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SURFACE-INITIATED POLYMERIZATIONS ON INITIATOR ANCHORED SUBSTRATES: SYNTHESIS AND CHARACTERIZATION OF NANOMETER THICK FUNCTIONAL POLYMER FILMS

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SURFACE-INITIATED POLYMERIZATIONS ON INITIATOR ANCHORED SUBSTRATES: SYNTHESIS AND CHARACTERIZATION OF NANOMETER THICK FUNCTIONAL POLYMER FILMS

By

Zhiyi Bao

A Dissertation

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

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ABSTRACT

SURFACE-INITIATED LIVING POLYMERIZATIONS ON INITIATOR ANCHORED SUBSTRATES: SYNTHESIS AND CHARACTERIZATION OF NANOMETER THICK FUNCTIONAL POLYMER FILMS

By

Zhiyi Bao

We describe the surface-initiated ring-opening polymerization (ROP) of lactide from poly(2-hydroxyethyl methacrylate) (PHEMA) brushes anchored to Au substrates. The resulting comb polymers have a "bottle brush" architecture. During hydrolytic degradation of PLA in pH 7.4 buffer at 55 °C, large, highly symmetric domains (~50-100 μ m) unexpectedly formed. The purpose of the research described in this chapter was to devise a model that describes their formation. Control experiments during degradation study link high lactide polymerization temperature to the formation of the defects. A likely mechanism is the scission of Au-S bonds at high temperatures, causing defects that swell when placed in the buffer solution.

We demonstrated enhanced control over polymer brushes through variation of the areal density of the immobilized initiators used for their growth. Reaction of mercaptoundecanol monolayers on Au with both an acyl bromide initiator and a structurally similar acyl bromide diluent yields monolayers whose composition reflects the ratio of the acyl bromides in solution. Similarly, derivatization of SiO₂ with an initiator and a diluent monochlorosilane also affords control over initiator density. The

thickness of polymer films grown from these modified substrates drop dramatically when the fractional coverage of the surface by initiator decreases below 10% of a monolayer because the area per polymer chain increases. However, reduced termination at low initiator coverage results in substantial increases in initiator efficiency as measured by film growth rates normalized by the fractional coverage of the surface by initiator. Variation of chain density also affords control over film swelling. PHEMA films prepared with 0.1% initiator densities swell 20-fold more in water than films grown from monolayers containing only initiators. Such control should prove valuable in the use of brushes for immobilization of active, accessible biomacromolecules such as singlestranded DNA or antibodies.

We report the remarkably rapid synthesis of polymer brushes under mild conditions (50 °C) using surface-initiated polymerization. The use of the highly active atom transfer radical polymerization catalyst Cu(I)1,4,8,11-tetramethyl-1,4,8,11tetraazacyclotetradecane allows synthesis of 100 nm thick poly(*tert*-butyl acrylate) brushes from initiator-modified Au surfaces in just 5 minutes. Using the same catalyst, polymerization of hydroxyethyl methacrylate and methyl methacrylate yielded 100 nm thick films in 10 and 60 minutes, respectively. Such polymerization rates are an order of magnitude greater than those for traditional free-radical polymerizations initiated from surfaces. It is important to note that though these rapid polymerizations from surfaces are not "living", they retain some features of controlled radical polymerizations such as the ability to form block copolymer brushes. Such rapid polymerization from a surface will be very important in potential applications of polymer brushes as skin layers in separation membranes and as substrate coatings for probe immobilization in gene and protein chips. To My Family

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LIST OF ABBREVIATIONS

| AIBN | 2,2'-Azobisisobutyronitrile |
|------------------------|--|
| AFM | Atomic force microscopy |
| ATR | Attenuated total reflectance |
| ATRA | Atom transfer radical addition |
| ATRP | Atom transfer radical polymerization |
| A _p | Average cross-sectional area of polymer chains |
| 2-BPB | 2-Bromopropionyl bromide |
| 2-MPB | 2-Methylpropionyl bromide |
| BPMA | N,N-bis(2-pyridylmethyl)amine |
| BPMOA | N,N-bis(2-pyridylmethyl)octylamine |
| bpy | 2,2'-Bipyridine |
| CL | <i>e</i> -Caprolactone |
| CYCLAM | 1,4,8,11-Tetraazacyclotetradecane |
| DETA | Diethylenetriamine |
| dHbpy | 4,4'-Diheptyl-2,2'-bipyridine |
| DMF | N,N-dimethylformamide |
| dNbpy | 4,4'-Di(5-nonyl)-2,2'-bipyridine |
| dnNbpy | 4,4'-Di(n-nonyl)-2,2'-bipyridine |
| DP | Degree of polymerization |
| EtOAc | Ethyl acetate |
| FTIR | Fourier transform infrared |
| GC | Gas chromatography |
| GMA | Glycidyl methacrylate |
| GPC | Gel permeation chromatography |
| HEMA | 2-Hydroxyethyl methacrylate |
| HMTETA | 1,1,4,7,10,10-Hexamethyltriethylenetetramine |
| k _p | Polymerization rate constant |
| k _t | Termination rate constant |
| k _{act} | Activation rate constant |
| k _{deact} | Deactivation rate constant |
| lactide | 3,6-Dimethyl-1,4-dioxane-2,5-dione |
| LB | Langmuir-Blodgett |
| LCST | Lower Critical Solution Temperatures |
| MA | Methyl acrylate |
| Me | Methyl |
| Me ₄ Cyclam | 1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane |
| Me ₆ TREN | tris[2-(Dimethylamino)ethyl]amine |
| μCP | Microcontact printing |
| MMA | Methyl methacrylate |
| <i>M</i> _n | Number average molecular weight |
| MS | Mass spectroscopy |
| MUD | Mercaptoundecanol |

| м | Weight average molecular weight |
|----------------|---|
| MWNIT | Multiwalled carbon nanotubes |
| N. | Avogadro's number |
| | Nitrovide-mediated nolymerization |
| NMP | Nuclear magnetic resonance |
| OTE | Triflate |
| | Poly(complic soid) |
| | Poly(activity actual) |
| PDA | Poly(n-buly) activate) |
| PCL | Poly(e-caprolactone) |
| PDI | Polydispersity index calculated as M_w/M_n |
| PDMS | Polydimethylsiloxane |
| PEI | N-propionylethylenimine |
| PEG | Poly(ethylene glycol) |
| PGMA | Poly(glycidyl methacrylate) |
| Ph | Phenyl |
| PHEMA | Poly(2-hydroxyethyl methacrylate) |
| phen | 1,10-Phenanthroline |
| PLA | Poly(lactide) |
| PMA | Poly(methacrylate) |
| PMEMA | Poly(2-(N-morpholino)-ethyl methacrylate) |
| PMMA | Poly(methyl methacrylate) |
| PMDETA | N,N,N',N',N"-pentamethyldiethylenetriamine |
| PNIPAAM | Poly(N-isopropylacrylamide) |
| PS | Polystyrene |
| PtBA | Poly(<i>tert</i> -butyl acrylate) |
| PTFE | Poly(tetrafluroethylene) |
| PVP | Poly(4-vinyl pyridine) |
| QR | Quenching and re-initiation |
| RAFT | Reversible addition-fragmentation chain transfer |
| ROMP | Ring-opening metathesis polymerization |
| ROP | Ring-opening polymerization |
| R _p | Rate of polymerization |
| SAM | Self-assembled monolayer |
| SEM | Scanning electron microscopy |
| t | Film thickness |
| tBA | tert-Butyl acrylate |
| TEMPO | 2,2,6,6-Tetramethylpiperidinyloxy |
| TETA | Triethylenetetramine |
| THF | Tetrahydrofuran |
| TMEDA | Tetramethylethylenediamine |
| TMSCl | Trimethylchlorosilane |
| tNtpv | 4,4',4"- <i>Tris</i> (5-nonvl)-2,2':6',2"-terpyridine |
| TPMA | Tris[(2-pyridyl)methyllamine |
| tov | 2.2':6'.2"-Terpyridine |
| TREN | Tris[2-aminoethyl]amine |
| TREN | Tris[2-aminoethyl]amine |

| UV | Ultraviolet |
|------|----------------------------------|
| 4-VP | 4-Vinyl pyridine |
| XPS | X-ray photoelectron spectroscopy |
| ρ | Density |

Chapter 1.

Introduction

I. Polymer Brushes

I-1. Their Definition and Physical Properties

As a defined by Milner, a polymer brush refers to an assembly of polymer chains tethered by one end to a surface or an interface.¹ The physical properties of polymer brushes largely depend on the chain length, grafting density, backbone flexibility, and excluded volume. Alexander² and de Gennes³ first developed the scaling theories for polymers irreversibly attached by one end to a surface. Three different regimes were identified that depend on the graft density and the distance between neighboring surfaceattached polymer molecules (Figure 1.1). The simplest case is when the distance between chains is larger than the characteristic size of the polymers. The polymers do not overlap, and in this case, the conformation of the polymer depends on the interaction between the polymer segments and the surface. Strong interactions lead to polymer segments adsorbing to the surface and a "pancake" conformation for the tethered polymer. Nonabsorbing polymers are described as having a mushroom conformation, where the chain segments avoid contact with the surface leading to a coiled polymer tethered through a short, terminal polymer segment. A high chain density leads to substantial inter and intramolecular segment-segment interactions, forcing the polymers to extend from the surface. This conformation is termed a "polymer brush".

In polymer brushes, the polymer chains may be tethered to the surface of a solid substrate, at an interface between two liquids, between a liquid and air, or between melts or solutions of homopolymers. Anchoring polymer chains to surfaces or interfaces can be reversible or irreversible. All of the polymer brush systems shown in **Figure 1.2** have a configuration different from that of a free chain in solution.^{1, 4, 5}



Figure 1.1. Schematic illustration of the conformation of polymers end-attached to a surface: (a) "pancakes"; (b) "mushrooms"; (c) "brushes".







diblock copolymer

adsorbed diblock copolymers

polymer micelle

melt



graft copolymers at fluid-fluid interfaces





end-grafted polymers

Figure 1.2. Examples of polymer systems comprising polymer brushes. (Redrawn with permission from *Prog. Polym. Sci.* 2000, 25, 677-710. Copyright 2000 Wiley-VCH.)

block copolymers at

fluid-fluid interfaces

I-2. Polymer Brushes on Various Substrates and their Applications

Polymer brushes may be useful in a broad range of applications because their mechanical and chemical robustness can be augmented by inclusion of a variety of functional groups and nanostructures. In the early 1950s, grafting polymer chains onto colloidal particles was found to be an effective strategy for preventing flocculation.⁶⁻⁹ In these "steric stabilized" systems, the attached polymer chains prefer the suspension

solvent to the colloid particle surface, and their extension into the solvent stabilizes colloids by their resistance to chain-chain overlap. The repulsive force between particles ultimately arises from the high osmotic pressure inside the brushes. More recent applications of polymer brushes include new adhesive materials,¹⁰ protein-resistant biosurfaces,¹¹ chromatographic devices,¹² lubricants,¹³ polymer surfactants¹ and polymer compatibilizers.¹ Some polymer brushes have Lower Critical Solution Temperatures (LCSTs) near room temperature and exhibit different wetting properties above and below the LCST.¹⁴ Polymer brushes covalently tethered on porous membranes can act as pH sensitive, photosensitive, and redox sensitive chemical gates.¹⁵⁻¹⁷ Suter et al. prepared polystyrene brushes on high surface area mica for the fabrication of organic-inorganic hybrid nanocomposites,^{18, 19} and patterned thin organic films have been investigated for applications in microelectrics,²⁰ controlled cell growth,²¹ biomimetic material fabrication,²² as microreaction vessels and for drug delivery.²³ The broad spectrum of polymer brush applications also stems from their compatibility with various substrates, including flat surfaces, particles or macromolecules (Figure 1.3).

STR/1535



polymer brushes on flat surface

polymer brushes on non-planar surface



polymer brushes on macromolecules

Figure 1.3. Examples of polymer brushes tethered from various substrates, such as flat wafers, particles, colloids and polymers.

I-3. Polymer Brushes on Flat Surfaces

Polymer brushes on flat wafers and surfaces are the most extensively investigated systems, partly due to well-developed surface characterization methods such as ellipsometry, contact angle measurements, x-ray photoelectron spectroscopy (XPS), scanning electron microscopy (SEM), atomic force microscopy (AFM), and fourier transform infrared (FTIR), but also from potential applications in advanced responsive materials, nanoprinting, and biotechnology.

The responsive nature of some polymer brushes upon changes in solvent,²⁴⁻²⁶ ionic strength,²⁷ or temperature^{27, 28} also lead to altered film morphologies, thickness, and/or barrier properties. A number of these stimuli-responsive or "smart" brushes have been synthesized and characterized. Block copolymer brushes grown from flat substrates have been widely studied because their conformation changes with changes in their environment. Brittain et al. grew ABA triblock copolymer brushes from flat silicon substrates where the physicochemical properties of the middle block are different from the end blocks.²⁶ As shown in Figure 1.4, the film should adopt an extended brush configuration when exposed to a good solvent for all the blocks, but when exposed to a good solvent for only the middle, the brush will fold to minimize exposure of the terminal A block to solvent. Experimentally, poly(methyl acrylate)-b-polystyrene (PMA-b-PS) brushes synthesized from a planar silicon surface show ~20° change in the advancing water contact angle when exposed to dichloromethane and cyclohexane. "Smart" polymer brushes can also be prepared by attaching poly(N-isopropylacrylamide) (PNIPAAM) brushes, which exhibit an LCST of ~ 32-33 °C. Below the LCST, the polymer is an extended brush and the surface is hydrophilic due to intermolecular H- bonding between PNIPAAM chains and water. Above the LCST, the water is expelled, and intermolecular hydrogen bonding renders the collapsed polymer structure hydrophobic. By tethering these polymer brushes to a well-defined rough surface, Jiang et al. created polymer films that switch between superhydrophobicity (contact angle \sim 150°) and superhydrophilicity (contact angle \sim 0°) over a \sim 10 °C change in temperature.²⁹ Similar temperature responsive behavior for other systems, may prove to be important in thermally responsive drug-delivery vehicles and temperature-controlled gates or switches.^{30, 31}

Polymer brushes grown from flat surfaces also are useful materials for many biological applications such as substrates for protein microarrays, which allow high throughput studies of protein-protein specific interactions. However, many biological systems tend to physically adsorb onto solid substrates without specific receptor-recognition interactions (nonspecific adsorption), and the background noise associated with nonspecific adsorption typically reduces the efficiency of protein microarrays. Poly(ethylene glycol) (PEG) is often used for biological applications because it is nontoxic, non-immunogenic, and resists protein and cell adhesion. Chilkoti et al. polymerized PEG-containing acrylate monomers from a flat gold surface and found that the polymer brushes successfully resisted protein and cell adhesion.³² Andruzzi et al. also produced PEG-containing polymer brushes that resisted protein and cell adsorption.³³



Figure 1.4. Reversible response of triblock-copolymer brushes to different solvents.

Polymer brushes anchored to flat surfaces are compatible with a number of patterning and microfabrication strategies. Various techniques such as standard photolithography,³⁴ ultraviolet litrhography,³⁵ microcontact printing (μ CP),^{36, 37} nanoshaving,²⁵ electron-beam lithography,³⁸ and dip-pen lithography³⁹ were used to produce micro to nano-sized features in polymer brushes attached to surfaces. Microcontact printing^{36, 37} and ultraviolet light lithography³⁵ generally enable rapid patterning of large surface areas (up to a few cm²). Serial processes such as electron beam lithography produced features as small as 70 nm with reasonable throughput.³⁸ AFM-based techniques that use the AFM tip to remove and backfill areas (nanoshaving)²⁵ or deposit molecular components (dip-pen lithography)³⁹ can in principal produce submicrometer features with site-specific control over features.

I-4. Polymer Brushes on Particles and Non-planar Surfaces

A variety of non-planar surfaces have also been used as substrates for polymer **brushes**, including gold,^{40, 41} silica,⁴²⁻⁴⁶ alumina,⁴⁷ clay,⁴⁸ latex,⁴⁹ dextran,⁵⁰ magnetic

particles,⁵¹ and carbon nanotubes.⁵²⁻⁵⁷ Nearly any substrate may be suitable as long as the surface can be functionalized and it is compatible with the method used to tether the brush. Most modifications of non-planar substrates are motivated by the need to alter the interactions of these materials with the surrounding environment. Substantial work has been devoted to non-planar surfaces in chromatographic supports, nanoparticles and nanotubes. In separations research, the emphasis has been functionalizing materials to improve selectivity while nanotube and particle research emphasizes dispersion of these materials in solvents, encapsulating particles in a polymer film to protect them from chemical or mechanical damage, or preparing well-defined nanostructures.

Surface modification is widely used to improve the selectivity of separation process.^{44, 58, 59} Buchmeiser et al.^{44, 60} used ring opening metathesis polymerization (ROMP) to grow functionalized norbornenes from silica surfaces for the chromatographic separation of phenols, anilines, lutidines, and hydroxyquinolines. Preparing supports by coating polymer solutions onto silica tends to clog pores and reduce surface area. Anchoring polymer brushes to surfaces avoids clogging and provided improved separations. They also used reverse-phase chromatography to separate biomolecules using copolymers of 2-norbornene and 1,4,4a,5,8,8a-hexaydro-1,4,5,8-exo,endodimethano-naphthalene grafted onto borosilicate monoliths.⁵⁹ Separation of the various proteins was dependent on the physicochemical properties and microstructure of the grafted monoliths.

There also has been substantial interest in polymer brushes tethered to particles that range from micrometer to nanometer in size. As noted earlier, research on polymer brushes attached to particles has mainly focused on increasing their solubility or dispersibility in solutions. As an example, carbon black has wide applications as a reinforcing agent for rubbers, pigments for coatings, inks and toners. However, small carbon blacks (10-75 nm) easily fuse into aggregates that range from 50-500 nm in size. Grafting polymers onto the surface of carbon black provides steric stabilization against flocculation and greatly improves their dispersal in resins and solvents.^{61, 62} Other efforts have been devoted to the synthesis of novel materials. Blomberg et al. created hollow nanospheres by attaching poly (styrene-*co*-vinylbenzocyclobutene) or poly (styrene-*co*-maleic anhydride) brushes on 600 nm size silica nanoparticles.⁶³ Both polymers are cross-linkable at high temperatures, and after cross-linking the polymer brushes, the silica core was etched away with HF leaving a hollow polymer capsule. The protection or gradual release of an inner substance such as drugs and dyes was suggested as an application for nanocapsules.

Single walled and multi-walled carbon nanotubes have the potential to be used in a variety of applications (molecular wires, sensors, and composite materials) due to their extraordinary mechanical and electrical properties.^{52, 55} However, the poor solubility in most solvent hinders their processability.⁵⁴ Tethering polymer brushes to carbon nanotubes renders them soluble in common solvents with minimal changes in the nanotube structure. Qin et al. successfully attached PS brushes to carbon nanotubes, and observed that in addition to good solubility in common organic solvents, the initial carbon nanotube bundles tend to separate into small bundles or even individual tubes during the attachment process.⁵² Kong et al. synthesized poly(methyl methacrylate) (PMMA)-*b*-poly(2-hydroxyethyl methacrylate) (PHEMA) polymer brushes from carbon nanotubes, and the solubility of the resulting nanotubes was dependent on solvent, with good solvents for PHEMA providing effective solvation,⁵³



Figure 1.5. Tapping mode AFM image of a molecular brush cast onto a mica substrate possessing a main chain DP = 400 and poly(*n*-butyl acrylate) side chains of DP = 30. (Reprinted with permission from *Macromolecules*. 2001, *34*, 8354-8360. Copyright 2001 American Chemical Society.)

I-5. Polymer Brushes Tethered on Macromolecules

Densely grafted linear or dendritic copolymers are described as "molecular brushes." Due to the high local concentration of tethered chains, the grafted chains must extend away from the polymeric backbone to minimize steric crowding effects. Initially, the attention to molecular brushes was largely driven by their possible visualization by AFM. When densely grafted brushes are deposited on surfaces, favorable interactions between the graft chains and the surface cause the chains to spread on the surface, enabling AFM imaging with single chain resolution. Shown in **Figure 1.5** is such an example, where Matyjaszewski et al. used AFM to image a molecular brush with poly(n-butyl acrylate) (PBA) grafted side chains that had been deposited on mica.^{64, 65} These materials were recently applied as templates for the directed mineralization of inorganic nanocrystals⁶⁶ and for the formation of high-aspect-ratio nanowires.⁶⁷

II. Surface-initiated Polymerizations

II-1. Preparation of Polymer Brushes

There are two general ways to prepare polymer brushes: physisorption and covalent attachment. While physisorption processes use multiple weak polymer-surface interactions to anchor the polymer to the substrate, both the "grafting to" and "grafting from" (surface-initiated polymerization) approaches connect the polymer to the surface through strong covalent bonds.

Physisorption is a reversible process for tethering of polymer chains to a solid surface, usually achieved by the self-assembly of polymeric surfactants or end-functionalized polymers on the surface.⁶⁸ Homopolymers, block copolymers and graft copolymers have been successfully tethered onto substrate surfaces via physisorption.⁶⁹⁻⁷² The resulting polymer brushes are often thermally and solvolytically labile due to the weak van der Walls forces or hydrogen bonding interactions, and exposure to a good solvent or more strongly adsorbing species may cause desorption.
In a "grafting to" approach, pre-formed end-functionalized polymer molecules react with an appropriate substrate to form polymer brushes. This approach is now more widely used than physisorption for the preparation of polymer brushes since the covalent bond formed between surface and polymer chain makes the polymer brushes more robust. The substrate surface is usually modified to accommodate the functional groups at the terminus of the polymer chain by modifying the surface with coupling agents or SAMs. Koutos et al.^{73, 74} synthesized a series of thiol-terminated polystyrenes with a low PDI, and these polystyrene chains were end-grafted to a gold surface via formation of goldthiolate Using hydrosilation, successfully bonds. Yang al. prepared et poly(methylhydrosiloxane) brushes on silicon surfaces that had been modified with vinvlterminated SAMs.⁷⁵ In most "grafting to" cases, only a small amount of polymer can be immobilized onto the surface since polymer chains must diffuse through the existing polymer film to reach the reactive sites on the surface. As the film thickness increase, this steric barrier becomes more severe. Thus, polymer brushes obtained by the "grafting to" approach generally have a low grafting density and low film thickness.

Comparing to physisorption and the "grafting to" method, the "grafting from" approach can provide polymer brushes with a high grafting density. "Grafting from" is accomplished by covalently anchoring initiators on a surface, and activating the initiators to start the polymerization. Recent progress in polymer synthesis techniques makes it possible to produce polymer chains with controllable lengths. Polymerization methods used to synthesize polymer brushes include cationic, anionic, ring opening, free radical and controlled radical polymerization. The following sections will emphasize the

synthesis of polymer brushes using these various surface-initiated polymerization methods.

II-2. Surface-initiated Cationic Polymerizations

In the early 1980s, Vidal et al.^{76, 77} used surface-initiated cationic polymerization to graft polyisobutylene to a silica surface. 2-(Chloromethylphenyl)ethyldimethyl chlorosilane was anchored to the silica surface, and the reaction of diethylaluminum chloride with the immobilized initiator produced carbocationic species which initiated the polymerization of isobutylene. Jordan and Ulman⁷⁸ reported performed surface-initiated cationic polymerization of *N*-propionylethylenimine (PEI) on gold surfaces. (Scheme 1.1) They first formed a hydroxy-terminated SAM on gold surfaces and then exposed the monolayer to a stream of trifluoromethanesulfonic anhydride vapor to convert the hydroxy groups to triflates. After polymerization of PEI for 7 days under reflux, ellipsometry measurements indicated formation of a 10 nm polymer brush, which they confirmed by external reflection FTIR and contact angle measurements. Scheme 1.1. Surface-initiated cationic polymerization of 2-oxazolines. (Redrawn with permission from *J. Am. Chem. Soc.* 1998, 120, 243-247. Copyright 1998 American Chemical Society.)



Recently, Zhao and Brittain⁷⁹ successfully synthesized PS brushes via surfaceinitiated cationic polymerization. 2-(4-Trichlorosilylphenyl)-2-methoxy-d₃-propane was immobilized on a silica substrate and addition of TiCl₄ initiated polymerization of a 34 nm thick brush. The initiator efficiency estimated by FTIR-ATR (attenuated total reflectance) was ~ 7%, and additional initiator was consumed by termination reactions.

Because cationic polymerizations are ionic reactions, factors such as solvent polarity and Lewis base additives will influence the brush thickness.

II-3. Surface-initiated Anionic Polymerizations

Anionic polymerization, the most widely used living polymerization technique, has also been adapted to the synthesis of polymer brushes *via* the "grafting from" approach. Jordan et al. used anionic polymerization to synthesize polystyrene brushes on gold substrates.⁸⁰ As shown in **Scheme 1.2**, a SAM of 4'-bromo-4-mercaptobiphenyl on gold reacted with *sec*-BuLi to form a monolayer of biphenyllithium. Addition of styrene initiated the polymerization, eventually forming 18 nm thick PS brushes. Based on the ellipsometric data from *in situ* swelling experiments, the grafting density was calculated to be 3.2-3.6 nm²/chains. The initiating efficiency was estimated to be ~ 8%.



Scheme 1.2. Surface-initiated anionic polymerization of styrene on gold





Qingye et al. also polymerized styrene from clay surfaces using anionic polymerization.⁸¹ A linear relationship was found between the monomer concentration and the M_n of the cleaved polymers, which is consistent with a living anionic polymerization mechanism. Ingall et al. polymerized acrylonitrile from SiO₂ using a similar strategy.⁸² A SAM formed from 3-bromopropyltrichlorosilane was lithiated with lithium di-*tert*-butylbiphenyl, and subsequent addition of monomer to the system initiated the anionic polymerization (Scheme 1.3). Polymerization for 8 days yielded tethered poly(acrylonitrile) films with thicknesses up to 245 nm.

II-4. Surface-initiated Ring-opening Polymerization

Surface-initiated ring-opening polymerization (ROP) is an attractive route for coating surfaces with thin layers of polycaprolactone, polylactide and other polymers. Husseman and coworkers prepared a SAM terminated with di(ethylene glycol) moieties,³⁶ and using the pendent OH groups for initiation, they carried out the aluminum alkoxide catalyzed ROP of ε -caprolactone (CL). They obtained 70 nm thick PCL brushes after a few hours at room temperature. Terminating the SAM with di(ethylene glycol) gave more reproducible polymer brush growth and better long-term stability than simple long chain alcohol SAMs.

In related work, Choi and Langer formed an oligo(ethylene glycol) terminated SAM on gold, and used tin(II) (2-ethylhexanoate)₂ (Sn(Oct)₂) to catalyze the ROP of Llactide from Au and silicon substrates⁸³ (Scheme 1.4). Poly(lactic acid) (PLA) is an important biodegradable polymer used in medical applications, and PLA brushes present a possible route to well-defined surfaces with controlled release properties. Polymerization for 3 days at 40 °C provided PLA brushes up to 12 nm thick, and 70 nm thick PLA brushes were obtained from silicon surfaces after polymerization for 3 days at 80 °C. The PLA brushes were reported to be chiral and crystallized on the surface.

Scheme 1.4. Surface-initiated ring opening polymerization of lactide. (Redrawn with permission from *Macromolecules* 2001, *34*, 5361-5363. Copyright 2001 American Chemical Society.)



It has been suggested that coating conductive substrates with well-defined polymer brushes such as functionalized norbornenes can be useful in the production of polymer electronic devices. These strained cyclic monomers are usually polymerized by ROMP. As shown in **Scheme 1.5**, various norbornene-derived polymer brushes were grown from silicon surfaces by Whitesides and co-workers.⁸⁴ The surface-bound catalytic sites were produced by forming a trichlorosilane-derived SAM containing norbornene groups, and then exposing the SAM to a solution of a Grubbs-type ROMP catalyst. Addition of the monomer initiated a rapid, but controlled polymerization, producing 90 nm thick brushes in 30 min. The formation of block copolymer brushes and the use of microprinting to produce patterned surfaces also was described.

Scheme 1.5. Surface-initiated ring opening metathesis polymerization of functionalized norbornenes. (Redrawn with permission from *Macromolecules* 2000, *33*, 2793-2795. Copyright 2000 American Chemical Society.)



Poly(norbornene) brushes were also grown from silicon substrate by Grubbs and co-workers using surface-initiated ROMP⁸⁵ using an alternative initiator attachment scheme. A direct Si-C bond to the surface was used to anchor the initiator instead of the Si-O bond formed via condensation of chlorosilanes. The polymer brushes grown from the initiatiators was very thick (up to 5.5 μ m).

II-5. Surface-initiated Free Radical Polymerization

In a typical surface initiated radical polymerization, the immobilization of the radical initiators usually involves a series of steps. In an early example Boven et al. initiated radical polymerization of methyl methacrylate (MMA) chains from immobilized azo initiators.⁸⁶ Sugawara and Matsuda used a similar strategy to graft PS on poly(vinyl alcohol) film, and poly(acrylamide) on poly(ethylene terephthalate) film.⁸⁷ The reactive azo initiators were attached onto the surface by coating the substrate with partially derivatized poly(allylamine).

Minko et al. studied surface initiated radical polymerization using both theoretical and experimental approaches.⁸⁸⁻⁹³ In their experimental work, azo or peroxide initiators were attached on solid substrates by either physisorption or chemical immobilization. Initiator anchoring comprised of priming surfaces with 3-glycidyloxypropyltrimethoxysilane followed by the reaction with 4,4'-azobis(4-cyanovaleric acid). The surface-initiated radical polymerization was followed by *in situ* ellipsometric measurements of the amount of grafted chains. The resulting kinetics showed a linear dependence of the polymerization rate on the surface concentration of the initiator and an

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Scheme 1.6. Synthesis of polystyrene brushes on silica and cleavage of the polymers

from the surface

inverse square root dependence on the initiator concentration in solution, which is consistent with conventional free radical polymerization. However, their method of anchoring initiator led to low initiator densities and side reactions.

To circumvent this problem, Rühe et al. developed a one step initiator anchoring strategy to initiate free radical polymerization from surface.^{45, 94-96} As shown in **Scheme 1.6**, their initiator system includes three important components: (1) an azo group that produces free radicals upon heating or irradiation by UV (ultraviolet), (2) a chlorosilane acting as the linker between the initiator and substrate surface, and (3) an ester that can be hydrolyzed to detach the polymer brushes from the surface. The initiator was self-assembled on the surface, and following free radical polymerization of styrene or other monomers, the ester bonds that connected the polymer brushes to the surface were cleaved. The molecular weights of the detached polymers were determined and compared to the free polymer formed in solution polymerization. The density of chains on the surface was calculated based on the molecular weight and the mass of the grafted polymers. They found that the average distance between tethered PS chains was 2-3 nm, smaller than the radii of gyration of the corresponding polymer molecules.

Wittmer *et al.* predicted significant differences between polymer brushes grown from surfaces and polymers generated in solution during the free radical polymerization.⁹⁷ They suggested that polymer brushes formed from the surface should have a higher polydispersity (PDI) than those formed in the solution. Due to their high mobility, long chains should be easily accessible to monomers and thus more efficient at adding monomers compared to short ones. The PDIs of the detached polymer brushes prepared by Prucker and Rühe ranged from 1.5 to 2, close to the PDI expected for free radical polymerizations in solution. Consequently, they concluded that surface immobilization does not cause excessive broadening of the molecular weight distribution. Figure 1.6 shows the molecular weights and polydispersities of the detached polymer brushes.



Figure 1.6. Time-dependent properties of polymer chains grown by surface-initiated free radical polymerization of styrene: (a) molecular weight M_n , (b) grafting densities $\delta(PS)$, and (c) polydispersity of the covalently attached polymers. Reprinted with permission from *Macromolecules* 1998, 31, 602-613. Copyright 1998 American Chemical Society.

Rühe and coworkers extended their surface-initiated free radical polymerization strategy to the preparation of block copolymer brushes, where one block was synthesized by ROP. A PCL macroinitiator containing azo groups was physisorbed on a silicon oxide surface to initiate the radical polymerization of the other monomer. This simple physisorbed macroinitiator system allows the creation of hydrophobic layers on hydrophilic surfaces.

II-6. Surface-initiated Controlled Radical Polymerization

Compared to conventional free radical polymerization, controlled radical polymerizations such as atom transfer radical polymerization (ATRP), nitroxidemediated polymerization (NMP), and reversible addition-fragmentation chain transfer (RAFT) provide several advantages for brush synthesis, principally the simple preparation of block copolymer brushes. The living character of these polymerization systems could provide a better control of molecular weight and polydispersity.

The living character of NMP depends on the reversible capping of the active chain-end radical with a nitroxide leaving group. As shown in **Scheme 1.7 (a)**, Husseman et al. described the first example of NMP applied to the synthesis of polymer brushes.⁹⁸ They first attached alkoxyamine initiators onto the surface and then heated the system to 120 °C to initiate radical polymerization. The stable nitroxide radical 2,2,6,6-tetramethylpiperidinyloxy (TEMPO), cleaves during the initiating process and reversibly caps the chain-end radicals to control radical propagation. The addition of free alkoxyamine initiator provides better control over the molecular weight, but induces polymerization in solution. Later, Hawker et al.⁶³ formed crosslinked, hollow

nanoparticles by using NMP (Scheme 1.7 (b)) to prepare random copolymer brushes of styrene and 4-vinylbenzocyclobutene anchored to silicon nanoparticles. The benzocyclobutenes are sites that readily cross-linked upon heating to 220 °C to form polymer-coated nanoparticles. Using hydrofluoric acid, the silica core was removed to give hollow cross-linked polymer spheres, which can be used for drug delivery.

Scheme 1.7. Polystyrene brushes and copolymer brushes grown by nitroxide-mediated polymerization (NMP). (a) Polystyrene, (b) random copolymer, leading to cross-linked hollow nanoparticles.



Hawker and coworkers combined photolithography with NMP to yield patterned polymer brushes with well-defined hydrophobic and hydrophilic domains (Figure 1.7).⁹⁹ Poly(*tert*-butyl acrylate) (PtBA) brushes (hydrophobic) was synthesized by surfaceinitiated NMP and their hydrolysis formed poly(acrylic acid) (PAA) brushes, which is hydrophilic.



Figure 1.7. Optical micrographs of patterned surfaces: (a) 10-µm features in a continuous polymer brush showing regions of poly(*tert*-butyl acrylate) (dark) and poly(acrylic acid) (light) and (b) interaction of a water droplet with 200-µm features showing an unusual wetting profile and preferential interaction with poly(acrylic acid) brush domains. Reprinted with permission from *J. Am. Chem. Soc.* 2000, *122*, 1844-1845. Copyright 2000 American Chemical Society.

Scheme 1.8. Polymer brushes grown by RAFT polymerization. (a) PMMA, (b) PS



RAFT is another important technique for controlled radical polymerization. Chain growth is initiated using a conventional radical initiator such as 2,2'azobisisobutyronitrile (AIBN), but propagation is mediated by a dithioester chain transfer agent that reversibly adds to chain ends to provide the polymerization its living character. As shown in **Scheme 1.8**, Brittain et al. synthesized PMMA, poly(N,N-dimethylacrylamide), and PS brushes from silica surfaces using surface-initiated RAFT polymerization.¹⁰⁰ The initiator was anchored via formation of SAM monolayer that contains an azo initiator or a dithiobenzoate group. Although RAFT polymerization is relatively slow compared to techniques such as ATRP and NMP, it is highly living, supported by the easy re-initiation of the polymer chains.

III. Atom Transfer Radical Polymerization

III-1. Introduction

Due to its compatibility with many monomers, free radical polymerization is widely used to prepare commercial polymers. With knowledge of the kinetic steps associated with initiation, propagation and termination, it is relatively easy to synthesize polymers of predictable molecular weight. However, the inevitable radical coupling and disproportionation reactions that occur during free radical polymerization prevent the synthesis of polymers with narrow molecular weight distributions, block copolymers, and more complicated polymer architectures. The past decade has seen the development of several schemes for controlled radical polymerization methods such as NMP, RAFT and ATRP. Since its independent development by Swamoto¹⁰¹ and Matyjaszewski,¹⁰² ATRP has become one of the most studied methods for controlled radical polymerization.

Scheme 1.9 compares radical formation in ATRP with conventional formation of radicals by photochemical or thermal decomposition of initiator precursors. The principal difference between ATRP and conventional free radical polymerizations is the reversible nature of radical formation in ATRP. Strategies for controlled polymerization exploit reversible radical formation to maintain a low radical concentration during polymerization, thus minimizing the bimolecular coupling and disproportionation reactions that are responsible for termination of the kinetic chain in radical polymerizations. In ATRP, the mechanism used to control radical concentration is a reversible one-electron reduction that transfers a halide from an initiator to a catalyst, leaving a radical capable of adding monomer in a step identical to that of conventional polymerizations. Setting the equilibrium to favor dormant initiator (oxidized) over the

active state (reduced, radical) minimizes, but does not eliminate termination reactions. Therefore, ATRP is not a true living polymerization and is often described as "controlled". In living polymerizations, there are no termination reaction and the chain ends continue to grow as long as monomer is added to the polymerization.

Scheme 1.9 Radical generation in conventional and atom transfer radical polymerization

i) Conventional Free Radical Polymerization

$$N \equiv C - C - N = N - C - C \equiv N \xrightarrow{heat or UV} 2 N \equiv C - C + N_2 \uparrow$$

$$CH_3 \qquad CH_3 \qquad CH_3$$

ii) Atom Transfer Radical Polymerization

Ethyl 2-bromoisobutyrate

ATRP has its roots in the Kharasch addition reaction.^{103, 104} As shown in **Scheme 1.10**, atom transfer radical addition (ATRA) corresponds to one cycle of ATRP, involving reduction of an organohalide by a metal complex to form a carbon centered radical, addition of one monomer, and transfer of the halide to the organic radical to form the addition product and regenerate the catalyst.





III-2. Mechanism and Kinetics

Scheme 1.11 shows a simple scheme that captures the salient features of ATRP. The principle difference between ATRP and ATRA is the repeated reversible activation of a substrate that allows the growth of a polymer chain. Matyjaszewski in particular has carried out detailed studies to understand the kinetics of ATRP. The initial step in ATRP is the reduction of initiator to form the radical species R·, which can either add a monomer with a rate constant k_p , terminate, or deactivate with a rate constant k_{deact} . In ATRP, k_{deact} is normally greater than k_{act} to minimize termination. As the radical concentration builds, an equilibrium is set up between R· and the dormant initiator RX. From detailed studies of ATRP for styrene,¹⁰⁵ MA,¹⁰⁶ and MMA^{107, 108} under homogeneous conditions, Matyjaszewski estimated the steady state concentration of radicals in ATRP to be as low as 10^{.7} to 10^{.8} M. Assuming rapid establishment of equilibrium and excluding termination effects leads to the rate law shown in equation 1 (for a Cu(I) catalyzed polymerization), and the evolution of the polydispersity (M_w/M_n) as a function of conversion in equation 2. As shown in equation 1, the rate of

polymerization is inversely proportional to the deactivator (Cu(II)). The equilibrium constant k_{eq} is equal to the k_{act}/k_{deact} , which is also proportional to the polymerization rate.

Scheme 1.11 Transition-Metal-Catalyzed ATRP

$$R-X + M_{n}^{t}-Y - \frac{k_{act}}{k_{deact}} R + X - M_{n}^{t}-Y / Ligand$$

$$(k_{p})^{t} + k_{t}^{t} + \frac{k_{t}}{k_{t}} + \frac$$

$$R_{\rm p} = k_{\rm p} \frac{k_{\rm act}}{k_{\rm deact}} [M][I]_0 \frac{[{\rm Cu}^{\rm I}]}{[{\rm XCu}^{\rm II}]} \qquad \text{eq. 1}$$

$$\frac{M_w}{M_n} = 1 + \left(\frac{k_p[I]_0}{k_{\text{deact}}[XCu^{II}]}\right) \left(\frac{2}{p} - 1\right) \qquad \text{eq. 2}$$

The first-order kinetics with respect to monomer, initiator, and catalyst (Cu(I)) concentration have been confirmed experimentally. Using ATRP of styrene at 110 °C (1 mol % initiator and catalyst), Matyjaszewski estimated the time intervals, τ , for various steps in the polymerization.¹⁰⁹ At 30 % conversion, the chain end is activated to a radical every 22 sec, and then is deactivated to its dormant species after 0.018 msec. Since the deactivation rate is seven times faster than propagation ($\tau = 12$ msec), one

monomer adds to a polymer chain in seven activation/deactivation cycles (2.5 min). Under these conditions, it would take 4 hours to grow a polymer with a degree of polymerization of 100.

ATRP can provide well-defined polymers with low-polydispersities (1.05 < $M_w/M_n < 1.5$). As shown in equation 2, the low polydispersities are due to a high deactivation rate and low radical concentration. If $k_{act} \gg k_{deact}$, the polymerization resembles a conventional redox-initiated radical polymerization, resulting in high polymerization rates and high polydispersities. Adding Cu(II) species favors deactivation and decreased radical concentration and termination. Controlled polymerization is achieved at the cost of a slower polymerization rate, but ATRP provides access to polymer structures that cannot be prepared by other methods.

III-3. Monomers, Catalysts and Initiating Systems

Because it is a radical polymerization, ATRP is compatible with a broad range of monomers including styrenes, acrylates, methacrylates, acrylamides, and acrylonitrile (Scheme 1.12). Each monomer has a unique atom transfer equilibrium constant for its active and dormant species, which is mainly dependent on the structure of the monomer. Whether a monomer performs well in ATRP depends on the structure of the dormant chain end. Removal of a halide from the chain end must be facile, reversible, and lead to a stabilized radical. Methacrylates are particularly well-suited to ATRP and polymerize at 50 °C; styrenes require temperatures near 100 °C. Two major classes of monomers not yet been successfully polymerized by ATRP, acidic monomers and the alkyl substituted olefins. The former fail because they react with the N-containing ligands

of most Cu-based systems, while the latter have a very low radical stability and are difficult to polymerize by any radical mechanism.



Scheme 1.12. Various monomers polymerized by ATRP

A variety of metal catalysts have been successfully used in ATRP, including copper,^{110, 111} iron,^{105, 112} ruthenium,^{101, 113} nickel,^{114, 115} and rhodium complexes.¹¹⁶ The metal center of a good catalyst must have two readily accessible oxidation states separated by one electron and have a reasonable affinity toward the halide in the initiator. In addition, strong ligand binding is helpful as it ensures a stable catalyst, a requirement often satisfied by the use of chelating ligands. The most popular ATRP catalyst systems are copper halide complexes having bipyridine or related ligands, which are particularly effective catalysts for polymerization of (meth)acrylate monomers.

A variety of initiators, including halogenated alkanes, benzylic halides, α bromoesters, α -haloketones and sulfonyl halides (Scheme 1.13) have been used successfully in ATRP. A good initiator system provides faster initiation than propagation. The halogen atom plays a very important role in the radical generation step. Bromine and chlorine are most commonly used halides, with brominated initiators more reactive that chlorinated initiators. (The C-Cl bond energy in benzyl chloride is~ 284.7 kJ/mol vs. 213.5 kJ/mol for benzyl bromide.) Because of their instability, iodide initiators are seldom used. The functional groups α to the halide also play a very important role, and stabilize radicals in the order of CN > C(=O)R > C(=O)OR > Ph > Cl > Me. As these groups are commonly found in monomers that undergo radical polymerization, a common strategy is to match the reactivity of the initiator to the dormant polymer chain by choosing an initiator whose structure mimics that of the monomer.

Usually the initiator, catalyst, and deactivator have the same type of halogen atom in the initiator and in the metal salt. However, Matyjaszewski found that a mixed initiator system of R-Br/CuCl provides fast initiation, but better control than R-Br/CuBr.¹¹⁷ The use of CuCl presumably increased the deactivation rate due to the formation of the stronger alkyl-chloride bond.





i) halogenated alkanes and benzylic halides

III-4. Ligands, Solvents and Other Factors

Ligands. The metal ligand in ATRP plays two important roles, to render the transition-metal salt soluble in organic, and in some cases, aqueous media, and to adjust the redox potential of the complex so that the metal center has the appropriate reactivity to carry out the activation/deactivation steps at the heart of the ATRP reaction. The most common ligands include nitrogen chelates for Cu-based catalysts,¹¹⁸ and phosphorus ligands for transition metals including rhenium,¹¹⁹ ruthenium,¹⁰¹ iron,¹¹⁸ rhodium,¹²⁰ nickel,¹¹⁴ and palladium.¹²¹ Ligands based on metal coordination to oxygen and sulfur have also been described, but are used infrequently.

The extensive use of Cu-catalyzed ATRP has motivated extensive research on the reactivity of nitrogen-based Cu complexes. In particular, Matyjaszewski et al. tested a large number Cu catalysts having multidentate nitrogen ligands (Scheme 1.14) and developed structure-activity relationships for the catalysts. In general, the activity of nitrogen-based ligands in ATRP decreases with the number of coordinating sites (N4 > N3 > N2 >> N1) and with the number of linking C-atoms (C2 > C3 >> C4). It also decreases in the order alkyl amine \approx pyridine > alkyl imine >> aryl imine > aryl amine. The activity of bridged and cyclic systems is normally higher than for linear analogs. These results were interpreted in terms of catalyst activity decreasing as the ligand stabilizes the Cu(I) state of the catalyst and favors deactivation.



i) bidentate ligands bpy dNbpy, when R = 5-nonyl phen TMEDA dnNbpy, when R = n-nonyl dHbpy, when R = n-heptyl ii) tridentate ligands R R R BPMA, when R = H tpy, when R = H DETA, when R = H BPMOA, when R = n-noctyl tNtpy, when R = 5-nonyl PMDETA, when R = methyl iii) tetradentate ligands R -R N' .R Ŕ CYCLAM, when R = H TETA, when R = H TREN, when R = H **TPMA** HMTETA, when R = methyl Me₄Cyclam, when R = methyl Me₆TREN, when R = methyl

Bipyridine (bpy) is probably the most commonly used ligand in ATRP,^{102, 122} but the poor solubility of the Cu(II) complex limits use to relatively polar solvents and monomers. The Cu(II) complexes of alkyl-substituted bipyridines such as 4,4'-diheptyl2,2'-bipyridine (dHbpy) and 4,4'-di(5-nonyl)-2,2'-bipyridine (dNbpy) are more soluble and provide better control over ATRP in nonpolar solvents.^{105, 123} The use of catalysts with multidentate amine ligands such as N,N',N',N'',N''-pentamethyldiethylenetriamine (PMDETA), 1,1,4,7,10,10-hexamethyltriethylenetetramine (HMTETA), and tris[2-(dimethylamino)ethyl]amine (Me₆TREN) provides faster polymerization rates than Cubpy complexes.^{124, 125} Me₆TREN-CuBr and structurally related complexes have lower redox potentials than copper-bpy complexes.¹²⁶ Compared to bpy, Me₆TREN increases the polymerization rate by shifting the dormant species/radical equilibrium to favor a higher radical concentration. Obviously, the increased radical concentration also favors increased termination and there is some loss of control compared to the bpy system. The higher activity of Me_6TREN enables activation at lower temperatures. MA was successfully polymerized at ambient temperatures when Me₆TREN was used as the ligand in ATRP,¹²⁵ while the corresponding dNbpy-based complex required polymerization at 90 °C.¹⁰⁶ ATRP of MMA using PMDETA as the ligand significantly deviates from the first order kinetics.¹²⁴

Solvents. ATRP can be run in bulk, in solution, or even in a heterogeneous system (emulsion and suspension polymerization). Solvents are commonly used since the catalyst must be soluble to effect the deactivation step in ATRP. Catalyst solubility is a common problem with Cu-based ATRP since the Cu(II) complexes often have lower solubilities and precipitate from nonpolar solvents, leading to loss of control over the polymerization.¹²⁷ The ATRP of *n*-butyl acrylate in benzene was poorly controlled with a PDI of 2.4, but switching to the more polar ethylene carbonate provided good control over molecular weight and a low PDI.¹²⁸ In addition, some polymers such as

polyacrylonitrile, are poorly soluble in their monomer. In general, solvents compatible with radical polymerization and the catalyst are acceptable for ATRP, and those used include benzene, toluene, anisole, diphenyl ether, ethyl acetate, acetone, dimethyl formamide, ethylene carbonate, alcohol, water, carbon dioxide, and many others.

ATRP in aqueous media is particularly attractive. Armes reported the accelerated ATRP of methoxy-capped oligo(ethylene glycol) methacrylate in water using a Cu(I)/bpy catalyst.¹²⁹ The fast polymerization rate was ascribed to the high polarity of water, which promoted the formation of $[Cu(bpy)_2]^+$ a very active mononuclear catalyst. Similar results were reported by Huck and Bruening and Baker in the aqueous ATRP of MMA and 2-hydroxyethyl methacrylate (HEMA).^{31, 130}

Temperature. In general, the rate of polymerization in ATRP increases with increasing temperature because both the radical propagation rate constant and the atom transfer equilibrium constant increase with the temperature However, chain transfer and other side reactions may also occur more at elevated temperatures.

Additives. Because of its tolerance to a variety of functional groups, additives are normally not required. However, in some cases, additives proved essential for a successful ATRP. For example, polymerization rates for styrene and MMA were greatly accelerated when a small amount of copper(0) was added to the ATRP systems.^{131, 132} Also, Lewis acids (such as aluminum alkoxides) are required for the controlled polymerization of MMA catalyzed by RuCl₂-(PPh₃)₃ and similar complexes.^{101, 133}

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III-5. Surface-initiated ATRP

Because of its wide compatibility with various functionalized monomers, and its controlled nature, surface initiated ATRP has become the most common "grafting from" approach for surface modification. Of the "grafting from" methods described earlier, surface initiated anionic and cationic polymerizations require rigorously dry conditions; other controlled radical polymerization methods such as NMP, and RAFT either require more complex initiator attachment steps or relatively high temperatures. The synthesis of thiol and silane initiators for surface-initiated ATRP and their attachment to Au and silicon substrates is straight forward, as shown in **Scheme 1.15**.





Fukuda and coworkers published the first example of surface initiated ATRP in 1998.¹³⁴ Using the Langmuir-Blodgett (LB) technique, they attached a well-ordered monolayer with aryl sulfononyl chloride head groups to a surface. Immersing the substrate in monomer and adding CuCl initiated the ATRP of MMA from the sulfonyl chlorides (Scheme 1.16). The polymerization was not well controlled, but the addition of free initiator to the polymerization solution increased the Cu(II) concentration, the deactivation rate, and control of the polymerization. Concurrently, PMMA formed in solution and was characterized by conventional methods. However, the formation of free polymer requires extensive washing to remove physically adsorbed free polymer.

By adding a Cu(II) complex instead of free initiator as a deactivator, Matyjaszewski et al. achieved controlled polymerization of PS, PMMA, and PMA.¹³⁵ The linear relationship between the thickness of polymer brush and polymerization time confirmed controlled polymerization.

Scheme 1.16. Schematic illustration of ATRP initiator immobilization on Si by the LB technique. (Redrawn with permission from *Macromolecules* 1998, *31*, 5934-5936. Copyright 1998 American Chemical Society.)



The first diblock copolymer brushes, PS-*b*-PMMA, were reported by Zhao and Brittain using sequential carbocationic polymerization and ATRP.¹³⁶ Like Fukuda's example, the addition of free initiator during ATRP was necessary to ensure a sufficient concentration of deactivating Cu(II) species, otherwise the polymerization was not controlled. Matyjaszewski et al. synthesized several block copolymer brushes such as PS-*b*-PMA, PS-*b*-PtBA, and PS-*b*-PAA by sequential ATRP.¹³⁵ For example, a 10 nm PS film was re-initiated to form a PS-*b*-PMA block polymer film. However, a significant fraction of active chain-ends were either buried in the polymer brush or lost via termination during growth of the PS block, since the initiator efficiency for the growth of the second block was reduced. Growth of the 90 nm PMA took much longer (20 hrs) than expected.

Kim et al. used a simple but effective quenching and re-initiation (QR) approach to grow PMA-*b*-PMMA-*b*-PHEMA triblock copolymer brushes on Au (Scheme 1.17).¹³⁷ Polymerization was effectively stopped by quenching a growing polymer brush with a concentrated CuBr₂/ligand solution, preserving the Br atoms at the chain ends for subsequent re-initiation of the next polymer block. It was found that the efficiency of the QR scheme was better than a simple solvent washing procedure, which resulted in a higher loss of active chains.



Surface initiated ATRP has also been applied to the synthesis of polymer brushes from non-planar substrates such as nanoparticles, carbon nanotubes, and polymer supports. Huang and Wirth synthesized polyacrylamide brushes from porous silica gel by surface initiated ATRP and used them for the separation of proteins by size exclusion.⁴⁶ Armes and coworkers synthesized poly(2-(N-morpholino)-ethyl methacrylate) (PMEMA) from a silane initiator on the silica particles.¹³⁸ The PMEMA-silica particles began aggregating at the LCST of PMEMA and re-dispersed upon cooling. Yan and coworkers⁵³ initiated ATRP from multiwalled carbon nanotubes (MWNT) as shown in **Scheme 1.18**. To attach the ATRP initiator, the MWNT was treated sequentially with HNO₃, and SOCl₂, and finally ethylene glycol to produce a hydroxyl-covered surface. The ATRP initiators was readily anchored to the surface by reaction with α bromoisobutyl bromide. ATRP of MMA provided a PMMA covered MWNT, and sequential polymerization of MMA and HEMA yielded carbon nanotubes coated with amphiphilic PMMA-*b*-PHEMA polymer brushes.



Scheme 1.18. ATRP of MMA from multi-walled carbon nanotubes (MWNT).

Genzer et al. recently used a technique they called mechanically assisted polymer assembly to produce polymer brushes of polyacrylamide on a cross-linked polydimethylsiloxane (PDMS) surface.¹³⁹ After stretching the PDMS substrate and generating silanol (Si-OH) groups on the surface by exposure to UV/O₃, they attached a trichlorosilane ATRP initiator onto the surface from the vapor phase. The substrate was kept stretched until the poly(acrylamide) brushes were formed by ATRP at 130 °C. They then released the strain, allowing the PDMS substrate to return to its former size. One advantage of this approach is that the brush grafting density can be controlled by altering the stretching extent of the PDMS substrate. Bontempo et al. synthesized a variety of polymer brushes from polystyrene microspheres using surface initiated ATRP in aqueous media.¹⁴⁰ Guerrini and coworkers grew poly(2-hydroxyethyl acrylate) and other polymer brushes from cross-linked poly(styrene-*co*-2-(2-bromopropionyloxy)) latex particles to form particles with a hydrophobic core and a hydrophilic shell.⁴⁹

Surface initiated ATRP can also be applied to form patterned polymer brushes by microprinting as other "grafting from" methods. Shah and coworkers reported the use of surface-initiated ATRP to amplify patterned initiator layers on gold films.³⁷ PMMA, PHEMA, PtBA, and poly(dimethylaminoethyl methacrylate) were grown from spatially patterned initiators and then the pattern was transferred into the substrates by using the brushes as barriers to wet chemical etching of gold (Scheme 1.19).

Scheme 1.19. Surface patterning by microcontact printing, surface-initiated ATRP, and etching. (Reprinted with permission from *Macromolecules* 2000, *33*, 597-605. Copyright



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Chapter 2

Controlled Growth and Degradation of PLA Films Grafted to PHEMA Brushes on Au Substrates

I. Introduction

Polylactide (PLA) is environmentally degradable and its precursor, lactic acid, is available from renewable resources such as corn, sugar and starch. Because of its favorable properties and its degradability, PLA was recently introduced as a commodity polymer for fibers and packaging materials. The biodegradability and biocompatibility of PLA have led to significant applications in medicine such as surgical sutures, tissue scaffolds, and bone screws. In addition to bulk PLA, thin films of PLA are especially important for applications in drug delivery systems¹ and as drug-eluting coatings on medical devices.²⁻⁴ The thickness of a coating and its degradation profile are important factors that must be considered in designing materials for controlled drug release. Therefore, precise control over the thickness of the PLA layer is indispensable.

Thin films can be coated on surfaces by a variety of methods including solvent casting, spin-coating, and spray deposition. Physically adsorbed layers are often thermally unstable due to weak interactions between the polymer and the solid substrate and lack resistance to solvents and friction, while covalently attached films should offer improved thermal stability and mechanical properties. Surface initiated polymerizations should provide robust polymer films since the polymers are anchored to surfaces through covalent bonds. There are a few examples where the ring opening polymerization (ROP) of lactide^{5, 6} and related monomers was used to grow aliphatic polyesters from surfaces.

Poly(ε -carprolactone) (PCL) was grown from polymer⁷ and gold surfaces⁸ by ROP. Langer and Choi used $Sn(2-ethylhexanoate)_2$ to catalyze the surface-initiated polymerization of L-lactide from gold and silicon oxide surfaces, coating each surface with a biocompatible and biodegradable poly(L-lactide) film,⁹ while Hedrick and coworkers reported the Sn(OTf)₂-catalyzed ROP of lactide from gold.¹⁰ In these two examples, lactide polymerization was initiated from -OH or -NH₂ groups at the termini of long chain alkyl thiolates on gold or silica surfaces. Kim et al. reported the growth of lactide from poly(2-hydroxyethyl methacrylate) (PHEMA) chains anchored to Au substrates. This approach is analogous to several syntheses of "molecular brushes" where ROP was initiated from solution-phase PHEMA. Kim described the surfaceinitiated ATRP of 2-hydroxyethyl methacrylate (HEMA) from Au substrates, followed by the controlled ROP of lactide from the -OH groups of PHEMA brushes.¹¹ The resulting comb polymers have a "bottle brush" architecture as shown in Scheme 2.1. The kinetics of polymer growth, derived from IR and ellipsometric analyses, show the ROP is well-controlled, and spectroscopic analyses of the hydrolytic degradation of the PHEMA/PLA comb polymer in pH 7.4 buffer at 55 °C were unremarkable. However, visual inspection of the polymer film revealed development of an unusual pattern of large, symmetric defects, some of which had regular geometric shapes (Figure 2.1).¹² The defects eventually were associated with bubble-like defects that formed in the first few hours of degradation, well before IR could detect any loss of the polylactide component.

To understand the formation of these unusual features, we tested how changes in experimental parameters affect the formation of the domains. We found that the temperature used to carry out the ROP of lactide largely determines the size and distribution of these features.



Scheme 2.1. Synthetic pathway for PHEMA-g-PLA



Figure 2.1. Optical micrographs of PHEMA (177 nm)-g-PLA (353 nm) showing the evolution in surface morphology during the drying of water-swollen films, the films were aged for 6 h in pH 7.4 buffer at 55 °C. (Kim, J. B. Surface-Initiated Living Polymerizations on Gold: Synthesis and Characterization of Nanometer Thick Polymer Films. Ph.D., Michigan State University, East Lansing, MI, 2002.)

II. Experimental Section

II-1. Materials

Triethylamine (Aldrich, 99.5%) was distilled from calcium hydride under an argon atmosphere at reduced pressure. 2,2'-Bipyridine (bpy) (Aldrich, 99%) was recrystallized from hexane and then sublimed. 3,6-Dimethyl-1,4-dioxane-2,5-dione

(lactide) (Aldrich) was recystallized twice from 8:2 (v:v) EtOAc/hexane and then sublimed. HEMA (Aldrich, 97%) was passed through a 10 cm column of basic alumina to remove inhibitors. Tris[2-(dimethylamino)ethyl]amine (Me₆TREN) was synthesized by a literature procedure.¹³ THF (Aldrich, HPLC grade) and acetonitrile (Aldrich, 99.8%) for polymerizations were passed through an activated basic alumina column and filtered through 0.2 μ m PTFE syringe filters. Toluene (Aldrich, anhydrous) was distilled from sodium benzophenone ketyl. After purification, HEMA, solvents and all required liquid chemicals were transferred to Schlenk flasks, de-gassed using three freeze-pump-thaw cycles and then transferred into a drybox. 11-Mercapto-1-undecanol (MUD) (Aldrich, 97%), 2-bromopropionyl bromide (2-BPB) (Aldrich, 97%), 4,4'-dinonyl-2,2'-bipyridyl (dnNbpy) (Aldrich, 97%), Cu(I)Br (Aldrich, 99.999%), Cu(I)Cl (Aldrich, 99.999%), Cu(II)Br₂ (Aldrich, 99.999%), and methanol (Aldrich, 99.93%) were used as received.

II-2. Characterization Methods

Film thicknesses were obtained with a rotating analyzer ellipsometer (model M-44; J. A. Woollam) at an incident angle of 75°. Thickness measurements were taken at least three spots on each substrate. Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80°) attachment. Changes in surface roughness of the polymer films during the hydrolytic degradation of PHEMA-g-PLA were observed using a Nikon Optiphot2-POL polarizing optical microscope equipped with a video camera.

II-3. Synthesis of PHEMA Brushes from Au Substrates

PHEMA brushes were synthesized by surface-initiated ATRP from initiatoranchored Au substrates using a diluted catalyst system to minimize contamination from the copper catalyst. To prepare monomer solutions, Cu(I)Br (4.5 mg), Cu(II)Br₂ (1.6 mg), and Me₆TREN (8.9 mg) were dissolved in 5 mL of CH₃CN:THF (5:1, v/v) in a drybox. HEMA (15 mL, 0.123 mol) was added and the solution was diluted to 35 mL with the cosolvent. The concentrations of each component were: Cu(I)Br/Me₆TREN (0.9 mM), Cu(II)Br₂/Me₆TREN (0.2 mM), and HEMA (3.5 M). The initiator-immobilized substrates were immersed in the monomer solution and polymerized for 5 h at 40 °C. After polymerization, the samples were removed from the monomer solution and immersed in anhydrous DMF to remove catalyst and residual monomer. The sample surface was rinsed with EtOAc, EtOH, and de-ionized water, and then dried under a flow of N₂. The PHEMA films were characterized by ellipsometry and surface reflectance FTIR.

II-4. Synthesis of PHEMA Brushes from Au by Surface-Initiated ATRP - Kinetics Experiments

PHEMA brushes on Au substrates were synthesized using a previously described procedure.¹⁴ For polymerization in methanol, 0.63 g (4.0 mmol) of bipyridine was added to 20 mL of a solution of monomer (HEMA/methanol, 1:1 v:v) in a Schlenk flask. The mixture was stirred until homogeneous, and then was degassed using three freeze-pump-thaw cycles. CuBr (0.26 g, 1.8 mmol) and CuBr₂ (0.04 g, 0.18 mmol) were added quickly into the flask under Ar, and this mixture was sonicated for one minute and transferred into a glove bag filled with N₂. The concentrations of each component were: CuBr (90

mM), CuBr₂ (9.0 mM), bpy (0.20 M), and HEMA (3.5 M). For polymerization in water, 0.61 g (3.9 mmol) of bipyridine was added to 20 mL of a solution of monomer (HEMA/H₂O, 1:1 v:v) in a Schlenk flask. The mixture was stirred until homogeneous, and then was degassed using three freeze-pump-thaw cycles. CuCl (0.14 g, 1.4 mmol) and CuBr₂ (0.09 g, 0.40 mmol) were added quickly into the flask under Ar, and this mixture was sonicated for one minute and transferred into a glove bag filled with N₂. The concentrations of each component were: CuCl (70 mM), CuBr₂ (20 mM), bpy (0.20 M), and HEMA (3.5 M). After stirring the catalyst mixture for an hour in the glove bag, the solution was poured into a second vial containing an initiator-covered Au substrate. The polymerization was allowed to proceed at room temperature for a set reaction time of 0.5-8 h, and then the vial was removed from the glove bag. The substrate was removed from the vial, washed sequentially with water, ethyl acetate, ethanol, and water, dried under a stream of N₂ and characterized by ellipsometry and reflectance FTIR.

II-5. Ring-opening Polymerization of Lactide from PHEMA - Kinetic Study

The ring-opening polymerization of lactide from the PHEMA followed the procedure of Kim.¹¹ A saturated solution of lactide was prepared in a drybox by stirring an excess of lactide in toluene (120 mL) at room temperature for one hour. The homogeneous solution was decanted from undissolved lactide, and the concentration of the lactide solution was determined by gravimetry to be ~0.13 M. Sn(2-ethylhexanoate)₂ catalyst (0.0844 g) was added to the lactide solution (100 mL) to give a catalyst concentration of ~2.1 mM. To perform ring opening polymerization of lactide in a N₂-filled drybox, Au substrates coated with PHEMA brushes were immersed in the lactide

(0.13 M) and Sn(2-ethylhexanoate)₂ (2.1 mM) solution. Silanized glass vials (15 mL) with silicon rubber caps were used as reaction vessels to avoid polymerization from surface silanol groups. The vials were suspended in an oil bath from copper wires, and a hot plate was used to heat the bath to 90 °C. Vials were removed from the oil bath at various intervals, and the samples were removed from the vial and were sequentially immersed in a series of vials containing toluene, ethyl acetate, ethanol, and de-ionized water to clean the surface. The surface was dried under a flow of N₂ and characterized by reflectance FTIR and ellipsometry.

II-6. Hydrolytic Degradation of PLA Films

To study the hydrolytic degradation of PHEMA-g-PLA on gold, substrates were immersed in phosphate buffer solution (pH 7.40) at 55 ± 0.1 °C. At predetermined times, the sample was removed from the buffer, washed thoroughly with de-ionized water, and dried under a flow of N₂. The sample was characterized by surface reflectance FTIR and optical microscopy, and then the sample was returned to the proper buffer solution.

II-7. Observation of PHEMA-g-PLA Films During Hydrolytic Degradation

Changes in surface roughness of the polymer films during the hydrolytic degradation of PHEMA-g-PLA were observed using a Nikon Optiphot2-POL polarizing optical microscope equipped with a video camera. Digital images of the dried polymer surface and changes in the surface morphology during the drying process were captured as graphic files.

III. Synthesis of PHEMA-g-PLA

Scheme 2.1 outlines the synthesis of PHEMA-g-PLA polymer brushes tethered to silicon wafers coated with a 200 nm layer of sputtered Au. The detailed experimental procedure is similar to that of Kim and is described in the experimental section. Using this approach. Kim et al. reported the growth of controlled polymerization of lactide from PHEMA brushes.¹¹ resulting in increases in film thickness as high as 450 nm. A selfassembled monolayer was prepared on the Au surface using mercaptoundecanol (MUD) and converted into an initiator monolayer by reaction with 2-bromopropionyl bromide as described previously. Initiator immobilization was apparent from the appearance of a carbonyl peak at 1743 cm⁻¹ in the reflectance FTIR spectrum (Figure 2.2, a). Polymerizations of HEMA from the initiator-anchored surfaces were run in a dry box to avoid contamination from oxygen. The catalyst system was a mixture of Cu(I)Br/Me₆TREN (0.3 mol% based on monomer) and Cu(II)Br₂/2 equivalents of dnNbpy in a 5:1 (v/v) solution of acetonitrile and THF. The Cu(II) complex (40 mol%, relative to Cu(I), ensures the deactivation of active radicals and provides some control over the polymerization. Polymerizations of HEMA were run at 40 °C for 5 h. The formation of PHEMA was apparent from the appearance of a carbonyl peak at 1733 cm⁻¹ and a broad hydroxy peak at 3200-3600 cm⁻¹ in the reflectance FTIR spectrum (Figure **2.2, b)**.

Using the hydroxy groups of PHEMA side chains as initiators, *rac*-lactide was polymerized in toluene at 90 °C using $Sn(2-ethylhexanoate)_2$ as the catalyst. The IR data in **Figure 2.2** show the growth of PLA from PHEMA. The initial PHEMA spectrum (b) showed a single carbonyl peak at 1733 cm⁻¹ from PHEMA, but after 4 h of lactide

polymerization, the carbonyl peak broadened (**Figure 2.2**, c) and shifted to higher wave numbers. Eventually, the PLA carbonyl peak dominated the spectrum and only a single peak at 1767 cm⁻¹ was observed (**Figure 2.2**, d). Parallel growth in the methyl stretching peak at 2993 cm⁻¹ and a decline of the hydroxy peak at 3200-3600 cm⁻¹ also confirms PLA formation. Since H₂O could be the competing initiator during polymerization of lactide, we tried to exclude H₂O by working in a dry box, using dry solvents, and silanizing reaction vials.



Figure 2.2. Reflectance FTIR spectra of (a) the initiator layer anchored to the Au surface, (b) a 170 nm PHEMA polymerized from the initiator layer, (c) a PHEMA (170 nm)-g-PLA (85 nm) film formed after 4 h of lactide polymerization, (d) a PHEMA (170 nm)-g-PLA (226 nm) film formed after 24 h.

IV. Kinetics of Polymerization of HEMA from Au Surfaces

To test the effects that different film compositions and thickness have on the formation of defects during the degradation of PHEMA-g-PLA films, we measured the film growth rates for PHEMA and PHEMA-g-PLA. ATRP is described as a "controlled" polymerization because the irreversible termination reactions that consume radicals are suppressed. In absence of termination, one should observe a linear growth in the thickness of polymer films during surface-initiated ATRP. We measured the film growth rate for the ATRP of HEMA from the initiator-anchored gold substrates by immersing the substrates in a solution of monomer and catalyst. A mixture of monomer (HEMA), catalyst (CuBr), ligand (bpy), deactivator (CuBr₂), and solvent (methanol) was stirred until a homogeneous dark brown solution formed. At fixed times ranging from 30 min to 48 h, the substrates were removed from the solution, washed with THF, dried and characterized by ellipsometry and FTIR. The kinetic data (Figure 2.3, \blacksquare) showed a steady but nonlinear growth in film thickness with polymerization time.

We investigated two refinements to the polymerization protocol to achieve more control over the polymerization. Matyjaszewski and co-workers reported that mixed halide initiation systems provide better control of ATRP because C-Cl bonds are more stable than C-Br bonds,¹⁵ and Armes reported that ATRP of hydrophilic monomers can greatly accelerated in aqueous media.^{16, 17} Thus, we altered the catalyst system to CuCl/CuBr₂ (30 mol %) and used water as the solvent for ATRP of HEMA. As shown in **Figure 2.3**, we observed a faster polymerization rate, 144 nm of HEMA in 8 h using water as the solvent vs. 58 nm in 8 h in methanol, but no significant improvement in the linearity of the thickness vs. time relationship.



Figure 2.3. Evolution of the film thickness with polymerization time during the surface initiated ATRP of HEMA from initiators anchored on Au: \blacksquare , using H₂O as the solvent and CuCl/CuBr₂ as the catalyst; \Box , using methanol as the solvent and CuBr/CuBr₂ as the catalyst.



V. Kinetics of Lactide Polymerization from PHEMA Surfaces

Two groups of PHEMA substrates were used to define the kinetics of the ROP of lactide. One group of PHEMA films had ellipsometric thicknesses of ~ 174 nm, while the other substrates were thinner, ~49 nm. The films were immersed in a 90 °C solution of rac-lactide in toluene (prepared as a saturated solution at room temperature) and the ROP initiator, Sn(2-ethylhexanoate)₂. At various times, films were removed from the solution, rinsed with THF, and dried under a stream of nitrogen. The growth of the PLA film was followed by monitoring the change in the film thickness with time. Plotted in Figure 2.4 are the net increases in the thickness of the PLA layer, calculated by subtracting the thickness of the PHEMA film from the total film thickness. The ROP of lactide follows a "coordination-insertion" mechanism,¹⁸ and the data of Figure 2.4 should show a linear increase in film thickness with polymerization time. Kim et al. reported linearity for comparable polymerizations through 8 hours, with the thickness saturating at longer times.¹¹ The data of Figure 2.4 have more scatter but show similar trends, a fast early growth that tails at longer times, and a faster film growth rate from thicker PHEMA films. The structure of PHEMA-g-PLA should be viewed as a graft copolymer, with at least some comb-like character.



Figure 2.4. The evolution of thickness with polymerization time for the ROP of PLA from PHEMA using: **•**, 174 ± 2 nm thick PHEMA substrates, **•**, 49 ± 1 nm thick PHEMA substrates. The ellipsometric thicknesses were measures at three different spots on a sample and the error bars are smaller than the symbols.

VI. Defect structures in PHEMA-g-PLA films

Kim investigated the hydrolytic degradation of PHEMA-g-PLA in phosphate buffer (pH 7.40) at 55 °C. During degradation, the sample surfaces quickly became rough, and reliable ellipsometric thicknesses could not be measured. When observed under an optical microscope, the surface was initially covered with highly symmetrical surface domains that continued to evolve with further degradation. The goal of the research described in this chapter was to understand the formation of these regularly patterned surface domains

The surface-grafted PHEMA-g-PLA films prepared in this study were immersed in the buffer solution and were removed at intervals and characterized by FTIR. The spectra, shown in **Figure 2.5**, show data from a representative polymer brush, PHEMA (153 nm)-g- PLA (362 nm). During hydrolytic degradation, the methyl stretching peak at 2993 cm⁻¹ and the carbonyl peak at 1767 cm⁻¹ decreased, while the hydroxy peak at 3200-3600 cm⁻¹ increased as expected for the hydrolytic loss of the PLA graft chains. As shown in **Figure 2.6**, PHEMA (153 nm)-g-PLA (362 nm) films are initially smooth before degradation (5a), but after 6 h of degradation, the dried surface was covered with numerous gear-shaped domains (5b). With further degradation, the domains evolved into a "dendrimer-like" pattern (5c), and eventually a flower-like motif separated by mottled areas (5d). These results are similar to those reported by Kim, although the details of the defect patterns differ somewhat.

To confirm that these features form via the same pathway seen by Kim, samples were pulled from the buffer solution and immediately observed by optical microscopy. As shown in **Figure 2.7**, the surface of a sample that had been degraded for 6 h was

decorated with blister-like domains that collapsed as the surface dried, eventually forming gear-like domains. These data confirm the same general features seen by Kim, blister formation followed by collapse of the blister and formation of regular domain structures.



Figure 2.5. Reflectance FTIR spectra of (a) PHEMA (153 nm)-g-PLA(362 nm) before degradation, (b) PHEMA-g-PLA films after 6 h hydrolytic degradation, (c) PHEMA-g-PLA films after 10 days hydrolytic degradation, (d) PHEMA-g-PLA films after 15 days hydrolytic degradation.



Figure 2.6. Surface images of PHEMA (153 nm)-*g*-PLA (362 nm) obtained by optical microscopy during hydrolytic degradation in pH 7.4 buffer at 55 °C: (a) before degradation, (b) after 6 hrs of degradation of PLA, (c) after 18 hrs of degradation of PLA, (d) after 42 days of degradation of PLA.



Figure 2.7. Surface images of PHEMA (153 nm)-g-PLA (362 nm) obtained by optical microscopy after 6 h of hydrolytic degradation in pH 7.4 buffer at 55 °C: (a) water-covered substrate, (b)-(c) substrates drying in air, (d) completely dry substrate.

We examined the effects of film composition and the temperature used to add the PLA grafts to the PHEM brushes. The data clearly show that the polymerization temperature significantly affects defect formation. When the lactide polymerization was run at 70 °C, the substrates failed to develop defects, (**Figure 2.8**), a few formed at 80°, and the number increased with temperature. Polymerizations at 110 °C (not shown in Figure 2.7) resulted in complete delamination of the PLA-*g*-PLA film from the substrate. The images in **Figure 2.9** further implicate temperature as the cause of domain formation. Both films were prepared at 90 °C, but the lactide polymerization lasted 26 h for the film shown in panel **a**, and 12 h for the film in panel **b**. The longer exposure of **a** to high temperatures led to a morphology similar to the sample shown in **Figure 2.8d** which was prepared at 100 °C.

These observations suggest that surface domain formation is related to the Au-S bonds that link the film to the substrate. It is well known that Au-S bonds are not stable above 60 °C.¹⁹⁻²¹ The temperature used for most lactide polymerizations was >70 °C, but if some of the Au-S bonds are cleaved, polymer chains will not desorb from the surface since the PHEMA film is partially cross-linked. However, chains that desorbed and fail to reform Au-S bonds may act as latent defects. During degradation, we believe water diffuses to sites on the gold surface where the film has detached, leading to localized blistering from swelling, irreversibly stretching the polymer film. With removal of the water, the blisters collapse from the center, forming a circular domain, with a ridge at the outer edge of the blister. As the film continues to dry, the ridge is under compression and eventually buckles to give the characteristic geometric patterns seen in some of the dried films. The results in **Figure 2.8** generally show an increase in the number of domains

(defects) with the polymerization temperature, as expected for increased scission of Au-S bonds at higher temperature, leading to more sites for swelling by water.



Figure 2.8. Surface images of PHEMA-g-PLA obtained by optical microscopy after 6 h of hydrolytic degradation in pH 7.4 buffer at 55 °C: (a) PHEMA (168 nm)-g-PLA (65 nm), polymerization of PLA at 70 °C; (b) PHEMA (188 nm)-g-PLA (336 nm), polymerization of PLA at 80 °C; (c) PHEMA (153 nm)-g-PLA (362 nm), polymerization of PLA at 90 °C; (d) PHEMA (183 nm)-g-PLA (367 nm), polymerization of PLA at 100 °C.

25 µm

25 µm



(b)

Figure 2.9. Surface images of PHEMA-g-PLA obtained by optical microscopy after 6 h of hydrolytic degradation in pH 7.4 buffer at 55 °C: (a) PHEMA (183 nm)-g-PLA (520 nm), polymerization of PLA at 90 °C; (b) PHEMA (153 nm)-g-PLA (362 nm), polymerization of PLA at 90 °C.

VII. Conclusions

(a)

Nanometer thick films of PHEMA-g-PLA were synthesized by the sequential ATRP of HEMA and the ROP of *rac*-lactide initiated from the hydroxy groups of PHEMA. The degradation of the PLA grafts in pH 7.4 buffer at 55 °C produces interesting and unexpected defect structures in the surface films. Control experiments link formation of the defects to lactide polymerization temperatures (> 70 °C). A likely mechanism is the scission of Au-S bonds at high temperatures, causing defects to swell when placed in the buffer solution.

VIII. References

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Chapter 3

Control of the Density of Polymer Brushes in Surface-Initiated ATRP from Au Surfaces

I. Introduction

The growth of dense arrays of polymers from solid substrates represents a new and exciting approach to the modification of surfaces.¹⁻¹⁰ Recent advances in the growth of polymer brushes on a variety of substrates enable experiments that address the fundamental questions related to polymer brush conformations on surfaces and their response to external stimuli.¹¹⁻¹³ In addition, the development of diverse methods for polymer brush synthesis suggests important applications of these materials as protective coatings that exploit the high density of chains on the surface, as environmentally responsive surfaces derived from phase changes in block copolymers triggered by changes in solvent quality,¹²⁻¹⁷ and more recently, as functional coatings.^{18, 19} Among the many procedures for preparing polymer brushes, atom transfer radical polymerization (ATRP) from immobilized initiators is especially attractive for its control over the molecular weight of the grafted polymers, tolerance to water and impurities, compatibility with a variety of functionalized monomers, as well as the option of carrying out polymerizations at relatively low temperatures. Moreover, because it is a controlled technique, ATRP is capable of producing thick surface-grafted polymers, binary polymers, and block copolymers.^{2, 3, 5, 10, 20-25}

Along with several other methods for producing polymer brushes, ATRP yields dense polymer films, which is important for the use of these materials as anticorrosion coatings,²⁶⁻²⁸ etch masks,^{29, 30} and lithographic coatings.^{29, 31-33} However in some

applications, such as attachment of accessible biomacromolecules to gene or protein chips, open films are desirable. If brushes are to be used to increase the sensitivity of sensors based on immobilized molecules, the entire brush should be available during both probe-molecule attachment and sensing. As an example,²⁷ poly(2-hydroxyethyl methacrylate) (PHEMA) brushes are accessible to small molecules such as perfluorooctanoyl chloride, and reaction of PHEMA with this molecule occurs in near-quantitative yield. However, when we used PHEMA brushes to initiate the ring opening polymerization of lactide to give a polymer brush having a bottle brush architecture,³⁴ the degree of polymerization for lactide was only ~6. This suggests that lactide polymerization is sterically limited and could be improved by using PHEMA brushes with lower areal densities of polymer chains. More importantly, covalent immobilization of proteins to modified PHEMA seems to occur only at the film surface, so open films will be required for depositing more than a monolayer of biomacromolecules.

This work aims at developing methods for reducing and controlling the density of polymer brushes grown from a surface using ATRP. Such control requires a technique for decreasing the areal density of active, immobilized initiators, and two basic strategies can be used for this purpose. In the first, either the number of available initiators (e.g. control of initiator concentration) or the length of time the initiator solution is in contact with the surface is used to limit the density of immobilized initiator. This strategy is difficult to apply because it requires either precise knowledge of the kinetics of the attachment reaction or fine control of a very low concentration of initiator molecules. Luzinov et al. employed the reaction of carboxylic acids with epoxides along with vapor-phase dosing of the carboxylic acid to control the amount of initiator anchored to glycidyl methacrylate

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on SiO₂.³⁵ Bohn et al. recently reported an electropolymerization approach to gradients of poly(acrylic acid) and poly(acrylamide) on surfaces.³⁶ A related strategy is to chemically activate or deactivate sites on surfaces using photochemical or scanning probe techniques,^{33, 37} but these methods generally are limited to flat surfaces. Analogs of this approach are photochemical or thermally-initiated free radical polymerization from azo or cholorosulfonyl³⁸ initiators anchored on surfaces, where the number of chains initiated is related to the quantum yield and half-life of the initiator. However, these methods should yield brushes with a high polydispersity.

A second strategy for controlling initiator density is to fully functionalize a surface with a mixture of the initiator and an inert analog. Assuming both molecules have the same reactivity for the surface, it should be possible to generate an arbitrary concentration of active initiator homogeneously diluted in a matrix of inactive molecules. Advantages of this strategy include insensitivity to the kinetics of the anchoring step, the ability to cover surfaces of arbitrary size and shape, and generalization to surfaces ranging from inorganic oxides to natural materials such as cellulose. Huck et al. described the co-deposition of the ATRP initiator mercaptoundecyl α -bromoisobutyrate and undecanethiol on Au.³⁹ They found that initiation of the ATRP of methyl methacrylate from these surfaces gave film thicknesses that were proportional to the fraction of initiator in the self assembled monolayer (SAM), implying constant initiator efficiency. This result is at odds with the expectation that bimolecular coupling should decrease with dilution of the initiator and lead to an increase in initiator efficiency. (Several studies suggest that only one in 10 initiators in a 100% initiator monolayer lead to polymerization.^{2, 24, 35}) One possible explanation for this finding of constant initiator
efficiency is that the two thiols phase separated to give islands of pure initiator embedded in undecanethiol. Such segregation of thiols in mixed self-assembled monolayers is well precedented.^{40, 41} Within each island, initiation efficiency would be constant, and dilution of initiators would simply decrease the number or size of islands. Similar phase separation effects were reported by Ejaz et al. during the co-deposition of a triethoxysilane terminated initiator (2-(4-chlorosulfonylphenyl)ethyltrimethoxysilane) and *n*-octadecyltrimethoxysilane, an inert diluent.²¹

This chapter describes methods for controlling the density of surface-initiated polymer brushes to create arbitrarily dense arrays of polymers on Au surfaces. To overcome "island effects" caused by phase separation in SAMs of thiols on Au, we first transform the Au surface to an alcohol-terminated monolayer using mercaptoundecanol. Treating this surface with mixtures of α -bromopropionyl bromide and α -methylpropionyl bromide yields active initiators dispersed in a matrix of inactive α -methylpropionate esters. Because the resultant initiator and diluent molecules differ only in the replacement of a bromo group by a methyl group, little phase separation is expected. Polymerization from Au surfaces yields films whose thickness depends greatly on initiator density when the fraction of initiator in the monolayer drops to <10% so initiation efficiency is high. Moreover, control of the density of PHEMA brushes allows swelling in water that ranges from 85 – 2000%.

II. Experimental Section

II-1. Materials

11-Mercapto-1-undecanol (MUD) (Aldrich, 97%), 2-bromopropionyl bromide (2-BPB, 1) (Aldrich, 97%), Cu(I)Br (Aldrich, 99.999%), Cu(I)Cl (Aldrich, 99.999%), Cu(II)Br₂ (Aldrich, 99.999%), phosphorus tribromide (Aldrich, 99%), and 1-hexadecanol (Aldrich, 99%) were used as received. 2,2'-Bipyridine (bpy) (Aldrich, 99%) was recrystallized from hexane and then sublimed. Triethylamine (Aldrich, 99.5%) was distilled from calcium hydride under an argon atmosphere at reduced pressure. Methyl methacrylate (MMA) (Aldrich 99%), glycidyl methacrylate (GMA) (Aldrich, 97%) and 2-hydroxyethyl methacrylate (HEMA) (Aldrich, 98%) were passed through a 10 cm column of basic alumina to remove inhibitors. After purification, the monomers, solvents and all required liquid chemicals were transferred to Schlenk flasks, de-gassed using three freeze-pump-thaw cycles and then transferred into a drybox.

II-2. Characterization Methods

Film thicknesses were measured using a rotating analyzer ellipsometer (model M-44; J. A. Woollam) at an incident angle of 75° using 44 wavelengths of light between 414.0 nm and 736.1 nm. Thickness measurements were taken on at least three spots on each substrate. For films with thicknesses greater than 40 nm, both thickness and refractive index were calculated, while the refractive index of thinner films was usually assumed to be 1.5. (Assuming refractive indices of 1.45 or 1.6 result in thickness changes of only ~10 %). For swelling measurements, Au wafers modified with PHEMA brushes were placed in a trapezoidal cell containing glass windows aligned perpendicular to the light beam. After measuring the ellipsometric parameters of the film/substrate in the air-filled cell, the cell was filled with deionized water. Two min later, ellipsometric measurements were performed on the swollen films immersed in water. The optical constants of water were obtained from literature data,⁴² and the refractive indices determined for the swollen films reflected the approximate volume fractions of water (refractive index around 1.333) and polymer (refractive index of 1.5) in the film. For example, swollen films suggesting a composition of ~95% water had refractive indices around 1.334, while films containing 50% water had refractive indices around 1.416. Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80°) attachment. Unless otherwise specified, routine ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were carried out in CDCl₃ using a Varian UnityPlus-500 spectrometer with the residual proton signals from the solvent as the chemical shift standard. Mass Spectral Analyses were carried out on a VG Trio-1 Benchtop GC-MS.

II-3. Synthesis of 2-Methylpropionyl Bromide (2-MPB) (2)

Phosphorus tribromide (15.2 mL, 0.164 mol) was added dropwise to well-stirred isobutyric acid (6.4 mL, 0.068 mol) at 0 °C. After the addition was complete, the reaction was stirred at 0 °C for 3 h and then at room temperature for 15 h. Fractional distillation of the reaction mixture under N₂ gave 2-MPB as a clear liquid in 75% yield. bp 110 °C (Lit.⁴³ bp 107-113 °C). ¹H NMR δ 3.00 (septet, 1H, CH), 1.26 (d, 6H, CH₃). ¹³C NMR δ 175.0 (C=O), 51.0 (CH), 18.8 (CH₃). EI-MS: m/z = 151.

II-4. Determination of the Relative Reactivity of 2-Bromopropionyl Bromide (2-BPB, 1) and 2-MPB with Alcohols

Using a literature procedure for the synthesis of the esters as a guide.² mixtures of 2-BPB and 2-MPB (various ratios of 2-BPB : 2-MPB, 14.8 mmol total) were added by syringe to a well-stirred solution of hexadecanol (2.986 g, 12.34 mmol) in 150 mL CH₂Cl₂ at 0 °C under N₂. After stirring at 0 °C for 1 h and then at room temperature for 12 h, the mixture was washed with aqueous 2 N sodium carbonate saturated with NH_4Cl . The organic layer was evaporated to dryness and the crude product was purified by flash chromatography (ethyl acetate : hexane = 1:10). Removal of the solvent gave a colorless oil in quantitative yield. The ratio of two esters in the product was determined using integration of the α -methyl peaks in ¹H NMR. Hexadecyl-2-bromopropanoate. ¹H NMR δ 4.33 (q, 1H, CH), 4.13 (m, 2H, CH₂), 1.79 (d, 3H, CH₃), 1.63 (m, 2H, CH₂), 1.19-1.32 (m, 26H, CH₂), 0.85 (t, 3H, CH₃). ¹³C-NMR δ 170.2 (C=O), 66.0 (CH₂), 40.2 (CH), 31.9 (CH₂), 29.7 (CH₂), 29.5 (CH₂), 29.4 (CH₂), 29.3 (CH₂), 29.1 (CH₂), 28.4 (CH_2) , 25.7 (CH_2) , 22.7 (CH_2) , 21.6 (CH_3) , 14.1 (CH_3) . EI-MS: m/z = 377. Hexadecyl-2methylpropanoate. ¹H NMR δ 4.03 (t, 2H, CH₂), 2.51 (septet, 1H, CH), 1.60 (d, 2H, CH₂), 1.17-1.32 (m, 26H, CH₂), 1.14 (d, 6H, 2CH₃), 0.86 (t, 3H, CH₃). ¹³C NMR δ 177.2 (C=O), 64.4 (CH₂), 34.0 (CH), 31.9 (CH₂), 29.7 (CH₂), 29.6 (CH₂), 29.5 (CH₂), 29.3 (CH₂), 29.2 (CH₂), 28.7 (CH₂), 25.9 (CH₂), 22.7 (CH₂), 19.0 (CH₃), 14.1 (CH₃). EI-MS: m/z = 312.

II-5. Preparation of Initiator-Immobilized Au Substrates

Au-coated Si wafers (200 nm of Au sputtered on 20 nm of Cr on Si (100) wafers) were UV/O₃ cleaned for 15 min before use and transferred into a N₂-filled glove bag. A hydroxy-terminated SAM was formed by immersing the Au-coated substrates in a vial containing a 1 mM ethanolic solution of 11-mercapto-1-undecanol (MUD) for 24 h. After removing the vial from the glove bag, the substrates were rinsed sequentially with ethanol and water, and dried under a stream of N₂. The ellipsometric thickness of the MUD layer was 10-15 Å. MUD-coated substrates were transferred to a dry box filled with N₂ and were dipped in a solution of 0.12 M triethylamine in anhydrous THF at ~0 °C. After 1 min, a mixture of 2-BPB and 2-MPB in anhydrous THF (0.1 M) was added dropwise to the solution to achieve initiator immobilization. The reaction time was limited to 2-3 min since thiol-terminated SAMs could be unstable in the presence of acid bromides. After rinsing with THF in the dry box, the Au substrates were removed from the dry box, rinsed with ethyl acetate, ethanol and Milli-Q water (18 MΩcm) sequentially and dried under a stream of N₂.

II-6. Surface-Initiated Polymerizations of MMA

Polymerizations of MMA were carried using a procedure developed by Huck and coworkers as a guide.³⁹ In an N₂-filled drybox, MMA (10 g, 100 mmol), bipyridine (312 mg, 2.0 mmol) and CuBr (143 mg, 1.0 mmol) were added to a 30 mL scintillation vial containing well-stirred MeOH (8 mL). After removing the vial from the drybox, deionized water (2 mL) was added to the mixture with a syringe, and this vial along with a second vial containing an initiator-modified Au or SiO₂ substrate were transferred into

a glove bag filled with N_2 . The deionized water was not degassed and some reaction of Cu(I) with O_2 may yield Cu(II) to help control the polymerization. After stirring the catalyst mixture for an hour, the solution was poured into the vial containing the initiator-modified substrate to initiate polymerization. Following a 0.5-8 h reaction time, the vial was removed from the glove bag and the substrate was washed sequentially with water, ethyl acetate, ethanol and water and dried under a stream of N_2 .

II-7. Surface-Initiated Polymerization of HEMA

The polymerization of HEMA was based on a previously described procedure.²⁸ In a Schlenk flask, 244 mg (1.56 mmol) of bipyridine was added to 20 mL of an aqueous solution of monomer (HEMA/H₂O, 1:1 v:v). The mixture was stirred until homogeneous, and then was degassed using three freeze-pump-thaw cycles. CuCl (55 mg, 0.55 mmol) and CuBr₂ (36 mg, 0.16 mmol) were added quickly into the flask under Ar, and this mixture was sonicated for one minute and transferred into a glove bag filled with N₂. After stirring the catalyst mixture for an hour in the glove bag, the solution was poured into a second vial containing an initiator-covered Au or SiO₂ substrate. The polymerization was allowed to proceed at room temperature for a set reaction time of 0.5-8 h, and then the vial was removed from the glove bag. The substrate was removed from the vial, washed sequentially with water, ethyl acetate, ethanol, and water and dried under a stream of N₂.

II-8. Surface-initiated ATRP of GMA

Polymerizations of GMA were carried using a procedure developed by Huck and coworkers as a guide.³⁹ In a drybox filled with N₂, GMA (14 g, 0.1 mol), bipyridine (312 mg, 2.0 mmol) and CuBr (143 mg, 1.0 mmol) were added to a 30 mL scintillation vial containing well-stirred MeOH (8 mL). After removing the vial from the drybox, deionized water (2 mL) was added to the mixture with a syringe, and this vial along with a second vial containing an initiator-modified Au substrate were transferred into a glove bag filled with N₂. The concentrations of each component were: Cu(I)Br (42 mM), bipyridine (84 mM), and GMA (4.2 M). After stirring the catalyst mixture for an hour, the solution was poured into the vial containing the initiator-modified substrate to initiate polymerization. Following a 0.5-8 h reaction time, the vial was removed from the glove bag and the substrate was washed sequentially with water, ethyl acetate, ethanol and water and dried under a stream of N₂.

II-9. Detachment of Polymer Brushes from Au Substrate Surfaces

Polymer brushes were detached from gold surfaces by immersing the polymercoated substrates in a 4 mM solution of I_2 in CH₂Cl₂ for 15 h at room temperature. After rinsing the surface with fresh CH₂Cl₂ and drying under a flow of N₂, the reflectance FTIR spectrum was measured to confirm that the polymer chains were detached from the surface. The initial CH₂Cl₂ solution was collected and transferred to a pear-shaped flask that was connected to a closed vacuum line. The solution was frozen in liquid N₂, and after opening the vacuum line, the bath was withdrawn, and the solvent was slowly removed under reduced pressure. After evaporation of CH₂Cl₂, a purplish thin coating remained on the inside of the flask. The flask was kept at 60 ± 10 °C in an oil bath and as I_2 was removed by sublimation under vacuum, the thin film coating on the flask walls became pale yellow. For GPC measurements, all of the remaining material in the flask was dissolved in ~150 µL of THF and injected into the instrument. Assuming full recovery of the polymer from a 380 Å-thick PMMA film on ~8 cm² of gold surface, the concentration of detached polymer brushes in 150 µL of THF should have been ~0.2 mg/mL.

III. Preparation of Au Substrates with Controlled Initiator Densities

Our strategy for controlling the areal density of chains in polymer brushes is to vary the concentration of the immobilized ATRP initiators from which they grow. **Scheme 3.1** outlines the synthetic pathway for anchoring initiators on sputtered Au substrates and controlling their density. We first generate an alcohol-terminated SAM, and then react the terminal hydroxy groups with a mixture of 2-BPB and 2-MPB to obtain ATRP initiators (α -bromoesters) dispersed among inert diluent molecules (α methylesters). The reaction of 2-BPB and 2-MPB with the surface hydroxy groups should be non-selective since the two acyl bromides are similar in terms of their steric demands.

To verify that these molecules have similar reactivities, we carried out a competitive reaction of 2-BPB and 2-MPB with hexadecanol in CH_2Cl_2 . As expected, ¹H NMR analysis of the reaction products showed essentially identical reactivities for the two acyl bromides (**Figure 3.1**). We assume that the lack of selectivity shown in solution

will also occur for reactions with the hydroxy-terminated SAM, and that the surface composition will mirror the ratio of 2-BPB and 2-MPB used to derivatize the monolayer.

Scheme 3.1. Surface-initiated ATRP of MMA from diluted-initiator monolayers on Au substrates



Moreover, self-organization processes that might lead to phase separation in the film should be insignificant since a 3 min reaction time is sufficient to anchor acyl bromides to the surface, and the size and hydrophobicity of the initiator and diluent are very similar. The appearance of a carbonyl peak (1743 cm⁻¹) in reflectance FTIR spectra of derivatized monolayers confirmed reaction of the surface with the acid bromides (**Figure 3.2**), but it could not provide a ratio of initiator to diluent in these films because both molecules contain ester groups.



Figure 3.1. Results from ¹H NMR analysis of the reaction of 2-BPB and 2-MPB with hexadecanol. The ratio of the two esters in the product was determined by integration of the α -methyl peaks in the ¹H NMR spectrum.



Figure 3.2. Reflectance FTIR spectra of diluted-initiator monolayers on gold substrates prepared from mixtures of 1 and 2. (a) 100% 1, (b) 50% 1, (c) 25% 1, (d) 1% 1.



Figure 3.3. Evolution of the ellipsometric brush thickness with time for the polymerization of MMA (methyl methacrylate) from diluted-initiator monolayers on Au substrates at 28 °C. (\Box , 100% 2-BPB (2-bromopropionyl bromide); \blacksquare , 50% 2-BPB; \triangle , 5% 2-BPB; \triangle , 1% 2-BPB). Polymerization conditions: [MMA] = 5M, [CuBr] = 0.05M, [2,2'-bipyridine] = 0.1 M, in 10 mL 4:1 (v:v) MeOH/H₂O. The points are the average of data from two independent runs, and the limits of the error bars are the measured film thicknesses from the two runs. The lines are least square fits to the data constrained to intersect the origin.

IV. Polymerization of MMA from Diluted Initiators Anchored to Au Substrates

PMMA brushes were grown from Au substrates with initiator densities ranging from 100% to 1% 2-BPB by immersing the substrates in water/methanol solutions containing an ATRP catalyst system and monomer. **Figure 3.3** shows ellipsometric thicknesses for MMA brushes grown from Au substrates modified with different initiator densities. Consistent with previous studies of this catalyst system using 100% initiator, all of the initiator concentrations yielded a near-linear increase in film thickness as a function of time, indicating that the polymerization is controlled. If termination and chain transfer are unimportant, the film growth rate (slopes of the lines in **Figure 3.3**) should be proportional to the density of initiation sites.

The data in **Figure 3.4** and **Table 3.1** clearly show that the dependence of growth rate on initiator concentration is more complicated than this. The polymerization rate is nearly constant (7-9 nm/h) from substrates with 25-100% 2-BPB, and then decreases with further dilution to 1.5 nm/h for 1% 2-BPB. FTIR and ellipsometric data show no evidence for polymer growth from a control surface with 0% 2-BPB. The most likely reason for the nonlinear relationship between film growth rate and initiator concentration is bimolecular termination. Initiators on flat surfaces are localized in a plane and since their effective concentration is very high, we expect that radical recombination near the surface should be facile early in the polymerization. (After the initial rapid radical combination, termination must slow dramatically to allow for a constant growth rate.) This picture is in accord with earlier results that showed that about 1 out of 10 initiators successfully grow high molecular weight polymers from flat surfaces.²⁴ Thus, the

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dependence of the film growth rate on initiator coverage should be weak until initiator concentration decreases to 10%, and this is consistent with the data in **Table 3.1**.

| initiator composition ^b (% 2-BPB) | initiator density ^c (nm ² /per chain) | PMMA thickness at 8 h (nm) | film growth rate ^d (nm/hr) | normalized rate ^e (nm/hr) |
|--|--|----------------------------------|--|---|
| 100 | 0.25 | 53 | 7.1 ± 0.4 | 7.1 ± 0.4 |
| 75 | 0.33 | 69 | 8.5 ± 0.3 | 11.3 ± 0.4 |
| 50 | 0.50 | 65 | 8.4 ± 0.3 | 16.8 ± 0.6 |
| 25 | 1.0 | 55 | 6.9 ± 0.1 | 27.6 ± 0.2 |
| 10 | 2.5 | 47 | 5.9 ± 0.1 | 59 ± 1.2 |
| 5 | 5.0 | 41 | 5.1 ± 0.1 | 102 ± 1.4 |
| 1 | 25 | 11 | 1.5 ± 0.1 | 150 ± 5.0 |

Table 3.1. MMA polymerization rate from Au substrates at various initiator densites^a

a. the conditions for the polymerization are described in Figure 3.3. b. based on the ratio of 2-BPB (2-bromopropionyl bromide) and 2-MPB (2-methylpropionyl bromide) used in the anchoring step. c. assuming full coverage = $0.25 \text{ nm}^2/\text{site.}^{44}$ d. defined as the slope of the line defined by least square fits to the data in Figure 3.3. The errors are the standard deviations derived from the linear fits to the data. e. defined as the film growth rate divided by fractional coverage of the surface by initiator.



Figure 3.4. Film growth rate (**•**) and normalized polymerization rate (\Box) (observed film growth rate/fractional coverage of the surface by initiator) in surface-initiated polymerization of MMA (methyl methacrylate) from diluted-initiator monolayers on Au substrates. The polymerization conditions are described in Figure 3.3.The error bars are derived from the standard deviations calculated from the linear fits to the data in Figure 3.3.

To obtain further insight into PMMA films on Au, we estimated the average

$$A_p = \frac{M_n}{N_A \rho t} \qquad \text{eq. 1.}$$

cross-sectional area of chains using GPC of polymers cleaved from Au wafers and equation 1, where ρ is the bulk density of PMMA (1.1 g/cm³), t is the film thickness, N_A is Avogadro's number, and M_n is the number-average molecular weight obtained from GPC experiments. **Table 3.2** shows the results for PMMA cleaved from 4-inch wafers. These data should be viewed with caution since the small sample size (~0.3 mg) leads to significant uncertainty in the GPC measurements, and some of the polymerizations on these 4-inch wafers do not give thicknesses as high as on diced pieces of wafer. However, the data do strongly suggest that the average thickness per chain is much higher for the film grown from 1% initiator.

Table 3.2. GPC Characterization of PMMA brushes grown from diluted-initiators

 anchored to Au substrates (brushes were detached from the surface before

characterization)

| initiator composition ^a (% 2-BPB) | Average thickness of PMMA (nm) | M _n (dalton) | PDI | PMMA density (nm ² /chain) | Initiating efficiency |
|--|--------------------------------------|-------------------------|-----|---|--------------------------|
| 100 | 25.4 | 65,500 | 1.3 | 3.89 | 5.1 |
| 75 | 31.1 | 108,000 | 1.4 | 5.25 | 5.1 |
| 25 | 26.0 | 79,700 | 1.3 | 4.63 | 17.3 |
| 5 | 47.2 | 190,700 | 1.5 | 6.12 | 65.4 |
| 1 | 17.4 | 226,300 | 1.6 | 19.6 | 102 |

a. based on the ratio of 2-BPB and 2-MPB used in the anchoring step.

Another remarkable finding from the GPC data is a very high initiation efficiency for the 1% initiator film. Assuming the area per molecule for a 1% 1 film is typical of that for SAMs, there should be 20-25 $\text{nm}^2/\text{initiator}$ in these monolayers, which is essentially the same as the area per chain (20 nm^2) in films grown from these initiators. (The fact that the area per chain is slightly smaller than the area per initiator reflects the uncertainty in the GPC measurements.) These results suggest that the initiation efficiency from monolayers containing dilute initiators approaches 100%. As shown in **Figure 3.5**, the initiator efficiency of surface-initiated ATRP of MMA does increase with the dilution of the initiators, which is in the accordance with the result we calculated from kinetics data.



Figure 3.5. The initiating efficiency in the ATRP of MMA from surfaces with various initiator densities (data calculated from GPC results).



Figure 3.6. Evolution of the ellipsometric brush thickness with time for the polymerization of HEMA (2-hydroxyethyl methacrylate) from diluted-initiator monolayers on Au substrates at 28 °C. (\blacksquare , 100% 2-BPB (2-bromopropionyl bromide); \Box , 5% 2-BPB; \blacktriangle , 1% 2-BPB; \triangle , 0.1% 2-BPB). Polymerization conditions: [CuCl] = 27.5 mM, [CuBr₂] = 8.0 mM, [2,2'-bipyridine] = 78 mM, in 20 mL of a 1:1 (v:v) mixture of HEMA and H₂O ([HEMA] = 4M). The points are the average of data from two independent runs, and the limits of the error bars are the measured film thicknesses from the two runs. The lines are a least square fit to the data constrained to intersect the origin.



Figure 3.7. Film growth rate (**\square**) and normalized polymerization rate (\square) (observed film growth rate/fractional coverage of the surface by initiator) in surface-initiated polymerization of HEMA (2-hydroxyethyl methacrylate) from diluted-initiator monolayers on Au substrates. The polymerization conditions are described in Figure 3.6. The error bars are derived from the standard deviations calculated from the linear fits to the data in Figure 3.6.

V. Polymerization of HEMA from Diluted Initiators Anchored to Au substrates

Polymerization of HEMA from Au (Figures 3.6 and 3.7, Table 3.3) shows similar trends. The relatively constant rate of film growth again suggests a controlled polymerization on this surface, and relative to films grown from surfaces with 100% initiator, thickness decreases 6-fold for films grown from monolayers with 1% initiator.

| initiator composition ^b (% 2-BPB) | initiator density ^c (nm ² /per chain) | PHEMA thickness at 8 h (nm) | film growth rate ^d (nm/h) | normalized rate ^e (nm/h) |
|--|--|-----------------------------------|---|--|
| 100 | 0.25 | 128 | 16.2 ± 0.3 | 16.2 ± 0.3 |
| 50 | 0.50 | 133 | 16.0 ± 0.8 | 32.0 ± 1.5 |
| 5 | 5.0 | 84 | 10.6 ± 0.3 | 212 ± 5.2 |
| 1 | 25 | 22 | 2.8 ± 0.2 | 280 ± 16 |
| 0.1 | 250 | 1.5 | 0.20 ± 0.02 | 190 ± 20 |

Table 3.3. HEMA polymerization rate from Au substrates at various initiator densites^a

a. conditions for the polymerizations are described in Figure 3.6. b. based on the ratio of 2-BPB (2-bromopropionyl bromide) and 2-MPB (2-methylpropionyl bromide) used in the anchoring step. c. assuming full coverage = $0.25 \text{ nm}^2/\text{site.}^{44}$ d. defined as the slope of the line defined by least square fits to the data in Figure 3.6. The errors are the standard deviations derived from the linear fits to the data. e. defined as the film growth rate divided by fractional coverage of the surface by initiator.

VI. Aqueous Swelling of PHEMA Films Grown from Au Substrates

All of the data presented thus far suggest that films prepared from 100% initiator should have much higher chain densities than films prepared from 1% initiators. Lower chain densities should result in greater swelling when films are exposed to a good solvent because the chains in the less dense film will likely be less extended prior to exposure to solvent. We examined the swelling of PHEMA in water, and the results are shown in **Table 3.4** and **Figure 3.8**. Percent swelling increases from 85% to 2000% when using films prepared from 0.1% rather than 100% initiator.

We should note that swelling of PHEMA chains in water is complicated by the fact that PHEMA films grown from a surface are probably lightly cross-linked. At lower initiation densities, both lower cross-linking and lower chain densities could lead to an increase in swelling. Moreover, the extremely high swelling at 0.1% should be viewed with caution because the refractive index of the film is nearly the same as that of the ambient water, making a thickness determination by ellipsometry difficult. Nonetheless, these data clearly show that film density can have a dramatic effect on physical properties.

| initiator composition ^b (% 1) | PHEMA film thickness in air ^c (nm) | PHEMA film thickness in water ^d (nm) | % increase in thickness |
|---|--|--|-------------------------|
| 100 | 43 | 77 | 77 |
| 50 | 38 | 62 | 62 |
| 5 | 47 | 83 | 76 |
| 1 | 17 | 45 | 180 |
| 0.1 | 4.2 | 75 | 1600 |

Table 3.4. Aqueous swelling of PHEMA brushes on Au substrates^a

a. average film thicknesses based on two data sets. b. based on the ratio of 2-BPB (2bromopropionyl bromide) and 2-MPB (2-methylpropionyl bromide) used in the anchoring step c. obtained using 1.5 as the film refractive index d. both film thickness and refractive index were obtained from fits to ellipsometric data.



Figure 3.8. Aqueous swelling of brushes prepared by polymerization of HEMA from diluted-initiator monolayers on gold substrates. The points are the average of measurements from two data sets, and the limits of the error bars are the % increase in thickness measured from the two runs.

VII. Polymerization of GMA from Diluted Initiators Anchored to Au Substrates

The results for polymerizations of GMA from Au surfaces as a function of initiator density are shown in **Figure 3.9.** GMA polymerizes much more rapidly than MMA, and GMA polymerizations from 100% initiator are so uncontrolled that the polymerization almost stops after 1 h, yielding thinner films than HEMA and MMA, \sim 8 nm after 2 hours. Dilution of the initiator to 75% or 50% increases polymerization rate and the film thickness. With the exception of the slow polymerization for 100% initiator,

GMA shows the same trends are seen with MMA and HEMA. Because of poor control over the polymerization, we did not investigate GMA further.



Figure 3.9. Evolution of the ellipsometric brush thickness with time for the polymerization of GMA from diluted-initiator monolayers on Au substrates at 28 °C. (•, 100% 2-BPB; •, 75% 2-BPB; \circ , 50% 2-BPB; \Box , 10% 2-BPB). Polymerization conditions: [GMA] = 4.2 M, [CuBr] = 42 mM, [2,2'-bipyridine] = 84 mM, in 10 mL 4:1 (v:v) MeOH/H₂O. The data sets are from a single polymerization at each initiator concentration.

VIII. Conclusions

In conclusion, we prepared Au substrates with various immobilized initiator densities using systems that should lead to a homogeneous distribution of initiator on the surface. Changes in the polymerization rate as a function of initiator density are consistent with both a decrease in bimolecular termination as the initiator density decreases and a decrease in the number of chains on the surface when the initiator density drops below 10% on Au. Finally, decreases in chain density lead to increases in film swelling in a good solvent, probably because chains are less extended prior to exposure to solvent when they are less dense. Future studies will examine the immobilization of macromolecules in polymer brushes as a function of film density.

IX. References

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Chapter 4

Control of the Density of Polymer Brushes in Surface-Initiated ATRP from Silicon Substrates

I. Introduction

Surface initiated polymerization is a powerful technique for preparing chemically modified surfaces. Studies aimed at understanding the fundamentals of polymer growth often use self-assembled monolayers (SAMs) as the initiator layer. SAMs provide certain advantages regarding surface modification, especially the formation of a closely packed, well-ordered, and stable configuration on the surface.¹ Most SAMs are generated on metal surfaces, such as Au, Ag, and Cu, using thiol chemistry,^{2, 3} or alkylsiloxanes anchored to hydroxy-terminated surfaces, such as Si/SiO₂, Al/Al₂O₃, and glass, using siloxy linkages.^{4, 5} Less frequently used is the Langmuir–Blodgett (LB) deposition of fatty acids or bifunctional amphiphiles.^{6,7}

The previous chapter described an effective method for controlling the initiator densities on the Au surfaces, which led to successful control over the density over the grafted polymer chains. The critical step was the use of a mixture of the initiator and an inert analog during the formation of the initiator layer, which avoids the tendency of SAMs to phase separate and segregate into islands. While monolayers of alkanethiolates on gold are probably the most studied to date, the deposition of silanes on the hydroxylated surfaces of Si/SiO₂ has more technological importance since glass and silicon are the most common inorganic materials used as optical and electrical materials. The driving force to form a SAM monolayer using alkylchlorosilanes, alkylalkoxysilanes, and alkylaminosilanes is the formation of covalent bonds with the surface silanol groups (-SiOH) via Si-O-Si bonds. Hydroxylated substrates, such as silicon oxide,⁸⁻¹² aluminum oxide,^{13, 14} quartz,¹⁵⁻¹⁷ glass,⁸ mica,¹⁸⁻²⁰ zinc selenide,^{8, 13} and germanium oxide,⁸ have been successfully modified by SAMs.

Previous methods for controlling the density of polymer brushes on silicon surfaces include Genzer and Fukuda's approaches. Genzer et al. used an evaporation process to deposit a continuous gradient of trichlorosilane-terminated initiators on SiO₂.^{21,} ²² Initiation of polymerization from these surfaces generated films that smoothly varied from dense brushes (full coverage of the surface by initiator) to isolated chains.²² Eiaz et al. controlled the density of polymer brushes by surface initiated polymerization from the co-deposited monolaver triethoxysilane terminated initiator of a (2-(4chlorosulfonylphenyl)ethyltrimethoxysilane) and *n*-octadecyltrimethoxysilane, an inert diluent.²³

Here we show that obtaining a homogeneous distribution of monochlorosilane initiators in monolayers requires matching both the reactivity and size of the initiator with a diluent. It is well known that the anchoring trichlorosilanes onto SiO₂ surfaces generates complex structures instead of a simple monolayer²⁴ (Figure 4.1). Thus, we used a mixture of a monochlorosilane initiator and an inert analog to form simple monolayers on SiO₂ surface with controlled initiator densities.



Figure 4.1. Possible reaction products of alkylchlorosilanes with SiO_2 surfaces. (Reprinted with permission from *Langmuir* 2000, *16*, 7268-7274. Copyright 2000 American Chemical Society.)

II. Experimental Section

II-1. Materials

Cu(I)Br (Aldrich, 99.999%), Cu(I)Cl (Aldrich, 99.999%), Cu(II)Br₂ (Aldrich, 99.999%), chlorodimethylsilane (Aldrich, 98%), hydrogen hexachloroplatinate(IV) hydrate (Aldrich, 99.9%), and 1-hexadecanol (Aldrich, 99%) were used as received. 2,2'-Bipyridine (bpy) (Aldrich, 99%) was recrystallized from hexane and then sublimed. Triethylamine (Aldrich, 99.5%) was distilled from calcium hydride under an argon atmosphere at reduced pressure. Methyl methacrylate (MMA) (Aldrich 99%) and 2-hydroxyethyl methacrylate (HEMA) (Aldrich, 98%) were passed through a 10 cm column of basic alumina to remove inhibitors. After purification, the monomers, solvents and all required liquid chemicals were transferred to Schlenk flasks, de-gassed using three freeze-pump-thaw cycles and then transferred into a drybox.

II-2. Characterization Methods

Film thicknesses were measured using a rotating analyzer ellipsometer (model M-44; J. A. Woollam) at an incident angle of 75° using 44 wavelengths of light between 414.0 nm and 736.1 nm. Thickness measurements were taken on at least three spots on each substrate. For films with thicknesses greater than 40 nm, both thickness and refractive index were calculated, while the refractive index of thinner films was usually assumed to be 1.5. (Assuming refractive indices of 1.45 or 1.6 result in thickness changes of only ~10 %). Unless otherwise specified, routine ¹H NMR (500 MHz) and ¹³C NMR (125 MHz) spectra were carried out in CDCl₃ using a Varian UnityPlus-500 spectrometer with the residual proton signals from the solvent used as the chemical shift standard. Mass Spectral Analyses were carried out on a VG Trio-1 Benchtop GC-MS.

II-3. Synthesis of (11-(2-Bromo-2-methyl)propionyloxy)-undecyldimethylchloro silane (1) and (11-(2,2-Dimethyl)propionyloxy)-undecyldimethylchlorosilane (2)

10-Undecen-1-yl-2-bromo-2-methylpropionate²⁵ (14.4 g, 45.1 mmol) and 49 mL of dimethylchlorosilane (451 mmol) were added to an oven-dried dry flask. The hydrogen hexachloroplatinate (IV) catalyst was then added (48 mg), and the mixture was stirred at room temperature overnight. The solution was then diluted in toluene and quickly filtered through a 5 cm plug of activated carbon to remove the catalyst. Removal of the solvent under reduced pressure gave 5.80 g of 1 as a colorless oil (31.1 %), which was stored in a drybox at 0 °C until used. ¹H-NMR δ 4.14 (t, 2H, CH₂), 1.90 (s, 6H, CH₃), 1.65 (m, 2H, CH₂), 1.37-1.24 (m, 16H, CH₂), δ 0.79 (t, 2H, CH₂), 0.37 (s, 6H, CH₃). ¹³C-NMR δ 171.69 (C=O), 66.11 (CH₂), 55.95 (C), 32.92 (CH₂), 29.54 (CH₂), 29.47 (CH₂), 29.42 (CH₂), 29.20 (CH₂), 29.13 (CH₂), 28.30 (CH₃), 25.75 (CH₂), 22.93 (CH₂), 18.94 (CH₂), 1.64 (CH₃).

A similar procedure was used to prepare (2) in 68.1 % yield. ¹H-NMR δ 4.02 (t, 2H, CH₂), 1.59 (m, 2H, CH₂), 1.37-1.24 (m, 16H, CH₂), 1.17 (s, 9H, CH₃), 0.79 (t, 2H, CH₂), 0.37 (s, 6H, CH₃). ¹³C-NMR δ 178.63 (C=O), 64.43 (CH₂), 38.70 (C), 32.94 (CH₂), 29.53 (CH₂), 29.47 (CH₂), 29.45 (CH₂), 29.21 (CH₂), 28.59 (CH₂), 27.19 (CH₃), 25.88 (CH₂), 22.95 (CH₂), 18.96 (CH₂), 1.64 (CH₃).

II-4. Determination of the Relative Reactivity of a Silane Initiator and Diluent with Alcohols

Using a literature procedure for the synthesis of the esters as a guide,²⁶ an equimolar mixture of initiator 1 and diluent 2 (4 mmol) was added by syringe to a wellstirred solution of hexadecanol (0.847 g, 3.5 mmol) in 15 mL CH₂Cl₂ at room temperature under N₂. After 24 h, the reaction was quenched by adding 100 mL of saturated aqueous NH₄Cl, and the mixture was extracted with diethyl ether (2 × 100 mL). The combined organic layers were dried over magnesium sulfate and the solvent was removed *in vacuo*. The ratio of two esters in the product was determined by integrating the corresponding methyl resonances in the ¹H NMR spectrum.

II-5. Preparation of Initiator-Immobilized SiO₂ Substrates

UV/O₃ cleaned Si wafers with an ellipsometrically determined oxide thickness of 16 Å were transferred to a dry box filled with N₂ and immersed in a toluene solution (20 mL) containing triethylamine (150 μ L) and 30 μ L of a mixture of initiator 1 and either diluent 2 or trimethylchlorosilane (TMSCl). (Initiator layers give thicker polymer brushes when they are prepared in solutions containing triethylamine.) After 48 h without stirring, the samples were removed from the solution, placed in fresh toluene and sonicated for 1 minute. Following additional rinsing with toluene, acetone, and ethanol, the substrates were dried under a stream of N₂. The ellipsometric thickness of the initiator layer was ~10 Å.

II-6. Surface-Initiated Polymerizations of MMA

Polymerizations of MMA were carried using a procedure developed by Huck and coworkers as a guide.²⁷ In an N₂-filled drybox, MMA (10 g, 100 mmol), bpy (312 mg, 2.0 mmol) and CuBr (143 mg, 1.0 mmol) were added to a 30 mL scintillation vial containing well-stirred MeOH (8 mL). After removing the vial from the drybox, deionized water (2 mL) was added to the mixture with a syringe, and this vial along with a second vial containing an initiator-modified Au or SiO₂ substrate were transferred into a glove bag filled with N₂. The deionized water was not degassed and some reaction of Cu(I) with O₂ may yield Cu(II) to help control the polymerization. After stirring the catalyst mixture for an hour, the solution was poured into the vial containing the initiator-modified substrate to initiate polymerization. Following a 0.5-8 h reaction time, the vial was removed from the glove bag and the substrate was washed sequentially with water, ethyl acetate, ethanol and water and dried under a stream of N₂.

II-7. Surface-Initiated Polymerization of HEMA

The polymerization of HEMA was based on a previously described procedure.²⁸ In a Schlenk flask, 244 mg (1.56 mmol) of bpy was added to 20 mL of an aqueous solution of monomer (HEMA/H₂O, 1:1 v:v). The mixture was stirred until homogeneous, and then was degassed using three freeze-pump-thaw cycles. CuCl (55 mg, 0.55 mmol) and CuBr₂ (36 mg, 0.16 mmol) were added quickly into the flask under Ar, and this mixture was sonicated for one minute and transferred into a glove bag filled with N₂. After stirring the catalyst mixture for an hour in the glove bag, the solution was poured into a second vial containing an initiator-covered Au or SiO₂ substrate. The

polymerization was allowed to proceed at room temperature for a set reaction time of 0.5-8 h, and then the vial was removed from the glove bag. The substrate was removed from the vial, washed sequentially with water, ethyl acetate, ethanol, and water and dried under a stream of N_2 .

III. Preparation of SiO₂ substrates with Controlled Initiator Densities

In the case of SiO₂ substrates, we controlled initiator density through silanization with mixtures of the two monochlorosilanes shown in Scheme 4.1. We utilized monochloroalkysilanes rather than trichlorosilanes because polymerization of tricholoralkylsilanes in the presence of trace amounts of water gives rise to a number of possible surface structures (Figure 4.1).²⁴ The monochloroalkylsilanes, 1 and 2, are structurally similar, but one is an α -bromoester capable of initiating ATRP, while the second is inert. Reactions of 1 and 2 with hydroxy groups in solution show that their reactivities are indistinguishable, and based on their similar sizes and shapes, we expect that their reactivities toward hydroxy-terminated surfaces should also be identical. Thus, the composition of a silane monolayer should accurately reflect the molar ratio of 1 and 2 in the solution used to modify the surface.

Since the reactivity of monochlorosilanes is lower than trichlorosilanes, we added triethylamine during the initiator anchoring step ensure a dense initiator monolayer. For comparison, we prepared initiator layers with and without adding triethylamine and polymerized HEMA from both substrates under the same conditions. As shown in **Figure 4.2**, the grafted PHEMA brush grown from the initiator layers formed using added
triethylamine was $\sim 20\%$ thicker than from the initiator layer prepared without triethylamine. Subsequently, all initiator anchoring experiments used triethylamine

Scheme 4.1. Surface-initiated ATRP of HEMA from diluted-initiator monolayers on

SiO₂ substrates





Figure 4.2. Evolution of the ellipsometric brush thickness with time for the polymerization of HEMA from 100% initiator monolayers on SiO₂ substrates at 28 °C. (**•**, from initiator monolayers prepared with added triethylamine; \Box , from initiator monolayers without added triethylamine). Polymerization conditions: [CuCl] = 27.5 mM, [CuBr₂] = 8.0 mM, [bpy] = 78 mM, in 20 mL of a 1:1 (v:v) mixture of HEMA and H₂O ([HEMA] = 4M). The points are the average of data from two independent runs, and the limits of the error bars are the measured film thicknesses from the two runs

IV. Polymerization of HEMA from Diluted Initiators Anchored on SiO₂ Substrates

Polymerization of HEMA from SiO₂ yielded results that are similar, though not identical, to polymerizations initiated from Au as shown in Figure 4.3. The rate of polymerization from initiators on SiO₂ decreased >30-fold on going from 100% to 1% initiator, but in this case the polymerization rate decreased monotonically as a function of initiator packing density (Figure 4.4 and Table 4.1). An important difference between Au and Si surfaces is the number and density of sites available on the surface for binding initiator. Studies of anchoring octadecyldimethylchlorosilane to a variety of silica surfaces²⁹ indicate a limiting area/molecule of 0.6 nm^2 , with typical values of ~0.65 nm^2 or ~ 1.54 chains/nm². Since this represents an areal density roughly 40% of that for a SAM on Au, the same initiator/diluent ratio applied to Au and SiO₂ will yield a larger average distance between initiators on SiO_2 . When the data are normalized on the basis of area/initiator, the polymerization rates from Au and SiO₂ are similar when the initiator is diluted to <10%, using the Au surface as the reference. More concentrated initiator layers show distinctly different behavior for SiO_2 and Au surfaces. HEMA polymerization rates from SiO₂ increase with initiator concentration, but the rates from Au are nearly constant.

We also found that surface initiated HEMA polymerization from Au is much slower than polymerization from SiO_2 surfaces using the same conditions. The reason for the difference is unclear, but could be related to surface effects at the early stages of polymerization, such as radical quenching by the metallic Au surface.



Figure 4.3. Evolution of the ellipsometric brush thickness with time for the polymerization of HEMA (2-hydroxyethyl methacrylate) from diluted-initiator monolayers on SiO₂ substrates at 28 °C. (\blacksquare , 100% 3; \Box , 50% 3; \blacktriangle , 5% 3; \triangle 1% 3). Polymerization conditions: [CuCl] = 27.5 mM, [CuBr₂] = 8.0 mM, [2,2'-bipyridine] = 78 mM, in 20 mL of a 1:1 (v:v) mixture of HEMA and H₂O ([HEMA] = 4M). The points are the average of data from two independent runs, and the limits of the error bars are the measured film thicknesses from the two runs. The lines are a least square fit to the 0-4 h data, constrained to intersect the origin.

| initiator composition ^b (% 1) | initiator density ^c (nm ² /per chain) | PHEMA thickness at 8 h (nm) | film growth rate ^d (nm/h) | normalized rate ^e (nm/h) |
|--|--|-----------------------------------|---|--|
| 100 | 0.6 | 213 | 36.2 ± 2.2 | 36.2 ± 2.2 |
| 50 | 1.2 | 150 | 27.7 ± 1.4 | 55 ± 3 |
| 10 | 6 | 23 | 4.9 ± 0.5 | 49 ± 5 |
| 5 | 12 | 16 | 3.7 ± 0.4 | 74 ± 8 |
| 1 | 60 | 5.7 | 1.3 ± 0.1 | 130 ± 12 |

Table 4.1. HEMA polymerization rate from SiO₂ substrates at various initiator densities^a

a. the conditions for the polymerization are described in Figure 4.3. b. based on the ratio of 1 and 2 used in the anchoring step. c. assuming full coverage = $0.65 \text{ nm}^2/\text{site.}^{29} d$. defined as the slope of the line defined by least square fits to the 0-4 h data in Figure 4.3. The errors are the standard deviations derived from the linear fits to the data. e. defined as the film growth rate divided by fractional coverage of the surface by initiator.



Figure 4.4. Film growth rate (**n**) and normalized polymerization rate (**n**) (observed film growth rate/fractional coverage of the surface by initiator) in surface-initiated polymerization of HEMA (2-hydroxyethyl methacrylate) from diluted-initiator monolayers on SiO₂ substrates. The polymerization conditions are described in Figure 4.3. The error bars are derived from the standard deviations calculated from the linear fits to the data in Figure 5. Film growth rates and normalized rates appear in Table 4.1.

V. Polymerization of MMA from Diluted Initiators Anchored on SiO₂ Substrates

Similar to the results described in Chapter 3 for Au surfaces, the rate of polymerization of MMA on SiO_2 decreased as a function of initiator packing density (>20-fold from 100% to1% initiator). Like the Au-based system, these data clearly show that decreasing the initiator density below a threshold value results in dramatic increases in the normalized polymerization rate. However, the decrease in growth rate with time (nonlinearity in **Figure 4.5**) suggests that there is significantly more termination with this system than on Au. Since the same pattern is seen for HEMA and MMA polymerizations, we speculate that the difference in the polymerization rates at high initiator concentrations on SiO_2 and Au is related to the decreased chain density on SiO_2 surfaces.



Figure 4.5. Evolution of the ellipsometric brush thickness with time for the polymerization of MMA from diluted-initiator monolayers on SiO₂ at 28 °C (\blacksquare , 100% 1; \Box , 50% 1; \blacktriangle , 10% 1; Δ , 5% 1; \bullet , 1% 1). Polymerization conditions: [MMA] = 5 M, [CuBr] = 0.05 M, [bpy] = 0.1 M, in 20 mL of 4:1 (v:v) MeOH/H₂O. The points are the average of data from two independent runs, and the limits of the error bars are the measured film thicknesses from the two runs.

VI. Controlling Initiator Densities by Using Trimethylsilyl Chloride as the Diluent

A reasonable question is whether the sizes and shapes of initiator and diluent need to be matched for effective control of initiator densities on SiO₂. Unlike SAMs on Au, the reaction of a chlorosilane with silanols on SiO₂ substrates forms covalent Si-O bonds and phase separation on SiO₂ surfaces is very slow.³⁰ To test for size effects in the anchoring process we prepared two 50% initiator layers, one using diluent 2 and a second where trimethylsilyl chloride substituted for 2. (Scheme 4.2) Trimethylsilyl chloride should have the same chemical reactivity as 2, and its cross-sectional area at SiO₂ should also be similar. Polymerizations were carried out from 50% initiator layers, one diluted with trimethylsilyl chloride and the other with 2.

Polymerizations from substrates with 100% initiator were run concurrently with each 50%-initiator substrate, enabling direct comparison of the growth rates from the two initiator dilution schemes. As shown in **Table 4.2** and **Figure 4.6**, substrates where the initiators were diluted to 50% with **2** have HEMA polymerization rates ~2/3 of those from 100% **1**. In contrast, polymerization rates decreased to 1/6th of the 100% control when trimethylsilyl chloride was used as the diluent, and we conclude that *the chain length on the diluent does matter*. (The polymerization rates for the two 100% control samples differed by less than 10%). We think that initially, both initiator and diluent have equal access to the surface and deposit homogeneously. However, as the surface is increasingly covered, initiators screen adjacent silanols and the shorter trimethylsilyl chloride competes more efficiently than **1** for surface silanols, resulting in lower than expected initiator densities and film growth rates. Thus, simply using the same functional group for anchoring initiator and diluent cannot guarantee homogeneous dilution of initiators on SiO_2 and other substrates.

Scheme 4.2. Surface-initiated ATRP of HEMA from diluted-initiator monolayers on



SiO₂ substrates using trimethylsilyl chloride

| initiator composition ^b (% 1) | initiator layer thickness (nm) | PHEMA thickness at 8 h (nm) | film growth rate (nm/h) ^c | normalized rate ^d (nm/h) |
|--|---|-----------------------------------|---|--|
| 100% 1 ^e | 1.4 | 212 | 31.6 ± 1.2 | 31.6 ± 1.2 |
| 50% 1, 50% 2 ^e | 1.4 | 151 | 24.0 ± 0.6 | 48.0 ± 1.2 |
| 100% 1 ^f | 1.4 | 220 | 35.5 ± 1.5 | 35.5 ± 1.5 |
| 50% 1 , 50% 3 ^f | 0.4 | 23 | 4.0 ± 0.3 | 8.0 ± 0.6 |

 Table 4.2. HEMA polymerization rates from silicon substrates using trimethylsilyl

 chloride (3) and 2 as diluents^a

a. the conditions for the polymerization are described in Figure 4.3. b. based on the ratio of initiator (1) and diluent (2) or TMSCl (3) used in the anchoring step. c. defined as the slope of the line defined by least square fits to the 0-4 hr data in Figure 4.6. The errors are the standard deviations derived from the linear fits to the data. d. defined as the film growth rate divided by fractional coverage of the surface by initiator. e samples and f samples were run concurrently.



Figure 4.6. Evolution of the ellipsometric brush thickness with time for the polymerization of HEMA (2-hydroxymethacrylate) from diluted-initiator monolayers on SiO₂ at 28 °C. (\circ , 100% 3; \bullet , 50% 3, diluted with 4; \blacksquare , 100% 3; \Box , 50% 3, diluted with trimethylsilyl chloride). The two data sets (squares and circles) are from independent runs and the two 100% initiator runs show the repeatability of the data. The conditions used for the experiments are identical to those of Figure 4.3.

VII. Conclusions

We prepared SiO_2 substrates with various immobilized initiator densities using systems that should lead to a homogeneous distribution of initiator on the surface. Similar to ATRP from Au surfaces, changes in the polymerization rate as a function of initiator density are consistent with both a decrease in bimolecular termination as the initiator density decreases, and a decrease in the number of chains on the surface when the initiator density drops below 10% on SiO₂. Control experiments using trimethylsilyl chloride as the diluent show that both the size and the anchoring chemistry of initiator and diluent must be matched to ensure dilution of initiators on SiO₂ substrates.

VIII. References

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Chapter 5

Rapid Growth of Polymer Brushes from Immobilized Initiators

I. Introduction

Growth of polymers from surfaces using controlled polymerization schemes such as Atom Transfer Radical Polymerization (ATRP),^{1,2} Reversible-Addition-Fragmentation Transfer polymerization (RAFT)³ and nitroxide-mediated polymerization (NMP)^{4, 5} has become a powerful strategy for anchoring well-defined polymers to substrates. These approaches to polymer brush synthesis limit the concentration of active chain ends (radicals) to minimize bimolecular termination reactions, thus providing control over the length of the chains and enabling the synthesis of block copolymers and other complex architectures. However, a consequence of gaining control is a substantial reduction in the polymerization rate, which can limit practical applications of polymer brushes. In this report we describe unusually fast growth of polymer brushes using the highly active catalyst Cu(I)1,4,8,11-tetramethyl-1,4,8,11-tetraazacyclotetradecane (Cu(I)-ATRP Me₄Cyclam). Growth of 100 nm thick poly(tert-butyl acrylate) (PtBA) brushes from initiator-modified Au surfaces occurs in just 5 minutes. Polymerization of hydroxyethyl methacrylate (HEMA) in water and methyl methacrylate (MMA) in dimethylformamide/anisole mixtures using the same catalyst provided 100 nm thick films in 10 and 60 minutes, respectively.

Rapid growth of PtBA films has important technological implications since these coatings are readily hydrolyzed to hydrophilic poly(acrylic acid) (PAA) films. The pendent carboxylic acids of PAA can chelate metals, induce changes in surface properties

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as a function of pH, and serve as scaffolds for anchoring chemical reagents, proteins, and other biomolecules. An early approach to PAA-decorated surfaces employed grafting of hyperbranched PAA to substrates.⁶ Although the graft-on-graft process is inherently slow, this technique yields relatively thick films for anchoring chemical reagents and biomolecules. Compared to "grafting to" strategies, direct growth of polymers from surfaces provides polymer brushes with greater thicknesses and chain densities. Albritton et al. recently reported rapid photoinitiated polymerization of acrylic acid from benzophenone adsorbed in polydimethylsiloxane films.⁷ The growth rates (100 nm/min) are remarkably fast and provide a direct route to PAA from polymer substrates. The methods presented in this work allow comparable films to be created on inorganic substrates and should be applicable to opaque supports with unusual geometries that are inaccessible to photopolymerization techniques. Moreover, more complicated architectures such as block copolymers can be created.

Ideally, we would like to directly grow PAA brushes from surfaces using accelerated ATRP techniques. However, ATRP of acrylic acid is problematic since carboxylic acids may react with the copper-amine catalysts typically used for ATRP. A partial solution is to polymerize *tert*-butyl acrylate (tBA) from a surface, and then hydrolyze PtBA to PAA. While widely used for preparing block copolymers containing PAA,^{8, 9} application of this approach to surface-initiated polymerization is limited by slow polymerization rates (<5 nm/hr) and low film thicknesses (<20 nm).⁹⁻¹³ The process described here provides a uniquely rapid method for forming 100 nm-thick films of PAA and other polymer brushes. Polymerization of HEMA, for example, provides another surface that can be readily derivatized to form functional coatings.¹⁴

II. Experimental Section

II-1. Materials

Unless otherwise noted, all chemicals were obtained from Aldrich. 11-Mercapto-1-undecanol (MUD, 97%), 2-bromopropionyl bromide (2-BPB) (97%), anisole (99.7%), N,N-dimethylformamide (DMF, 99.8%), Cu(I)Br (99.999%), Cu(II)Br₂ (99.999%), Me₄Cyclam (99%) and 4,4'-dinonyl-2,2'-bipyridyl (dnNbpy, 97%) and 1,1,4,7,10,10hexamethyltriethylene-tetramine (HMTETA) (97%) were used as received. Tris[2-(dimethylamino)ethyl]arnine (Me₆TREN) was synthesized as previously described.¹⁵ 2,2'-Bipyridine (bpy, 99%) was recrystallized from hexane and then sublimed. Triethylamine was distilled from calcium hydride under an argon atmosphere at reduced pressure. MMA (99%), tBA (98%), styrene (99%), 4-vinyl pyridine (4-VP) (95%) and HEMA (97%) were passed through a 10 cm column of basic alumina to remove inhibitors. After purification, the monomers and solvents were transferred into a drybox. *Note: For best results, solvents and monomers must be scrupulously purified and deoxygenated*.

II-2. Preparation of Immobilized Initiators on Gold Substrates

Au-coated Si wafers (200 nm of Au sputtered on 20 nm of Cr on Si (100) wafers) were UV/O₃ cleaned for 15 min before use and transferred into a N₂-filled glove bag. Hydroxy-terminated SAMs were formed by immersing the Au-coated substrates in a vial containing a 1 mM ethanolic solution of MUD for 24 h. After removing the vial from the glove bag, the substrates were rinsed sequentially with ethanol and water, and dried under a stream of N₂. The ellipsometric thickness of the MUD layer was 10-15 Å. MUDcoated substrates were transferred to a dry box filled with N₂ and were dipped in a 10 mL solution of 0.12 M triethylamine in anhydrous THF at ~0 °C. After 1 min, 10 mL of a solution of 2-BPB in anhydrous THF (0.1 M) was added dropwise to the solution to form the immobilized initiator layer. The reaction time was limited to 2-3 min since thiolterminated SAMs could be unstable in the presence of acid bromides. After rinsing with THF in the dry box, the Au substrates were removed from the dry box, rinsed with ethyl acetate, ethanol and deionized water (Milli-Q, 18 MΩcm) sequentially and dried under a stream of N₂.

II-3. Preparation of Immobilized Initiators on Si Substrates

UV/O₃ cleaned Si wafers with an ellipsometrically determined oxide thickness of 16 Å were transferred to a dry box filled with N₂ and immersed in a toluene solution (20 mL) containing triethylamine (150 μ L) and 30 μ L of (11-(2-bromo-2-methyl) propionyloxy)undecyldimethylchlorosilane. (Initiator layers give thicker polymer brushes when they are prepared in solutions containing triethylamine.) After 48 h without stirring, the samples were removed from the solution, placed in fresh toluene and sonicated for 1 min. Following additional rinsing with toluene, acetone, and ethanol, the substrates were dried under a stream of N₂. The ellipsometric thickness of the initiator layer was ~10 Å.

II-4. Polymerization of tBA, MMA, Styrene and 4-VP from Initiators Immobilized on Au and Si Substrates

In a N₂-filled drybox, 5.74 mg (0.04 mmol) of CuBr, 4.47 mg (0.02 mmol) of CuBr₂, 10.26 mg (0.04 mmol) of Me₄Cyclam, and 16.35 mg (0.04 mmol) of dnNbpy were added to a round bottom flask containing 20 mL of a solution of monomer in DMF/anisole (tBA/DMF/anisole = 2:1:1 v:v:v, [tBA] = 3.5 M). The mixture was well-stirred and heated with an oil bath to 50 °C until a transparent light green solution formed. The prepared solution was then transferred into a small vial containing an initiator-modified Au or Si substrate to start the surface-initiated polymerization. After a set reaction time at 50 °C, the substrate was removed from the vial, washed with ethyl acetate and THF sequentially, and then was dried under a flow of N₂ in the drybox. The same conditions were used for polymerization of methyl methacrylate ([MMA] = 4 M), styrene ([styrene] = 4.6 M) and 4-vinyl pyridine ([4-VP] = 4.5 M).

II-5. Polymerization of HEMA from Initiators Immobilized on Gold Substrates

HEMA was polymerized in a N₂-filled glove bag. For polymerization using $Me_4Cyclam$ as the ligand, an 18 mL solution of monomer (HEMA/H₂O, 5:4, v:v) was stirred in a Schlenk flask until homogeneous, degassed using three freeze-pump-thaw cycles, and then transferred into a glove bag filled with N₂. At the same time, a 2 mL DMF solution containing 5.74 mg (0.04 mmol) of CuBr, 4.47 mg (0.02 mmol) of CuBr₂, 10.26 mg (0.04 mmol) of Me₄Cyclam, and 16.35 mg (0.04 mmol) of dnNbpy was prepared in a N₂-filled drybox and transferred into the glove bag with the monomer solution. After mixing the monomer and catalyst solution and stirring for half an hour in

the glove bag, the solution ([HEMA] = 4 M) was poured into a second vial containing an initiator-covered Au substrate. The polymerization was allowed to proceed at room temperature for a set reaction time, and the vial was removed from the glove bag. The substrate was removed from the vial, washed sequentially with water, ethyl acetate, ethanol, and water and dried under a stream of N₂. For polymerization using bpy as the ligand, 244 mg (1.56 mmol) of bpy was added to a Schlenk flask containing 20 mL of an aqueous monomer solution (HEMA/H₂O, 1:1 v:v). The mixture was stirred until homogeneous, and then was degassed using three freeze-pump-thaw cycles. CuCl (55 mg, 0.55 mmol) and CuBr₂ (36 mg, 0.16 mmol) were quickly added to the flask under Ar, and the mixture ([HEMA] = 4 M) was sonicated for one minute and transferred into a glove bag filled with N₂. After stirring the catalyst mixture for an hour in the glove bag, the solution was poured into a second vial containing an initiator-covered Au or Si substrate. The polymerization was allowed to proceed at room temperature for a set reaction time of 0.5-8 h, and then the vial was removed from the glove bag. The substrate was removed from the vial, washed sequentially with water, ethyl acetate, ethanol, and water, and dried under a stream of N_2 .

II-6. Characterization Methods

Film thicknesses were measured using a rotating analyzer ellipsometer (model M-44; J. A. Woollam) at an incident angle of 75°. The data were analyzed using WVASE32 software, and thickness and refractive index determinations were performed on at least three spots on each substrate. The refractive index of the films was assumed to be 1.5 and then fitted with the film thickness. Reflectance FTIR spectroscopy was performed using a Nicolet Magna-IR 560 spectrometer containing a PIKE grazing angle (80 °) attachment.

III. Synthesis of PAA Brushes from Au Substrate Surface

Scheme 5.1 shows the synthetic route to thick PAA films on Au. (Analogous work on other surfaces is also possible, and data for polymerization from silicon are presented later). Formation of a mercaptoundecanol self-assembled monolayer on a Aucoated silicon wafer followed by reaction with α -bromopropionyl bromide yielded a dense initiator monolayer.¹⁶ Immersion of the initiator-coated substrate in a mixture of monomer, Cu(I)Me₄Cyclam, and Cu(II)dnNbpy₂ dissolved in a 1:1 mixture of DMF and anisole initiated rapid polymerization of tBA at 50 °C. At predetermined times, the substrates were removed from the solution, and after washing with solvent to remove residual catalyst and monomer and drying with N₂, the films were characterized by FTIR spectrom of the film from the appearance of a large carbonyl peak at 1740 cm⁻¹ and *tert*-butyl ester peaks at 1390 cm⁻¹ and 1180 cm⁻¹ (*Figure 5.1*, spectrum b) No film was detected on a control substrate (no initiator anchored on the surface) placed in the same polymerization solution.

Scheme 5.1. Preparation of PAA brushes via surface-initiated polymerization of tBA and

 $Au - S - (CH_2)_{11} - O Br \xrightarrow{\text{tBA/anisole/DMF}} Au - S - (CH_2)_{11} - O (CH_2 - CH_3)_{11} - O (CH_3 - CH_3)_$

subsequent hydrolysis.

Hydrolysis of a 150 nm thick film of PtBA using 150 mM methanesulfonic acid in 10 mL CH₂Cl₂ for 10 min yielded a 60 nm PAA film.¹⁷ The formation of PAA was apparent from a broad carboxylic acid peak at 3000-3500 cm⁻¹ and disappearance of the *tert*-butyl ester peaks (*Figure 5.1*, spectrum c). To prove essentially quantitative conversion of the *tert*-butyl ester to the corresponding acid, we treated the film with a pH 10 sodium diphosphate solution followed by rinsing with ethanol. The resulting FTIR spectrum showed the loss of the OH band at 3000-3500 cm⁻¹ and the disappearance of the acid carbonyl peak at 1740 cm⁻¹, as well as the growth of characteristic carboxylate peaks at 1610 cm⁻¹ and 1450 cm⁻¹ (*Figure 5.1*, spectrum d). The disappearance of the acid carbonyl peak upon deprotonation did not reveal an underlying ester carbonyl peak, confirming complete hydrolysis.



Figure 5.1. Reflectance FTIR spectra of gold substrates coated with (a) an immobilized initiator layer; (b) 150 nm PtBA brushes grown from the initiator layer; (c) 60 nm PAA brushes prepared by a 10 min hydrolysis of the PtBA film in a 150 mM solution of CH_3SO_3H in CH_2Cl_2 ; and (d) PAA brushes after immersion in a pH 10 buffer solution for 10 min and rinsing with ethanol. A UV/O₃ cleaned gold slide was used as a background.

IV. Kinetic Study of Rapid Polymerization of tBA from Immobilized Initiators

Figure 5.2 shows the evolution of film thickness with time for polymerization of tBA The high polymerization rate and thicknesses for PtBA are unusual for ATRP systems, which generally provide control over molecular weight and polydispersity by maintaining a low concentration of active (radical) chain ends. The nonlinear relationship between film thickness and time for PtBA (Figure 5.2) suggests that in this case a relatively high concentration of radicals leads to both termination and a high polymerization rate, especially early in the polymerization (see inset to Figure 5.2). However, the loss of some control in this polymerization system is more than compensated by the possibility of growing thick films in a few minutes. A 90 nm PtBA film was synthesized from a Au substrate at room temperature in 1 h. The polymer was detached from the Au substrate using iodine and after isolation, its molecular weight was measured by GPC. The number average of molecular weight was 265,000 daltons with a polydispersity of 1.64. While such measurements on small amounts of sample involve significant uncertainty, the data are consistent with a rapid polymerization with some control (polydispersity <2).



Figure 5.2. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates at 50 °C. The polymerizations were carried out using a mixture of CuBr/Me₄Cyclam (2 mM) and CuBr₂(dnNbpy)₂ (1 mM) in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/anisole solution ([tBA] = 3.5 M). The filled squares show the average of three independent runs, and the error bars correspond to the standard deviation. The inset shows data from 0-10 min. The open squares are data from the polymerization of tBA from initiators anchored on SiO₂ using the same polymerization conditions.

Polymerizations using the structurally related Me₆TREN and HMTETA ligands under the same conditions were not accelerated and yielded <20 nm films in 60 minutes (Figure 5.3). While the Me₄Cyclam/CuBr system seems to be unique, other combinations of ligands and polymerization conditions also may yield ultra-fast polymerizations. To examine to what extent the polymerization exhibits features of a controlled polymerization, we used CuBr₂(Me₄Cyclam)₂ as the Cu(II) source. Prior research showed that the use of Me₄Cyclam/CuBr for the solution ATRP of dimethylacrylamide^{18, 19} and 2-vinyl-4,4-dimethyl-5-oxazolone²⁰ provides marginal control over the molecular weight, most likely due to an inefficient back reaction ($R^{\bullet} + CuX_2 \rightarrow RX + CuX$) and hence, insufficient deactivation of chain ends.²¹ When CuBr₂(Me₄Cyclam)₂ was used as the Cu(II) source in tBA polymerizations, the initial polymerization rate increased as expected for an uncontrolled polymerization, and ultimately yielded thinner films due to a rapid decrease in polymerization rate after initiation (Figure 5.4). Using CuBr₂(dnNbpy)₂, the initial polymerization rate is slower, but the polymerization yields thicker films, indicating some level of control in polymerizations using CuBr₂(dnNbpy)₂.



Figure 5.3. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates using three different ligand systems: [CuBr] = 2 mM, $[CuBr_2] = 1 \text{ mM}$, [ligand] = 6 M, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/Anisole solution ([tBA] = 3.5 M); \Box , Me₄Cyclam; \bullet , Me₆TREN; \blacktriangle , HMTETA. Polymerizations were performed in a N₂-filled drybox at 50 °C.



Figure 5.4. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates using Me₄Cyclam and dnNbpy as the Cu(II) source. **•**, [CuBr/Me₄Cyclam] = 2 mM, [CuBr₂(dnNbpy)₂] = 1 mM, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/Anisole solution ([tBA] = 3.5 M); \Box , [CuBr/Me₄Cyclam] = 2 mM, [CuBr₂(Me₄Cyclam)₂] = 1 mM, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/Anisole solution ([tBA] = 3.5 M); \Box , [CuBr/Me₄Cyclam] = 2 mM, [CuBr₂(Me₄Cyclam)₂] = 1 mM, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/Anisole solution ([tBA] = 3.5 M). The polymerizations were performed in a N₂-filled drybox at 50 °C.



Figure 5.5. Reflectance FTIR spectra of gold substrates coated with (a) 97 nm PtBA brushes grown from the initiator layer; (b) PtBA (97 nm)-*block*-PMMA (210 nm) copolymer brushes grown from the PtBA brush layer. A UV/O₃ cleaned gold slide was used as a background.

A more rigorous test was the successful formation of block copolymers. A 97 nm PtBA film (Figure 5.5, a) was grown in 5 minutes, rinsed with solvent and dried under N_2 . The sample was removed from the dry box, and characterized by ellipsometry and

FTIR spectroscopy. After 24 hours, the substrate was returned to the dry box, and a PMMA film with a thickness of 210 nm (Figure 5.5, b) was grown from the PtBA film in 1 h using the Me₄Cyclam-based catalyst. Formation of the block was confirmed by an increase in the carbonyl peak in FTIR spectra. Interestingly, the PMMA block is comparable in thickness to a PMMA film grown directly from surface anchored initiators, suggesting that a substantial fraction of the chains were active after polymerization of the initial PtBA block.

V. Other Relevant Factors in the Rapid tBA Polymerization System

We examined other experimental parameters to better understand the scope of polymerization conditions. Polymerizations were run in different solvents **Figure 5.6**; no significant differences were found which eliminated anisole as a significant contributor to the high polymerization rate. Polymerization of PtBA at at 30 °C (**Figure 5.7**) generated a 50 nm film in just 5 minutes, suggesting the possibility of running polymerizations at subambient temperatures. The effects of monomer concentration (**Figure 5.8**) were also examined. When the monomer concentration decreased by one half, the film thickness decreased to 1/3 to 1/4 of its original value. Varying the ratio of Cu(I)/Cu(II) (**Figure 5.9**) suggests some element of control in these polymerizations. Using CuBr₂(dnNbpy)₂ as the Cu(II) source and the metric of film thickness at 60 minutes, the thickest films were obtained using a 2:1 Cu(I)/Cu(II) ratio, suggesting that the added Cu(II) provides some control over the polymerization.



Figure 5.6. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates using different solvent systems. Catalyst system: $[CuBr/Me_4Cyclam] = 2 \text{ mM}$, $[CuBr_2(dnNbpy)_2] = 1 \text{ mM}$, in 20 mL **a**, 2:1:1 (v:v:v) tBA/DMF/Anisole solution ; \Box , 2:2 (v:v) tBA/DMF solution ([tBA] = 3.5 M). Polymerization was performed in a N₂-filled drybox at 50 °C.



Figure 5.7. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates using the same catalyst system at three different temperatures: $[CuBr/Me_4Cyclam] = 2 \text{ mM}$, $[CuBr_2(dnNbpy)_2] = 1 \text{ mM}$, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/Anisole solution ([tBA] = 3.5 M). \Box , 50 °C; •, 40 °C; •, 30 °C. Polymerization was performed in a N₂-filled drybox at 50 °C.



Figure 5.8. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates at different monomer concentrations. $[CuBr/Me_4Cyclam] = 2 \text{ mM}, [CuBr_2(dnNbpy)_2] = 1 \text{ mM}, \text{ in 20 mL 1:1}$ (v:v) DMF/Anisole solution (\Box , [tBA] = 3.5 M; \blacktriangle , [tBA] = 1.8 M; \blacksquare , [tBA] = 0.9 M). Polymerizations were performed in a N₂-filled drybox at 50 °C.



Figure 5.9. Evolution of the ellipsometric brush thickness with time for the polymerization of tBA from initiator monolayers on Au substrates at 50 °C at various Cu(I)/Cu(II) ratios, in 20 mL of a 2:1:1 (v:v:v) tBA/DMF/anisole solution ([tBA] = 3.5 M).

- \diamond , [CuBr/Me₄Cyclam] = 2 mM, [CuBr₂(dnNbpy)₂] = 0.67 mM;
- •, $[CuBr/Me_4Cyclam] = 2 \text{ mM}$, $[CuBr_2(dnNbpy)_2] = 1 \text{ mM}$;
- $\Box, [CuBr/Me_4Cyclam] = 2 \text{ mM}, [CuBr_2(dnNbpy)_2] = 1.34 \text{ mM},.$

VI. Rapid Synthesis of Various Polymer Brushes from Au and SiO₂ Substrates

The unusually high growth rates for PtBA films prompted us to examine other monomers to see if they too could be polymerized rapidly to provide thick films. As shown in Figure 5.10, polymerization rates for styrene, methyl methacrylate and vinyl pyridine were slower than for tBA, and the limiting film thicknesses were also lower. However, the polymerization rates were still significantly higher than those described to date. For example, Huck et al. reported the growth of 35 nm thick PMMA films from Au in 2 h.²² whereas the Me₄Cyclam/CuBr system gave a 100 nm thick PMMA film in just 1 hour. Husson et al. grew a 40 nm thick polystyrene film in 25 h from a silicon substrate at 50 °C.²³ compared to a 30 nm film from Au in just 1 h at 50 °C with the Me₄Cyclam/CuBr system. Despite the potential utility of poly(4-vinyl pyridine) (PVP) brushes, we are unaware of only one example of the polymerization of 4-vinyl pyridine from a surface, Rühe's growth of 430 nm thick films from surface anchored azo initiators in 14 h.²⁴ However, Husson et al. reported very slow growth rates for poly(2-vinyl pyridine), (6 nm in 5 h).²⁵ In the case of PHEMA (Figure 5.11), polymerization occurred in aqueous solution, and the initial rate of polymerization was approximately 70 times faster than when using a bipyridine catalyst under similar conditions. Thus, PHEMA provides a second polymer system that can be rapidly polymerized and readily derivatized to control functionality. The reflectance FTIR spectra of polystyrene, poly(4vinyl pyridine), PMMA, and PHEMA polymer brushes grown from immobilized initiators are shown in Figure 5.12.


Figure 5.10. Evolution of the ellipsometric brush thickness with time for the polymerization of *tert*-butylacrylate (tBA, \blacksquare , the error bar is the standard deviation from results of 3 independent runs), methyl methacrylate (MMA, \Box), styrene (•), 4-vinyl pyridine (4-VP, \circ) from initiator monolayers on Au substrates. Polymerization conditions: [CuBr/Me₄Cyclam] = 2 mM, [CuBr₂(dnNbpy)₂] = 1 mM, in a 20 mL solution of 2:1:1 (v:v:v) monomer/DMF/anisole ([tBA] = 3.5 M; [MMA] = 4 M; [styrene] = 4.6 M; [4-VP] = 4.5 M). Polymerization was performed in a N₂-filled glovebox at 50 °C.



Figure 5.11. Evolution of the ellipsometric brush thickness with time for the polymerization of HEMA from initiator monolayers on Au substrates using two different catalyst systems: **•**, polymerization conditions: $[CuBr/Me_4Cyclam] = 2 \text{ mM}$, $[CuBr_2(dnNbpy)_2] = 1 \text{ mM}$, in 20 mL of a 5:1:4 (v:v:v) HEMA/DMF/H₂O solution ([HEMA] = 4M). \Box , Polymerization conditions: [CuCl] = 27.5 mM, $[CuBr_2] = 8.0 \text{ mM}$, [bpy] = 78 mM, in 20 mL of a 1:1 (v:v) mixture of HEMA and H₂O ([HEMA] = 4M). Polymerization was performed in a N₂-filled glovebag at 28 °C.



Figure 5.12. Reflectance FTIR spectra of gold substrates modified with polymer brushes grown from immobilized initiators for 1 h. (a) 50 nm polystyrene; (b) 100 nm poly(4-vinyl pyridine), after polymerization for 24 h; (c) 120 nm poly(methyl methacrylate); and (d) 160 nm poly(2-hydroxy ethyl methacrylate). A UV/O₃ cleaned gold slide was used as a background.

Comparison of the polymerization rates of tBA, MMA, styrene, and 4-vinyl pyridine in DMF/anisole suggests that the unusually rapid growth of PtBA films stems from a combination of tBA's fast propagation rate and reduced bimolecular coupling due to the steric bulk of the monomer. Neglecting chain transfer processes, the degree of polymerization realized in a chain-growth polymerization is defined by the relative probabilities of a growing chain by adding a monomer or terminating. Since most syntheses of polymer brushes from surfaces are carried out at high monomer concentrations that are approximately constant during the polymerization, the ratio of k_p to k_t , the rate constants for propagation and termination, serves as an indicator of the likelihood that a reaction will reach high degrees of polymerization before termination. Moreover, preliminary data show that tBA polymerizations show a strong dependence on monomer concentration (**Figure 5.8**). The order of the limiting film thicknesses shown in **Figure 5.11** is consistent with the relative values of k_p / k_t for the monomers.²⁶

As can be anticipated from the data presented in earlier chapters, this fast polymerization system can be transferred from Au to silicon substrates (**Figure 5.13**). We observed rapid polymerization tBA, MMA, styrene, and 4-vinyl pyridine. Polymerization of 4-vinyl pyridine was much faster from silicon than from Au, which may be related to the difference in polymerization rates seen for Au and SiO₂ as described in Chapter 4.



Figure 5.13. Evolution of the ellipsometric brush thickness with time for the polymerization of *tert*-butylacrylate (tBA, \blacksquare), methyl methacrylate (MMA, \square), styrene (•), 4-vinyl pyridine (4-VP, \circ) from initiator monolayers on SiO₂ substrates. Polymerization conditions: [CuBr/Me₄Cyclam] = 2 mM, [CuBr₂(dnNbpy)₂] = 1 mM, in a 20 mL solution of 2:1:1 (v:v:v) monomer/DMF/anisole ([tBA] = 3.5 M; [MMA] = 4 M; [styrene] = 4.6 M; [4-VP] = 4.5 M). Polymerization was performed in a N₂-filled glovebox at 50 °C.

VII. Conclusions

The use of the Me₄Cyclam/CuBr catalyst system allows rapid polymerization of a variety of monomers. Such rapid polymerization from a surface will be very important in potential applications of polymer brushes as skin layers in separation membranes and as substrate coatings for probe immobilization in gene and protein chips. It is important to note that while these rapid polymerizations from surfaces are not "living", they do allow formation of block copolymers and their high growth rates are very attractive for forming functional films.

VIII. References

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