

Another interesting result comes from comparing the estimated initiator density of 8 ± 1 initiators/nm\(^2\) to the values of graft density reported in Table 3.1. The ratio of graft density to initiator density provides an estimate of the initiator efficiency. From my measurements, I estimate that 2.1–4.3% of initiator sites produce a grafted polymer chain.

### 3.4 Conclusions

Thick polystyrene brushes were synthesized from PGMA/BPA-modified silicon substrates by ATRP at temperatures well below \( T_g \) for PS. I showed that at temperatures \( \leq 75 \, ^\circ \text{C} \), the polymer growth does not appear to be limited by mass transfer of monomer to propagation sites. Constant growth rates were obtained, indicating indirectly that polymerization was controlled. AFM, contact angle, and swelling studies confirmed that
homogeneous PS layers were formed with high graft densities. This methodology provides many opportunities for the formation of uniform, grafted polymer nanolayers with independent varying grafting densities that can be used to modify polymeric membranes for separation applications.

Table 3.1. Swelling experiment results for PS grafted layers.

<table>
<thead>
<tr>
<th>h_{dry} (nm)</th>
<th>h_{ellip}^{*} (nm)</th>
<th>h_{swollen}^{*} (nm)</th>
<th>N</th>
<th>R_{g} (nm)</th>
<th>σ (chains/nm²)</th>
<th>D (nm)</th>
<th>swelling ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td>30.9 ± 0.1</td>
<td>63.4 ± 0.3</td>
<td>84.5 ± 0.4</td>
<td>1412± 102</td>
<td>13.9 ± 0.6</td>
<td>0.159 ± 0.036</td>
<td>2.9 ± 0.3</td>
<td>2.05 ± 0.02</td>
</tr>
<tr>
<td>61.8 ± 1.2</td>
<td>97.5 ± 1.8</td>
<td>130 ± 2.4</td>
<td>2026± 76</td>
<td>17.2 ± 0.3</td>
<td>0.185 ± 0.010</td>
<td>2.6 ± 0.1</td>
<td>1.58 ± 0.06</td>
</tr>
<tr>
<td>116 ± 6</td>
<td>190 ± 9.8</td>
<td>253.3 ± 9.8</td>
<td>4032± 337</td>
<td>26.0 ± 1.3</td>
<td>0.176 ± 0.023</td>
<td>2.7 ± 0.2</td>
<td>1.64 ± 0.18</td>
</tr>
</tbody>
</table>

a: polymerization temperature = 60 °C  b: polymerization temperature = 75 °C


4.1 Introduction

Surface-initiated polymerization has gained significant attention in recent years because it provides the opportunity to modify and control the surface properties of materials precisely. Some of the surface properties that can be altered by grafting polymer films from the surface are tribology, wettability, conductivity, and adhesion. Polymer brushes have been used as modifying layers to produce stimuli-responsive and switchable surfaces [Luzinov et al., 2004; Minko et al., 2003; Zhao, 2000], media for chromatographic separations [Nagase et al., 2008; Sulitzky et al., 2002; Van Zanten, 1994], and membranes for separation applications [Jain et al., 2007; Singh et al., 2005; Singh et al., 2008; Bhut et al., 2008; Ito et al., 1997; Yang and Ulbricht, 2008]. Different techniques, grafting to and grafting from, have been used to create polymer brushes on substrates. In general, denser polymer brushes result from application of the “grafting from” technique, and the layer thickness can be controlled independently of graft density [Kim et al., 2000; Singh et al., 2007; Mei et al., 2005; Wu et al., 2003; Wu et al., 2007]. Grafting from approaches that employ controlled free radical methods also enable block copolymers to be made with high reinitiation efficiencies [Zhao and Brittain, 2000; Boyes et al., 2002; Huang et al., 2002; Bao et al., 2006].
In Chapter Three, I reported data on the surface-initiated atom transfer radical polymerization (ATRP) of styrene at low temperature. Constant growth rates were obtained for this system, indicating indirectly that polymerization was controlled, even without pre-addition of Cu(II) or sacrificial initiator. That study showed that at temperatures of 50–75 °C, continuous polymer growth could be achieved by minimizing thermal self-polymerization in solution, the associated viscous mass-transfer resistance for monomer from solution to surface reaction sites, and other side reactions.

Kinetic studies of the solution-phase ATRP of styrene at temperatures greater than the glass transition temperature of 95 °C for PS showed that the polymerization rate was first order with respect to monomer concentration [Matyjaszewski et al., 1997; Percec et al., 1996; Wang et al., 2005]. Herein, I report the results of a kinetic investigation of the low temperature, surface-initiated ATRP of styrene. Specifically, this chapter describes the kinetics of surface-initiated ATRP of styrene at 60 °C using the CuBr/PMDETA catalyst/ligand system. A wide range of monomer concentration was studied in order to determine the reaction order with respect to the monomer concentration. In anisole, the polymerization rate was first order with respect to monomer concentration up to a monomer concentration of approximately 3.5–4.3 M; thereafter, it unexpectedly became apparent zero order for higher monomer concentrations. A kinetic model is developed to explain this change in rate order.
4.2 Experiments

4.2.1 Materials

Chemicals were used as received, except styrene, which was dehibited by passing it through a column of Al₂O₃ prior to use. They were styrene (≥ 99%, Aldrich), aluminum oxide (~150 mesh, Aldrich), copper (I) bromide (Cu(I)Br, 99.999%, Aldrich), toluene (Certified A.C.S., Fisher), 1,1,4,7,7-pentamethyldiethylenetriamine (PMDETA, 98%, Alfa Aesar), methyl ethyl ketone (MEK, 98%, Baker), glycidyl methacrylate (97%, Aldrich), 2,2-azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich), and 2-bromo-2-methylpropionic acid (BPA, 98%, Acros).

Experimental details regarding the preparation and functionalization of silicon substrates with poly(glycidyl methacrylate) (PGMA) and initiator groups and the surface-initiated ATRP of styrene were reported in Chapter Three. In this study, polymerization reactions were performed for a minimum of four different styrene concentrations using anisole as the solvent, covering a range from 0.86 M to 8.6 M (bulk). Polymerizations were carried out in a nitrogen atmosphere at 60 °C using CuBr catalyst concentrations of 21.5 mM, 43.0 mM and 86.0 mM. For each catalyst concentration, I looked at how the polymer thickness changed with monomer concentration. Each initiator-functionalized PGMA layer was brought in contact with the specific polymerization solution for 5 h. After treatment, the surfaces were soaked in MEK for 10 minutes and rinsed with MEK three times, and polymer layer thicknesses were measured using ellipsometry, as described in Chapters Two and Three.
4.3 Results and Discussion

Gopireddy and Husson showed that surface-initiated ATRP from a flat surface is first-order in monomer concentration [Gopireddy and Husson, 2002]. Using a simple kinetic model, they showed that for controlled ATRP in the absence of chain transfer, the layer thickness, $h$, increases with time, $t$, according to the following rate equation:

$$\frac{dh}{dt} = k'_p [I][Cu(I)][M]$$  \hspace{1cm} (4.1)

where $[I]$, $[Cu(I)]$, and $[M]$ represent the initiator, catalyst, and monomer concentrations in solution, and $k'_p$ is an apparent propagation rate constant that collects other rate parameters and constants, as described in detail by Sankhe et al. [Sankhe et al., 2006].

In order to determine the reaction order with respect to the monomer concentration for my system, a reaction rate order diagram (Figure 4.1) was prepared using initial layer growth rates (in nm/hr) at each monomer concentration (in M). Reaction rate order was determined by a linear, least-squares regression of the data. As seen in Figure 4.1, for all three catalyst concentrations, up to a monomer concentration of approximately 3.5–4.3 M, the reaction is first order in $[M]$. A plateau is reached for higher $[M]$ indicating that the reaction became apparent zero order with respect to monomer concentration. This transition from first- to zero-order reaction kinetics was not seen for solution-phase ATRP of PS using the CuBr/dNbipy catalyst/ligand system at 110 °C [Matyjaszewski et al., 1997]. Based on my knowledge, this transition in reaction order has not been reported in the literature for the surface-initiated ATRP.
In ATRP, the transition metal catalyst operates as a reversible halogen atom transfer reagent that establishes a dynamic equilibrium between active and dormant species. Polymerization rate is first order with respect to the catalyst concentration. To rationalize the behavior observed in Figure 4.1, I first considered the possibility that the system was experiencing a change from diffusion-limited growth at low monomer concentrations to reaction rate-limited growth at high monomer concentrations. If growth is diffusion limited in the low concentration range, then adding more catalyst should have no impact on the growth rate. To test this idea, polymerizations were done at different catalyst concentrations covering a wide range from 21.5 mM to 86.0 mM. Figure 4.1 shows that growth rates increased with increasing catalyst concentration, with an apparent first-order dependence on catalyst concentration, which is the expected behavior for ATRP. A second reaction rate order diagram (Figure 4.2) was prepared using initial layer growth rates (in nm/hr) at each catalyst concentration (in M) for three different monomer concentrations. Figure 4.2 shows the results of a fit to first-order rate equation. These results show a close fit to the first order reaction in \([Cu(I)]\). The linear, least-squares regressions of the three sets of data give a slope of 0.8 for the monomer concentration of 2.15 M, 1.0 for the monomer concentration of 4.3 M, and 1.2 for the monomer concentration of 8.6 M. It should be noted that the slope of the line represents the reaction order with respect to the catalyst concentration, \([Cu(I)]\).

From the above analysis, I conclude that the growth rate is not diffusion limited at low monomer concentrations. It should be emphasized that the complexes of CuBr and PMDETA were fully soluble in styrene/anisole mixtures over the entire styrene
concentration range. This fact is confirmed by the behavior of the system as a function of catalyst concentration. By simple phase-equilibrium thermodynamics, if the catalyst solubility was limiting, then I would have seen no impact of adding additional catalyst on the surface-initiated growth rates for this system as only the dissolved catalyst has the opportunity to activate growth from the surface. As such, catalyst solubility cannot be a factor to describe the observed rate order transition.

Given the transition from first- to zero-order reaction kinetics, I also considered the possibility that the PS brushes might be experiencing a phase transition as a result of differences in the solution composition. If the polymer brushes were to experience a phase transition (from collapsed to extended state), then that would affect the rate of polymer growth. In this hypothetical situation, at low monomer concentration (i.e., high anisole concentration), the rate could be low because the chains are collapsed, and reactive chain ends are less accessible for reaction. As styrene concentration increased, the chains would extend more and more into this good solvent, thereby increasing the rate. Then, at some high enough concentration of styrene, the chains would be fully extended. Adding more styrene would not extend them any further, so the rate would stabilize to a constant value.

To test this idea, PS brushes with similar dry layer thicknesses were brought into contact with pure anisole, pure styrene, and a 2.15 M styrene solution in anisole, and solvent-swollen layer thicknesses were measured by ellipsometry using a fluid cell described in Chapter Three. The results displayed in Table 4.1 indicate that the PS brushes behave similarly in these different solutions. Therefore, I conclude that the
behavior seen in Figure 4.1 is not caused by a phase transition due to the variation in the solution composition.

To further support this result, the solubility parameters were analyzed. They were reported to be 9.1 (cal/cm$^3$)$^{0.5}$ for polystyrene [Sperling, 2001], 9.3 (cal/cm$^3$)$^{0.5}$ for styrene [Shen and Fong, 1994], and 9.7 (cal/cm$^3$)$^{0.5}$ for anisole [Paul, 2004]. It frequently is found that solvents having solubility parameters within about one unit (cal/cm$^3$)$^{0.5}$ of a polymer are considered to be good solvents for that polymer. Based on this rule of thumb, styrene and anisole are both considered to be good solvents for polystyrene, as supported by swelling measurement results displayed in Table 4.1.

Given that the transition from first- to zero-order reaction rate is not associated with a change from diffusion- to rate-limited growth, nor due to a phase transition due to differences in PS-brush solvency in solutions of different monomer concentration, I initially hypothesized that the formation of an intermediate, as suggested by the reaction mechanism shown in Appendix B, is responsible for the change in reaction order that is observed in Figure 4.1. After studying the reaction mechanism more closely, I considered that one possible ‘intermediate’ could be the monomer adsorbed to the periphery of the PS film. There are many adsorption isotherm models, such as the Langmuir adsorption isotherm, that show saturation in adsorbed amount (in this case of monomer) with increasing solution concentration of adsorptive (monomer). Therefore, I hypothesized that the observed behavior here could be explained by the classic adsorption/reaction model. The reaction mechanism shown here might be responsible for the change in reaction order that is observed in Figure 4.1:
Similar types of mechanism have been suggested for catalytic reactions that take place in a polymer. In that case, the reactants must be first transported into the polymer and then combine chemically with the catalytic groups. The adsorption/desorption mechanism is not only valid for polymeric catalysts, but for reaction on solids in general [Gates, 1992]. Here, I consider the adsorption of the monomer (M) from solution onto the flat surface (S). As shown in Equation 4.3, the adsorbed monomer (M*) may desorb and return to solution or react with the radical species (I*) if it is in close enough proximity to an active chain end. Direct adsorption onto the reactive radical sites is not included in this set of equations because, as a result of the ATRP equilibrium, the concentration of radical chains is negligible compared to the concentration of dormant chains.

Adsorption data frequently are reported in the form of adsorption isotherms. Here, the isotherm model represents the amount of monomer adsorbed on a solid at different monomer concentrations.

In deriving a rate law for the rate of adsorption of the monomer onto the vacant sites on the surface, the reaction shown in Equation 4.3 can be treated as an elementary reaction. The rate of adsorption of the monomer molecules to the surface is proportional to the number of collisions that these molecules make with the surface. The collision rate is proportional to monomer concentration. Since the monomer molecules adsorb only

\[
\begin{align*}
I + Cu(I) & \underset{k_d}{\overset{k_i}{\rightleftharpoons}} I^+ + Cu(II) \quad \text{(4.2)} \\
M + S & \underset{k_2}{\overset{k_1}{\rightleftharpoons}} M^* \quad \text{(4.3)} \\
I^+ + M^* & \overset{k_p}{\rightarrow} IM^* \quad \text{(4.4)}
\end{align*}
\]
onto vacant sites, the rate of adsorption is also proportional to the fraction of vacant sites. Therefore, the rate of monomer adsorption can be written as follows:

\[ r_{\text{ads}} = k_{\text{ads}} [M] \theta_v \]  

(4.5)

where \( \theta_v \) is the fraction of vacant sites and \([M]\) is the monomer concentration in solution.

The rate of desorption of the monomer molecules from the surface is a first-order process and is directly proportional to the concentration of sites occupied by the monomer molecules:

\[ r_{\text{des}} = k_{\text{des}} \theta_M \]  

(4.6)

where \( \theta_M \) is the fraction of sites occupied by the monomer molecules.

The adsorption and desorption rates are equal at equilibrium and \( \theta_v + \theta_M = 1 \). Therefore,

\[ k_{\text{ads}} [M] \theta_v = k_{\text{des}} \theta_M \]  

(4.7)

By substituting \((1 - \theta_M)\) for \( \theta_v \) and \( K_M \) for \( k_{\text{ads}}/k_{\text{des}} \),

\[ \theta_M = \frac{K_M [M]}{1 + K_M [M]} \]  

(4.8)

\( \theta_M \) can be written as follows:

\[ \theta_M = \frac{[M^*]}{[S]_T} \]  

(4.9)

where \([M^*]\) is the concentration of the monomer adsorbed to the surface, and \([S]_T\) is the total concentration of sites on the surface. \([S]_T\) is assumed to remain constant. The free radical that is formed on the surface adds adsorbed monomer (if it finds one or more in its proximity) via free radical attack, as shown by the reaction in Equation 4.4. The rate of
monomer consumption can be written as follows:

$$-r_M = k_P [I^g][M^+]$$  \hspace{1cm} (4.10)

Substituting Equation 4.9 into Equation 4.8 and then substituting the resulting expression for $[M^+]$ into Equation 4.10 yields

$$-r_M = \frac{k_p K_M [S][I^g][M]}{1 + K_M [M]}$$  \hspace{1cm} (4.11)

In Equation 4.11, the initiator and the catalyst concentrations are embedded in $[I']$ because, at steady state,

$$[I'] = \frac{k_a[I][Cu(I)]}{k_d[Cu(II)]}$$  \hspace{1cm} (4.12)

Under ATRP conditions, the deactivation rate constant ($k_d$) is much greater than the activation rate constant ($k_a$). Therefore, the denominator in Equation 4.12 is much larger than the product of $k_a$ and $[Cu(I)]$ in the numerator, even though the Cu(II) concentration is very low [Chen et al., 2006; Kim et al., 2003].

As pointed out explicitly by Sankhe et al. [Sankhe et al., 2006], the rate expression given by Equation 4.11 can be re-expressed in terms of a rate of layer thickness increase through a proportionality constant $\beta$. As given by Sankhe et al. [Sankhe et al., 2006], I define an apparent propagation constant, $k_p' = \frac{\beta k_p k_a K_M [S]}{(k_d[Cu(II)])}$. Substituting Equation 4.12 into Equation 4.11 and introducing this apparent propagation constant yields the final form of the rate equation in terms of layer thickness.
Equation 4.13 describes the growth rate behavior seen in Figure 4.1. At low monomer concentration such that \( I \gg K_M[M] \), the reaction rate is first order in monomer concentration. At high enough monomer concentration such that \( I \ll K_M[M] \), the reaction rate is apparent zero order in monomer concentration. Equation 4.13 also shows that the reaction rate is first order with respect to the catalyst concentration over the entire range of monomer concentration, as observed experimentally in Figure 4.2.

Figure 4.3 shows best fits of the growth rate data presented in Figure 4.1 to the rate equation given by Equation 4.13. It is worth reiterating that monomer concentration remains effectively constant during this type of surface-initiated polymerization [Gopireddy and Husson, 2002]. Clearly, Equation 4.13 captures the features of the experimental data closely. This transition from first- to apparent zero-order reaction kinetics has not been observed for ATRP of PS as mentioned before. One possible reason might be that the previous studies have been done at elevated temperatures, and as the temperature increases the adsorption equilibrium constant \( (K_M) \) decreases such that the term \( K_M[M] \) in the denominator of Equation 4.13 becomes negligible compared to a value of one, and the reaction becomes first- order with respect to the monomer concentration over the full range of monomer concentration.
Figure 4.1. Monomer rate order diagram for surface-initiated ATRP of styrene at 60 °C from poly(glycidyl methacrylate)-coated silicon substrates. Symbols represent experimental data; lines provided to guide the eye show the transition from first-order to zero-order reaction kinetics.
Figure 4.2. Catalyst rate order diagram for surface-initiated ATRP of styrene at 60 °C from poly(glycidyl methacrylate)-coated silicon substrates. Symbols represent experimental data; lines represent fits to a first-order rate equation. Slopes of best-fit lines are 0.8, 1.0, and 1.2 for catalyst concentrations of 2.15 M, 4.30 M, and 8.60 M.
Figure 4.3. Best fits of the growth rate data presented in Figure 4.1 to the rate equation given by Equation 4.13.

Table 4.1. Swelling experiment results for grafted PS layers.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>Dry layer thickness, nm</th>
<th>Layer thickness in solvent, nm</th>
<th>% increase in thickness&lt;sup&gt;a&lt;/sup&gt;</th>
</tr>
</thead>
<tbody>
<tr>
<td>Anisole</td>
<td>125.0 ± 0.5</td>
<td>244.6 ± 6.0</td>
<td>96 ± 6</td>
</tr>
<tr>
<td>2.15 M Styrene</td>
<td>120.4 ± 0.4</td>
<td>250.9 ± 4.4</td>
<td>108 ± 4</td>
</tr>
<tr>
<td>8.6 M Styrene</td>
<td>119.6 ± 0.4</td>
<td>248.6 ± 0.7</td>
<td>108 ± 1</td>
</tr>
</tbody>
</table>

<sup>a</sup>Defined as (thickness in solvent – dry layer thickness)/dry layer thickness × 100 %. 
4.4 Conclusions

A shift was observed in the reaction order (from first to apparent zero order) with respect to the monomer concentration for the surface-initiated ATRP of styrene at 60 °C. I contend that the adsorption/reaction model proposed here, in which a monomer molecule adsorbs to a vacant surface site and then reacts or desorbs without reaction, is responsible for the change in apparent reaction order.


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CHAPTER FIVE
PREPARATION OF POLY(IONIC LIQUID) THIN-FILM COMPOSITE
MEMBRANES FOR CO₂ SEPARATION USING SURFACE-INITIATED
ATOM TRANSFER RADICAL POLYMERIZATION

5.1 Introduction

Fossil fuel consumption continues to increase resulting in a drastic increase in atmospheric CO₂ concentration. This increase in CO₂ concentration has contributed to global warming, which has become a major environmental concern today [Sun et al., 2005]. In Chapter One, I summarized the most widely practiced methods for CO₂ capture. Here, I focus discussion on the use of membrane technologies.

Relative to other gases such as methane and nitrogen, carbon dioxide has been found to have good solubility in ionic liquids [Tang et al., 2005]. The extent of CO₂ solubility in ionic liquids depends on the ionic liquid cation, anion, and substituents, with anions playing a major role [Hu et al., 2006]. The drawback of separation using room temperature ionic liquids (RTILs) [Baltus et al., 2005] is that the volume of the RTIL solvent required is proportional to the volume of the gas to be processed. Therefore, there would be a large volume of RTIL required to separate CO₂ at low concentration from large volume flue gas streams. RTIL cost prohibits this technique for large-scale commercial usage. Supported ionic liquid membranes (SILMs) have been proposed as an alternative platform for CO₂ separation in order to avoid using a large volume of RTIL.
SILMs, which are porous membranes filled with room temperature ionic liquids, have been used at the laboratory scale for CO$_2$ separation [Bates et al., 2002; Camper et al., 2004; Scovazzo et al., 2004]. Yet, a major weakness of SILMs is that the ionic liquid is held in the membrane pores by capillary forces such that, when the transmembrane pressure is high enough, the ionic liquid is pushed out of the membrane.

While ionic liquids may not fulfill their promise for gas separations for the reasons cited, it has been shown that poly(ionic liquids) (PILs) can have higher CO$_2$ absorption capacity than room temperature ionic liquids [Tang et al., 2005]. PIL-based membranes have been prepared by casting, which has resulted in non-porous membranes with thicknesses in the range of 80–200 μm [Hu et al., 2006]. It is important to note that these membranes have been prepared as copolymers, whereby the IL monomer provided selectivity and the comonomer adjusted the mechanical properties [Hu et al., 2006].

Permeation of CO$_2$ through the dense PIL layer is expected to occur via the well-known solution-diffusion mechanism. Gas transport across the membrane involves diffusion through the boundary layer at the membrane-gas interface, sorption into the selective layer on the upstream side of the membrane, diffusion through the selective layer, and desorption from the downstream side of the membrane. Each of these steps imposes a resistance to mass transport. In the solution-diffusion mechanism, the gas typically is absorbed by the selective polymeric membrane on the high pressure (feed) side. The amount of gas that is absorbed is directly proportional to the gas pressure and the proportionality constant is the solubility coefficient. The absorbed gas diffuses through the selective layer as a result of a chemical potential gradient across the layer, as
described in Chapter One. The flux (F), which is the rate of gas transport per unit area through the membrane, can be obtained by the following equation at low values of pressure, where the ideal gas law applies:

\[ F = \frac{DS(P_H - P_L)}{L} \]  

(5.1)

L is the thickness of the selective layer, D is the diffusion coefficient for transport through the membrane, and S is the solubility coefficient in the selective layer. Oftentimes, this equation is written in terms of the permeability (or permeability coefficient) (P) of a gas, which is the product of its solubility coefficient and its diffusion coefficient. As seen in Equation 5.1, the flux is inversely proportional to the selective layer thickness. Therefore, having a thinner selective layer would be beneficial for improving flux. Since the permeability is independent of the thickness of the membrane, unlike flux, it is truly a property of the polymeric material and the processing history. The diffusion coefficient of the gas in the polymer is determined largely by the relative motion of the polymer chains and the penetrant inside the selective layer. The ideal permeability selectivity, which also is called permselectivity, is determined on the basis of the permeabilities of pure components A and B. Permselectivity is calculated by the following equation [Patel et al., 2004]:

\[ \alpha_{A,B} = \frac{P_A}{P_B} = \left( \frac{D_A}{D_B} \right) \times \left( \frac{S_A}{S_B} \right) \]  

(5.2)

This factoring of the thermodynamic and kinetic factors allows the effects of detailed changes in the characteristics of the polymer backbone to be analyzed [Koros et al., 1992].
Here, I report a solution to the leaking problem of SILMs and also address the need for high selectivity, high flux membranes for CO₂ capture. Surface-initiated atom transfer radical polymerization (ATRP) was used to graft PIL nanolayers covalently from the surfaces of commercial membrane supports such as low molecular weight cutoff (MWCO) regenerated cellulose ultrafiltration (UF) membranes. Because the PIL nanolayer is attached to the membrane surface covalently, there is no concern for leakage from the support. Relative to the PIL membranes prepared by solvent casting [Hu et al., 2006], these composite membranes offer an ultrathin selective layer (roughly 1000 times thinner), with uniform coverage ensured by the ATRP process.

Experimentally, poly[2-(methylacryloyloxy)ethyl-trimethylammonium chloride] (poly[METAC]) layers were grown from the membrane support, and ion exchange was used to replace Cl⁻ with BF₄⁻. The resulting poly(ionic liquid) thin-film composite membranes were characterized by ATR-FTIR spectroscopy, FE SEM, and XPS. A set of experiments was performed on a model flat substrate in order to measure the polymer layer growth kinetics and guide the design of experimental polymerization conditions for the membrane work. Pure-component CO₂ and N₂ permeabilities were measured for unmodified and modified membranes using a home-built permeation cell test apparatus.

5.2. Experimental

5.2.1. Materials

Composite membranes comprising a regenerated cellulose (RC) ultrafiltration layer on an ultrahigh molecular weight polyethylene support was provided as a generous
gift from Millipore Corporation. These membranes have a nominal MWCO of 30 kDa. The 30 kDa molecular weight cut off membrane is designed in a way such that roughly 90% of molecules with a molecular weight of 30 kDa would be rejected by the membrane. The thickness of the porous RC layer is 40 μm, and the thickness of the porous polyethylene support is 200 μm. The membrane was cut into circular disks with a diameter of 52 mm before use. The resistance to flow of gas through this support would be negligible in comparison to the resistance to diffusion through the dense PIL layer. Thus, this relatively thick membrane support provides the mechanical strength without negatively impacting flux. Commercial thin-film polyamide NF membranes (FILMTEC BW30, Dow NF-270), and macroporous RC membrane discs (average effective pore diameter 1.0 μm, 47 mm diameter, 100 μm thickness) purchased from Whatman, Inc. also were used.

These chemicals were used as received, with purities reported in wt.%: anhydrous acetonitrile (99.8%, Aldrich), anhydrous tetrahydrofuran (THF, 99.9%, Aldrich), 2,2-azobis(2-methylpropionitrile) (AIBN, 98%, Aldrich), 2-bromo-2-methylpropionic acid (BPA, 98%, Acros), 2-bromo-2-methylpropionic acid (BIB, 98%, Aldrich), 2,2'-bipyridyl (bipy, >99%, Aldrich), copper(I) chloride (≥99.995%, Aldrich), copper(II) chloride (99.99%, Aldrich), ethanol (99.5%, Aldrich), glycidyl methacrylate (97%, Aldrich), HPLC water (Aldrich), hydrogen peroxide (30% in water, VWR), methanol (99.8%, Aldrich), methyl ethyl ketone (MEK, 98%, Baker), [2-(methylacryloyloxy)ethyl]trimethylammonium chloride (METAC, 75% solution in water), triethylamine (≥99.5%, Aldrich), and sulfuric acid (95~98%, EMD).
Silicon wafers (Silicon Quest International) with a crystal orientation of $<1-0-0>$ were diced into 1 cm × 3 cm sample sizes and used as substrates for nanolayer growth studies. Prior to use, the silicon substrates were cleaned by sonication in deionized water for 30 minutes, treated with a 3:1 mixture by volume of concentrated $\text{H}_2\text{SO}_4$ and $\text{H}_2\text{O}_2$ (Caution: This mixture reacts violently with organic compounds. Minimal volumes should be used with appropriate gloves, goggles, and a face shield for protection) for 1 hour at approximately 70 °C, and then rinsed thoroughly with HPLC water.

5.2.2. Surface-initiated ATRP

RC membranes were soaked in water for 15 minutes in order to remove glycerine, which is used to preserve the structure of these membranes during the manufacturer drying process. The membranes were rinsed with methanol in order to remove water so that it will not react with 2-BIB, and then equilibrated with anhydrous THF. The advantage of using methanol is that it has a higher vapor pressure than water, and, therefore, membranes dry faster.

The NF-270 membranes were prepared as follows: The polyamide membranes were immersed in a solution of 50% (v/v) ethanol, 45% water, and 5% sulfuric acid for 24 hours. This step generates reactive amine groups for incorporation of 2-BIB as a surface initiator.

Several methods were studied for incorporating ATRP initiator groups into the base membrane supports. First, I describe direct immobilization of the initiator precursor, 2-BIB. RC membranes were brought in contact with a solution of 3 mM 2-BIB and 3 mM
triethylamine in anhydrous THF (solvent) for 2 hours. A volume of approximately 60 ml was used for each membrane disc (with a diameter of approximately 52 mm). For NF-270 membranes, the membranes were immersed in a 2 mM solution of 2-BIB in anhydrous acetonitrile for 3 hours.

Initial work found that the RC membranes had the tendency to roll after the initiator incorporation reaction and drying. Re-flattening of the membrane would result in cracking of the membrane. Therefore, two interlocking Teflon rings with diameters of 50 mm and 48 mm were designed and made by personnel in Clemson University Machining and Technical Services. The membranes were held flat between the two rings during reaction and drying, which prevented them from rolling up and preserved the initial shape of the membrane. After reaction, the initiator-functionalized membranes were washed thoroughly with HPLC water and methanol.

For improving performance for CO₂ separation, I also considered the possibility of coating the RC membranes with poly(glycidyl methacrylate) (PGMA) with two different molecular weights (Mₙ = 46,971 g/mol and a PDI of 3.7 and Mₙ = 300,000 g/mol and a PDI of 2.1 as determined by GPC). The PGMA was prepared by radical polymerization of glycidyl methacrylate in MEK at 60 °C using AIBN as initiator.

As described in the first method, RC membranes provide the necessary reaction sites for surface modification without pretreatment. But surface treatment with PGMA may cover any possible surface defects (i.e., cracks, non-uniform pore-size distribution). The pre-made PGMA was grafted to the surface of the RC membrane, and then residual epoxy groups of PGMA were used as additional reactive sites to attach initiator groups.
Depending on the type of initiator precursor molecules used, one can control which functional groups on the membrane are reacted (epoxy groups of PGMA only, or epoxy and bulk –OH groups of the base membrane). My primary goal in this initial study was to form a dense PIL nanolayer on the membrane surface and to confine this grafted polymer layer to the membrane surface, as opposed to modifying the pore surfaces of the membrane (leading to pore filling).

As mentioned previously, PGMA can react with hydroxyl groups on the surface of regenerated cellulose membranes. The regenerated cellulose membrane was placed in 20 ml of 0.2 wt% PGMA solution in MEK for 1 minute. The PGMA coated membrane was then annealed at 40 °C overnight. Higher temperatures were avoided, as they damaged the membrane. Subsequent rinsing with MEK removed non-bonded PGMA from the membrane. The PGMA coated membrane was reacted either with a solution of 3 mM 2-BIB and 3 mM triethylamine in anhydrous THF (solvent) for 2 hours or with a solution of 3 mM BPA in MEK for 2 hours. It is important to note that both initiator precursors yield the same surface initiator group on the membrane following reaction. After treatment, the surfaces were soaked in MEK for 30 minutes and rinsed with MEK three times. One important note is that the BPA initiator could not be attached by vapor deposition as described in Chapter Three, as that reaction protocol resulted in delamination (i.e., peeling of the cellulose layer from the polypropylene support). Therefore, all the initiator attachment reactions were done in solution, which preserved the membrane integrity.
Poly[METAC] nanolayers were grown from the initiator-functionalized membranes by ATRP. For the ATRP reaction, a mixture of two parts by mass solvent (80:20 (v/v) methanol-water) and one part by mass monomer was used. Cu(I)Cl, Cu(II)Cl₂, and bipy were added to the mixture in the following molar proportions: [METAC]:[Cu(I)Cl]:[bipy]:[Cu(II)Cl₂] = 100:2:5:0.1 and 100:2:5:0.2. The mixture was degassed using three freeze-pump-thaw cycles, as described in Chapter Three. The reaction mixture was then transferred into an oxygen-free glove box, and the initiator-functionalized membranes were put in the polymerization solution for different times. After polymerization, the membrane with grafted poly[METAC] was washed with HPLC water and methanol and dried in a stream of nitrogen. NaBF₄ (14.5 g) was dissolved in HPLC water (150 ml) and brought in contact with the poly[METAC]-modified membranes at room temperature overnight in order to exchange the Cl⁻ anions for BF₄⁻.

For nanolayer growth studies, poly[METAC] was grafted from the PGMA-coated silicon substrates using the same conditions used for the membrane surface modification. The PGMA coating of silicon substrates was done using the exact same protocol described in Chapter Three. A kinetic study was done to study the poly[METAC] layer thickness as a function of time. The Cu(I)/Cu(II) molar ratio was used as an independent variable in order to control polymer growth rate from the flat silicon surfaces.

5.2.3. Permeation Test Setup

Figure 5.1 shows the constant-volume, constant-temperature, variable-pressure permeation test setup built by members of the Advanced Membranes Creative Inquiry
group and members of Dr. Christopher Kitchen’s group at Clemson. This permeation test setup is enclosed in a constant-temperature chamber (not shown) that maintains the temperature to ± 2 °C. A similar type of setup has been described by different groups in previous publications [Lin et al., 2000; Patel et al., 2004]. For each measurement, the test membrane was sandwiched between two pieces of aluminum tape. The pieces of aluminum tape both had an opening with an area of 3.8 cm$^2$ that exposed the membrane to the test gas. The membrane was mounted tightly in the permeation cell to avoid leakage. Initially, the entire system was evacuated to a measured pressure of about 13 Pa using a vacuum pump. A known gas pressure was applied on the upstream side, and the downstream pressure was measured as a function of time.

5.2.4. Characterization

5.2.4.1. Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR)

Attenuated total reflectance Fourier-transform infrared spectroscopy (ATR-FTIR) was used to analyze the surface chemistry of unmodified (base) and polymer-modified membranes. Details of the instrument and measurement conditions are given in Chapter Two.

5.2.4.2. Field emission scanning electron microscope (FE SEM)

Field Emission Scanning Electron Microscopy (FE-SEM, Hitachi 4800) was used to study the morphologies and porosities of the membrane surfaces before and after
surface modification. Membranes were cut into 0.5 cm² with a razor, and they were attached to aluminum stabs with a carbon tape. They were then coated with a layer of platinum a few nanometers thick to make them conductive. The SEM measurements were done at an accelerating voltage of 5 kV.

5.2.4.3. X-ray photoelectron spectroscopy (XPS)

XPS data were collected using a Kratos Axis Ultra photoelectron spectrometer with Al Kα radiation (15 kV, 225 W). All spectra were collected at an electron takeoff angle of 90° to the sample surface. Survey scans were recorded over the 0–1200 eV binding energy range using a pass energy of 80 eV. High-resolution spectra of the C 1s, O 1s, and N 1s core levels also were recorded. Spectral analysis was done using casaXPS software, and all binding energies were referenced to the C 1s binding energy of 285 eV.

5.2.4.4. Ellipsometry

Multi-angle ellipsometry (Beaglehole Instruments Picometer™) was used to measure PIL dry layer thicknesses. Thickness was measured at three or more locations on each sample, with assumed refractive index values of 1.500 for PIL, 1.525 for PGMA, and 1.500 for BPA. Ellipsometric data were fit to a multilayer Cauchy model (Igor Pro software) to determine layer thickness. Further details of the instrument and method were given previously in Chapter Two.
5.3. Results and Discussion

5.3.1. Kinetics of surface-initiated ATRP of poly[METAC]

To guide the subsequent membrane modification work, the polymer layer growth kinetics first were measured from a 3-dimensional PGMA layer structure that represents the membrane surface more closely than a 2-dimensional surface. Compared to a self-assembled monolayer of initiator, the relatively higher initiator density generated by the PGMA [Liu et al., 2004] better reflects the cellulose membrane surface, where initiator can attach throughout the 3-dimensional structure of the cellulose membrane threads and not just at the surface [Singh et al., 2008]. Poly[METAC] was grown from PGMA-coated silicon substrates that had been functionalized with an ATRP initiator. The procedures for deposition of the anchoring PGMA layer on the surface and attachment of the initiator to
the PGMA-modified surface allow regulation of the initiator surface density. As Liu et al. [Liu et al., 2004] discussed, by varying the PGMA layer thickness, one can control the amount of BPA attached to the surface. They showed that there is a linear correlation between the PGMA layer thickness and the density of the anchored initiator. They also showed that for a constant PGMA layer thickness, one could control the initiator density by controlling the temperature and duration of BPA vapor exposure [Liu et al., 2004]. The initiator grafting density can be estimated by multiplying the initiator thickness by the bulk initiator density. Calculation of ‘initiator thickness’ was done as follows: The thickness of the anchoring PGMA layer was measured first. Then, the thickness of the PGMA film treated with BPA was measured. The difference in thickness between the untreated and treated PGMA layer was used as the ‘initiator thickness’ in the estimation of initiator density. Appropriate units (initiator molecules/area) can be obtained by multiplying by Avogadro’s number and dividing by the initiator molecular weight. The density of BPA (1.93 g/cm³) and the BPA molecular weight (167 g/mol) were obtained from the supplier. Using the dry layer thickness increase upon initiator attachment (1.2 ± 0.2 nm), I approximated the initiator density to be 8 ± 2 molecules/nm² for my system. This site density is higher than the approximately 3 initiator molecules/nm² that typically result from self-assembled monolayers of ATRP initiators [Jones et al., 2002]. With this system, initiator densities as high as 40 molecules/nm² have been reported [Liu et al., 2004]. I should mention that unlike the PGMA work presented in Chapter Three, the initiator layers have not been as uniform in this work, and, in some cases, I had major issues with PGMA uniformity.
Poly[METAC] layer thickness was measured as a function of time. The Cu(I)/Cu(II) molar ratio was used as an independent variable in order to control polymer growth rate from the PGMA-modified silicon surfaces. Ellipsometry was used to monitor the change in dry layer thickness as a function of time. Figure 5.2 shows results for two different Cu(II) concentrations. By increasing the molar ratio of Cu(II) (i.e., the deactivating agent) to Cu(I) catalyst, one can decrease the reaction rate and, as a result, increase the degree of control over the polymerization process. Based on reasoning that I presented in Chapter Three, controlled growth is indicated by a linear increase in dry layer thickness with time. As seen in Figure 5.2, for [Cu(I)Cl]:[Cu(II)Cl₂] = 2:0.1, the polymer layer thickness increases nonlinearly with time, indicating that there is a lack of control in polymerization. A now well-documented strategy is to add excess Cu(II) deactivator at the beginning of the polymerization reaction in order to improve the degree of control [Matyjaszewski and Xia, 2001]. In my work, by doubling the Cu(II) concentration ([Cu(I)Cl]:[Cu(II)Cl₂] = 2:0.2), I attained better control (i.e. more linearity) with an associated decrease in the rate of polymerization. It should be pointed out that even though the Cu(II) concentration is doubled, and according to the rate equation one would expect the initial rate (slope) to be halved, it appears from Figure 5.2 that the initial rate decreases by more than a factor of 2. The error bars in Figure 5.2 come from measurements for a different set of chips. Thus, the possible explanation for this behavior is that, unlike the PGMA-related studies that were done in Chapter Three, the variation in ‘initiator thickness’ was significant in this study. In this study, I demonstrated that I am able to grow reasonably thick (about 100 nm), by ATRP standards, PIL nanolayers. The
controlled growth behavior indicates that production of thicker nanolayers is possible if I extend the time of polymerization. In this work, having a thicker polymer layer may be useful to ensure that the membrane has a defect-free selective layer. On the other hand, increasing the thickness will result in lower flux values according to Equation 5.1.

5.3.2. Membrane surface characterization

Chemical functionalities of modified membranes were identified by ATR-FTIR. Figure 5.3 shows the ATR-FTIR spectra for unmodified and poly[METAC]-modified 30 kDa RC membranes prepared by surface-initiated polymerization for different times. A strong peak that appears at around 1735 cm$^{-1}$ corresponds to a strong C=O stretching mode in the methacrylate backbone of poly[METAC] and supports the successful growth of the polymer.
Figure 5.2. Growth of surface-initiated PMETAC at room temperature from PGMA-modified silicon surfaces with α-bromoester initiator. Closed symbols represent [METAC]/[CuI]/[Bipy]/[CuIICl2] = 100:2:5:0.1 and open symbols represent [METAC]/[CuI]/[Bipy]/[CuIICl2] = 100:2:5:0.2.
Figure 5.3. ATR-FTIR spectra for regenerated cellulose membranes: unmodified (bottom spectrum), PIL-modified membrane after 5 hours of polymerization (middle spectrum), and PIL-modified membrane after 24 hours of polymerization (top spectrum).
While peak intensity increases as the polymerization time increases, supporting the fact that the polymer thickness increases with time, one should not read too far into this result as no precaution was made to ensure exactly the same compression force between the membrane and the ATR crystal.

As mentioned in the materials section, commercial thin-film polyamide NF membranes (FILMTEC, Dow NF-270), and macroporous RC membranes discs also were considered for use initially. The polymerization from the NF membrane was successful as confirmed by the ATR-FTIR spectra shown in Figure 5.4, but I encountered delamination problems with NF membranes during polymerization. Specifically, the polyamide selective layer would partially peel off the support after polymerization. The layer would not completely peel off the support, thus allowing me to do ATR-FTIR studies. With the macroporous membranes, I soon discovered that PIL nanolayer thickness attained by ATRP is not high enough to fill in the pores completely. So even though these membranes would provide high flux, the CO₂/N₂ selectivity would be negligible. Thus, I decided to use the UF membranes for the bulk of the experiments in this study. While RC UF membranes come with a range of MWCO values, I selected the 30 kDa MWCO product because it 1) provides a relatively porous substrate (high flux), with 2) an estimated pore diameter (vide infra) less than the thickness values achieved in the kinetic study, and 3) was available in our lab.

My initial plan to examine the importance of PIL nanolayer chemistry on membrane performance was to prepare a variety of ammonium-based IL monomers, and to use these to grow PIL nanolayers from the membrane supports.
Figure 5.4. ATR-FTIR spectra for polyamide NF-270 membranes: unmodified (spectrum a), PIL-modified membrane after 3 hours of polymerization (spectrum b), PIL-modified membrane after 14 hours of polymerization (spectrum c), PIL-modified membrane after 26 hours of polymerization (spectrum d).
While the synthesis of the first monomer, 2-(methylacryloyloxy)ethyltrimethylammonium tetrafluoroborate (1 in Figure 5.5), was successful (the synthesis procedure and the NMR spectra are reported in Appendix D), it required a solution-phase purification step to isolate the product monomer. After this first experiment, I decided to approach the synthesis differently in order to avoid the monomer purification step. Rather than synthesize each monomer separately and then prepare PIL nanolayers, I decided to use a single, commercially available monomer, 2-(methylacryloyloxy)ethyltrimethylammonium chloride (METAC) (2 in Figure 5.7), to prepare the polymer nanolayers, and then carry out the ion exchange reaction on the grafted polymer. A simple rinse step replaces the monomer purification step. I recognized that the potential disadvantage of this approach is that the anion exchange reaction might not take place completely. Thus, I needed a way to study the extent of ion exchange.

![Figure 5.5. Ionic liquid monomers and PIL repeat units studied.](image)

Analysis was done using XPS, including survey scans and high-resolution C 1s spectra (Figures 5.6–5.8). Tables 2.1 and 2.2 summarize the elemental compositions for a control (blank) membrane, a membrane after polymerization before anion exchange,
and a membrane after polymerization after anion exchange with BF$_4^-$.

In all cases, polymerization was done for 24 hours using a [Cu(I)Cl]:[Cu(II)Cl$_2$] = 2:0.1. This ratio was selected as opposed to the ratio of 2:0.2, which was seen to give controlled growth, since my initial plan was to graft thick (100 nm) PIL nanolayers. Using the formulation with higher Cu(II) concentration would have taken over 3 days to reach this thickness. I decided to sacrifice some control for expedience. For the blank membrane, all the peaks in the XPS spectrum correspond to that of regenerated cellulose. The experimental C:O atomic ratio was calculated to be 1.4, which is close to the theoretical value of 1.2 for cellulose. After polymerization, two additional peaks corresponding to N and Cl appear at 400 eV and 196 eV, respectively. For poly[METAC], the N and Cl contents were lower than the theoretical values of 8 mol%. The O content is higher than the theoretical value. The C:O ratios for poly[METAC] and cellulose ((C$_6$H$_{10}$O$_5$)$_n$) are 4.5 and 1.2, respectively. However, the experimental ratios for before anion exchange and after anion exchange are 2.5 and 2.7, respectively. These intermediate values indicate that the cellulose layer underneath the polymer layer is seen in the region probed by XPS (around 100 Å). I did not expect this result, as one would expect from the kinetic data that the PIL layer thickness is greater than 30 Å, which would shield the underlying cellulose layer completely. But there is a possibility that the direct attachment of the initiator to the RC membrane does not result in a highly dense PIL layer on the outer surface of the membrane. However, this explanation may not seem reasonable based on my SEM images. Another possible explanation is that the cellulose is seen through a crack.
Figure 5.6. XPS survey scan of an unmodified regenerated cellulose membrane.
Figure 5.7. XPS survey scan of a P[METAC]-modified regenerated cellulose membrane.
Figure 5.8. XPS survey scan of a P[META][BF$_4$]-modified regenerated cellulose membrane.
Table 5.1. XPS results for poly[METAC] before anion exchange.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Experimental Atomic Conc. %</th>
<th>Theoretical Atomic Conc. %</th>
<th>Ratio</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>26.2</td>
<td>15</td>
<td>N:Cl</td>
<td>1</td>
<td>1.3</td>
</tr>
<tr>
<td>N</td>
<td>4.2</td>
<td>8</td>
<td>C:O</td>
<td>4.5</td>
<td>2.5</td>
</tr>
<tr>
<td>C</td>
<td>66.4</td>
<td>69</td>
<td>C:N</td>
<td>9</td>
<td>15.8</td>
</tr>
<tr>
<td>Cl</td>
<td>3.2</td>
<td>8</td>
<td>C:Cl</td>
<td>9</td>
<td>20.7</td>
</tr>
</tbody>
</table>

Table 5.2. XPS results for poly[METAC] after anion exchange with BF$_4^-$.

<table>
<thead>
<tr>
<th>Atoms</th>
<th>Experimental Atomic Conc. %</th>
<th>Theoretical Atomic Conc. %</th>
<th>Ratio</th>
<th>Theoretical</th>
<th>Experimental</th>
</tr>
</thead>
<tbody>
<tr>
<td>O</td>
<td>20.7</td>
<td>12.5</td>
<td>F:N</td>
<td>4</td>
<td>3.9</td>
</tr>
<tr>
<td>N</td>
<td>4.6</td>
<td>6.25</td>
<td>C:O</td>
<td>4.5</td>
<td>2.7</td>
</tr>
<tr>
<td>C</td>
<td>56.6</td>
<td>56.25</td>
<td>C:N</td>
<td>9</td>
<td>12.3</td>
</tr>
<tr>
<td>F</td>
<td>17.9</td>
<td>25</td>
<td>C:F</td>
<td>2.2</td>
<td>3.2</td>
</tr>
</tbody>
</table>
However, these results verified that ion-exchange reactions were quantitative. No residual Cl was seen in any of the PIL nanolayers (e.g., Figure 5.8), and the experimental atomic ratio of F:N was similar to the theoretical value.

Figure 5.9 shows SEM images for an initiator-functionalized and poly[METAC]-modified membranes. SEM images (a-b) and (c-d) represent membranes at 2000x and 10000x magnification, respectively. Presumably the membranes were damaged by the electron beam in these measurements. However, further studies have been done in our group to characterize RC membranes following each modification step. Bhut et al. [Bhut et al., 2008] showed by SEM that membrane pore morphology remains intact following initiator attachment and surface-initiated ATRP of polyamines.

5.3.3. Membrane performance testing

After successful development of the methodology to modify membranes with these PIL nanolayers, I turned my attention to their performance as separation agents. An undergraduate member (Ruben Kemmerlin) of our Advanced Membranes Creative Inquiry team used my modification protocol to prepare a set of membranes and tested their ability to selectively adsorb CO₂. Polymerization was done using the formulation with [Cu(I)Cl:Cu(II)Cl₂ ratio of 2:0.1]. Testing was done by this student using a specially modified Wicke-Kallenbach cell and analysis methods developed by Professor Seidel-Morgenstern at the Max Planck Institute for Dynamic Complex Technical Systems in Magdeburg, Germany [Cermáková et al., 2008]. CO₂ and N₂ adsorption isotherms were measured on PIL nanolayers grafted from cellulose membranes. Measurements with N₂
showed no measureable adsorption at the highest pressure studied. Measurements on unmodified cellulose showed no CO$_2$ uptake. CO$_2$ only adsorbed to PIL-modified membranes as expected. My colleague also discovered that the CO$_2$ capacity increased on membranes that had been modified by ATRP up to 12 hours of polymerization, but it remained constant for polymerization times greater than 12 hours, which is consistent with the growth rate data reported in Figure 5.2 (solid circles correspond to the formulation used in this study).

5.3.3.1. Permeation testing of non-PGMA coated membranes

Knowing that the PIL nanolayers adsorb CO$_2$ selectively over N$_2$, I investigated whether a membrane modified by a PIL nanolayer would selectively transport CO$_2$ over N$_2$. Measurements were made with membranes loaded into the permeation cell setup described earlier and shown in Figure 5.1. The cell is divided into an upstream side and a downstream side separated by the membrane. The downstream side volume was measured to be 150 cm$^3$ as described in Appendix C. The exposed membrane area was measured to be 3.8 cm$^2$. The downstream side of the cell was evacuated and the upstream side was pressurized from a cylinder with CO$_2$ or N$_2$. The upstream pressure was kept constant at $2.8 \times 10^5$ Pa. Downstream pressure was monitored over time. In experiments similar to this one, the downstream pressure initially increases nonlinearly and then linearly as a function of time. This linear increase at longer times is associated with a steady-state concentration profile in the membrane [Hu et al., 2006]. This behavior is not seen for my system due to a very low selective layer thickness.
Figure 5.9. SEM images for an initiator-functionalized (a-b) and poly[METAC]-modified membranes (c-d). SEM images (a-b) and (c-d) represent membranes at 2000x and 10000x magnification, respectively.
The permeability is calculated using Equation 5.3:

\[
P = \frac{VL}{ART \Delta p} \frac{dp}{dt}
\]

(5.3)

where \( P \) is the permeability in Barrer (1 Barrer = \( 7.5 \times 10^{-14} \) cm\(^3\)(STP)·cm/cm\(^2\)·s·Pa), \( V \) is the volume of the downstream chamber (in cm\(^3\)), \( A \) is the surface area of the membrane exposed to the gas (in cm\(^2\)), \( L \) is the membrane thickness (in cm), \( R \) is the universal gas constant (8308650 Pa·cm\(^3\)/(K·mol)), \( \Delta p \) is the pressure difference (in Pa) across the membrane, \( T \) is the absolute temperature (in K), and \( \frac{dp}{dt} \) is the rate of the downstream pressure increase (in Pa/min).

**Figure 5.10** shows the results for an unmodified 30 kDa regenerated cellulose thin-film composite membrane. There is no selectivity for either gas; both permeate through the membrane at the same rate, as was expected for this porous support. **Figure 5.11** shows the first result for a membrane modified by a PIL nanolayer. The polymerization time was 20 hours for this experiment. CO\(_2\) transport is much faster than N\(_2\) for this membrane. Furthermore, the rate of pressure increase for CO\(_2\) is similar to the unmodified membrane.

Using the data from **Figure 5.11**, along with a downstream volume of 150 cm\(^3\), exposed membrane area of 3.8 cm\(^2\), and temperature of 298 K, I calculated the permeability of CO\(_2\) through the membrane to be approximately 0.7 Barrer and the permeability of N\(_2\) to be approximately 0.02 Barrer. Therefore, the permselectivity was estimated to be 40 using Equation 5.2. It should be mentioned that the pressure
difference across the membrane for the case of a plain membrane was $2.8 \times 10^5$ Pa, and it was slightly lower ($2.3 \times 10^5$ Pa) for the PIL-modified membrane.

**Figure 5.10.** CO$_2$ and N$_2$ rate of pressure rise through an unmodified 30 kDa regenerated cellulose membrane.
Figure 5.11. CO$_2$ and N$_2$ rate of pressure rise through a PIL-modified 30 kDa RC membrane.
Comparing these data to those reported for polymeric membranes on a “Robeson plot”, it is clear that these PIL-modified membranes behave similarly to some polymeric membranes reported in the literature [Robeson, 2008]. In the area of gas separation membranes, Robeson [Robeson, 1991] presented a very simple approach for comparing membranes made from different materials and different manufacturers. The separation factor, which is equal to the ratio of the permeability of the more permeable gas to that of the less permeable species, was plotted as a function of the permeability of the more permeable gas on a log–log scale. Data for a large number of different membranes were all clustered below a critical line, or upper bound, which is often referred to in the gas separations community as the “line of death” since there are few (if any) membranes that provide a combination of selectivity and permeability above this limit. Comparing these data to those reported for casted P[METAC][BF$_4$]-g-PEG 2000 membranes [Hu et al., 2006], however, one finds that the CO$_2$ permeability is lower than the reported permeability value of ~100 Barrer. The permselectivity is, however, slightly higher than the reported value of 30 for P[METAC][BF4]-g-PEG 2000 [Hu et al., 2006]. The membranes reported in their work have thicknesses in the range of 80–200 μm, so their reported larger permeability values seem reasonable as compared to our low permeability values resulting from nanothin PIL layers. Adding PEG would also lower the polymer T$_g$ allowing them to produce thermally, chemically, and mechanically stable membranes. The selectivity for CO$_2$/N$_2$ separation is primarily due to the solubility differences, not the diffusivity differences [Hu et al., 2006], so using pure PIL probably shows higher
solubility in my case than in their case of using copolymer. This might be the reason that my permselectivity is slightly greater than theirs. From a processing point of view, high selectivity and high flux membranes are desired, and growing nanothin PIL layers as shown in my work is promising in the sense that it could provide high fluxes.

Despite this promising initial result, the results shown in Figure 5.11 were not reproducible, and, in subsequent gas permeation tests, the N\textsubscript{2} and CO\textsubscript{2} downstream pressures both reached the applied upstream pressure of 2.8 ×10\textsuperscript{5} Pa within the first minute. After running the first sets of experiments, I suspected that the membrane integrity is lost after the first set of permeation tests, and the membrane probably cracks or otherwise is damaged, resulting in the fast permeation of N\textsubscript{2} and CO\textsubscript{2}. It is important to point out the N\textsubscript{2} measurement was done first, so it is possible that the CO\textsubscript{2} data above correspond to permeation through a major crack in the membrane (nonselective transport). The N\textsubscript{2} permeability is similar to the values that will be reported throughout the Chapter for other modified membranes. Therefore, it is not certain that the CO\textsubscript{2} data reported here are representative of a dense film. It should be reiterated that the membranes used for these sets of permeation tests were prepared with direct attachment of the initiator to the RC layer and ATRP of IL monomer for 20 hours at room temperature. I also considered decreasing the upstream pressure to 1.4 ×10\textsuperscript{5} Pa to see if the membrane would function with a lower transmembrane pressure difference (\(\Delta p\)) but that did not solve the problem. To support my suspicion about membrane damage, I analyzed the membrane post permeation testing by SEM. Figure 5.12 clearly shows the formation of cracks after one set of permeation tests.
Figure 5.12. Surface SEM image of the PIL modified RC membrane showing a crack after one set of gas permeation measurements.
One path forward would be to consider using a co-monomer with a low glass transition temperature ($T_g$) in order to create a flexible nanolayer coating. To make the PIL membranes by solution casting less brittle, Hu et al. [Hu et al., 2006] grafted polyethylene glycol (PEG) chains onto the glassy PIL to reduce $T_g$. The $T_g$ of the copolymer can be estimated using the Fox equation [Sagle et al., 2009]:

$$\frac{1}{T_g} = \frac{w_{\text{PEG}}}{T_{g\text{PEG}}} + \frac{w_{\text{IL}}}{T_{g\text{PIL}}}$$

(5.4)

where $w_{\text{PEG}}$ and $w_{\text{IL}}$ are the weight fractions of PEG and ionic liquid monomer in the final copolymer, respectively. $T_{g\text{PEG}}$ is the glass transition temperature of pure PEG, and $T_{g\text{PIL}}$ is the glass transition temperature of pure PIL. Hu et al. [Hu et al., 2006] reported a $T_g$ of 218 °C for P[METAC][BF$_4$] and a $T_g$ of −80 °C for PEG. What we would use in our case to make a copolymer is, however, PEG-methacrylate with a $T_g$ of −40 °C. Using these data, a mixture of 60 wt % PEG and 40 wt % IL should be used to lower the $T_g$ to 30 °C (close to room temperature, where my experiments are conducted).

5.3.3.2. Permeation testing of PGMA-coated membranes

To prevent cracking or to seal any imperfections coming from the manufacturer, I decided to cover the RC membrane with the reactive primary PGMA layer. The $T_g$ of PGMA is 80 °C, so PGMA could potentially build in some flexibility to aid with cracking as well. A fraction of the epoxide functional groups react with the hydroxyl groups of the membrane to anchor the layer, and residual epoxide groups are functionalized with ATRP initiators. ATRP was then used to grow PIL from this functional polymer layer.
In gas permeation measurements with this set of membranes, $\text{N}_2$ and $\text{CO}_2$ hardly permeated through the PIL-modified membranes and showed almost no selectivity (Figure 5.13). The measured permeability values for $\text{N}_2$ and $\text{CO}_2$ were approximately 0.013 Barrer. Those results lead me to conclude that the grafted PGMA most likely is blocking the outer surface, as well as membrane pores. The membrane pore diameter has not been reported by the manufacturer for this specific 30 kDa membrane. However, they report an average pore diameter of 3 nm for their 1 kDa membrane product. PGMA with molecular weight of 46,970 g/mol was used in this first experiment. This polymer was estimated to have a radius of gyration ($R_g (\text{nm}) = 0.186 N^{0.5}$) of 3 nm. I used the same coefficient as the one given for PS in Chapter Three for estimation purposes, and the power of 0.5 was used for the degree of polymerization [Zhao and Brittain, 2000] since air can be considered a theta solvent for polymers. For rough estimation, I used the data for the 1 kDa membrane to calculate the diameter of the 30 kDa membrane. The pore diameter was assumed to be $2R_g$ (i.e., $R_g$ of 1.5 nm). Using the above equation relating $R_g$ to $N$, I determined the degree of polymerization for a hypothetical molecule that would ‘plug’ the 1 kDa membrane. Using 30N, I estimated the pore diameter of the 30 kDa membrane to be 16 nm. Therefore, it seems reasonable that PGMA with $R_g = 3$ nm may be ‘clogging’ the pores at the membrane surface.

As mentioned previously, my main goal was to create a dense, ultrathin nanolayer on the membrane outer surface, and to demonstrate $\text{CO}_2$ permeation through the $\text{CO}_2$-selective PIL nanolayer by the solution-diffusion mechanism. To ensure that the dense PIL layer was formed only on the outer surface, and that the PGMA did not diffuse into
the pores and block them, PGMA with a higher molecular weight of 300,000 g/mol was synthesized and used for membrane coating. This PGMA molecular weight would give an estimated radius of gyration of 9 nm, which is expected to be closer to the membrane average pore diameter. As shown in Figure 5.14, a CO$_2$ and N$_2$ permeability of 0.026 Barrer with almost no selectivity was obtained. A still higher MW PGMA or a lower MWCO base membrane may be needed. It is important to note that going to a higher MW PGMA did improve the permeability from the case of low MW PGMA. The permeability doubled indeed. One reason that there is no selectivity might be because the PGMA acts as the dense layer and it does not show any selectivity. In fact, I did permeability measurements on PGMA-modified membrane (high MW PGMA), and, as shown in Figure 5.15, the permeability and selectivity values are very close to what I measured for the PIL-PGMA-modified membrane. The pressure rise values for the PGMA-modified are significantly lower than the base membrane values shown in Figure 5.10.

It is important to note that the integrity of the PGMA-coated membranes were retained even after several permeation measurements. This was confirmed by repeating the experiment at least two times and obtaining the exact same permeability and selectivity values. While the data in Figure 5.15 indicate that the PGMA may be clogging the pores, there is also the possibility that PIL chains grown directly from the –OH groups of the membrane pores are clogging the pores. Therefore, I decided to do some initial studies to change the type of initiator used in order to create a dense, selective PIL nanolayer on the outer surface only of the RC membrane. I have attempted using BPA in
place of 2-BIB for attachment of the ATRP initiator to the PGMA-covered RC membranes.

**Figure 5.13.** CO$_2$ and N$_2$ rate of pressure rise through a PIL-modified 30 kDa RC membrane that had first been coated with low MW PGMA.
Figure 5.14. CO₂ and N₂ rate of pressure rise through a PIL-modified 30 kDa RC membrane that had first been coated with high MW PGMA.
Figure 5.15. CO₂ and N₂ rate of pressure rise a 30 kDa RC membrane that had been coated with high MW PGMA.
The idea is to use an initiator that would attach only to the epoxide groups of the PGMA as opposed to attaching to both PGMA and cellulose. This way, I would confine the PIL to the PGMA layer on the cellulose outer layer and would allow the bulk cellulose layer to remain porous. As mentioned before, the BPA initiator could not be attached by vapor deposition as it would result in peeling the cellulose layer off of the support. Therefore, all the initiator attachment reactions were done in solution. As shown in Figure 5.16, this initiator attachment and polymerization strategy yielded PIL-modified membranes. Ongoing research is focusing on manipulating modification conditions to create a dense, selective, mechanically stable PIL nanolayer on the outer surface of the RC membrane.

5.4. Conclusions

Atom transfer radical polymerization was used to modify the physical and chemical properties of a regenerated cellulose ultrafiltration membranes. Using this technique, CO₂-selective, poly(ionic liquid) nanolayers were grafted from the membrane surfaces. Ion exchange was used to replace Cl⁻ with BF₄⁻. XPS results confirmed that the ion-exchange reactions were quantitative. No residual Cl was seen in any of the PIL nanolayers. A kinetic study was done from flat surfaces to measure the poly[METAC] layer thickness as a function of time. By doubling the Cu(II) concentration, more control was obtained over the polymerization reaction. Pure-component CO₂ and N₂ permeabilities were measured for unmodified and modified membranes using a home-built permeation cell test apparatus. Retaining the membrane integrity was problematic
after running the first set of permeation measurements. Covering the outer surface of the
membrane with PGMA seems to have resolved that problem, but has resulted in low
permeability membranes, likely due to pore clogging. Several ideas were outlined to
improve the permeability values and avoid cracks in the selective PIL layer. These
include using a higher MW PGMA and/or lower MWCO membrane, restricting the PIL
to the outer PGMA layer using BPA initiator, and integrating a low Tg copolymer to
form more flexible PIL selective layer.
Figure 5.16. ATR-FTIR spectra for 30 kDa regenerated cellulose membranes: unmodified (bottom spectrum) and PIL-modified membrane after 20 hours of polymerization (top spectrum). BPA was used as the ATRP initiator, which was anchored to a PGMA layer.
References


CHAPTER SIX
CONCLUSIONS AND RECOMMENDATIONS

6.1 Conclusions

Through this dissertation, I report findings on surface-initiated atom transfer radical polymerization of styrene from poly(glycidyl methacrylate)-coated silicon substrates at low temperatures of ≤ 75 °C. This work was the first to report ATRP of styrene below its glass transition temperature. I showed that under these low temperature conditions thick PS brushes could be prepared, and the polymer growth does not appear to be limited by mass transfer of monomer to propagation sites. Constant growth rates were obtained, indicating indirectly that polymerization was controlled. One of the outcomes of the low temperature condition was that thermally-initiated self-polymerization was suppressed, meaning that the monomer concentration in solution remained constant. To confirm that uniform PS brushes with high grafting densities were formed, AFM, contact angle, and ellipsometric swelling measurements were conducted to characterize the polymer nanolayers. The advantage of using PGMA is that it provides a high potential initiator density, and it can be used as a primary modifier layer for the preparation of thin-film composite membranes. Thus, this methodology provides many opportunities for the formation of uniform, grafted polymer nanolayers with varying grafting densities that can be used to modify membranes for separation applications. Also, in addition to the advantages for controlled growth listed above, being able to
conduct ATRP at lower temperatures is advantageous for membrane modification, since many polymeric membranes that would be used as supports deteriorate at elevated temperatures.

I was also interested in studying the kinetics of surface-initiated ATRP of styrene at lower temperatures since the kinetics of surface-initiated ATRP has not received as much attention as the bulk and solution-phase ATRP kinetics. In my work, a shift was observed in the reaction order (from first to apparent zero order) with respect to the monomer concentration at 60 °C. I contend that the adsorption/reaction model proposed here, in which a monomer molecule adsorbs to a vacant surface site and then reacts or desorbs without reaction, is responsible for the change in apparent reaction order.

Finally, a kinetic study was done from flat surfaces to measure the ATRP growth of CO₂-selective, poly(ionic liquid) (poly[METAC]) nanolayers as a function of time. By increasing the Cu(II) concentration in the ATRP formulation, control was obtained over the polymerization reaction at the expense of slower growth. This model system was used then to grow poly(ionic liquid) nanolayers from regenerated cellulose ultrafiltration membranes, yielding PIL thin-film composite membranes for gas separations. Also, I demonstrated that post-polymerization anion exchange could be used to replace Cl⁻ with BF₄⁻. XPS results confirmed that the ion-exchange reactions were quantitative. No residual Cl was seen in any of the PIL nanolayers. Thus, this strategy could be used to create a series of PIL materials starting from the same base polymer, poly[METAC], using anion exchange to vary the PIL anion. Pure-component CO₂ and N₂ permeabilities were measured for unmodified and modified membranes. Covering the outer surface of
the membrane with PGMA seems to improve the membrane integrity during permeation measurements, but has resulted in low permeability membranes, likely due to pore clogging.

6.2 Recommendations

For surface initiated-ATRP studies of styrene at lower temperatures, it will be interesting to see how the system would behave under elevated temperature conditions. As the temperature increases, I would expect the adsorption equilibrium constant to decrease and the reaction to become first-order with respect to the monomer concentration over the full range of monomer concentration. It will be worthwhile to confirm that by doing the polymerization at temperatures greater than 100 °C. The data that were presented in Chapter Four were initial growth rate data. Therefore, by going to higher temperatures, I would not expect the thermal polymerization of the monomer to be significant in the first few hours.

For membrane modification, to improve the permeability values and avoid cracks in the selective PIL layer of the regenerated cellulose membrane, I recommend using a higher MW PGMA and/or lower MWCO membrane, restricting the PIL to the outer PGMA layer, and integrating a low T_g copolymer to form more flexible PIL selective layer. Based on my calculation method, I would recommend using a higher PGMA MW of 600,000 g/mol, which would have a radius of gyration of 12 nm, for the 30 kDa membranes (with a pore diameter of ~ 16 nm) used in this study. Perhaps one could also
purchase a commercially available 1 kDa membrane (with a pore diameter of ~ 3 nm) to
test with the PGMA MWs used in my study.

To restrict growth in the PGMA layer, I would recommend using BPA in place of
2-BIB for attachment of the ATRP initiator to the PGMA-covered RC membranes. This
way, the initiator is expected to only attach to the epoxide groups of the PGMA as
opposed to attaching to both PGMA and cellulose. The PIL would then be confined to the
PGMA layer on the cellulose outer layer and would allow the bulk cellulose layer to
remain porous, which will help to improve flux.

Poly(RTILs) are mechanically weak (brittle) and require a crosslinker or
copolymerization for effective testing as thin, flatsheet membranes. So I recommend
preparing a low $T_g$ (~ 30 °C) copolymer such as poly(RTIL)-co-poly(ethylene glycol)
(PEG) methacrylate to form more flexible PIL selective layer. Hu et al. [2006] showed
that poly(RTIL)-co-PEG exhibited enhanced CO$_2$ solubility and selectivity. If the gas
permeation tests show CO$_2$ plasticization, I would recommend crosslinking the PIL
network. Bara et al. [2007] recommended using 5 mol% of an appropriate, matching
cross-linking agent (divinylbenzene or 1,6-hexanediol diacrylate) and 1 wt% of a
photoinitiator (2-hydroxy-2-methylpropiophenone).

It will be interesting to find out if it would be useful to coat modified membranes
with a high boiling point, hygroscopic compound like glycerin to prevent cracking. The
manufacturer of the RC ultrafiltration membranes uses glycerin to keep the membranes
from drying out and experiencing pore collapse. One disadvantage of this approach that
would need to be evaluated is that water may interfere with the CO$_2$ selectivity of the
membranes. The use of a thin coating of silicone protectant, like some other researchers have proposed [Kurdi and Kumar, 2005], would be another option to test. Kurdi and Kumar [2005] coated the membranes used in the permeation test with silicon rubber. A solution of 3 Wt % Sylgard-184 in $n$-pentane was sprayed as a thin layer on the top surface of the membrane and the solvent was allowed to evaporate. Finally, the coated silicon rubber was cured in an air purging convection oven at 80 °C for 1 day [Kurdi and Kumar, 2005].
6.3 References


APPENDICES
The lines in the sketch below represent different segment density profiles of a polymer brush at equilibrium. The intention is that all three profiles describe a brush of the same average segment density. The dashed line represents the accepted structure of real, nearly monodisperse brushes: The segment density profile is parabolic with an exponentially decaying “tail” at brush/fluid periphery. The parabolic (lighter line) and box-like (heavy line) profiles are different constructs designed to represent (approximate) the structure of the brush. The box-like profile is often referred to as the Alexander-deGennes model, and the parabolic profile results from the SCF model of Milner et al. [Milner et al., 1988].
A relationship can be obtained between the heights predicted from the box-like and parabolic profiles, \( H_{\text{box}} \) and \( h^* \), respectively, by calculating the first moments of the segment density profiles, \( \Omega(z) \):

**Box-like profile:**

\[
\Omega(z) = s \quad \text{when} \quad z < H_{\text{box}}
\]

\[
\Omega(z) = 0 \quad \text{when} \quad z \geq H_{\text{box}}
\]

\( s \) is the maximum segment density

\[
Z_1 = \frac{\int_0^\infty z \Omega(z) \, dz}{\int_0^\infty \Omega(z) \, dz} = \frac{\int_0^{H_{\text{box}}} z \Omega(z) \, dz}{\int_0^{H_{\text{box}}} \Omega(z) \, dz} = \frac{H_{\text{box}}}{2}
\]

**Parabolic profile:**

\[
\Omega(z) = \left( \frac{B}{\omega} \right) \left( (h^*)^2 - z^2 \right) \quad \text{when} \quad z < h^*
\]

\[
\Omega(z) = 0 \quad \text{when} \quad z \geq h^*
\]

\[
Z_1 = \frac{\int_0^\infty z \Omega(z) \, dz}{\int_0^\infty \Omega(z) \, dz} = \frac{\int_0^{h^*} z \Omega(z) \, dz}{\int_0^{h^*} \Omega(z) \, dz} = \frac{\int_0^{h^*} (z(h^*)^2 - z^2) \, dz}{\int_0^{h^*} (h^*)^2 - z^2 \, dz} = \frac{3}{8} h^*
\]
Since the first moments represent the average segment densities, and since the profiles are meant to have the same average segment densities, I find the relationship between \( h^* \) and \( H_{\text{box}} \) to be

\[
h^* = \left(\frac{4}{3}\right) \cdot H_{\text{box}}
\]

Reference

Appendix B

Given that the transition from first- to zero-order reaction rate is not associated with a change from diffusion- to rate-limited growth, nor due to a phase transition due to differences in PS-brush solvency in solutions of different monomer concentration, I initially hypothesized that the formation of an intermediate, as suggested by the reaction mechanism shown in here, is responsible for the change in reaction order that is observed in Figure 4.1.

\[
\begin{align*}
I + Cu(I) & \overset{k_s}{\underset{k_{da}}{\rightleftharpoons}} I' + Cu(II) \quad \text{(B.1)} \\
I' + M & \overset{k_1}{\underset{k_2}{\rightleftharpoons}} IM \quad \text{(B.2)} \\
I'M & \overset{k_2}{\longrightarrow} IM' \quad \text{(B.3)}
\end{align*}
\]

Similar types of mechanism have been suggested for enzymatic reactions and those involving adsorption and reaction. Here, I hypothesize that once the radical species is formed via Equation B.1, it may form an intermediate complex (IM) (Equation B.2) that results from collision or interaction between the free radical and a monomer molecule from solution. This intermediate complex may dissociate to the radical and monomer species (reverse of Equation B.2) or react to form a covalent bond (Equation B.3).

A kinetic model to test the hypothesis can be formulated using the pseudo-steady state assumption, which assumes that the net rate of formation of the intermediate is zero. Writing the net rate of formation for the intermediate complex and using the pseudo-steady state assumption gives Equation B.4,
\[ r_{rM} = 0 = k_1 \left[ I^* \right] [M] - k_2 \left[ I'M \right] - k_p \left[ I'M \right] \]  \hspace{1cm} (B.4)

where \( k_1, k_2, k_p, [I^*], [M], [I'M] \) are the formation rate constant for the intermediate complex, dissociation rate constant for the intermediate complex, propagation rate constant, free surface radical concentration, monomer concentration, and concentration of intermediate complex, respectively.

The free surface radical concentration can be calculated by subtracting the concentration of intermediate complex from the total concentration of surface radicals \([I^*\text{tot}]\), according to \textbf{Equation B.5}.

\[ \left[ I^* \right] = \left[ I^*\text{tot} \right] - \left[ I'M \right] \]  \hspace{1cm} (B.5)

Substituting the expression for \([I^*]\) from \textbf{Equation B.5} into \textbf{Equation B.4} and solving for \([I'M]\) gives \textbf{Equation B.6}.

\[ \left[ I'M \right] = \frac{k_1 \left[ I^*\text{tot} \right][M]}{k_i[M] + k_2 + k_p} \]  \hspace{1cm} (B.6)

Again using the expression for \([I^*]\) from \textbf{Equation B.5}, the rate of monomer consumption can be written as

\[ -r_M = k_i \left( \left[ I^*\text{tot} \right] - \left[ I'M \right] \right)[M] - k_2 \left[ I'M \right] \]  \hspace{1cm} (B.7)

Substituting the expression for \([I'M]\) from \textbf{Equation B.6} into \textbf{Equation B.7} and collecting constants gives

\[ -r_M = \frac{k_p \left[ I^*\text{tot} \right][M]}{[M] + k_m} \]  \hspace{1cm} (B.8)
where \( k_m = (k_2 + k_p)/2 \). In \textbf{Equation B.8}, the initiator and the catalyst concentrations are embedded in \([I_{\text{tot}}]\) because, at steady state,

\[
[I^*_{\text{tot}}] = \frac{k_a [I] [Cu(I)]}{k_a [Cu(II)]}
\]  

\text{(B.9)}

Under ATRP conditions, the deactivation rate constant \((k_d)\) is much greater than the activation rate constant \((k_a)\). Therefore, the denominator in \textbf{Equation B.9} is much larger than the product of \(k_a\) and \([Cu(II)]\) in the numerator, even though the Cu(II) concentration is very low.

As pointed out explicitly by Sankhe et al., the rate expression given by \textbf{Equation B.8} can be re-expressed in terms of a rate of layer thickness increase through a proportionality constant \(\beta\). As given by Sankhe et al., I define an apparent propagation constant, \(k_p' = \beta k_p k_d/(k_d[Cu(II)])\). Substituting \textbf{Equation B.9} into \textbf{Equation B.8} and introducing this apparent propagation constant yields the final form of the rate equation in terms of layer thickness.

\[
\frac{dh}{dt} = \frac{k_p' [I] [Cu(I)] [M]}{[M] + k_m}
\]  

\text{(B.10)}

\textbf{Equation B.10} describes the growth rate behavior seen in \textbf{Figure 4.1}. At low monomer concentration such that \(k_m >> [M]\), the reaction rate is first order in monomer concentration. At high enough monomer concentration such that \(k_m << [M]\), the reaction rate is apparent zero order in monomer concentration. \textbf{Equation B.10} also shows that the reaction rate is first order with respect to the catalyst concentration over the entire range of monomer concentration.
Appendix C

Permeability Box: Procedure for Usage

1. Remove membrane holder (do not touch fittings that have Teflon tape). (9/16” & 7/16” wrenches needed).

2. Open up membrane holder with HEX key.

3. Put the membrane to be tested inside the membrane holder. The order inside the membrane holder is: small opening (where gas comes in), mesh, membrane, O-ring

4. Replace membrane holder into the box.

5. Close all valves initially.

6. Open valve 4, 5, 6, and 7.
7. Turn on the pump.

8. Let the downstream pressure go down until it reaches steady state.

Setting up upstream pressure:

1. After setting up the tank pressure (upstream pressure) at the desirable value, close the vacuum pump and valves 4 and 7. Then open valve 3 and either valve 1 or 2 (depending on which gas you want to test). Start recording the downstream pressure as a function of time.

*The chamber temperature can be adjusted/set using a fan that is located inside the box.

*Major precautions need to be taken as far as tightening the fittings and checking the o-rings as this system is very susceptible to leaking. The o-rings should be replaced after 4-5 set of experiments as the tightening and untightening the screws normally result in their deterioration.

*To measure the downstream volume, vacuum was pulled on the downstream side. Constant pressure syringe pump (Tytedyne ISCO) with an initial known volume was then attached to the downstream side. The volume of the syringe pump was adjusted automatically in order to equilibrate to the syringe pump pressure. The difference in the initial and final volumes gives the downstream volume.
Appendix D

Synthesis of the ionic liquid monomer ([METAC][BF₄])

Aqueous 2-(methlacryloyloxy)ethyl-trimethyl ammonium chloride solution (75 wt.%) (30 ml, 0.12 mol) was added into a 20 ml flask. After the water was removed under vacuum, NaBF₄ (14.5 g, 0.132 mole) and CH₃CN (150 ml) were added to the flask. The mixture was stirred overnight. A white precipitate formed. The precipitate was removed by filtration. The filtrate was concentrated using a rotavap, and then it was poured in ether. The white crystal was collected and dried in vacuum at room temperature. The NMR spectra shown below verifies the successful synthesis of the monomer. The ppm assignments are: δ 6.09 (1H, s), 5.75 (1H, m), 4.53 (2H, m), 3.70 (2H,m), 3.14 (9H, s), 1.91 (3H, s) [Tang et al., 2005].
Reference

Figure D1. $^1$H NMR spectra for [METAC][BF$_4$].
Figure D2. Typical $^1$H NMR spectra for [METAC][BF$_4$].
Figure D2. Typical $^{19}$F NMR spectra for [METAC][BF$_4$].