Abstract

TOMLINSON, MICHAEL RALPH. Surface-grafted Polymer and Copolymer Assemblies with Gradient in Molecular Weight and Composition. (Under the direction of Jan Genzer.)

The chief goal of this Ph.D. dissertation was to develop methodologies facilitating the formation of assemblies comprising grafted polymers on surfaces with gradually varying length (or, alternatively, molecular weight). Our additional goals accomplished include expansion of these methodologies to incorporate multiple monomer systems and block copolymer assemblies. Lastly we demonstrate the utility of these gradient assemblies to study some complex phenomena of scientific interest. Surface-grafted polymer gradients represent important tools in the combinatorial study of tethered polymer layers. This approach can lead to rapid screening of properties and development of new or more efficient technologies involving tethered polymer films. The areas/technologies of interest are cited throughout the work and span organic electronic materials, responsive surfaces, nonfouling coatings, drug delivery applications, and manipulation of matter on “small scales” leading to developments in nanotechnology.

In Chapter 3, I describe procedures, methods, and several evolutions of a gradient chamber designed to create homopolymer gradient assemblies. Chapter 3 also includes studies using polymer gradients to understand polymer surface growth kinetics and an introduction to the concept of orthogonal gradient samples. I include, as supplemental information, my studies involving Atom Transfer Radical Polymerization (ATRP) simulations using a step time based Fortran program.

Chapter 4 introduces the concept of block-copolymer gradients and describes my progress and major accomplishments in achieving my goal of formation of tethered
copolymers. I also discuss several studies involving these tethered copolymers. I use a combinatorial approach to create “step” multiblocks on one sample surface in order to study the efficiency and characteristics of growth of these multiblock layers. I describe how I was able to produce surface-grafted diblock copolymer gradients and how I was able to chemically modify these layers. A major portion of Chapter 4 is devoted to describing a study in which a tethered diblock copolymer gradient was subjected to two selective-solvent exposure procedures designed to collapse the top and bottom blocks, respectively. I was able to study, combinatorially, the formation of and characteristics of micellar and bicontinuous structures formed via these solvent exposure techniques. Clear AFM images, ellipsometric thickness, and wettability measurements made on this sample reveal a possible relationship between surface morphology and the rearrangement of the diblock surface. I also introduce a triangular triblock triple gradient, which I successfully created. Such gradients will yield a wealth of information when applied to the study of tethered triblock copolymers.
Surface-Grafted Polymer and Copolymer Assemblies with Gradient in Molecular Weight and Composition

by

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Dedication

I would like to dedicate this dissertation to my parents, Mike and Susan Tomlinson. They provided the foundation that allowed me to have an opportunity to achieve everything that I have worked for in my life.
Biography

Michael Ralph Tomlinson, Junior was born on December 8th 1976 in Mobile, Alabama. His loving parents, Susan Tomlinson and Michael Tomlinson, provided a healthy environment in which he was taught to enjoy learning, appreciate music, and believe in himself. He was active in the Boy Scouts of America for many years and received his Eagle Scout award, the highest honor in the organization, just before his 18th birthday. He attended public schools in Mobile until the end of his sophomore year at Davidson High School at which time he transferred to the Alabama School of Mathematics and Science. Thanks to many caring and intelligent teachers and some supportive friends, he was empowered with a love of diversity, a passion for thinking, and the self-confidence to succeed.

He attended Auburn University from 1995 to 2000 where he earned a bachelors degree in Chemical Engineering. He tutored physics, chemistry, and mathematics while at Auburn and was active in The American Institute of Chemical Engineering and the Auburn University Concert Choir. He received practical research experience both with the Auburn University Space Power Institute and the Auburn University Glass Shop.

Upon graduation he decided to seek higher education at North Carolina State University where he attended from 2000 to 2005 and earned his Masters degree and PhD in chemical engineering. While at NCSU, he was a member of the chemical engineering graduate recruiting team, a member of a Cappology 101 (an a cappella singing group), president of The Self Knowledge Symposium (a student-run organization devoted to self-growth), and ambassador to and member of the NCSU Interfaith Council and Interfaith Alliance of Raleigh.
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With every journey there are people who make the journey easier, more exciting, and worthwhile. Having completed my Ph.D., I look back on all those who have stood by me and helped me in their own ways.

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# Table Of Contents

List of Tables.................................................................................................................. viii
List of Figures................................................................................................................... ix
List of Abbreviations/Symbols......................................................................................... xiii
1. General Introduction and Project Goals........................................................................ 1
   1.1. Surface-Grafted Polymers..................................................................................... 1
   1.2. Controlled/Living Polymerizations....................................................................... 5
   1.3. Applications in Polymer Thin Films....................................................................... 8
       1.3.1. Selected Applications in Polymer Electronic Materials................................. 9
       1.3.2. Selected Applications in Responsive/”Smart” Surfaces................................. 12
   1.4. Combinatorial Science and Gradients................................................................. 14
       1.4.1. Importance of Combinatorial Methods in Research......................................... 14
   1.5. References............................................................................................................ 16
2. A Review of Surface-Grafted Macromolecular Gradients........................................... 27
   2.1. Introduction........................................................................................................... 27
   2.2. Review of Techniques of Preparation and Characterization of Polymer
       Gradients.................................................................................................................. 28
       2.2.1. Surface-Grafted Polymers Through Corona Treatment................................. 29
       2.2.2. Polymer Gradients Prepared by “Grafting onto” Technique............................. 29
       2.2.3. Gradients Prepared by “Grafting from” Technique............................................ 32
       2.2.4. Miscellaneous Methods for Immobilizing Polymers in Gradient Pattern.......... 33
       2.2.5. Gradient Graft Copolymers............................................................................. 34
       2.2.6. Methods of Characterizing Gradient Properties............................................. 36
   2.3. Anchored Polymers with Grafting Density Gradients........................................... 40
       2.3.1. Formation and Properties of the Gradient Initiator........................................ 40
       2.3.2. “Grafting from” on the Gradient Initiator Surfaces........................................ 42
       2.3.3. Properties of Grafted Polymer Layers........................................................... 43
2.3.4. Anchored Polymers with Molecular Weight Gradients.................................47

2.4. References........................................................................................................48

3. Methods, Procedure, & Equipment in Production of Surface-Grafted Macromolecular Gradients.................................................................66

3.1. Project Goals and Motivation........................................................................66

3.2. Initiator Deposition, Characterization, and Growing Brushes.........................67

3.3. The Evolution of the Gradient Chamber..........................................................69

3.3.1. 1<sup>st</sup> and 2<sup>nd</sup> Generation Exhaust Gradient Chamber......................69

3.3.2. 1<sup>st</sup> Generation Dipping Gradient Chamber.........................................72

3.4. Formation and Characterization of Polymer Brushes with Molecular Weight Gradients........................................................................................................73

3.4.1. Kinetics of Surface-Confined Polymerizations........................................73

3.4.2. Macroinitiator Reinitiation Efficiency Studies............................................79

3.4.3. Added Deactivator (AD) vs. Sacrificial Initiator (SI) in Control of ATRP...80

3.4.3.1. Gradient Study of Surface Growth Kinetics with SI for Control.............82

3.4.3.2. GPC Data Confirming Low PDI In-solution Polymer From AD System..................................................................................................................83

3.4.3.3. Fortran ATRP Simulations........................................................................84

3.5. Formation of Orthogonal Polymer Brush Gradients.........................................87

3.5.1. Orthogonal Homopolymer Molecular Weight / Grafting Density Gradients..................................................................................................................87

3.5.2. Application of Orthogonal Homopolymer Molecular Weight / Grafting Density Gradients......................................................................................................88

3.6. References..........................................................................................................91

4. Gradient Block Copolymer Assemblies..............................................................109

4.1. Formation of Tethered Copolymers.................................................................109

4.1.1. Necessary Conditions to Prepare Copolymers...........................................109

4.1.2. Adjusting Co-solvent to Promote Copolymerization of PMMA and PHEMA.................................................................................................................110

4.2. Studies of Grafted Diblock Copolymers..........................................................111
4.2.1. Macroinitiator Efficiency in Grafted Alternating Multiblock Copolymer
4.2.2. Surface-Grafted Diblock Copolymer Gradients
4.2.3. Chemically Modified Diblock Copolymer Gradients
4.3. The “Orthogonal Gradient”
4.3.1. Solvent Exposure Study of Tethered Diblock Copolymer Brushes
4.3.2. Study of Chain Conformations After Selective Solvent Treatment
   4.3.2.1. AFM Studies of Surface Morphologies
   4.3.2.2. Wettability Studies of Surface Morphologies
4.4. Studies of Grafted Triblock Copolymers
4.5. References
5. Outlook
   5.1. Polymer Gradients in Electronic/Photonic Materials
   5.2. Polymer Gradients in Biomedical Applications
   5.3. Polymer Gradients to Study Anti-fouling Surfaces
   5.4. Polymer Gradients in Polymer-Nanoparticle Composite Materials
   5.5. Polymer Gradients in Studying Polymer Surface Growth
   5.6. Conclusion
   5.7. References
List of Tables

Table 3.1 – Polymerization Recipe Used to Determine PDI of Polymer Grown from AD System

Table 3.2 – Polydispersity from Three PMMA AD Runs

Table 3.3a – Kinetic Parameters Used in Fortran ATRP Simulation

Table 3.3b – Initial Conditions Used in Fortran ATRP Simulation

Table 4.1 – Solubility of PHEMA and PMMA Polymers in Various Solvents

Table 4.2 – Co-solvent Recipe for Polymerization of PHEMA from PMMA Macroinitiator
List of Figures

Figure 1.1 – Formation of Surface-Anchored Polymer Assemblies by “Grafting onto” and “Grafting from” Methods………………………………………………………………………………..24

Figure 1.2 – Schematic of Surface-Anchored Polymer in Good and Poor Solvents……………………………………………………………………………………………………………………….24

Figure 1.3 – Polymer Architectures Formed via ATRP………………………………………………………………………………………………………………………………………………….25

Figure 1.4 – Diagram of an Organic Light Emitting Diode (OLED) ………………………………26

Figure 1.5 – Diagram of a Photoelectric (Solar) Cell…………………………………………………………..26

Figure 2.1 – Schematic of Surface-Anchored Polymers with Gradients in Grafting Density and Molecular Weight…………………………………………………………………………………54

Figure 2.2 – Schematic of Surface-Anchored Copolymer Gradients and Double Homopolymer Gradients with Variance in Composition and Length. ……………………………………54

Figure 2.3 - Schematic Showing Comb-like Poly(ethylene oxide) Gradient on Polymer Surface………………………………………………………………………………………………55

Figure 2.4 - Preparation of Ultra thin Tethered Polymer Layers with Gradually Changing Thickness by Utilizing a “Grafting to” Approach Using a Temperature Gradient……………………………..55

Figure 2.5 - Ellipsometric Mapping of PBA/P2VP Gradient Brush………………………………56

Figure 2.6 - Contact Angle at Different pH of PAA/P2VP Brush vs. Composition………………56

Figure 2.7 - Schematic Representation of Controlled Topologies, Compositions, and Functionalities and Molecular Composites Prepared by Atom Transfer Radical Polymerization (ATRP) ……………………………………………………………57

Figure 2.8 – Synthesis of Gradient Comb Copolymer of Poly(MMA-graft-nBuA) …………..58

Figure 2.9 – Chemical Formulas of PAAm, PMMA, PHEMA, PtBA, PAA, and PDMAEMA…………………………………………………………………………………………………..59

Figure 2.10 - Method of Preparing Surface-Grafted Polymer Assemblies with Gradients in Grafting Density………………………………………………………………………………60

Figure 2.11 – Carbon Edge PEY NEXAFS Spectra Collected from CMPE-SAM and OTS-SAM……………………………………………………………………………………………..61
Figure 2.12 – PEY NEXAFS Intensity Measured at E=284.2 eV as a Function of Position on the Substrate Containing Initiator Gradients …………………….61

Figure 2.13 – Dry and Wet Thickness of PAAm as a Function of Position on the Substrate Prepared from Initiator Gradients of CMPE. …………………….62

Figure 2.14 – Wet Thickness of PAAm as a Function of PAAm Grafting Density………………63

Figure 2.15 – Dry Thickness of PAAm and Contact Angle with DI Water for PAAm Grafting Density Gradient………………………………………………64

Figure 2.16 – Negative Cosine of Contact Angle as a Function of PAAm Grafting Density…………………………………………………………………….65

Figure 3.1 – BMPUS Initiator Deposited at 25˚C and –10˚C as a Function of Deposition Time………………………………………………….……………….96

Figure 3.2 – Growth Rate Data for PMMA Grown on Silicon Wafers Using Deposited BMPUS Initiator Monolayer…………………………….……………….96

Figure 3.3 - 1st Generation Gradient Chamber (Illustration) …………………………………97

Figure 3.4 – 1st Generation Gradient Chamber (photograph) …………………………………97

Figure 3.5 - 2nd Generation Exhaustive Gradient Chamber (Photograph) ………………………98

Figure 3.6 – 1st Generation Dipping Gradient Chamber………………………………………………99

Figure 3.7 – PAAM Gradient Showing Nonlinear Behavior of PAAM Growth………………99

Figure 3.8 – Two PAAM Gradients Formed with Different Pump Speeds…………………..100

Figure 3.9 – Variation of Pump Speed Changes Steepness of Slope in PMMA Gradients……………………………………………………..………100

Figure 3.10 – PMMA Gradients Showing Growth Rate Dependence on CuCl2/CuCl Ratio…………………………………………………………101

Figure 3.11 – Surface Kinetics Plot for PMMA Growth in Aqueous Methanol Media…………………………………………………………101

Figure 3.12 – PHEMA Gradients Showing Growth Rate Dependence on CuCl2/CuCl Ratio…………………………………………………………102

Figure 3.13 - Surface Kinetics Plot for PHEMA Growth in Aqueous Methanol Media…………………………………………………………102
Figure 4.7 – Contact Angle Data from Fluorinated PHEMA-b-PtBA
Before and after Hydrolysis of PtBA to PAA……………………………………………………………139

Figure 4.8 – PHEMA-b-PMMA Orthogonal Molecular Weight Gradient
Sample (Ellipsometric Data) …………………………………………………………………….140

Figure 4.9 – PHEMA-b-PMMA Molecular Weight Gradient Sample (Photograph)……141

Figure 4.10 – Diagram Showing Phase Predictions of Tethered AB Diblock Layer
Exposed to Theta Solvent for A (Bottom Block) and Poor Solvent for B (Top)………..141

Figure 4.11 - Morphology Diagram of Ethanol-Quenched PHEMA-b-PMMA
Brushes Based on Atomic Force Microscopy (AFM) Results Revealing the Existence
of Flat (F), Micellar (M), and Continuous (C) Morphologies……………………………………142

Figure 4.12 – Approximate Phase Diagram Produced from AFM Images.
Flat (F), Micellar (M), and Bicontinuous (BC) Regions are Labeled………………….143

Figure 4.13 – AFM Images of Transition (a) Across PHEMA-b-PMMA Orthogonal
Sample Exposed to Selective Solvent for Bottom (PHEMA) Block…………….144

Figure 4.14 – AFM Images of Transition (b) Across PHEMA-b-PMMA Orthogonal
Sample Exposed to Selective Solvent for Bottom (PHEMA) Block. ……………144

Figure 4.15 – AFM Images of Transition (c) Across PHEMA-b-PMMA Orthogonal
Sample Exposed to Selective Solvent for Bottom (PHEMA) Block. ……………145

Figure 4.16 – AFM Images of Transition (d) Across PHEMA-b-PMMA Orthogonal
Sample Exposed to Selective Solvent for Bottom (PHEMA) Block. ……………145

Figure 4.17 – “Spongy” Morphology Observed Over Most of Sample After Solvent
Treatment to Collapse Bottom PHEMA Block. ………………………………………146

Figure 4.18 – Transition at Intermediate PMMA Thickness (~12nm) from Short
to Long PHEMA. ………………………………………………………………………..147

Figure 4.19 – DI Contact Angle Data Taken after Solvent Treatment to Collapse
Top PMMA Block……………………………………………………………………….148

Figure 4.20 – DI Contact Angle Data Taken after Solvent Treatment to Collapse
Bottom PHEMA Block……………………………………………………………………….148

Figure 4.21 – PHEMA-b-PMMA-b-PDMAEMA Triangular Triblock Sample………..149
List of Symbols

AD = Added Deactivator

ATRP = Atom Transfer Radical Polymerization

BMPUS = (11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane (surface initiator)

BPY = 2,2'-dipyridyl

CMPE = Chloromethylpheylethyl trichlorosilane initiator

EBiB = Ethyl-α-bromoisobutyrate (in-solution initiator)

PAAm = Poly(acryl amide)

PDI = Polydispersity Index

PDMAEMA = Poly(dimethylaminoethyl methacrylate)

PHEMA = Poly(2-hydroxyethyl methacrylate)

PMDETA = N,N,N',N',N''-pentamethyl-diethylene-triamine

PMMA = Poly(methyl methacrylate)

PtBA = Poly(tert-butyl acrylate)

SI = Sacrificial Initiator

ρ = Volumetric Density

σ = Surface Grafting Density
Chapter 1: General Introduction & Project Goals

It would be appropriate to introduce two significantly important concepts before explaining the motivation and goals of my project. Those two broad areas are surface-grafted polymers and controlled/living polymerizations (specifically Atom Transfer Radical Polymerization). For those who need no introduction to these key subjects, please skip to 1.4 Project Goals and Motivation. For the rest, please enjoy the next sections.

1.1. Surface-grafted polymers

Polymer coatings offer an efficient and convenient way of modifying physico-chemical characteristics of material surfaces[1, 2]. Such polymer-modified surfaces are used extensively in a variety of applications, including photolithographic masks[3], adhesion promoters[4], lubricants[5], stabilizers of colloidal particles[6], non-fouling coatings[7-9], responsive materials[10], and others. Polymers serve as excellent candidates for surface modification on account of several reasons: (1) compared to low molecular weight coatings such as self-assembled monolayers (SAM), polymers have better and more tailorable mechanical properties (2), they can form thick films thus providing a large number of functional groups, (3) they offer a wide variety of functional groups to choose from, and (4) they can serve as multifunctional stimuli-responsive materials. More will be said on specific applications of polymer thin films in section 1.2.
Traditionally, polymer coatings are created by physically attaching a polymer layer to the surface of interest. Typical methods of forming physisorbed polymer coatings include spin casting or solution dip-coating. The nature of interaction between the polymer and the surface in these coatings is usually non-covalent. Although physisorbed polymer coatings serve their purpose immediately after the fabrication process, their performance diminishes over a protracted time period due to the erosion of the coating under harsh application conditions. In order to overcome these shortcomings, it is highly beneficial to chemically bind the polymers to the surface. Grafting polymers to a substrate provides a permanent chemical bond between each polymer molecule and the chosen surface. There are two ways of grafting polymers to a solid substrate (figure 1.1). In the “grafting onto” method, polymer molecules are grown in solution and then end-tethered onto the substrate. In the “grafting from” method, the surface is functionalized with initiator molecules and then a polymer brush is grown from the surface. A polymer brush can be defined as a relatively densely packed formation of grafted polymer molecules extending from the surface via the grafting points on the surface. The “grafting onto” method produces brushes with a low grafting density, due to a large entropy barrier for packing/extending the chain. The preferred “grafting from” method produces high-density polymer brushes and can be used to permanently modify many different surfaces with many types of polymers. Figure 1.2, which will be explained in more detail later, illustrates a brush conformation (expected for “grafting from” polymerizations) as well as a mushroom conformation (expected for “grafting onto” tethered polymers)

For growth of “grafted from” polymer brushes, several things must be accomplished: (1) choosing a surface/substrate for polymer brush growth, (2) synthesizing the polymer-
compatible initiator to begin polymerization, (3) tethering the initiator molecule to the substrate, and (4) growing the polymer brush. A variety of surfaces in different geometries (planar, nanoparticle, pores) have been modified with tethered polymer brushes including silicon, gold, alumina, germanium, mica, and polymeric substrates[11]. Once the surface is chosen there are a variety of functionalized molecules that may react and self-assemble with the chosen substrate. Self assembly has been known to occur with many different types of molecules. Thiols assemble on gold, and chloro- and alkoxy silanes assemble on metal oxides like SiO\textsubscript{2} [11]. The process of self-assembly produces a highly ordered and chemically bound monolayer of a given molecule to the chosen substrate. A reactive group, compatible as a polymerization initiator, must then be coupled with the reactive “tethering” functionality. This process produces a molecule that will self-assemble and allow a “grafted from” polymerization to take place directly off of the substrate surface. Polymerization schemes to produce well-ordered brushes will be discussed in the following section.

Conformations of tethered polymer chains are significantly different from those of free polymers in solution [12-14]. The main parameters governing the conformation of macromolecules in solution include the quality of the solvent (expressed in terms of the monomer-monomer interactions), chain stiffness, and the degree of polymerization, N. In good solvents, where favorable interaction between monomer and solvent molecules dominate the loss of entropy due to chain stretching, polymer molecules assume a relaxed conformation in the form of an expanded coil. In contrast, a poor solvent causes monomers to minimize contacts with solvent molecules as much as possible, consequently resulting in the formation of a collapsed globule. Under good solvent conditions entropy drives the polymer to minimize its contact with other monomer units. Under poor solvent conditions
entropy drives the polymer chain to minimize its contact with the solvent. In the case of theta solvents the polymer and solvent have equal interaction and thus produce chains with an intermediate radius of gyration between good and poor solvents. Radius of gyration of a polymer chain, which is a measure of average size of the chain, is given by $R_g \sim N^{3/5}$ under good solvent conditions. This scaling relationship shows a much weaker dependence on $N$ (or equivalently molecular weight) under poor solvent conditions with $R_g \sim N^{1/3}$. In the so-called theta solvents the chain dimension scales as the unperturbed radius of gyration, $R_g \sim N^{1/2}$. Grafting of polymer chains to a surface dramatically modifies the way in which the constraints of monomer-monomer interaction and chain stretching on polymer conformation are manifested. In addition to $N$, the conformation of end-tethered polymer chains is governed by the number of polymer chains grafted per unit area of the substrate, which is characterized by grafting density of chains on the surface, $\sigma$. When a few long polymer chains are attached to the substrate, they do not overlap and as long as there is no special interaction with the substrate, the conformation of these chains is similar to that in solution. Under good solvent conditions, the chains try to maximize the number of contacts with the solvent molecules while keeping chain stretching to a minimum. This behavior results in the formation of a so-called mushroom conformation (figure 1.2). Wet thickness of a polymer in the mushroom regime under good solvent conditions has been theoretically predicted and experimentally verified to scale as $H \sim N\sigma^0$ [13, 14]. It must be pointed out that the aforementioned scaling relations apply only to neutral grafted polymers, i.e. the polymers devoid of any chargeable functional groups along their backbone. As the grafting density of chains on the surface increases, the osmotic pressure among the chains increases and this forces the chains to stretch normal to the substrate. This equilibrium conformation,
in which polymer chains are stretched away from the grafting surface, has been coined as a polymer brush (Figure 1.2)[13]. The wet thickness of a brush in a good solvent scales as $H \sim N\sigma^{1/3}$. Thus, compared to free polymer chains in solution, the size of grafted chains exhibits a stronger dependence on $N$ and an additional dependence on grafting density. When placed in poor solvents, the surface-tethered polymers collapse, giving rise to collapsed chain conformations. At small $\sigma$ the individual chains remain isolated (Figure 1.2), with increasing $\sigma$ they form surface-bound collapsed aggregates of various shapes and sizes [14, 15].

As the conformation of the grafted polymer chains governs the effectiveness of the polymer thin film for a given application, it is desirable to be able to manipulate the conformation by controlling $N$ and $\sigma$ of the grafted chains. For example, it has been predicted that adsorption of small proteins (and the subsequent bio-fouling) on a surface can be minimized by using polymer brushes having high grafting density whereas thicker brushes (high $N$) are preferred to achieve similar repellency for larger proteins[8]. Polymer brushes are widely used to prevent coagulation of colloidal particles. This steric stabilization is best realized by using long grafted chains with a relatively high $\sigma$ [6]. Adhesion promotion between a polymer melt and brush-coated surface is found to depend critically on $\sigma$ and is best realized with long chains that are relatively sparsely grafted [16, 17]. Minimization of friction (for creating lubricating surfaces) via grafted brushes is heavily dependent on both grafting density and molecular weight. At high grafting densities the friction is dependent on the rheology of the brush layer while at sparse grafting densities the frictional stress is related nonlinearly with the surface velocity. [18]
1.2 Controlled/living polymerizations

Living polymerizations, first discovered in 1956 by Szwarc [19], allowed for the synthesis of polymers without irreversible chain transfer and termination. This process paved the way for complex macromolecular architectures since polymer chemists now had wide control over endgroup functionality and were able to synthesize block copolymers via sequential monomer addition. Controlled polymerization is a synthetic method to prepare polymers with well-defined topology (linear, star, dendritic, etc), terminal functionality, composition and arrangement of comonomers (e.g., statistical, periodic, block, graft, gradient). The combination of these two concepts brings us to controlled/living polymerizations, which are characterized by forming a variety of different polymer and copolymer architectures with a very narrow polydispersity index (PDI).

Since the introduction of controlled/living polymerizations, many different polymerization schemes have been developed. These schemes include living anionic polymerization, living cationic polymerization, living ring-opening polymerization (ROP), ring-opening metathesis polymerization (ROMP), nitroxide-mediated polymerization (NMP), reversible addition-fragmentation chain transfer polymerization (RAFT), and atom-transfer radical polymerization (ATRP). The well-known ability of anionic polymerizations to form highly monodisperse polymers first made this scheme popular from application to polymer brush growth, however the extremely low temperatures, immaculate purity of chemicals and glassware, and long reaction times required makes anionic polymerizations less friendly to non-chemists. Little work has been done with cationic polymerizations in reference to
polymer brush growth especially complex topologies and arrangement/composition of comonomer. Many industrially important polymers are synthesized via ROP, which has been successfully used in “grafting from” polymerizations on surfaces. For example, lactones, lactides, and lactic acid (producing a potentially important biodegradable polymer) have all been polymerized via this method. Polymer brushes may also be synthesized via ROMP. Many electronically active polymers and brushes made using ROMP may be very important in the future realm of electronic materials (see section 1.3). The last three schemes rely on the reversible end-capping of growing polymer radical chains. NMP relies on a nitroxide leaving group, RAFT on a dithiol ester, and ATRP on transition metal halide complexes. In all three schemes, the fundamental reactions are similar. Unlike other schemes, radical polymerizations can function well in a variety of solvents, at more reasonable temperatures, and with less rigorous cleanliness. The most widely used “controlled”/living radical scheme is atom transfer radical polymerization (ATRP) due to its increasing flexibility and ease of use (see eqn. 1.1 & 1.2). In strict radical polymerization the propagation step is much faster than the initiation step, which leads to polymers with wide PDI’s. ATRP, pioneered by the Sawamoto [20-24] and Matyjaszewski [25-28] groups, solves this problem by utilizing a mechanism in which the radicals used for polymerization are kept mostly inactive during polymerization due to halogen addition from a transition metal halide complex [eqn. 1]. In ATRP, the radical polymerization shifts from being monomer diffusion limited to being limited by the halogen exchange.

Halogen Exchange

\[ P-X + L_{n}M_{i}^{Z} \rightleftharpoons P^{*} + L_{n}M_{i}^{Z+1}X \]  

(Equilibrium favors halide-capped polymer)
Controlled Propagation

\[ P_n^* + \text{Monomer} \rightarrow P_{n+1} \]  \hspace{1cm} (1.2)

ATRP also allows for end-functionalized and body-functionalized polymers to be synthesized, thereby opening the doors to a variety of different polymer architectures such as block copolymers, multi-armed star, hyperbranched polymers, polymer combs, or brushes (figure 1.3). ATRP is a versatile and relatively inexpensive technique. Many types of polymers including acrylates, methacrylates, styrenes, vinylpyridines, acrylonitrile, and acrylamides [26, 29-33] have been synthesized via ATRP. Recently, ATRP of some acrylates, methacrylates, and modified styrenes, has been achieved in a room temperature water/methanol solvent system [34-39] making ATRP even simpler, more industrially sound (except perhaps when high conversions are expected), and more eco-friendly. The polar nature of the water/Methanol system increases solubility and activity of the catalyst and thereby increases the rate of polymerization. The rate of reaction is quickened such that the polymerization can take place at room temperature. Aqueous ATRP is ideal for precise modification of surfaces due to its many advantages: simplicity of procedure, mild experimental conditions, low solvent cost & low organic solvent use, low energy cost (low operating temperature), high rate of polymerization, and precise control of polymer structures and properties.
1.3 Applications in Polymer Thin Films

Polymer thin films have been studied for numerous applications including the realms of electronic materials, sensor technologies, photonics, organic memory storage devices, property-tailored coatings, biomedical applications, and responsive surfaces and materials. Polymers and copolymers have peaked interest in these areas due to their flexible/tailorable properties, low-cost, biocompatibility, stimuli-responsive nature, and relative ease of fabrication. In this section, we will introduce some more specific applications for polymers particularly in the thin film regime.

1.3.1 Selected Applications in Polymer Electronic Materials

The discovery of semiconducting and conducting polymers for applications in electronic materials was initially discovered in the 1970’s. Since then, conducting polymers have become their own unique class of materials for investigation. Polymeric light emitting diodes (PLEDs), organic light emitting diodes (OLED), based on luminescent semiconducting polymers evolved in the 1990’s along with other organic electronics applications such as photodiodes, photovoltaic cells, thin-film transistors, and lasers. Nowadays they are being implemented in flat panel displays in devices ranging from digital cameras, cell phones, and PDAs to large screen TVs. OLED displays are highly flexible, inexpensive to manufacture, and very efficient. They also come in a variety of colors and have excellent contrast. A typical OLED consists of sequential thin films of an electron-conductive cathode, an organic layer, and a transparent hole-conducting anode (figure 1.4). In a PLED a polymeric material is used as the organic layer. A small voltage across the polymer layer causes holes and electrons to be simultaneously injected through the layer.
Recombination of the electrons and holes excites the semiconducting polymer molecules and causes light to be emitted. PLEDs are on the way to being the next candidates for OLED-based displays[40-44]. The luminescent properties of PLEDs makes them attractive for other applications like IR optical communications technologies [45] or chemical sensors [46-48] (in which polymers interact with target molecules to induce luminescence quenching). In all PLED applications primary characteristics like the polymers chemical properties and physical properties are important as well as secondary properties including morphology, surface/interface contact and film preparation history. It will become evident in chapter 4 that polymer gradients may play an important role in characterizing and tuning specific morphological characteristics of thin polymer films.

Another contemporary area of research for polymer films is in solar cell or photovoltaic applications. In photovoltaics, light is collected by means of a semiconductor plate. A typical photocell consists of, from top to bottom, a transparent coating (anti-reflection), a conductive collector grid, n-type silicon, p-type silicon, and a back electrode (figure 1.5). Photons enter the anti-reflective layer and are channeled to the semiconductor plate where they are absorbed by the semiconductor. This causes electrons to be liberated from the semiconductors outer orbitals (simultaneously generating ‘holes’). The opposite of what happens in a diode, electron/hole flow to light, occurs in a photocell- light to electron flow. The interface where the p- and n-type silicon meet (referred to as the pn junction) creates a permanent electric field, which allows electrons to flow only one way. The electrons generated by the absorption of photons, tend to flow across this junction thereby creating voltage and current flow. Solar energy is free but the cells are expensive and lack efficiency. Polymer films have been studied in this realm to increase the efficiency of
existing cells as well as for fabrication of polymer or polymer composite solar cells. Several factors decrease the potential efficiency of existing solar cells. Electron-hole recombination proves to be a major impediment to solar cell efficiency. As the technology exists today, most photon-excited electrons produced in the cell are lost as they quickly recombine with electron “holes” also created during the photoexcitation. The best way to minimize this effect is to increase the surface area of the pn junction such that electrons and holes flow in opposite directions across the barrier fast enough that recombination is minimized. Polymer photocells would offer a less expensive and easily fabricated version of a traditional solar cell, but as it stands currently conversion efficiencies are only now reaching 3% [49].

Conjugated polymer systems are being studied for use in photovoltaic applications [50-53]. In this type of a solar cell, usually two types of semiconducting polymers – electron donating and electron withdrawing - are incorporated to replace the semiconducting film. Several factors must be improved to reach beyond the current 3% efficiency for polymer based solar cells. Lower band-gap polymers are needed to capture more photons from solar energy and also a higher charge/carrier mobility, more efficient exciton dissociation, and reduced electron/hole recombination. Some new lower bandwidth polymers are being studied now [54]. In order to optimize these new polymer based photocells, a fundamental understanding of all aspects of the semiconducting polymer/copolymer/polymer blend films is necessary. Typically, the way polymer films are used in this manner is a homopolymer blend or block copolymer is spin cast onto a hole collector plate. A collector grid is deposited on top and the solar cell works as normal. The difference in the most promising “bulk heterojunction” polymer based solar cells is the fact that there is no bilayer of n- and p-type semiconductor material. Instead, the polymer blend is forced to separate forming an
interconnected morphology. This can increase the efficiency of the cell orders of magnitude due to the huge increase in the surface area of the heterojunction [49]. As mentioned before, this increase in the surface area of the pn junction can help minimize electron-hole recombination. Arguably, the most tunable of polymer systems utilizes copolymers, whose highly controllable morphologies can form naturally bicontinuous interconnecting structures. It is likely that semiconducting block copolymer films will play an important role in developing efficient polymer-based solar cells. Unlike spin coated homopolymer blends, films of block copolymers form highly reproducible, highly tunable morphologies. The characteristics of the heterojunction interface is so important for these applications that some research is gearing toward studying the exact effects of morphology on the electrical properties of these types of films [55-57]. See section 4.3 for a detailed investigation of tethered copolymer film morphologies using grafted copolymer gradients.

1.3.2 Selected Applications in Responsive/”Smart” Surfaces

There is little argument that surfaces and interfaces play a very important role in the performance of many materials in all different areas of technology. Friction, shear, lubrication, abrasion, wetting, adhesion, adsorption, biocompatibility, and fouling properties are all important issues dealing directly with surfaces. Due to the increasing need for surfaces with dual, often opposite, properties (acidic/basic, hydrophilic/hydrophobic, adhesive/repellant, conductive/insulating) a current approach is to fabricate and study materials with properties that change due to external stimuli, so-called “smart” surfaces.

One major area in this field of responsive surfaces is fabrication of polymer and copolymer brushes as coatings. Polymer brushes can be readily attached to a variety of
surfaces and can be tailored to meet any of the dualistic criteria above. Poly(2-hydroxyethyl methacrylate) (PHEMA) as well as polysiloxane have been studied as surface responsive homopolymers [58, 59]. PHEMA begins with a relatively hydrophobic surface and becomes hydrophilic when exposed to water as the hydrophilic alcohol groups reorient to contact the water. Most homopolymers exhibit some degree of responsiveness but there are many ways to broaden the responsive nature of brushes. One method is to use end-group modification. Low energy fluorinated end-groups have been studied on a variety of different polymers as a way to create adaptive surfaces [60, 61]. These studies show an abundance of fluorine at the surface when the polymer layers are exposed to air causing hydrophobicity. These same surfaces demonstrated some rearrangement upon exposure to saturated water vapor. The location of functionalities along the chain backbone has also been shown to be important. A study by O’Rourke-Muisener et al. [62] using self-consistent mean field (SCF) theory determined that the optimal distribution of groups to provide surface segregation was to have similar functionalized units grouped sequentially on a chain. Surface segregation was always best when two functional groups of like character were next to each other as opposed to two of opposite character. It was concluded that low surface energy releasing polymers were conveniently formed when adjacent low energy functionalities were present at one end of the polymer chain, high energy adhesive surfaces were best formed when high energy functionalities were placed adjacently in the middle of the chain.

Block copolymers offer additional tailorability in that they can form a myriad of rearrangeable morphologies. Amphiphilic block copolymers (polymers composed of hydrophobic and hydrophilic blocks) have been shown to exhibit surface rearrangement [63-65]. At equilibrium in air, these block copolymers rearrange thus hiding the hydrophilic
block beneath the surface. Upon exposure to water, channels open up and allow contact with the underlying hydrophilic block. Russell adequately comments that this system could easily be used as a time-release drug delivery mechanism [2]. Combining clever placement of specific functionalities along the chain, choosing a polymer backbone that is flexible or rigid, introducing sidechains of specific functionality, and creating blocky or random copolymers, polymers provide unique flexible-property materials for responsive surfaces.

1.4 Combinatorial Science and Gradients

1.4.1 Importance of Combinatorial Methods in Research

Traditional “one-sample” preparation and characterization has been and is now the primary tool by which experimental scientists explore the properties of different materials. A great deal of time is spent simply preparing each sample when essentially only one data point for each type of characteristic being tested is generated. A significant number of data points must usually be taken before trends are identified and the researcher can begin to calculate or guess what must be varied in the future to optimize sample characteristics. Also, simple unavoidable environmental variances between sample preparations can introduce considerable error. A better answer to sample preparation may be found with combinatorial methods. Combinatorial methods are being applied in catalysis [66-69], drug discovery [70-74], fuel cell applications [75-80] polymer science [75-80], organic light emitting diode (OLED) screening[81], and many other fields. The efficiency and practicality of these methods have produced many new combinations of materials yielding optimized properties. Characterization of new polymeric materials is driven by their applications in structural materials, packaging, microelectronics, coatings, bioengineering, and nanotechnology. Many
variables and properties (i.e. monomers used, degree of polymerization, block polymer composition, and annealing conditions) that combine to make unique polymer materials make traditional characterization extremely slow and cumbersome. Combinatorial methods offer ways to circumvent these difficulties simultaneously. Using combinatorial methods polymer materials with broad ranges of properties may be simultaneously synthesized and tested making characterization of these materials much more efficient and accurate.

Typically, discrete arrays are employed in combinatorial methods. Arrays are prepared by systematically varying composition of small sample points down rows and columns along a single sample tray or surface. This way, with rows and columns, two variables (polymer type, polymer fraction, temperature, thickness, etc) may be simultaneously varied. Alternatively, gradients may be prepared with continuously varying characteristics. A few particular characteristics of gradients allow them to be more advantageous than simple arrays. While arrays allow many different polymer materials to be synthesized at once, they are not continuous and therefore do not allow for screening of polymer materials with the maximum resolution of the surface. The resolution of arrays is directly dependent on how many rows and columns of sample points you prepare. A gradient prepared in a similar arrangement will contain all possible combinations of two variables between finite boundaries of the variables. In many instances gradients are more easily prepared than arrays since preparation of arrays usually requires machinery to distribute exact quantities of materials to be tested. In conclusion, continuous gradients offer a simple, convenient, and powerful way to screen materials for a variety of technologies. In this
dissertation, methodologies and techniques for preparation and characterization of polymer gradient assemblies will be described.
1.5 References


Figure 1.1  Schematic illustrating the formation of surface end-anchored polymer assemblies by utilizing the “grafting to” and “grafting from” methods. Cartoon resembles extended “brush” conformation, however, “grafting onto” can produce much less dense polymer grafts.

Figure 1.2  Schematic representation of surface-anchored polymers in brush (left) and mushroom (middle) conformations in good solvents. Also shown is the conformation of surface-tethered polymer under poor solvent conditions.
Figure 1.3 - Some polymer architectures formed via ATRP
Figure 1.4 – Typical example of an Organic Light Emitting Diode (OLED). Organic layer is excited by hole/electron recombination driven by the voltage across the layer.

Figure 1.5 – Typical Photoelectric Cell. Electron donating (N-si) and electron withdrawing (P-si) layers may be replaced with donor/acceptor copolymer layers to create organic polymer-based photocells.
Chapter 2: A Review of Surface-Grafted Macromolecular Gradients

2.1 Introduction

Gradient surfaces offer powerful avenues enabling systematic variation of one or more brush properties. Employing a gradient surface to study a complex, multivariate phenomenon enables unambiguous interpretation of the system’s response to a given stimulus. Since all other properties of the system remain constant, the system’s response can be unequivocally attributed to the gradually changing surface property along the gradient. Additionally, gradient surfaces offer combinatorial platforms for quick and inexpensive investigation of the multivariate phenomenon [1, 2]. Similar study by traditional methods typically requires preparation of numerous samples, ostensibly under similar experimental conditions. Various types of surface-grafted polymer gradients are illustrated in Figure 2.1 (homopolymer gradients) and Figure 2.2 (copolymer, mixed polymer gradients). These can be gradients in polymer chain length, grafting density, composition (lateral as well as transverse) or a combination of any of these parameters. These polymer gradients not only work as combinatorial substrates for investigation of a complex phenomenon but they also serve as soft-matter templates, thus allowing fabrication of gradient assemblies of non-polymeric objects. From a materials point of view, polymer gradients offer a unique material platform wherein physico-chemical characteristics such as wetting, or chemical composition change gradually, typically over a broad range of properties. Such surfaces with unidirectional variation of material properties may be useful in directing motion of liquid
droplets or nano-objects thus acting as a molecular motor. Some of these applications are addressed in greater detail towards the end of this chapter.

While the field of surface-bound polymer gradients is still in its nascent stages, it has a great potential for further exploration. Accordingly, the goal of this review is to familiarize the reader with existing methodologies that enable the formation and characterization of surface-attached polymer gradients, with an emphasis on their utility to study complex phenomena. Specifically, we will elaborate on the role of gradient structures in advancing basic knowledge of polymer behavior in confined spaces as well as fabricating functional devices. We restrict the review to polymer gradients that are chemically bound to a substrate. Although industrially relevant, we will not venture into the area of gradient polymer coatings that lack a chemical bond between polymer chains and substrate [1, 2].

2.2. Review of techniques of preparation and characterization of polymer gradients

Although a multitude of methodologies exist for the creation of gradient assemblies of short organic modifiers [3], relatively few techniques are available for generating gradients of surface-bound polymers. Most of them rely on selective physical or chemical ”cure” of surfaces before or during growth/attachment of polymer. These treatments include creation of density gradient of surface sites used for adsorbing or growing polymers, gradual immersion or withdrawal of a substrate from a polymerization solution, regulation of radiation intensity during photoimmobilization, exposing substrate to temperature gradient etc. A brief review of these strategies is presented below.
2.2.1 Surface-grafted polymers through corona treatment

In this technique, radio-frequency corona discharge treatment was first used to create oxygen-rich moieties on a polyethylene (PE) substrate [4, 5]. The density of these moieties on PE sheet was varied by continuously increasing the power of the corona discharge from a knife-type electrode as the substrate was gradually exposed to the electrode. PE substrate was then dipped in monomer solution maintained at an elevated temperature. At this temperature, oxygen-rich moieties on the surface decomposed into free radicals, which served as initiators for “grafting from” polymerization. The density gradient of oxygen-rich moieties on the substrate thus resulted in density gradient of grown polymers. Typical monomers used were acrylic acid, sodium p-styrene sulfonate, and N,N-dimethylaminopropyl acrylamide. These gradients were employed to investigate the effect of wettability, functional group density and charge on protein adsorption and cell growth on these surfaces [4, 5]. Although this technique was successful in creating density gradients of functional groups, no information about the molecular parameters of these surface-bound gradients, such as N or $\sigma$, was provided.

2.2.2 Polymer Gradients prepared by the “grafting onto” technique

As mentioned previously, the “grafting onto” method involves the preparation of substrate-bound polymers wherein pre-formed polymer chains are simply attached to the substrate through a chemical reaction between a functional group on the substrate and a
functional group (typically end-group) on the polymer. Lee and coworkers prepared grafting
density gradients of comb-like poly(ethylene glycol) (PEG) on PE substrate (cf. figure 2.3)
[6, 7]. To achieve this, the researchers first subjected PE sheet to a corona discharge
treatment, with the corona power increasing gradually along the length of the sheet. As
mentioned in section 2.2.1, this type of corona treatment produces a density gradient of
oxygen-rich moieties on PE surface. At elevated temperatures, these moieties served as
binding sites for the attachment of poly(ethylene glycol) methacrylate (PEG-MA) chains.
Immersion of a PE sheet with a continuous gradient in binding sites in a solution of PEG-MA
maintained at high temperature resulted in the formation of grafted polymers with a gradient
in grafting density of chains. In PEG-MA gradient, the chain length of PEG-MA remained
presumably constant along the substrate; only the density of chains varied. Since PEG is
well known for its protein-resistant nature, Lee et al. used the PEG-comb gradients to study
plasma protein and platelet adsorption. They found that as the surface density of PEG chains
increased, protein and cell adsorption decreased [6, 7] and the surfaces became more non-
fouling. Major advantages of their gradient approach were that it reduced the number of
experiments as well as the methodological error associated with those experiments.

Ionov et al. employed temperature gradient to create grafting density gradient of
surface-attached polymer chains (cf. Figure 2.4, left) [8]. For this purpose, they first either
dip-coated a silica wafer with a thin layer of poly(glycidyl methacrylate) or attached a
monolayer of epoxy silane, which served as an anchoring layer for further attachment of
polymer chains. A layer of end-functionalized polymer was spin-coated on top of the
anchoring layer and the whole assembly was heated above the glass transition temperature of
spin-cast polymer. The substrate was kept on a heating stage with a temperature gradient
along the length of the stage. Temperature was varied from a few degrees below glass transition temperature ($T_g$) to tens of degrees above $T_g$. Due to the temperature-dependent grafting kinetics, the extent of grafting of polymer chains at a given point on the surface depended on the temperature prevailing at that point. Consequently, the temperature gradient along the substrate was translated into grafting density gradient of anchored chains. The right portion of Figure 2.4 shows that the amount of polymer attached increases as grafting temperature increases along the substrate. The gradient also displayed a continuous change in morphology (cf. Figure 2.4, left part) and wetting properties.

Recently, Ionov and coworkers used their gradient formation technique to form a mixed brush grafting density gradient [9]. In this assembly, gradients of two different polymers run counter to each other, i.e., grafting density of one polymer increases in one direction along the substrate whereas that of the other decreases, and vice versa (cf. Figure 2.2b). To create such a two-component polymer gradient assembly, the authors first formed a gradient of poly(tert-butyl acrylate) (PtBA) according to technique described in above paragraph. This gradient was then “backfilled” by poly(2-vinyl pyridine) (P2VP) by utilizing the same procedure as was used for grafting the first polymer. The resultant structure comprised a mixed polymer brush gradient with a constant thickness and a variable concentration of the PtBA and P2VP grafted polymers (cf. Figure 2.5). After converting PtBA into poly(acrylic acid) (PAA), the wettabilities along the substrate were shown to switch from hydrophilic to hydrophobic upon varying pH (cf. Figure 2.6).
2.2.3 Gradients prepared by the “grafting from” technique

The “grafting from” method generates surface-bound polymers with a high grafting density due to the minimal diffusion resistance offered to monomer molecules as the polymerization proceeds on the surface. For a given polymer molecular weight ($M_n$), higher grafting density of polymers grafted to a surface increases the thickness ($h$) of the resulting film, $h=\sigma M_n/(\rho N_A)$, where $M_n$ and $\rho$ are molecular weight and density of polymer, respectively, and $N_A$ is Avogadro's number. Such thick and dense coatings are useful in a number of applications, such as etch-barrier material in photolithography. Although a large variety of polymerization reactions can be used to grow polymers from surface bound initiators, controlled/“living” polymerizations are preferred because: (1) they retain the simplicity of the radical reactions while producing nearly monodisperse polymers due to fast initiation and minimal termination, (2) high molecular weight polymers can be routinely synthesized due to the controlled nature of the polymerization, and (3) they potentially allow for tailoring the chain microstructure (linear, grafted, star, and others) and facilitate the synthesis of block copolymers. The controlled polymerization techniques that have been applied to create surface-grafted polymer assemblies include [10]: living anionic polymerization [11, 12], living cationic polymerization [13], living ring opening polymerization [14-16], ring opening metathesis polymerization [17, 18], living radical polymerization, mainly nitroxide mediated polymerization [19], reversible addition-fragmentation chain transfer polymerization, [20] and atom transfer radical polymerization (ATRP) [21, 22]. Of all these techniques, ATRP has emerged as a robust and versatile polymerization technique capable of synthesizing a large range of functional polymers on a variety of surfaces [23-26]. With the discovery of ATRP as a controlled/”living” radical
polymerization technique, the interest in the field of surface-initiated polymerization has shown a dramatic surge. This is predominantly due to the ease with which ATRP can be carried out on surfaces. Unlike ionic polymerizations, ATRP is not as demanding with regard to monomer and solvent purity, the presence of moisture and oxygen, etc. A large number of functional monomers that do not undergo ionic polymerization, such as water-soluble monomers, can be easily polymerized by ATRP [23, 24, 27, 28]. ATRP is especially powerful in synthesizing polymers with novel topologies, composition profiles, and functionalities on flat as well as curved semiconductor, metal, polymer surfaces (cf. Figure 2.7).

Our group has used ATRP extensively to synthesize a variety of “grafted from” polymer gradients. These include gradients in (1) grafting density of polymer chains, (2) polymer molecular weight, (3) polymer chain composition, and (4) a combination of these gradients. While these gradients are schematically illustrated in Figures 2.1 and 2.2, their synthesis, characterization and applications are described in detail later in this chapter and in chapter 3.

2.2.4 Miscellaneous methods for immobilizing polymers in gradient pattern

Recently, a few novel approaches involving the formation of gradient grafted polymer assemblies have emerged. For example, Ito and coworkers used a photomask with a gradient pattern to selectively immobilize a biomolecule – epidermal growth factor (EGF) - on a polystyrene tissue culture plate [29]. Specifically, they coated a polystyrene substrate with polyallylamine-tagged EGF and exposed the coating to ultraviolet rays through the gradient
photomask. Grafting of EGF took place only on those parts of the substrate that were
exposed to UV rays. The EFG gradient pattern was visualized by immunostaining with anti-
EGF antibody. The EGF gradient facilitated quantitative evaluation of cell growth as a
function of the concentration of immobilized biomolecule. In a similar study, a
thermoreponsive polymer was attached to a polystyrene substrate using the gradient
micropattern [30]. This gradient was employed to examine the effect of concentration of
immobilized thermoresponsive polymer and temperature on the adhesion of fibroblast cells.
Hu and coworkers used laser activation to generate a microscale gradient of a protein tagged
to a photoactive cross-linking agent [31]. For this purpose, they rastered the laser beam over
a protein-coated surface at progressively faster speeds, thereby varying the laser exposure
time across the length of the sample. Since the immobilization of protein on the surface was
proportional to the laser exposure time, the raster pattern of the beam produced a gradient
pattern of immobilized protein.

2.2.5 Gradient graft copolymers

Graft copolymers are systems, in which one type of polymer (say A) is grafted
chemically to the backbone of another polymer (say B). The grafting density of A is dictated
by the distribution of the grafting sites along B; these can be perfectly ordered or “perfectly
random”. Alternatively, there may be a gradient in the density of the grafting sites along B.
Growth of polymer A from the backbone having gradient in grafting sites results in the
formation of gradient graft copolymers. Synthesis of such copolymers with gradients in the
grafting density of A has recently been reported by the Matyjaszewski group [32].
Copolymers with composition gradient are needed as precursors for the synthesis of gradient graft copolymers. In the composition gradient copolymer the local concentration of one monomer unit along the polymer backbone varies continuously from one end of the chain to the other (cf. Figure 2.7) [33, 34]. As far as the sequence of the two co-monomers along the backbone is concerned, the gradient composition copolymers can be considered to be intermediate between random and block copolymers. This sequence distribution along the backbone can result either from the differences in the reactivity ratios of the two monomers (spontaneous gradient) or from different rates of addition of the two monomers in the reaction vessel (forced gradient). The reactivity ratio is defined as the ratio of the rate constant of homo-propagation (i.e., tendency of active species to react with species of its own kind) to that of cross-propagation (i.e., predisposition of a monomer species to react with species of other kind in preference to species of its kind). When one monomer tends to homo-propagate but the other prefers to cross-propagate, the resulting copolymer is a gradient composition copolymer, where the two ends of the polymer are enriched with two monomers and the middle part of the polymer has a composition gradient. The compositional breadth of such spontaneous gradient is determined by the reactivity ratios of the two monomers. To create a forced composition gradient copolymer, the feed rates of one or both monomers are varied either continuously or periodically throughout the course of the reaction. The width of the gradient is predominantly determined by the differences in the feed rates of the two monomers. Properties of the gradient copolymers are significantly different from those of random or block copolymers [34]. Thus a judicious choice of the two co-monomers and their feed rates can result in the formation of a gradient copolymer having much improved properties compared to the two parent polymers. These gradient copolymers
are envisaged to be useful as polymer blend compatibilizers, pressure sensitive adhesives and as novel materials for vibration and noise dampening [35, 36].

As mentioned above, copolymers with compositional gradient can serve as precursors for generating gradient graft copolymers, where the number of side chains attached to the polymer backbone gradually decreases from one end of the backbone to the other [32]. Börner et al. synthesized such gradients according to the scheme shown in Figure 2.8. First, Börner and coworkers created a forced compositional gradient along the backbone by continuously adding one monomer in the reaction vessel while the other monomer is steadily consumed. One of the two monomers along the backbone then served as an initiator for growing side chains made of a third monomer. Since the backbone itself had a concentration gradient, the grafted copolymer showed a continuous change in side chain grafting density. Such grafted copolymer gradient brushes are highly anisotropic with a bulky head and a thin tail. For further details, reader is referred to excellent review articles by Matyjaszewski and coworkers dealing with the synthesis of gradient copolymers by controlled radical polymerization techniques [35, 36].

2.2.6 Methods of characterizing gradient properties

Characterization of gradient substrates involves determining the same physico-chemical characteristics as those measured on “conventional” non-gradient specimens. Since the physico-chemical characteristics of gradient samples vary laterally, a judicious choice of a technique is required. Such a choice is governed by the interplay among: 1) the lateral resolution of a given technique, 2) the lateral scanning ability of the technique, and 3) the
distance on the surface over which the gradient is present (gradient steepness). Only techniques in which the lateral resolution is better than the gradient steepness can be utilized. Depending on the lateral scanning ability of a given technique vis-à-vis gradient steepness, one can distinguish between two modes of operation. If the lateral scanning ability of the technique is comparable to or slightly larger than the gradient steepness, information content about the gradient substrate can be accessed in a single measurement. We refer to such a mode as “global”. If, however, the probe’s lateral scanning ability is much smaller than the distance over which the gradient exists, one has to repeat the measurement on various portions of the substrate along the gradient in order to fully characterize the specimen. We call this a “local” mode. In order to illustrate the difference between the two modes let us consider using chemical force microscopy (CFM) [37]. CFM measures the forces between the surface and a chemical moiety, such as end-functionalized alkanethiol, that has been covalently attached to the probing tip. Considering that the largest scanning area accessible with a single CFM measurement is ≈125 x 125 μm², CFM can be used as a “global” technique on gradient samples whose gradient steepness is equal to or smaller than ≈125 x 125 μm². If the gradient variation occurs over much larger lateral distance on the substrate, multiple individual measurements with CFM have to be carried out at various positions on the substrate in order to characterize the entire specimen. In the latter case, CFM operates in the “local” mode. The following paragraphs offer a brief overview of several “local” techniques that have been utilized to characterize polymer gradients. Some of the most important properties of polymer gradients that need to be characterized are wettability, chemical composition, thickness of the surface layer, and morphology.
Static or dynamic contact angle measurements are the easiest and most widely available methods of determining wettability [38]. In static contact angle experiments, one measures the wetting angle of a small volume of probing liquid on the surface. The typical area on the surface probed by contact angle techniques ranges from hundreds of square micrometers to square millimeters. On homogeneous surfaces, contact angle measurements are typically performed under the conditions where the needle and the probing liquid are not separated. This allows for determining the so-called advancing and receding contact angles. However, contact angle measurements on wettability gradients are usually performed such that the needle is in contact with the probing liquid, so that the droplet does not move towards the more wettable region on the substrate. Separating the needle from the liquid would allow the liquid to move on the surface (see [38]), particularly in gradients with steep boundaries between the hydrophobic and hydrophilic regions. The dynamic contact angle (DCA) measurements are usually performed using the Wilhelmy plate. Examples of the DCA measurements on gradient substrates can be found elsewhere [39]. While useful in providing macroscopic level information about the chemistry on the gradient surfaces, contact angle methods are not capable of delivering information about the structural properties of the gradients on a molecular level (such as concentration of a particular chemical group, orientation of molecules, etc).

For acquiring molecular-level information, one has to turn to more sophisticated probes. Ruardy and coworkers discuss the utilization of x-ray photoelectron spectroscopy (XPS) [40] and infrared spectroscopy (IR) for determining concentration of a particular species along molecular gradients [39, 41]. Recently, near-edge x-ray absorption fine structure (NEXAFS) spectroscopy [41] has emerged as a powerful tool for characterizing
gradients [42, 43], because it allows for simultaneous investigation of both the surface chemistry and the molecular orientation. NEXAFS involves the resonant soft X-ray excitation of a K or L shell electron to an unoccupied low-lying antibonding molecular orbital of $\sigma$ or $\pi$ symmetry, $\sigma^*$ and $\pi^*$, respectively. The initial state K or L shell excitation gives NEXAFS its element specificity, while the final-state unoccupied molecular orbitals provide NEXAFS with its bonding or chemical selectivity. A measurement of the intensity of NEXAFS spectral features enables the identification of chemical bonds and determination of their relative population density within the sample. Because of the fixed geometry between the sample and the X-ray beam and the fact that the $1s \rightarrow \sigma^*$ and $1s \rightarrow \pi^*$ excitations are governed by dipole selection rules, the resonance intensities vary as a function of the direction of the electric vector $\mathbf{E}$ of the incident polarized X-ray relative to the axis of the $\sigma^*$ and $\pi^*$ orbitals. This, coupled with the fact that sharp core level excitations for elements C, N, O, and F occur in the soft X-ray spectral region, makes NEXAFS an ideal technique for probing molecular orientations of organic molecules.

Spectroscopic ellipsometry (SE) is the most commonly employed technique to determine thickness of the polymer layer in a gradient sample. SE relates thickness of the film to the change in the polarization state of light incident on the film. Specifically, SE measures two values, $\Delta$ and $\Psi$, which describe the polarization change in the sample and which are related to the ratio of Fresnel reflection coefficients, $R_p$ and $R_s$ for p- and s-polarized light, respectively. $\Delta$ and $\Psi$ profiles as functions of wavelength of light are used to obtain film thickness by performing fitting to the $\Delta$ and $\Psi$ data. The lateral variation of polymer thickness along the gradient is measured by taking SE scans on various parts of the specimen.
While not described in this review, there are several novel experimental probes that may be applied in the near future to characterize gradient substrates with a high lateral resolution (ranging from tens of square nanometers to square micrometers). These include the scanning near-field optical microscopy (SNOM) [44], imaging ellipsometry [45], imaging IR, imaging XPS [46], X-ray photo emission electron microscopy (X-PEEM) [46].

2.3 Anchored polymers with grafting density gradients

In the following sections we will describe recent research efforts in the Genzer group in the area of gradient polymer assemblies. For clarity, the chemical formulas of the polymers used in our experiments are shown in Figure 2.9. Surface-anchored polymers with a grafting density gradient represent macromolecular systems, in which the number of polymers per unit area of the surface changes gradually as a function of the position on the surface. Figure 2.10 depicts the technological steps leading to the formation of surface-bound polymer assemblies with gradients in grafting density. These structures can be prepared by first generating a concentration gradient of the polymerization initiator on the surface, followed by the “grafting from” polymerization [47].

2.3.1 Formation and properties of the Gradient Initiator

We formed gradients of polymerization initiator on flat silica substrates using the methodology proposed by Chaudhury and Whitesides [48] (cf. Figure 2.10a). Specifically, 1-trichlorosilyl-2-(m/p-chloromethylphenyl) ethane (CMPE) was mixed with paraffin oil
(PO) and the mixture was placed in an open container that was positioned close to an edge of a silicon wafer. As CMPE evaporated, it diffused in the vapor phase and generated a concentration gradient along the silica substrate. Upon impinging on the substrate, the CMPE molecules reacted with the substrate -OH functionalities and formed a SAM. The breadth and position of the CMPE molecular gradient can be tuned by adjusting the CMPE diffusion time and the flux of the CMPE molecules. The latter can be conveniently adjusted by varying the chlorosilane:PO ratio and the temperature of the CMPE:PO mixture. In order to minimize any physisorption of monomer and/or the polymer formed in solution on the parts of the substrate that do not contain the CMPE-SAM, we backfilled the unexposed regions on the substrate (containing unreacted -OH functionalities) with n-octyltrichlorosilane, (OTS). After the OTS-SAM deposition, any physisorbed CMPE and OTS molecules were removed by thoroughly washing the substrates with warm deionized (DI) water (75°C, resistivity>16 MΩ m) for several minutes.

Near-edge x-ray absorption fine structure (NEXAFS) spectroscopy was used to provide detailed chemical and structural information about the SAMs on the substrate [1][49]. The NEXAFS spectra were collected in the partial electron yield (PEY) at the normal (θ=90°), grazing (θ=20°), and so-called “magic” angle (θ=55°) incidence geometries, where θ is the angle between the sample normal and the polarization vector of the x-ray beam. In Figure 2.11 we plot the carbon edge K-edge PEY NEXAFS spectra taken from the CMPE-SAM (top) and OTS-SAM (bottom) samples. The NEXAFS spectra collected at the “magic” angle were indistinguishable from those recorded at the normal and grazing incidence geometries, revealing that the CMPE-SAMs are not oriented, rather they formed a “liquid-like” structure. This observation is in accord with recent studies from Chaudhury and
Allara groups who studied the transition between the “liquid-like” and “semi-crystalline-like” structures in hydrocarbon SAMs [50, 51]. The NEXAFS spectra in figure 2.11 both contain peaks at 286.0 and 288.5 eV that correspond to the 1s→σ* transition for the C-H and C-C bonds, respectively. In addition, the spectrum of CMPE also exhibits a very strong signal at 284.2 eV, which can be attributed to the 1s→π* transition for phenyl C=C*. The latter signal can thus be used as an unambiguous signature of CMPE in the sample. With the x-ray monochromator set to 284.2 eV, we collected the PEY NEXAFS signal by rastering the x-ray beam across the gradient. The lines in Figure 2.12 depict the variation of the PEY NEXAFS intensity measured at 284.2 eV across the gradient samples prepared by diffusing CMPE for 2 minutes from mixtures with various CMPE:PO ratios equal to 1:1 (solid line), 1:2 (dashed line), 1:5 (dotted line), and 1:10 (dash-dotted line). For clarity, we refer to such substrates as S1, S2, S5, and S10, respectively. The data in Figure 2.12 reveal that the PEY NEXAFS intensity from the C=C phenyl bond, and thus the concentration of CMPE in the sample, decreases as one moves from the CMPE side of the sample towards the OTS-SAM; the functional form closely resembles that of a diffusion-like profile. Experiments using spectroscopic ellipsometry (SE) confirmed that only a single monolayer was formed along the substrate.

2.3.2 “Grafting from” on the gradient initiator surfaces

The polymerization of poly(acryl amide) (PAAm) was performed by atom transfer radial polymerization (ATRP), as described earlier [52-54]. In addition, PAAm brushes were grown on silica gels using the procedure outlined by Huang and Wirth [52]. The PAAm
polymers were grown and purified using the same conditions as were used for growing polymer on flat silica wafers. The PAAm chains were then cleaved from the silica support and their molecular weight was measured using size exclusion chromatography ($M_w = 17$ kDa, polydispersity index = 1.7).

2.3.3 Properties of grafted polymer layers

SE was used to measure the thickness of the dry polymer film, $h$, as a function of the position on the substrate. In Figure 2.13 the values of $h$ for samples prepared on the (a) S1 (open squares), (b) S2 (open circles), and (c) S5 (open triangles) substrates are plotted. From Figure 2.13, $h$ decreases gradually as one moves across the substrate starting at the CMPE edge. Note the agreement between the variation of $h$ and the concentration profiles of the CMPE initiator (solid lines). Because the polymers grafted on the substrate all have roughly the same degree of polymerization (see discussion below), the variation of the polymer film thickness can be attributed to the difference in the density of the CMPE grafting points on the substrate. The polymer grafting density can be calculated from $\sigma = h \rho N_A/M_n$, where $\rho$ is the density of PAAm ($=1.302$ g/cm$^3$).

The substrates with the grafted PAAm were placed into a solution cell that was filled with DI water (pH 7), a good solvent for PAAm, and incubated for at least 5 h. The thickness of PAAm grafted polymer in DI water (“wet thickness”), $H$, was measured using SE. The data in Figure 2.13 indicate that for all samples H decreases as one traverses across the substrate stating at the CMPE side. The maximum brush height at the CMPE edge of the sample decreases with decreasing CMPE concentration on the substrate (S1 > S2 > S5).
In Figure 2.14 we plot the wet polymer thickness as a function of the PAAm grafting density on the substrate for all three samples, S1, S2 and S5. The data reveal that at low $\sigma$, $H$ is independent of the grafting density. Hence the chains are in the mushroom regime. At higher polymer grafting densities, $H$ increases with increasing $\sigma$, indicating the brush behavior. The crossover between the two regimes occurs at $\sigma \approx 0.065 \ \text{nm}^{-2}$. By fitting the data in the brush regime to $H \sim N\sigma^n$ we obtain $n$ equal to $0.37\pm0.04$ (S1), $0.39\pm0.05$ (S2), and $0.40\pm0.06$ (S5). We note that $n$ obtained by fitting the experimental data is slightly higher that the predicted value of $n=1/3$; this observation is in agreement with recent reports [55]. A remark has to be made about the possible variation of the chain length with grafting density. Jones and coworkers recently reported on studies of grafting from polymerization of poly(methyl methacrylate) using ATRP from substrates having various surface densities of the polymerization initiator, $\omega$-mercaptoundecyl bromoisobutyrate [56]. Their study revealed that the grafting density of the polymer depends on the grafting density of the initiator. However, based on the data presented, it is difficult to discern whether the kinetics of the polymerization also depends on the grafting density of the initiator. Currently we have no means of measuring the molecular weight of the grafted brushes directly on the gradient substrate. While we cannot exclude the possibility that the length PAAm chains polymerized on the various parts of the molecular gradient substrate varies with $\sigma$, we note that the fact that the curves in Figure 2.14 superimpose on a single master curve indicates that the polymers have likely very similar lengths, which is not surprising for the rather short anchored polymers synthesized in this work.

In addition to the measurement of the wet brush thickness, we have also performed wettability experiments as a function of the PAAm grafting density on the substrate [57].
Our aim was to corroborate the ellipsometric data and provide more insight into the polymer packing in the surface grafting density gradient. In Figure 2.15 we plot the dry PAAm thickness, \( h \), (closed symbols) and the contact angles of DI water, \( \theta_{\text{DIW}} \), (open symbols) as a function of the position on the substrate for samples prepared on the S1 (squares) and S5 (triangles) substrates. In both samples, the dry thickness of PAAm decreases gradually as one moves across the substrate starting at the CMPE edge. The \( \theta_{\text{DIW}} \) values increase as one traverses across the substrate stating at the CMPE side. The increase in \( \theta_{\text{DIW}} \) is not monotonous, it follows a “double S”-type shape. While the “double S”-type dependence of \( \theta_{\text{DIW}} \) on the position on the sample is detected in both S1 and S5 samples, there are differences in the plateau values. Specifically, while for the S1 sample, the three plateaus are located at \( \theta_{\text{DIW}} \approx 40^\circ, \approx 83^\circ, \text{ and } \approx 100^\circ \) the corresponding values for the S5 sample are \( \theta_{\text{DIW}} \approx 47^\circ, \approx 70^\circ, \text{ and } \approx 97^\circ \). Based on the dry thickness data and our previous discussion, the three plateaus in the contact angle behavior can be attributed to the wetting characteristics inside the brush, mushroom, and OTS (no PAAm) regions. At distances far away from the CMPE edge, where the \( \theta_{\text{DIW}} \) values are high, there is no grafted PAAm on the sample. The contact angle experiments detect the presence of the OTS monolayer. By moving closer towards the CMPE edge, the contact angles decrease by \( \approx 20-30^\circ \) indicating that some polymers are present on the substrate. However, their grafting densities are low so that the probing liquid can penetrate between the grafted chains; the measured contact angles represent a weighted average between the PAAm and OTS. Upon approaching the mushroom-to-brush transition region, the contact angle further decreases. The decrease is steeper for PAAm on the S1 substrate and more gradual for the S5 sample, indicating that the density of PAAm increases more rapidly in the former case. The contact angles in the lowest
plateau are $\theta_{\text{DIW}} \approx 40^\circ$ and $\approx 47^\circ$ for samples S1 and S5, respectively. In independent experiments, we have established that the $\theta_{\text{DIW}}$ of a pure PAAm is $\approx 35-38^\circ$ [2]. Because in both cases the PAAm polymers grafted on the substrate have roughly the same degree of polymerization, the variation of the polymer film thickness can be attributed to the difference in the density of the CMPE grafting points on the substrate. Specifically, close to the CMPE edge, the PAAm macromolecules form a dense brush on the S1 substrate and a “semi-dense” brush on the S5 substrate.

The previous discussion revealed that $\theta_{\text{DIW}}$ depends on the grafting density of the PAAm chains on the substrate. Earlier we have shown that the wet thickness of PAAm prepared on substrates with various CMPE concentrations can be collapsed on a single master curve when plotted as $H$ vs. $\sigma$. One would also expect that the wettabilities of the substrates plotted versus the PAAm grafting density should exhibit similar universal behavior. In Figure 2.16 we plot the negative cosine of $\theta_{\text{DIW}}$ as a function of the grafting density of PAAm on substrates S1 (squares) and S5 (triangles). As anticipated, the data collapse on a single master curve. A close inspection of the results present in Figure 2.16 shows that the data can be divided into three distinct regions. For $\sigma>0.1$ nm$^{-2}$, the chains are expected to be in a brush regime – the wettabilities are close to the pure PAAm ($-\cos(\theta_{\text{DIW}}) \approx -0.79$). For $\sigma<0.02$ nm$^{-2}$ the PAAm chains form mushroom conformations on the substrate. In this regime, the wettabilities change slightly because the distance between the chains also changes, although they are already loosely separated on the substrate. At grafting densities $0.02$ nm$^{-2}<\sigma<0.1$ nm$^{-2}$, the slope of $-\cos(\theta_{\text{DIW}})$ changes rather rapidly. The data in Figure 2.16 show that the position of the mushroom-to-brush crossover determined using the
wettability approach is in accord with the ellipsometric measurements (the transition location was established to be at $\sigma \approx 0.065 \text{ nm}^{-2}$). However, in the former case, the transition region extends over almost one order of magnitude in $\sigma$, which is broader, as expected [58-61], than the transition region predicted by the $H$ vs. $\sigma$ data. We speculate that the small difference between the widths of the mushroom-to-brush region inferred from both types of experiments is likely associated with the inaccuracy in $H$, which was obtained indirectly by the model fitting of the SE data.

2.3.4 Anchored polymers with molecular weight gradients

In addition to the polymer grafting density, polymer molecular weight is another important molecular parameter that profoundly influences the properties of surface-anchored polymers. As discussed earlier, the thickness of the grafted polymer layer is proportional to the degree of polymerization of the anchored polymer. For some applications to be discussed subsequently in this review, it would be convenient to have samples with anchored polymers having variable degrees of polymerization. We have recently designed a few methodologies leading to the preparation of surface-anchored polymers with a variable degree of polymerization. The preparation techniques and subsequent study of these structures constitute the major trust of my research and will be discussed in depth in chapters 3 and 4.
2.4 References


49. In *The NEXAFS experiments were carried out on the U7A NIST/Dow Materials Soft X-ray Materials Characterization Facility at the National Syncrotron Light Source at Brookhaven National Laboratory.*


Figure 2.1 - Schematic illustrating a) conformations of surface-anchored polymers, and polymer brush assemblies with a b) grafting density gradient, and c) a gradient in polymer length. Part d) depicts polymer conformations on a substrate comprising grafting density and polymer length orthogonal gradients.

Figure 2.2 - Schematic illustrating a) conformations of grafted homopolymer brushes made of two chemically distinct polymers and diblock copolymers, b) mixed homopolymer brushes with gradually changing grafting densities, c) grafted diblock copolymers with a constant length and gradually changing composition, and d) grafted diblock
Figure 2.3 Schematic diagram showing comb-like poly(ethylene oxide) gradient produced on polymer surface. [Reproduced with permission from B.J. Jeong et al, J. Colloid Interface Sci. 178, 757 (1996)]

Figure 2.4 (left) Preparation of ultrathin tethered polymer layers with gradually changing thickness by utilizing a “grafting to” approach using a temperature gradient created on a heating stage. (right) Grafted amount of carboxylic acid-terminated polystyrene (PS-COOH) film grafted through (open circles) 3-glycidoxypropyl trimethoxysilane (GPS, annealing time=4 hrs), (closed circles) poly(glycidyl methacrylate) (PGMA, annealing time=4 hrs), and (closed triangles) PGMA (annealing time=12 hrs) anchoring layers. [Reproduced with permission from L. Ioniv et al, Macromol. Rapid Commun. 25, 360 (2004)].
Figure 2.5 Ellipsometric mapping of PBA/P2VP gradient brush, total thickness (■), PtBA layer (●), P2VP layer (△). (b) Fraction of PtBA versus the point coordinate on the sample [Reproduced with permission from the American Chemical Society].

Figure 2.6 Contact angle at different pH: 2.2 (■), 2.54 (●), 3.24 (○), 4.95 (□), 9.95 (▲) of PAA/P2VP brush vs. composition [Reproduced with permission from the American Chemical Society].
Figure 2.7  Schematic representation of controlled topologies, compositions, and functionalities and molecular composites prepared by atom transfer radical polymerization (ATRP). [Reproduced with permission from K. Matyjaszewski and J. Xia, *Chem. Rev.* **101**, 2921 (2001)]
Figure 2.8  Subsequent synthesis of the macroinitiator precursor (I), the macroinitiator (II) amd macromolecular brush copolymer (III). [Reproduced with permission from H.G. Börner et al, *Macromolecules* 35, 3387 (2002)]
Figure 2.9  Chemical formulas of poly(acrylamide) (PAAm), poly(methyl methacrylate) (PMMA), poly(2-hydroxyethyl methacrylate) (PHEMA), poly(β-butyl acrylate) (PtBA), and poly(acrylic acid) (PAA), and poly(dimethyl aminoethyl methacrylate) (PDMAEMA).
Figure 2.10  Methods of preparing surface-grafted polymer assemblies with gradients in grafting density.  a) ATRP initiator gradient on a solid substrate is formed by mixing 1-trichlorosilyl-2-(m-p-chloromethylphenyl) ethane (CMPE) with paraffin oil (PO) and placing the mixture in an open container heated at 88°C close to an edge of a silicon wafer.  As CMPE evaporates, it diffuses in the vapor phase and generates a concentration gradient along the silica substrate.  Upon impinging on the substrate, the CMPE molecules react with the substrate -OH functionalities and form a self-assembled monolayer (SAM).  In order to minimize any physisorption of monomer and/or the polymer formed in solution on the parts of the substrate that do not contain the CMPE-SAM, the unexposed regions on the substrate containing unreacted –OH functionalities are backfilled with n-octyl trichlorosilane, (OTS).  After the OTS-SAM deposition, any physisorbed CMPE and OTS molecules are removed by thoroughly washing the substrates with warm deionized water (75°C, >16 MΩ cm) for several minutes.  b) Surface-grafted polymer assemblies are formed on the substrates by using “grafting from” ATRP.  a) Schematic illustrating polymer conformations in the mushroom (height $H_m$) and brush (height $H_b$) regimes and the mushroom-to-brush transition.
Figure 2.11 Carbon K-edge Partial electron yield (PEY) NEXAFS spectra collected from the CMPE-SAM (top) and OTS-SAM (bottom). The arrow marks the position of the $1s \rightarrow \pi^*$ transition for phenyl C=C, present only in the CMPE-SAM sample. [Reproduced with permission from T. Wu et al, Macromolecules 36, 2448 (2003)]

Figure 2.12 Partial electron yield (PEY) NEXAFS intensity measured at $E=284.2 \text{ eV}$ as a function of the position the substrates containing the initiator gradients made of CMPE:PO mixtures (w/w) 1:1 (solid line), 1:2 (dashed line), 1:5 (dotted line), and 1:10 (dash-dotted line).
Figure 2.13  Dry thickness, $h$, (open symbols) and wet thickness, $H$, (closed symbols) of poly(acryl amide) (PAAm) and the 1-trichlorosilyl-2-(m-p-chloromethylphenyl) ethane (CMPE) concentration (solid line) as a function of the position on the substrate for samples prepared on substrates containing the initiator gradients made of CMPE:PO mixtures (w/w) a) 1:1 ($\square$, ■), b) 1:2 ($\bigcirc$, ○), and c) 1:5 ($\triangle$, ▲). [Reproduced with permission from T. Wu et al, Macromolecules 36, 2448 (2003)]
Figure 2.14  Wet thickness of PAAm as a function of the poly(acryl amide) (PAAm) grafting density for samples prepared on substrates containing the initiator gradients made of CMPE:PO mixtures (w/w) 1:1 (■), 1:2 (●), 1:5 (▲). The inset shows a cartoon illustrating the polymer behavior. [Reproduced with permission from T. Wu et al, Macromolecules 36, 2448 (2003)]
Figure 2.15  Dry thickness of poly(acryl amide) (PAAm), $h$, (closed symbols) and contact angle of DI water, $\theta_{\text{DIW}}$, (open symbols) as a function of the position on the substrate for samples prepared on substrates containing the initiator gradients made of CMPE:PO mixtures (w/w) 1:1 a) (□, ■) and b) 1:5 (△, ▲). The contact angle data have an error better than ±1.5 deg and ±1 mm on the vertical and horizontal scales, respectively. [Reproduced with permission from T. Wu et al, *Macromolecules* **36**, 2448 (2003)]
Figure 2.16 - Negative cosine of the contact angle of DI water as a function of the poly(acryl amide) (PAAm) grafting density on the substrate for samples prepared on substrates containing the initiator gradients made of CMPE:PO mixtures (w/w) 1:1 (□) and 1:5 (△). The lines are meant to guide the eyes.
Chapter 3: Methods, Procedure, & Equipment in Production of Surface-Grafted Macromolecular Gradients

3.1 Project Goals and Motivation

As discussed in Chapter 2, gradients represent a powerful way to systematically vary one or more properties in surface-grafted polymers. Employing a gradient surface to study a complex, multivariate phenomenon enables unambiguous interpretation of the system’s response to a given stimulus. Since all other properties of the system remain constant, the system’s response can be unequivocally attributed to the gradually changing surface property along the gradient. Additionally, gradient surfaces offer combinatorial platforms for quick and inexpensive investigation of the multivariate phenomenon. Similar study by traditional methods typically requires preparation of numerous samples under similar experimental conditions.

Realizing the importance of this combinatorial method of study in polymer science, I sought to gear my project to create these structures and study their properties in application to several projects from polymer physics and chemistry. My project goals were as follows: (1) To devise a method to synthesize surface-grafted homopolymer molecular weight gradients, (2) to expand this method to preparation of multiple monomers and block copolymers, and (3) to demonstrate the ability of these structures to study complex phenomena involving surface-grafted polymers.
3.2 Initiator Deposition, Characterization, and Growing Brushes

For growth of “grafted from” polymer brushes, several things must be accomplished: (1) choosing the surface/substrate for polymer brush growth, (2) synthesizing the polymer-compatible initiator to begin polymerization, (3) tethering the initiator molecule to the substrate, and (4) growth of the polymer brush. A flat silicon substrate covered with a thin layer of its native oxide (silica, SiO$_x$) was used in our experiments. This substrate can be easily functionalized by depositing chloro- or alkoxysilane based self-assembled monolayers (SAMs). Silicon is also amenable to IR spectroscopy, ellipsometry, and contact angle measurements making initial characterization quick and easy. The task of synthesizing and attaching an initiator was the next big step to take. A synthesis scheme was adopted to make a bromoisobutyric-terminated 15-carbon tricholorsilane \[ \text{[1]} \]. This particular molecule [(11-(2-bromo-2-methyl)propionyloxy) undecyltrichlorosilane] (heretofore known as BMPUS) reacts with the surface of a UVO-treated silicon wafer in a dilute anhydrous toluene solution at –10°C overnight. When used in previous papers, this initiator was deposited at 25°C. A lower deposition temperature seemed to produce a better monolayer. Our experiments at 25°C show a slow formation of the initiator layer, which does not reach thicknesses achieved at -10°C even after 18 hours (cf. figure 3.1). Also, subsequent detachment of tethered polymers occurred with samples made from 25°C deposition. Experiments using near-edge x-ray absorption fine structure spectroscopy (NEXAFS) revealed that the lower deposition temperature produced a nicely organized and densely packed monolayer[2]. The ellipsometric thickness after 18 hrs was about 19 Å, a value expected of a well-organized monolayer of this type. The BMPUS molecules were previously shown to initiate the growth of polystyrene (PS), and poly-\textit{tert}-butyl acrylate (PTBA) [1]. Similar bromopropionic-
terminated initiators have also been used to synthesize brushes of poly(methyl methacrylate) (PMMA), polyacrylamide (PAAm), poly(2-hydroxyethyl methacrylate) (PHEMA) [3, 4].

This initiator system was used to synthesize PMMA from silicon wafers by utilizing the “grafting from” methodology. In our polymerization we adopted aqueous/methanol based ATRP, which was previously used to synthesize acrylates and methacrylates [5-10]. The grown polymer is very soluble in its own monomer. According to Jones and Huck, the polymerization media should comprise approximately 50% monomer, 10% water (high dielectric), and 40% methanol (water monomer compatibilizer) [11, 12]. We modified this system to make it more controllable by adding 2-20% CuCl, the deactivator for ATRP (see chapter 1, sec 1.2). This concentration was found to produce a homogeneous system that dissolves PMMA. The polymerization rate and polydispersity index can be changed by simply varying the CuCl/CuCl\textsubscript{2} ratio. After the halogen exchange equilibrium is established, the polymerization rate increases linearly with the CuCl/CuCl\textsubscript{2} ratio (figure 3.2). At low growth rates the growing chain spends most of its time in the dormant state. Hence, the ATRP mechanism is better controlled and the chain polydispersity is relatively low (below 1.10). In addition to the CuCl/CuCl\textsubscript{2} ratio, the type of solvent(s) used also influences the polymerization. Higher dielectric solvents (like water, methanol, and acetone) tend to increase the rate of reaction. This is thought to result from an increase in solubility and activity of the metal/ligand complex.
3.3 The Evolution of the Gradient Chamber

3.3.1 1st and 2nd Generation Exhaust Gradient Chamber

After proving that the initiator formed a well-ordered monolayer and could grow polymers via ATRP, the next step was to build an apparatus that would allow us to form polymer molecular weight gradients. The apparatus was designed based on the initial thought that we could “dip” the wafer slowly into the polymerization media. Since we are using controlled/”living” polymerization, the polymer growth (in molecular weight and thickness) would be linear with time. The time of initiation would, however, change according to the length down the wafer. Assuming a constant rate of dipping, the dry length profile of the polymer layer would increase linearly down the wafer. This concept was put aside and replaced with a very similar notion based on withdrawal of the polymerization media at a constant rate. This “exhaust” method works in a similar manner, hence changing the time of reaction termination rather than initiation time. This exhaustive chamber would prove to be less costly and time-consuming than the dipping chamber. We were successful in creating molecular weight gradients as we had proposed. The full apparatus is shown in cartoon form and actual form below (figures 3.3 & 3.4).

This glass chamber was fabricated with the ability to be purged with nitrogen and sealed prior to use. It also contained an output valve connected to a variable-rate peristaltic pump. The wafer was suspended in a special holder under the purged nitrogen environment in the main chamber. The custom-designed polymerization chamber is charged with a solution comprising 37.45 g of monomer, 25.5 g of methanol (MeOH), 7.0 g of deionized water (DIW), 2.33 g of bipyridine (BiPy), 0.66 g of CuCl and CuCl₂ (usually varying between 1/5 to 1/30 molar amount relative to CuCl). To commence a gradient experiment
the wafer is immersed into the media following the pump being turn on. This causes the solution level to decrease along the wafer and creates a gradient structure along the wafer surface. The actual gradient structures formed using this apparatus will be discussed later in this chapter.

This polymerization chamber was proven to produce gradient structures in a very reproducible manner, but not without a couple of drawbacks. The amount of polymerization media required for each run was also maintained at a minimum (<100ml). After several successful trials using a variety of monomer systems, however, the drawbacks of our first chamber became apparent. The first of two major drawbacks was that this chamber had no easy way to control the temperature of the polymerization media. In normal polymerization procedures a temperature bath would be used to maintain a certain temperature of the media. Most polymerizations have a marked temperature dependency, as does ATRP, in which changing temperature will affect the rate of radical transfer as well as the chemical equilibria associated with the metal/ligand catalyst. This chamber was designed to operate at room temperature and therefore suffered only minor temperature fluctuations. However, many other monomer systems require higher temperatures to reach appreciable rates of polymerization. The second drawback to this first chamber was that the sample width was limited to 1 cm. As will become apparent later in this study, it became necessary to produce samples wider than 1 cm in order to generate so-called orthogonal gradient specimens. We identified these new requirements and proceeded to design a second chamber.

The second chamber required a slightly more complex design in order to incorporate temperature control and larger sample sizes. The new design (figure 3.5) consisted of a larger main chamber that required a solution volume that was more than 250 ml. A
temperature control jacket was constructed around the main chamber to allow for accurate temperature control from approximately 10ºC to over 60ºC. Several complex gradient structures, also to be discussed later, were formed using this chamber.

As successful as the evolution of the exhaustive chambers was, we recognized that some limitations needed to be addressed. The first concern was the meniscus effect due to wettability at the substrate/solution/gas interface. As a polymer layer formed the surface wettability at the wafer/solution interface often changed quite dramatically. Since the wafer was immersed into the monomer solution described above, the beginning contact angle was an advancing contact angle with the surface. As the run progressed, the solution level decreased and the contact angle became a receding contact angle. Especially in the case of more hydrophilic monomers, the advancing to receding contact angle often changed as much as 40 degrees or more. This induced a lag time in the beginning of the run as the low-wettability monolayer was reacted away and a higher energy polymer brush surface arose. Depending on how fast the solution level was being exhausted, this could produce erroneous data for a large portion of the initial polymerization time.

The second concern involved the reluctance of more hydrophilic monomers to dewet from the surface as the solution level decreased. Monomer solution could sometimes be seen adhering to the surface long after the solution level had receded. This created an unknown error in the actual polymerization time relative to the surface. In addition, as the monomer solution dewetted, there were often deposits left from the drying monomer/catalyst solution. This, in itself, did not seem to affect the gradient or efficiency of the macroinitiator layer to grow a second block. The presence of the deposits, however, required that we wash the surface thoroughly and, at times, sonicate the layer to remove dried copper catalyst. We
found it necessary to minimize the treatment of the macroinitiator layer if we wished to produce a second block, otherwise, some inefficient initiation and, presumably, dead macroinitiator chains were produced.

Lastly, experimental runs tended to be somewhat complex and time-consuming, which often caused considerable experimental error. Solvent effects on the pump tubing for different monomers, changing tubes, and tube degeneration combined to make a pumping rate calibration nearly impossible over long-term use. Run times had to be monitored from start to finish to capture the exact endpoint of the reaction (while the end of the wafer was still in solution). When preparing diblock copolymer gradients (described in chapter 4), the chamber had to be cleaned, dried, and a new monomer solution had to be prepared for each block. Run times, not including solution preparation and purging, tended to range from 4 to 20 hours.

3.3.2 1st Generation Dipping Gradient Chamber

The success of our first two designs urged us to revisit the original idea of a “dipping” chamber. By creating a dipping chamber many of the aforementioned concerns from the exhaustive chambers could be avoided. The dipping chamber (figure 3.6) was designed to provide the same benefits of temperature control and large sample size as the second exhaustive chamber. The sample is held by a Teflon® clip on the end of a steel rod. The steel rod is attached to a screw drive, which is turned by a stepper motor. The stepper motor/screw drive assembly was calibrated to raise and lower the sample holder at precise intervals. The stepper motor was controlled through a programmed motor controller connected to a PC with programmable software. The full range of motion of the sample
holder allows for a sample up to approximately 8 cm to be completely immersed into a solution contained in a beaker within the carousel. The sample may also be withdrawn into a Teflon® cylinder above the carousel without removing the wafer from the inert environment. The carousel, with six beaker holders, was built inside the main chamber. The beaker carousel and the screw drive can be controlled by the same software. The chamber is fitted with a purge inlet to allow a flow of nitrogen to purge the inner chamber for 1 hour prior to each experimental run. A micro-hotplate was built directly into the chamber base and connected to a temperature controller so that the temperature may be kept constant for each solution. Temperature can be monitored with a thermocouple probe entering the Teflon® cylinder, which is immersed in the beaker solution when the cylinder is lowered. The setup is completely automated so that each experimental run may be programmed ahead of time and the wetted sample is never exposed to the outside oxygenated atmosphere. Exact rates of dipping/withdrawing can be programmed into the controller allowing for precise relation between the grown thickness and immersion time.

3.4 Formation and Characterization of Polymer Brushes with Molecular Weight Gradients

3.4.1 Kinetics of Surface-Confined Polymerizations

The solution “exhaust” apparatus was first used to grow gradients of PMMA, PHEMA, and PAAm brushes. BMPUS SAMs deposited onto flat silicon wafers were used to grow PMMA and PHEMA gradients in a controlled manner. While PAAm was also
grown, the polymerization proceeded in a non-linear fashion indicating a lack of well-controlled ATRP (Figure 3.7). We suspect that, under the conditions used, the growing PAAm chains tended towards radical coupling or irreversible halogen acceptance and grew uncontrolled to the point of termination. Other research has also concluded that the growth of PAAm is typically uncontrolled yielding high polydispersity polymers with loss of living character [13-17]. Despite the nonlinear growth of PAAm, gradients prepared under the same conditions yielded consistent results. Using two PAAm gradients grown under similar polymerization conditions but different solution exhaust speeds, we were able to show the utility of the gradient chamber to tune the PAAm layer thickness while still keeping an accurate record of thickness vs. polymerization time (figure 3.8). PMMA, PHEMA, and PAAm could all be polymerized to brushes in aqueous media. The growth of each type of polymer is fast enough to produce several tens of nanometers thick layers of polymer on a silicon surface within a few hours. Inspection of the ellipsometric length profiles of these gradients reveals their character whether controlled or not. For a given polymer grafting density ($\sigma$), the dry thickness ($h$) is proportional to the molecular weight of the grafted polymer, $h=\sigma M_n/(\rho N_A)$, where $M_n$ and $\rho$ are molecular weight and density of polymer, respectively, and $N_A$ is Avogadro's number. Having established this, we can see that the growth rate of PAAm (cf. figure 3.8) is non-linear with time. In contrast to PAAm, PMMA growth is highly linear for even very high CuCl/CuCl$_2$ ratios (figure 3.9). PHEMA also grows almost linearly with a slight leveling off at thicknesses greater than 50 nm. The latter effect has been reported earlier in literature for PHEMA brushes and is thought to occur due to interactions of the alcohol group in PHEMA with the catalyst [4]. Regardless of the non-linear profile, PHEMA ATRP is known to remain well-controlled [18, 19].
The aqueous PMMA polymerization was studied in greater detail due to the fact that the system represents an ideal polymerization set-up being both controlled and living. A silicon wafer (≈1x5 cm) was first covered with a BMPUS SAM, which served as an initiator for the ATRP. Experiments using variable angle spectroscopic ellipsometry (VASE, J.A. Woollam, Co.) confirmed that only a monolayer of BMPUS was formed on the substrate and that the BMPUS molecules were homogeneously distributed on the substrate. The polymerization of MMA was carried out at room temperature using 32.7 g of MMA, 25.5 g of methanol (MeOH), 7.0 g of deionized water, 2.06 g of bipyridine (BiPy), 0.66 g of CuCl and 0.04 g of CuCl$_2$. Tubing, attached at the bottom of the chamber, is connected to a micropump, which controls the solution flow rate removal from the chamber. Figure 3.9 shows the dry thickness of PMMA (measured by VASE) as a function of the position on the substrate. The inset shows the dependence of the dry PMMA thickness on the polymerization time. The data in the inset demonstrate that the brush thickness increases linearly with polymerization time, which concurs with previous reports [20, 21]. We tested the effect of varying the volumetric flow of the drained solution on the polymer properties along the substrate. The arrows in Figure 3.9 mark the instances where the solution removal speed was reduced. As apparent from the data in Figure 3.9, changing the draining rate of the solution from the chamber does not affect the polymerization rate (defined as the slope of the dry polymer thickness vs. polymerization time, see discussion below) but influences the “steepness” of the gradient.

Figure 3.10 depicts the dry PMMA thickness as a function of the polymerization time for various CuCl$_2$/CuCl ratios. In this set of experiments we used the same quantities of the
MMA, MeOH, H$_2$O, BiPy and CuCl and varied the amount of CuCl$_2$. The results in Figure 3.10 reveal that the dry thickness of the surface-anchored PMMA increases linearly with increasing polymerization time. Moreover, this increase is more rapid for smaller CuCl$_2$/CuCl ratios. This finding is not that surprising given the nature of the reaction. The key reaction in ATRP is the reversible activation-deactivation process using metal (M)/ligand (L) complexes.[21]

$$P-X + M^I/X/2L \rightleftharpoons P^* + M^{II}X_2/2L,$$  \hspace{1cm} (3.1)

where $k_a$ and $k_d$ are the rate constants for activation (forward reaction), and deactivation (reverse reaction), respectively, M is usually Cu, and X is Cl or Br. The propagating radical, $P^*$, produced by the halogen atom transfer from P-X to the $M^I/X/2L$ complex, will undergo polymerization until it is deactivated by the $M^{II}X_2/2L$ complex. The quick speed of the activation-deactivation cycles compared to rate of polymerization and the low concentration of the active species (relative to the P-X ones) results in polymers with narrow polydispersities. MCl$_2$ may be added to the reaction mixture to regulate the reaction rate and chain polydispersity. The combinatorial design of our system is conveniently suited for such studies because it allows for complete probing of the anchored polymer properties and studying the polymerization kinetics in confined geometries.

More insight into the ATRP polymerization on solid substrates can be obtained by evaluating the polymerization rate as a function of the CuCl$_2$/CuCl ratio. Matyjaszewski and coworkers established that the rate of ATRP polymerization, $R_p$, is given by Eq. 3.2, [21, 22]

$$R_p = k_p \frac{k_a}{k_d} [PMMACl][MMA][CuCl] \frac{[CuCl]}{[CuCl_2]}$$  \hspace{1cm} (3.2)
where \( k_p \) is the rate constant for propagation, \([\text{PMMA-Cl}]\) is the concentration of the growing ends of the grafted polymer, \([\text{MMA}]\) is the concentration of the free monomer in the solution, and \([\text{CuCl}]\) and \([\text{CuCl}_2]\) are the concentrations of CuCl and CuCl\(_2\), respectively. The dry thickness of PMMA on the substrate, \( h \), is related to the polymer molecular weight, \( M_{\text{PMMA}} \), through Eq. 3.3,

\[
h = M_{\text{PMMA}} \frac{\sigma}{\rho_{\text{PMMA}} N_A}
\]  

(3.3)

where \( \sigma \) is the polymer grafting density, \( \rho_{\text{PMMA}} \) is the PMMA density, and \( N_A \) is the Avogadro’s number. Recognizing that \( R_p \sim \frac{dh}{dt} \) and lumping the terms that stay constant during the polymerization, one arrives at Eq. 3.4,

\[
\frac{dh}{dt} \sim \left( \frac{[\text{Cu}^{(II)}\text{Cl}]}{[\text{Cu}^{(I)}]} \right)^{-1}
\]

(3.4)

Figure 3.11 depicts the \( \frac{dh}{dt} \) obtained by fitting the dry thickness vs. polymerization time data (\textit{cf.} Figure 3.10) as a function of the CuCl\(_2\)/CuCl ratio. By placing the data on a line on a logarithmic scale (figure 3.11) we obtain a relationship between \( \frac{dh}{dt} \) and CuCl\(_2\)/CuCl. The slope approaches \(-1\), predicted by the scaling argument presented in Eq. 3.4, only in the mid CuCl\(_2\) concentrations, corresponding to the CuCl/CuCl\(_2\) ratios ranging from 5-30. The growth rate at both higher and lower CuCl\(_2\) concentrations is less than expected from the linear prediction in the mid regions. There are two likely explanations for this effect. First, at higher CuCl\(_2\) concentrations the increased amount of CuCl\(_2\), having a more positive chelating center than CuCl, can reduce the effectiveness of the in solution ligand to bind and
solubilize the activating CuCl species. Second, in the regions of low CuCl₂, the reaction can become highly uncontrolled causing irreversible termination. Both of these facts cause an apparent lowering of thickness growth kinetics. While the former effect leads to a slower growth in the molecular weight vs. time, the latter effect causes early irreversible termination lowering the total grafting density of active chains. Additionally, the scaling argument shown in Eq. 3.4 is derived from the ATRP rate of polymerization that has been derived for bulk polymerization and does not take into account any constraints due to confinement effects.

Final estimation of the growth kinetics of PMMA in aqueous methanol media results in Eq. 3.5.

\[
\log(R_g) = -\log(\text{CuII/CuI}) - 1.66
\]  

(3.5)

\(\text{CuII/CuI} = \text{molar copper ratio}\)

\(R_g = \text{growth rate in Å/min}\)

<table>
<thead>
<tr>
<th>Polymerization Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>MMA</td>
<td>50.0ml (0.467mol)</td>
</tr>
<tr>
<td>Methanol</td>
<td>46.0ml (1.136mol)</td>
</tr>
<tr>
<td>Water</td>
<td>10.0ml (0.555mol)</td>
</tr>
<tr>
<td>Bipyridine</td>
<td>3.0g (1.92×10⁻³ mol)</td>
</tr>
<tr>
<td>CuCl + CuCl₂ = BPY/2</td>
<td>9.6×10⁻³ mol</td>
</tr>
<tr>
<td>CuCl / CuCl₂ =</td>
<td>5-30</td>
</tr>
<tr>
<td>Temp =</td>
<td>25°C</td>
</tr>
</tbody>
</table>

Similar polymerization rate analysis was carried out for PHEMA brushes. In Figure 3.12 we plot the time-dependent dry thickness of PHEMA for four different CuCl₂/CuCl concentrations. In Figure 3.13 we present the polymerization rate as a function of the CuCl₂/CuCl ratio. The data in Figure 3.13 reveals that similar to the PHEMA case,
growth rate of PHEMA brushes in aqueous/methanol media deviates from the theoretical prediction.

\[ \log(R_g) = -1.26 \log(CuII/CuI) - 1.37 \]  

\( CuII/CuI = \text{molar copper ratio} \)

\( R_g = \text{growth rate in Å/min} \)

<table>
<thead>
<tr>
<th>Polymerization Parameters</th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>HEMA = 50.0ml (0.412mol)</td>
<td></td>
</tr>
<tr>
<td>Methanol = 46.0ml (1.136mol)</td>
<td></td>
</tr>
<tr>
<td>Water = 10.0ml (0.555mol)</td>
<td></td>
</tr>
<tr>
<td>Bipyridine = 3.0g (1.92x10^-2 moles)</td>
<td></td>
</tr>
<tr>
<td>( \text{CuCl} + \text{CuCl}_2 = \text{BPY}/2 = 9.6x10^{-3} \text{ mol} )</td>
<td></td>
</tr>
<tr>
<td>( \text{CuCl} / \text{CuCl}_2 = 5-30 )</td>
<td></td>
</tr>
<tr>
<td>Temp = 25ºC</td>
<td></td>
</tr>
</tbody>
</table>

3.4.2 Macroinitiator Reinitiation Efficiency Studies

Several factors can limit the reinitiation efficiency when trying to grow multiple blocks on a surface. The most obvious potential difficulty is the fact that each sample is usually taken out of solution, rinsed, and dried after each block formation. From our experiments, we know that the macroinitiator is quite stable in solution throughout the polymerization. However the exact effect of rinsing and drying (which collapses the brush) between each block formation is unknown. The flexibility and control that the 1st generation dipping apparatus provides a way to easily study this phenomenon.

In order to study the reinitiation efficiency of a PMMA homopolymer brush on flat substrates, a 1 cm x 5 cm silicon wafer covered with the BMPUS initiator was loaded vertically into the dipper chamber with a PMMA polymerization solution. The wafer was dipped in the ATRP media for a controlled period of time in order to grow a PMMA block.
After polymerization, the wafer was removed from the monomer solution and thoroughly rinsed and dried. Repeating these two steps, while dipping the wafer 1 less centimeter for each repetition, produced multiple PMMA thickness “steps” on the same wafer as seen in Figure 3.14. The reinitiation efficiency of the PMMA could be determined by measuring the thickness via VASE and calculating the growth rate of each layer. By plotting the step heights as a function of the total immersion time (= total polymerization time) we conclude that the PMMA growth is highly linear (figure 3.15). The PMMA growth rate (cf. Figure 3.16) determined from each polymerization step is approximately equal, indicating that that length of the macroinitiator does not influence the rate of polymerization.

3.4.3 Added deactivator(AD) vs. Sacrificial Initiator(SI) in Control of ATRP

Since the inception of ATRP as a means to produce well-controlled polymers of low polydispersity, many studies have been done using this system. Most research utilizes a SI to produce the controllability of the reaction. In most cases we utilize AD without SI and our reasoning will become apparent in this section. In a SI system, activator (i.e. CuCl, CuBr), ligand (i.e. BPY, PMDETA, HMTETA), monomer, and solvents are used along with an amount of in-solution initiator (usually equal molar amount to activator), which serves two purposes. First, some of the in-solution initiator initiates polymer chain growth to produce polymer (eq. 3.8). Second, some of the in-solution initiator irreversibly self terminates with other initiator radicals thereby leaving the same molar amounts of deactivator, which serves to give the reaction the controlled/”living” characteristics found in ATRP. This method relies on the ability of the initiator to quickly establish enough deactivator in solution to give a controlled polymerization.
\[
I-X + M^I X/2L \leftrightarrow I^* + M^{II} X_2/2L \quad (3.7)
\]
\[
I^* + M \rightarrow P^* \quad (3.8)
\]
\[
I^* + I^* \rightarrow I \quad (3.9)
\]

In fact, it has become a common practice in determining whether or not a given initiator/metal halide/ligand/monomer/solvent system is well controlled, to simply add SI in equal molar amounts to the activator, grow polymer, and measure molecular weight and polydispersity. This method, having many advantages, does have its shortcomings in that it may overlook some ATRP systems which may be well-controlled with an AD system. Also, the in-solution initiator must be added in a fairly large amount. This may, in some instances, cause polymer chain termination and lead to high PDI polymer. I will discuss an example of such a system in section 3.4.3.3 on ATRP simulations.

Our choice of primarily using an AD (CuCl₂) recipe for our surface-confined polymerizations gives several advantages over the sacrificial initiator method. First, we do not have to thoroughly extract/sonicate our samples after growth to remove adsorbed polymer. In the case of SI systems a lot of in-solution polymer is produced in the process. This polymer tends to adsorb to the surface and can even interfere with the surface polymerization. Second, the surface growth in the AD system is always linear. Only a small fraction of monomer (enough to produce a few nanometers of surface polymer) is actually used up in the polymerization process, therefore the monomer concentration remains constant. This is not the case with SI systems as monomer is slowly used up in the process. Third, in SI systems there will always be a maximum molecular weight – usually less than
30k- that may be reached via a controlled/”living” process. This is due to the fact that a fairly large amount of in-solution initiator is required to produce the necessary deactivator. The molecular weight of the polymer in solution and on the surface will be limited by the ratio of initiator to monomer. In an ideal system the final degree of polymerization at 100% conversion would be equal to the ratio of the monomer to the initiator. In AD systems much higher molecular weight polymers may be synthesized without losing the controlled/”living” character.

3.4.3.1 Gradient Study of Surface Growth Kinetics with SI for Control

In order to study the kinetics, growth, and controlled/”living” character of surface tethered PMMA using a SI system instead of the AD, we designed a simple gradient experiment that would illustrate these characteristics. This experiment truly exhibits the ability of surface-tethered polymer gradients to study time-dependent surface polymerization. A solution was prepared using a modified recipe of the one found in section 3.4.1. In this modified recipe, the CuCl\(_2\) was left out and a molar amount of ethyl-2-bromoisobutyrate (EBiB) equal to the CuCl was added after the run was started. A 1cm x 7cm wafer was prepared with a BMPUS monolayer. The run was started by dipping the wafer into the solution at a constant rate. After the wafer was immersed ½ cm into the solution, the EBiB was added. The surface polymerization continued for 90 minutes. As a result, a nonlinear gradient of PMMA was formed on the wafer surface (figure 3.17). The run was quenched by adding excess CuCl\(_2\) at 90 minutes. The wafer was rinsed, dried, and the layer was measured using a VASE ellipsometer. The wafer was then placed back into an AD MMA solution to reinitiate and polymerize a second layer. The percent growth of the second layer was
measured with respect to the growth at the end of the wafer exhibiting only the BMPUS monolayer (assumed to be 100%). Changes in the percent growth along the gradient could only be due to termination of the macroinitiators via polymer-polymer terminations or polymer-initiator terminations.

Results from the second layer growth indicate that the percent of macroinitiators, relative to 100% at the BMPUS monolayer, decrease linearly from 100% to 55% as the wafer stays immersed in the solution (figure 3.18). The gradient wafer also indicates a leveling off of the second layer growth on the section of the wafer representing surface initiation prior to the addition of the EBiB in-solution initiator. This is significant because it indicates that the primary mode of macroinitiator termination is by polymer-initiator termination rather than by polymer-polymer terminations. We can deduce that, due to polymer-initiator termination, it is likely that this aqueous methanol SI system would produce polymer (in-solution and tethered) with a fairly high PDI.

3.4.3.2 GPC data confirming low PDI in-solution polymer from added CuCl₂ systems

It was necessary for us to determine the degree to which our AD system was controlled, thus we made several runs to test the PDI as a function of added CuCl₂. Based on data obtained from gradient growth rates shown above, we suspected that the polymerization would be controlled when the CuCl/CuCl₂ ratio was less than 30. We had no alternative but to use a small amount of in-solution initiator, which actually made our AD system a hybrid AD/SI system. We added the SI in a molar amount that was comparable to or less than the added CuCl₂ and since only a small fraction of the initiator actually dissociates to increase
the deactivator, we assumed this quantity to be negligible. The recipe used is shown in table 3.1. The results of the runs are given in table 3.2.

We discovered that the polydispersity is fairly low for each of these runs. As expected the lowest PDI was found on the polymer with the highest deactivator concentration. The polymer produced exhibited low PDI’s in all cases, however. We were led to believe that, in the case of the lowest deactivator concentration, the in-solution initiator may have played more of a role in reducing the PDI.

3.4.3.3 Fortran ATRP simulations

ATRP is a relatively new polymerization scheme, but many groups are studying ATRP systems both experimentally and theoretically. Simulations have been useful in predicting the outcomes and mechanisms of various scenarios in ATRP. Several groups, in collaboration with Matyjaszewski, have used simulations to produce Mw vs. time data for various monomer/catalyst systems in ATRP [23, 24]. All of these models are quite similar in how they operate due to the fact that ATRP can be modeled using several fairly simple reactions and equilibria. Assumptions within these models are usually due to not having all of the parameters measured. Many groups are exploring methods to obtain kinetic parameters so that more accurate models may be produced[25-35]. The relevant equations to model a typical ATRP system, and the equations we used to produce our model, are shown below:

Initiation

\[ I_X + M^I \rightleftharpoons I^* + M^{II}X_2/2L \quad [k1/k2] \quad (3.10) \]
\[ I^* + M \rightarrow P_1 \quad [k_i] \quad (3.11) \]
Propagation

\[ P_n^* + M \rightarrow P_{n+1}^* \quad [kp] \quad (3.12) \]

\[ P_nX + M^{I}X/2L \rightleftharpoons P_n^* + M^{II}X_2/2L \quad [ka/kd] \quad (3.13) \]

Termination

\[ I^* + I^* \rightarrow I-I \quad [kiit] \quad (3.14) \]

\[ P_n^* + P_m^* \rightarrow P_{n+m}^* \quad [kt] \quad (3.15) \]

\[ P_n^* + I^* \rightarrow P_nI \quad [kipt] \quad (3.16) \]

A variable step time method using Runge-Kutta algorithms was used to produce the model in Fortran. Run times were on the order of five to twenty minutes per six hours simulated polymerization time. Run times were reasonable only after transferring to Fortran and applying the variable time step and Runge-Kutta. No other simplifications were made to the equations listed above. Four simulations are discussed below. The first two compare end results obtained from PMMA polymerization using CuBr/PMDETA catalyst system initiated with EBiB initiator. The first uses a SI system in which no deactivator is added. In the second, a smaller amount of EBiB is added along with a small amount of deactivator. The last two represent a system in which a sluggish initiator is used to attempt ATRP (A benzyl-type initiator would be an example). Our results are in agreement with Zhang and coworkers [33] who have stated that a small amount of added deactivator at the beginning of a polymerization can significantly improve PDI’s. Kinetic parameters and initial values used in the initial simulation are shown in tables 3.3a and 3.3b respectively. Highlighted parameters are changed for the four simulations and discussion will follow.
Figure 3.19 shows the results from two simulations designed to model a PMMA CuBr/PMDETA system at 35°C. The data in red denotes the system with added value of in-solution SI equal in molar amount to the activator (CuBr). The data in black denotes the system with a small amount of deactivator added at the beginning of the reaction along with only 1/10 of the molar amount of SI. In both these simulations initiator equilibrium (eq. 3.10) parameters were set to be the same as the polymer equilibrium (eq. 3.13) (i.e. \( k_1/k_a = k_2/k_d = 1 \)). The data reveals a significant difference in PDI’s obtained for both systems. The polymerization is more likely to run out of control during the first few minutes until enough deactivator is formed from SI termination, thereby causing huge PDI’s early on.

Figure 3.20 shows the results from similar starting parameters designed to simulate a sluggish initiating system (i.e. phenylethyl bromide). Again the red and black denote the pure SI vs. AD systems. In these last two simulations the initiator equilibrium (eq. 3.10) parameters were set such that they would imitate a more sluggish phenylethyl bromide (i.e. \( k_1/k_a = 0.1 k_2/k_d = 4 \)). The sluggishness of the initiator causes the system to remain uncontrolled for much longer and thereby causes a much larger difference in PDI’s obtained. Whereas the AD system could be considered fairly well controlled (PDI < 1.2), the pure SI system exhibits very little control (PDI >>1.2). The results agree with the results of Zhang and coworkers [33] and may be generalized to greatly improve any ATRP process, especially those involving sluggish initiators.
3.5 Formation of Orthogonal Polymer Brush Gradients

3.5.1 Orthogonal Homopolymer Molecular Weight / Grafting Density Gradient

The concept of “Orthogonal Gradients” will be discussed in more detail in the next chapter in section 4.3. In an orthogonal gradient, two characteristics are varied simultaneously on one sample surface in orthogonal directions such that all combinations (within two specified ranges) of the two variables are created. Working with orthogonal gradient substrates not only saves time and resources but it also minimizes the systematic error associated with doing individual experiments. We have previously established that one can independently control the grafting density (σ) and molecular weight (MW) of grafted polymer brushes. These methods of forming separate gradients can be combined to form orthogonal polymer brushes in which σ and MW vary continuously along two perpendicular directions (cf. Figure 3.21).

Fabrication of a surface-grafted σ-MW orthogonal gradient entails two steps: (1) formation of concentration gradient of initiator molecules and (2) growth of surface-anchored chains with a molecular weight gradient in a direction perpendicular to that of the initiator concentration gradient (cf. Figure 3.22). To accomplish the first step we use the organosilane vapor diffusion technique described in Chapter 2. Gradient of initiator BMPUS molecules was formed by first generating a gradient of n-octyltrichlorosilane (OTS) and then “backfilling” the empty sites on the surface by BMPUS. Growing chains from such a concentration gradient of initiator results in grafting density gradient of grown brushes along the direction of initiator gradient (X-direction). In order to achieve MW gradient in a direction perpendicular to that of σ, we rotated the sample by 90° and immersed it in polymerization mixture (along Y-direction) placed in a de-aerated reaction chamber. By
continuously removing the polymerization medium from the chamber a MW gradient on the substrate was generated in the Y-direction. The MW of grafted polymer chains at various points along X-direction for a given Y should be approximately the same since all those points remain in the reaction media for the same period of time. We have succeeded in creating orthogonal gradient of grafted PHEMA using the methodology described above. In Figure 3.23 we plot the dry thickness profile of grown PHEMA in X (σ gradient) and Y (MW gradient) directions. As mentioned earlier, dry thickness of grafted polymer is given by \( h=\sigma M_n/(\rho N_A) \); thus, \( h \) depends on both MW and \( \sigma \) of the grown polymer. For a given value of Y on the sample, \( h \) increases continuously as one moves away from the OTS end along X direction. Similar trend in thickness is observed along Y direction for a given X as one moves from a region that was in the reaction media for a shorter period to a region that stayed in the mixture for longer time. These measurements indicate that orthogonal gradient was successfully formed.

3.5.2 Application of Orthogonal Homopolymer Molecular Weight / Grafting Density Gradients

This section contains descriptions of projects headed up primarily by Rajendra Bhat using developed techniques for creating molecular weight gradients described in this dissertation. For a more detailed discussion of these specific projects see the PhD dissertation and work of Rajendra Bhat.

Orthogonal gradients, when combined with a large pool of functional polymers, offer powerful combinatorial platforms for studying complex phenomena; they can be tailored to
serve as separation devices or as templates for organization of non-polymeric materials. Over the past 3 years, several efforts in the Genzer group have aimed at investigating complex problems in colloid and biomaterials science with the aid of $\sigma$-MW gradients. For example, recent work carried out in our group utilized a $\sigma$-MW combinatorial substrate to study the effect of MW and $\sigma$ on the assembly of nanoparticles on grafted polymer surfaces. Controlled fabrication of such surface-bound nanoparticles assemblies represents an important milestone along the path towards realization of the goal of nanotechnology. Orthogonal gradients formed from poly(dimethyl aminoethyl methacrylate) (PDMAEMA) were used to control the loading and spatial distribution of gold nanoparticles on surfaces [36]. The interaction between the particles and the underlying polymer was mediated via strong electrostatic interactions between negatively charged citrate groups attached to the particle and positive charges on PDMAEMA generated by lowering the solution pH to 6. We established that relatively large gold nanoparticles (diameter about 17 nm) resided on top of the PDMAEMA brushes. The concentration of nanoparticles was found to increase with increasing polymer coverage, accomplished via increasing either $\sigma$ or MW.

In another study, PHEMA $\sigma$-MW orthogonal brushes were used for protein adsorption studies. Systematic study of protein adsorption is important, as it is the first step in regulating a number of biological processes occurring around a biomaterial inserted into the body. This work was carried out by another member of the Genzer research group, Rajendra R. Bhat. The PHEMA $\sigma$-MW orthogonal gradient sample was subjected to adsorption of various proteins, including fibronectin (FN) and lysozyme. The results of the adsorption experiments revealed that the amount of protein decreased with increasing MW or $\sigma$ of PHEMA [36]. This observation is in accord with theoretical predictions and consistent
with the fact that upon increasing both MW and \( \sigma \), the fraction of the surface covered by PHEMA increases, which prevents further protein adsorption. Bhat and coworkers further utilized the density gradients of FN prepared on top of PHEMA \( \sigma \)-MW orthogonal brushes in cell culturing studies. Benefiting from the fact that FN serves as an anchor for the attachment of the osteoblastic cells though the RGD tri-peptide sequence present on the FN molecule [37], Bhat and coworkers established a correlation between the amount of FN (controlled by the PHEMA coverage) and the amount and morphology of cells [38]. Specifically, the cell density was found to decrease with increasing PHEMA coverage (decreasing amount of FN) on the surface. Cell morphology also changed as a function of the PHEMA (and hence FN) coverage. Cells attained the polygonal shape on regions of the substrate covered with large amount of FN and they elongate when there is little or no FN present. Thus, cells were better adhered to the thin PHEMA layer whereas on thicker PHEMA regions they have less traction.
3.6 References


Table 3.1 - Polymerization recipe used to test determine PDI of polymer grown from AD system.

| MMA = | 50.0ml (0.467mol) |
| Methanol = | 46.0ml (1.136mol) |
| Water = | 10.0ml (0.555mol) |
| Bipyridine = | 3.0g (1.92x10^{-2} mol) |
| EBI = | 28ul (1.9x10^{-4} mol) |
| CuCl + CuCl$_2$ = | BPY/2 = 9.6x10^{-3} mol |
| CuCl / CuCl$_2$ = | 11,62,125 |
| Temp = | 25°C |

Table 3.2 – Polydispersity from three PMMA AD runs.

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<th>CuCl/CuCl$_2$</th>
<th>$M_w$ (GPC)</th>
<th>PDI</th>
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<tr>
<td>11</td>
<td>8k</td>
<td>1.10</td>
</tr>
<tr>
<td>62</td>
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</tr>
<tr>
<td>125</td>
<td>18k</td>
<td>1.25</td>
</tr>
</tbody>
</table>

Table 3.3a: Simulation Kinetic Parameters

| $k_1^a$ = 4.3 M$^{-1}$s$^{-1}$ |
| $k_2^b$ = 4.3e7 M$^{-1}$s$^{-1}$ |
| $k_i^c$ = 438 M$^{-1}$s$^{-1}$ |
| $k_p^c$ = 438 M$^{-1}$s$^{-1}$ |
| $k_a^a$ = 4.3 M$^{-1}$s$^{-1}$ |
| $k_d^b$ = 4.3e7 M$^{-1}$s$^{-1}$ |
| $k_{ii}^d$ = 10$^8$ M$^{-1}$s$^{-1}$ |
| $k_{i}^d$ = 10$^8$ M$^{-1}$s$^{-1}$ |
| $k_{ip}^d$ = 10$^8$ M$^{-1}$s$^{-1}$ |

Table 3.3b: Simulation Initial Values

| IXo = | 0.047 |
| Mo = | 9.4 |
| CuIX = | 0.047 |
| CuIX$_2$ = | 0.0047 |


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a Pintauer, et al., Macromolecules 37,8,2679 
b Est from Keq, Zhang, et al. Macromolecules 43,18,6169 
c Matyjaszewski and Davis, “Handbook of Radical Polymerization” p.199. 
d Nikitin and Evseev, Macromol. Th. and Sim., 8,4,296
Figure 3.1 – Initiator Deposited at 25°C (■) shows steady increase but does not reach ideal thickness even after 18hr. Well ordered monolayer forms with –10°C (●) within 6hours. Conditions were 2.5μl in 20ml anhydrous toluene.

Figure 3.2 - Growth rate data for PMMA grown on silicon wafers using deposited BMPUS monolayer. Each data point is from one single sample. Trend seems linear w.r.t. Cu ratio < 30.
Figure 3.3 – 1st Generation gradient chamber with gradient sample forming.

Figure 3.4 – 1st generation gradient chamber.
Figure 3.5 – 2nd Generation exhaustive gradient chamber. Notice wider sample chamber and temperature control jacket.
Figure 3.6 – 1st Generation dipping gradient chamber. Full view of base and sample dipping tower (left). Base equipped with 4 insulated beaker holders and mini stirrer/heater for temperature control (right).

Figure 3.7 – PAAM gradient showing nonlinear behavior of PAAM growth. 3 gradients represent various amounts of CuCl2 and ligand with constant amount of CuCl.
Figure 3.8 – Two PAAM gradients formed with different pump speeds. Axes show substrate position as well as polymerization time illustrating that pumping rate does not affect apparent surface kinetics.

Figure 3.9 – Variation of pump speed changes steepness of slope in PMMA gradients. Main graph shows position on the wafer with 3 separate slopes for 3 pump speeds. Inset shows axis of polymerization time vs. thickness of same data.
Figure 3.10 – PMMA gradients showing growth rate dependence on CuCl\textsubscript{2}/CuCl ratio.

Figure 3.11 – Surface kinetics plot for PMMA growth in aqueous methanol media. MeOH : H\textsubscript{2}O : MMA : Cu : BPY (molar) = 1.0 : 0.49 : 0.41 : 0.0085 : 0.0169 T=25\degree C
Figure 3.12 – PHEMA gradients showing growth rate dependence on CuCl$_2$/CuCl ratio. Nonlinear behavior observed at low CuCl$_2$ concentrations.

Figure 3.13 - Surface kinetics plot for PHEMA growth in aqueous methanol media. Growth rate taken from most linear portion of PHEMA gradient found in the beginning of growth.

MeOH : H$_2$O : HEMA : Cu : BPY (molar) = 1.0 : 0.49 : 0.36 : 0.00828 : 0.0166

T=25ºC
Figure 3.14 – 10 step reinitiation of PMMA. Time steps are 45 min for first three steps, 90 min for next three steps, and 3 hours for last four.
Figure 3.15 – When step heights are placed on a graph relative to total immersion (polymerization) time graph is still highly linear. No effect of washing/collapsing brush apparent.

Figure 3.16 – Apparent growth rates (affected by actual growth rate and initiator efficiency) remain unchanged even after over 10 wash/dry/reinitiation cycles.
Figure 3.17 – (red) PMMA dipped gradient prepared with SI added 24 minutes into process. Time-dependent growth of PMMA observed. (green) 2nd PMMA layer grown homogeneously with normal AD system. Variance in thickness with 2nd layer assumed to be due to termination of macroinitiator.

Figure 3.18 – Percentage of chains growing as compared with growth on BMPUS monolayer. EBiB added at 24 minutes.

>24 minutes = kinetics as EBiB is reacting to create deactivator equilibrium.

0-24 minutes = uncontrolled kinetics, no AD.
Figure 3.19 – Simulation results for PMMA CuBr/PMDETA system. PDI is noticeably higher for SI system than for system with small added amount of deactivator. $k_1/k_a = 1$ ; $k_2/k_d = 1$

(SI) $M_o : Cu_I : Cu_{II} : IX_o = 200 : 1 : 0 : 1$

(SI+AD) $M_o : Cu_I : Cu_{II} : IX_o = 200 : 1 : 0.002 : 0.1$

Figure 3.20 - Simulation results for PMMA CuCl/PMDETA system using parameters for a more sluggish initiator. Difference in PDI from pure SI vs. AD systems is further exaggerated. $k_1/k_a = 0.1$ ; $k_2/k_d = 4$

(SI) $M_o : Cu_I : Cu_{II} : IX_o = 200 : 1 : 0 : 1$

(SI+AD) $M_o : Cu_I : Cu_{II} : IX_o = 200 : 1 : 0.002 : 0.1$
Figure 3.21 – Cartoon representation of a Molecular Weight / Grafting Density Gradient.

Figure 3.22 - Grafting Density / Molecular Weight Orthogonal Gradient. (a) Forming a gradient in OTS via diffusion (b) backfilling deposition of BMPUS initiator and (c) forming MW gradient orthogonally to the grafting density gradient.
Figure 3.23 - Orthogonal Grafting Density / Molecular Weight gradient of PDMAEMA. (Ellipsometric Dry Thickness)
4.1 Formation of Tethered Copolymers

4.1.1 Necessary Conditions to Produce Copolymers

Creating copolymer assemblies via ATRP required an added degree of complexity above that of homopolymers. At least two primary conditions must be satisfied. First, the macroinitiator must exhibit fast initiation to the second monomer under the experimental conditions of the second polymerization. Second, each homopolymer must be significantly soluble in and compatible with the polymerization solution of the opposite polymer.

Like monomers can usually be copolymerized with success, for example, combinations of most methacrylates with methacrylates, acrylates with acrylates, or styrene derivatives with styrene derivatives. In some instances, it may become necessary to produce block copolymers with completely different chemical formulas, in which case combinations of various different polymerization schemes must often be employed. Examples of this include combinations of ATRP with ring-opening polymerizations (ROPs), radical polymerization (RP), or with ionic (both cationic and anionic) polymerizations [1-6]. In many cases one may stick to the same polymerization scheme by changing the reactive endgroup. One well-known technique to enhance macroinitiator activity is to use a mixed halogen system. Matyjaszewski first described this technique in 1998 [7, 8]. This scheme involves using a more active halogen terminated initiator or macroinitiator and subsequently polymerizing with a less active halogen system. An example of this is growth of a diblock
consisting of poly(hydroxyethyl methacrylate) (PHEMA) and poly(methyl methacrylate) (PMMA) blocks, in which the PHEMA block was polymerized using a CuCl/CuCl$_2$:BPY from a macroinitiator comprising bromine-terminated PMMA. The order of activity of halogens would be I > Br > Cl.

The second condition can come into play when the first block is insoluble in the second monomer system or the polymer/monomer contains a functionality that changes the activity of the macroinitiator. The macroinitiator, in the case of insolubility, can collapse on itself and steric hindrance would become so great that the second polymer could not initiate from the first polymer. In this case, the chemical functionality of the polymer, monomer, or solvent/monomer system must be changed to compatibilize the two systems. Several synthetic schemes have been devised in order to minimize some of these drawbacks. For example acid, amino, or hydroxyl functionalities can be protected with groups like trimethylsilyl groups in order to compatibilize the systems [9, 10].

4.1.2 Adjusting co-solvent to promote copolymerization of PMMA and PHEMA

The primary system of copolymer we investigated in our work was a block copolymer comprising PMMA and PHEMA blocks. This copolymer was grown in aqueous media via ATRP as detailed in Chapter 3. While growth of PHEMA-b-PMMA copolymers in aqueous media had been reported previously, growing PHEMA in aqueous media from a PMMA macroinitiator proved more difficult. The first attempts were unsuccessful. Soon, we realized that the second condition mentioned above was not satisfied. Namely, PMMA was insoluble in the HEMA/MeOH/H$_2$O media. This system was particularly challenging since PHEMA is only appreciably soluble in alcohols and no other traditional solvents (i.e. toluene,
DMF, THF). PMMA, on the other hand, is only mildly soluble in some alcohol mixtures. As illustrated in Table 4.1, PMMA and PHEMA have opposite solubility characteristics. Only one other group [11] has succeeded in growing PHEMA from a PMMA macroinitiator. This was done by protecting the hydroxyl groups, thus adding an extra step in the polymerization process. Because this method did not use an aqueous system high polymerization rates were only achieved above 50°C. By maintaining the existing system and adding a small amount of acetone as a co-solvent, we were able to block-copolymerize PHEMA from a PMMA macroinitiator with only a slight decrease in the surface growth rate. Table 4.2 gives the recipe used for PHEMA block polymerization from PMMA macroinitiator.

4.2 Studies of Grafted Diblock Copolymers

4.2.1 Macroinitiator Efficiency in Grafted Alternating Multiblock Copolymer

There are many reasons to study effects of macroinitiator efficiency on tethered multiblock copolymers. By knowing the reinitiation efficiency and thus establishing how fast the subsequent blocks grow, one can synthesize and characterize grafted multiblock gradient samples without the need of exposing the sample to lengthy ellipsometric measurement in atmospheric conditions after each block is formed. To examine a simple case of multiblock formation of a PMMA-b-PHEMA tethered copolymer, a “step” multiblock sample (figure 4.1a) was formed by a similar method as described in detail in Chapter 3. The original procedure (section 3.4.3 in this Thesis) was modified by adding the second monomer solution and alternating from MMA to HEMA solution. The “step”
multiblock sample data are shown in Figure 4.1b. To our knowledge, this is the first multiblock of PMMA-b-PHEMA reported. An interesting phenomenon was observed in comparing growth rates in the beginning and middle of the block formations. It was expected that subsequent blocks may grow more slowly or less completely due to inefficiencies in initiation (thus a decrease in block grafting density). Contrary to our expectation, we found that the opposite was true. The first PMMA block actually grew the slowest, by far, of any of the block layers. The multiblock layers of PMMA were shown to grow at a rate that was 25% greater than that of the initial PMMA layer. We concluded that this result was most likely due to the increased solubility of the multiblock copolymer (due to the presence of PHEMA block) in the aqueous methanol mixture compared with the PMMA homopolymer. We believe this to be the first case of direct observation of the influence of chain conformation on the growth rate of the polymer chains. A tethered PMMA homopolymer would be expected to be much less soluble in the aqueous methanol media whereas a tethered copolymer with PHEMA would exhibit increased solubility and swelling of the brush.

In addition to PMMA-PHEMA multiblocks, copolymers comprising alternating blocks of PMMA and poly(dimethylaminoethyl methacrylate) (PDMAEMA) were synthesized. The literature reports indicate that although other methacrylate macroinitiators could be used to initiate a well controlled copolymer with PDMAEMA, loss of initiator activity was observed when PDMAEMA macroinitiators were used to initiate a copolymer [12, 13]. It was reported that a high percentage of dead chains (loss of end functionality) were formed which never initiated the copolymerization. We intended to establish whether the loss of end functionality occurred during the polymerization or during the precipitation
and purification of the first block. The latter case can be avoided when using surface-
tethered copolymers, such as those formed via surface-initiated polymerization, which does
not suffer from precipitation. PDMAEMA, as well as other nitrogen-containing polymers,
are well known for binding to the copper salts used in ATRP during and after the
polymerization process [14, 15]. This binding can affect the conformation of the chain as
well as the activity of the growing endgroup. The adsorbed catalyst may also remain active
when the polymer is precipitated and purified, thereby causing end-group functionality loss
after the homopolymerization is complete.

In Figure 4.2 we plot dry thickness data taken from an alternating diblock of PMMA-
b-PDMAEMA. Our analysis shows that the apparent growth rate of PMMA is greatly
decreased upon initiation from the first and second PDMAEMA blocks. Growth rate
decreases, relative to that of the initial PMMA block. Specifically, we detect a decrease by
27% and 15% for the second and third PMMA blocks, respectively. Interestingly, the growth
rate of the PDMAEMA blocks remains very similar. For example, the growth of the second
and third PDMAEMA blocks was 127% and 120%, respectively, of the original PDMAEMA
block growth rate. This indicates that there is no loss of end-functionality in the PDMAEMA
macroinitiator and that decrease in growth rate is likely due to either inefficient transfer to
PMMA or, more likely, to the interaction of the PDMAEMA with the copper catalyst. It has
been shown that the reactivity ratio of PDMAEMA and PMMA deviates significantly from
values calculated from conventional radical polymerization [16]. The relative coordination
of the copper catalyst to the polymer chains rather than in solution could be significantly
greater while attempting to polymerize PMMA rather than PDMAEMA. For PDMAEMA,
the system coordination would happen along the polymer as well as in solution with the
monomer. This could likely cause interruption during attempted PMMA polymerization on a PDMAEMA macroinitiator layers. Polymerization using a stronger ligand, e.g., PMDETA, or a mildly coordinating solvent, e.g., pyridine, could allow for more regular growth of subsequent PMMA layers.

The important overall conclusion of these experiments is that multiblocks of PMMA and PHEMA can be successfully grown via surface-initiated ATRP to above 35 nanometers in dry thickness with little or no decrease in growth efficiency. Furthermore, PMMA-b-PDMAEMA multiblocks can be grown, large decreases in polymerization rate are observed with PMMA layers grown from layers containing PDMAEMA. No “dead chains” or loss of functionality was observed in the PMMA-PDMAEMA layers and hence could not have caused the decrease in PMMA growth rate.

4.2.2 Surface-grafted diblock copolymer gradients

Having successfully prepared homopolymer molecular weight gradients, we attempted to generate diblock copolymer gradients. In true ATRP, the surface-bound polymer will remain halogenated so that subsequent blocks may be polymerized on top of the macroinitiator layer. PMMA and PHEMA have been copolymerized with each other forming PHEMA-b-PMMA polymers with well-defined molecular weights and polydispersities [11, 17]. The procedure for growing a gradient diblock is outlined in Figure 4.3. A homopolymer gradient is first grown in the gradient apparatus, as described in Chapter 3. The wafer with the macroinitiator gradient (PHEMA) is removed from the chamber, and washed with methanol. In order to grow the second block, the PHEMA-macroinitiator containing sample is either subjected to ATRP of MMA in order to grow a
constant length PMMA block (sample S1) or placed back in the gradient chamber in order to
grow a molecular weight gradient PMMA block (sample S2). The dry thicknesses of each
block are shown in Figure 4.4. These results illustrate that our first attempts at producing
these diblocks were quite successful. Figure 4.5 depicts contact angle data using deionized
(DI) water as a function of position on sample S2. PHEMA and PMMA exhibit different
contact angles with DI water. Being more hydrophobic, PMMA displays a contact angle
near 75°. In contrast, PHEMA has a contact angle around 45-50°. One would expect the
contact angle to increase as the polymer composition increases from 0 to 100% PMMA. An
interesting phenomenon is discovered, however, in taking the contact angles of these diblock
gradients (cf. Figure 4.5). After both acetone and water rinses, the contact angle did increase
with increasing PMMA content, but only at the end of the wafer with the thickest PMMA
(largest numbers along the position on the sample). A local minimum in contact angle was
observed with PMMA thickness of 5-8 nm and PHEMA thickness of 10-15 nm. The last
part of the wafer containing shorter PMMA exhibited a quick increase in contact angle
followed by a leveling off. It was not until more experiments were done that we realized this
occurrence was not simply an artifact of experimental error, but represented an interesting
phenomenon of surface rearrangement of the grafted copolymer. For more information on
this phenomenon see section 4.3.2.

4.2.3 Chemically modified diblock copolymer gradients

The use of surface-grafted polymers has been shown to be useful for a variety of
potential applications that benefit from tunable surfaces. At the end of Chapter 3 we
provided a few examples. Chemical modification of existing copolymers offers a useful
method of creating copolymers of blocks that may, under normal conditions, be difficult to synthesize. For instance, low surface-energy polymers often cannot be copolymerized with more polar/hydrophilic polymers due to their incompatibility. Recently, Brantly and Jennings [18] described a method of preparing hydrophilic polymer films via ATRP and subsequently modified them via acylation reaction with hydrocarbon or fluorinated hydrocarbon side groups. Starting from a PHEMA “backbone”, this procedure produces highly derivatized films with very low-energy surfaces. Several researchers have utilized the hydrolysis reaction of poly(tertbutyl acrylate) (PtBA) to form poly(acrylic acid) (PAA) [19, 20]. Similar reaction schemes are used to produce amphiphilic block copolymers by copolymerizing a hydrophobic block with PtBA and then cleaving the t-butyl group. It is of interest to see if the flexibility of these two techniques could be applied together. This would be advantageous since it would allow a hydrophilic block to be attached to PHEMA, which could be derivatized to form almost any type of diblock copolymer. In addition, the question arises: “How does block length, composition, and degree of derivatization affect the surface properties of these diblocks?” If a permanent gradient in hydrophilicity can be created on a surface, it could be used in microfluidics applications as in “lab-on-a-chip” devices.

The first step in preparing such an amphiphilic diblock copolymer was to grow a PHEMA molecular weight gradient on a silicon wafer using the methodology outlined earlier. In the next step, a PtBA layer was added by ATRP polymerization of tBA. In order to grow well-controlled diblocks via ATRP two main conditions must be met. First, the macroinitiator of the first block must initiate and transfer faster than the propagation rate of the second block. Second, the first block must be soluble in the media, in which the second block is formed. The first criterion was likely to be satisfied since methacrylates tend to...
form radicals nearly 10x as fast as acrylates. Since PHEMA is insoluble in most solvents except alcohols, we chose a solvent/monomer system that included alcohol. PHEMA was shown to dissolve well in this solvent. The PHEMA gradient wafer was prepared and allowed to polymerize with a second block of PtBA using the following conditions: 29.7 ml tBA, 29.7 ml acetone, 7.5 ml MeOH, 1.09 ml H$_2$O, 0.222 g CuBr, 0.01 g CuBr$_2$, 344 ul PMDETA at 50°C for 5 hours. This procedure produced a uniform layer of 5.5 nm of PtBA grown from the PHEMA macroinitiator (Figure 4.6). Modification of the PHEMA block was attempted via acylation of the alcohol group by following the method of Brantley and Jennings [18]. The wafer was added to an 80 mM pentafluorobenzoyl chloride, 100 mM pyridine solution in dichloromethane (DCM) and left for 12 hours. The amount of fluorination of PHEMA was established from thickness measurements. Our experiments reveal thickness increases of 55 to 60% (relative to the “bare” PHEMA thickness), which corresponds to ≈70% fluorination of PHEMA (Figure 4.6). Since this acylation should only be unstable when subjected to heat or base it was assumed that the acid hydrolysis of PtBA to PAA would not affect the fluorinated PHEMA layer. The fluorinated diblock was then subjected to an acid hydrolysis technique also used by Kong et al. [21]. The diblock layer was immersed in a 10% trifluoroacetic acid solution in chloroform at room temperature for 24 hours. Thickness measurements carried out on the specimen after the hydrolysis revealed a graded non-uniformity in thickness change. Specifically, while the part of the sample containing primarily thin fluorinated PHEMA exhibited ≈60% decrease in thickness, the thickness at the other side of the specimen decreased by only ≈20%. Based on the volume of the tert-butyl group, a decrease of ≈52% should have occurred. It is thus likely that the thick
fluorinated PHEMA layer acted to protect the PtBA from complete hydrolysis and as the fluorinated protective layer became shorter more hydrolysis was observed.

To test the surface wettability of these amphiphilic diblock copolymer layers, DI water contact angles were taken along various positions on the sample. The non-hydrolyzed fluorinated diblock had a very high contact angle (around 90-95°) except at the region covered with a thin fluorinated PHEMA layer. The contact angle maximum (=97°) was reached at the point that corresponded to approximately equal thicknesses of the fluorinated PHEMA the PtBA layers. There was a steady decrease in contact angle with increasing the fluorinated PHEMA layer thickness. Upon hydrolysis of the top PtBA block, an abrupt decrease in contact angle was observed on the whole sample. A much lower contact angle was observed for the end predominantly made of PtBA and a higher contact angle was observed for the end predominantly made of fluorinated PHEMA (figure 4.7). When a large water drop was placed on the hydrophobic end of the sample, it tended to spread towards the more hydrophilic side. If capillary sidewalls were modified with this diblock gradient spontaneous movement of liquid would likely occur.

4.3 The “Orthogonal Gradient”

Several researchers have reported on utilizing the surface-confined copolymer systems in controlling chain conformations by selectively swelling one of the blocks, while collapsing the other block. For instance, Brittain and coworkers demonstrated that selective swelling and collapse of poly(styrene-b-methyl methacrylate) brushes produced variable surface topologies[22, 23]. This simple method of tailoring the substrate roughness has led
in recent years to some exciting developments in utilizing surface-grafted polymer as potential “soft vehicles” capable of moving nano-sized objects[24]. In order to fully utilize the power of the copolymer in such applications, one needs to systematically explore the effect of the lengths of the two blocks and their composition on selective response to various solvents. The notion of orthogonal gradients, outlined earlier in Chapter 3, is very useful here. If one can prepare a sample in which both blocks can systematically vary, the phase behavior of surface-grafted copolymers can be studied readily. In this section we outline the procedure leading to the formation of such orthogonal copolymer gradients and discuss how these can be utilized to study the chain conformations upon exposure to solvents selective for each block.

4.3.1 Solvent exposure study of tethered diblock copolymer brushes

In order to demonstrate the effectiveness of tethered orthogonal copolymer gradients in combinatorial studies, we prepared a surface-tethered A-B block copolymer sample of poly(2-hydroxyethyl methacrylate)-b-poly(methyl methacrylate) (PHEMA-b-PMMA) with smoothly varying lengths of both blocks on a single substrate. We utilize such structures to systematically map out the influence of the block length on surface morphologies of PHEMA-b-PMMA in response to selectively collapsing the top (PMMA) block as well as the lower (PHEMA) block of the copolymer.

Silicon wafers were cut into 5x5 cm² pieces and a decorated with a monolayer of (11-(2-bromo-2-methyl)propionyloxy)undecyl-trichlorosilane (BMPUS), the initiator for subsequent atom transfer radical polymerization (ATRP) [25]. The orthogonal diblock gradient was formed by first forming a gradient in molecular weight of PHEMA by “grafting
from” polymerizing 2-hydroxyethyl methacrylate using the solution draining method (chapter 4), followed by rotating the sample by 90 degrees, and repeating the previous step by polymerizing methyl methacrylate (MMA). This procedure resulted in a PHEMA-b-PMMA diblock copolymer brush with position-dependent lengths of the two blocks on the substrate.

In Figure 4.8 we plot the dry thickness maps along the PHEMA-b-PMMA specimen. A photograph of the actual sample with visible gradients is shown in Figure 4.9. The thickness of each block was determined using ellipsometry after each synthesis step. PHEMA dry thickness increases linearly along the X (horizontal direction in Figure 4.8a) direction and the PMMA thickness increases linearly in the Y direction (vertical direction in Figure 4.8b). Because the grafting density, $\sigma$, of all polymers is approximately equal on the entire specimen, the dry thickness of each block, $h$ is directly proportional to its molecular weight, $M$ ($h= \sigma M/(\rho N_A)$, where $\sigma$ and $N_A$ are the density and Avogadro’s number, respectively. More information about the various copolymer compositions can be obtained by plotting the dry thicknesses of the PHEMA and PMMA blocks along the various directions indicated by arrows in Figure 4.8c. The horizontally pointing arrows denote copolymers having a constant PMMA length and a linearly increasing PHEMA length. Two cases are highlighted here, copolymers with a short (1) and long (1’) PMMA block (Figure 4.8d). The vertical arrows depict block copolymers with a linearly varying length of the PMMA block and a constant length of the bottom PHEMA block. As before, we mark the boundary cases involving a short (2) and long (2’) PHEMA block (Figure 4.8e). The diagonals in Figure 4.8c denote copolymers that have: (3) approximately constant fraction
of both blocks but an increased total length, and (3) those with a constant length but a linearly varying composition (Figure 4.8f).

The following solvent treatment (designated #1) was designed to swell the entire copolymer chain then selectively collapse the top PMMA block: The orthogonal gradient specimen was immersed in 40% ethanol/acetone (v/v) solution, a good solvent mixture for both blocks. The solution composition was changed gradually by adding ethanol. When the content of ethanol in the solution reached \( \approx 90\% \), the sample was immediately transferred to 100% anhydrous ethanol. In order to vitrify the surface morphology of the PHEMA-b-PMMA copolymers and minimize the reordering of the copolymer structures upon drying, the sample was immersed into liquid ethane (freezing \(-211^\circ C\), boiling \(-88^\circ C\)). The cold nonpolar ethane causes the polar PHEMA and PMMA to collapse and withdraws any solvent left behind. The ethane and the sample were allowed to increase in temperature until the ethanol was absorbed completely by the ethane phase. The sample was then immersed in liquid nitrogen and transferred to a vacuum oven at room temperature.

The following “reverse” solvent treatment (designated #2) was designed to swell the entire copolymer chain then selectively collapse the bottom PHEMA block: The orthogonal gradient specimen was immersed in 40% acetone/ethanol (v/v) solution, a good solvent mixture for both blocks. The solution composition was changed gradually by adding acetone (a nonsolvent for PHEMA). When the content of acetone in the solution reached \( \approx 90\% \), the sample was immediately transferred to 100% anhydrous acetone. In order to vitrify the surface morphology of the PHEMA-b-PMMA copolymers and minimize the reordering of the copolymer structures upon drying, the sample was immersed into liquid butane (freezing \(-138^\circ C\), boiling \(-0.5^\circ C\)). Butane was used in place of ethane due to the freezing point of
acetone being too high to use ethane. The butane and the sample were allowed to increase in temperature until the acetone was liquid and miscible with the butane phase. The sample was then immersed in liquid nitrogen and transferred to a vacuum oven at room temperature.

4.3.2 Study of chain conformations after selective solvent treatment

4.3.2.1 AFM studies of surface morphologies

Almost a decade ago, Balazs and coworkers studied the swelling of surface-tethered copolymers using selective solvents [26, 27]. Their self-consistent field (SCF) method calculations and scaling arguments revealed that grafted copolymers exposed to a solvent that is a theta solvent for the bottom block and a poor solvent for the top block exhibit several distinct morphologies: flat (I), pure B pinned micelles (PMB), A-legged micelles (MAB), star-like micelles (MA), and a bicontinuous phase (BAB) (figure 4.10). The type of morphology the copolymer adopts depends on the lengths of the individual blocks. Our sample design is ideally suited for testing the predictions of Balazs and coworkers. Having copolymers with independent and smoothly varying lengths of each block on a single sample, we can systematically screen the entire parameter space in a reproducible and fast manner. In order to explore the effect of solvent quality on the composition of the PHEMA-b-PMMA copolymer, the samples were exposed to the various selective solvents described earlier. The sample surface morphology was then probed with tapping mode atomic force microscopy (AFM). AFM images were taken from 25 equally spaced locations on the sample.

We commence with describing results obtained after selective solvent treatment #1 designed to collapse the top PMMA block. In Figure 4.11 we plot the morphology diagram based on multiple AFM scans collected from several areas on two different PHEMA-b-
PMMA orthogonal samples. The AFM results can be broken down into two basic effects: 1) the increase in size of the micelles (dependent primarily on the PHEMA block length) and 2) the ability of chains to aggregate (dependent primarily on the PMMA block length). These results may be somewhat counterintuitive as one might expect the micelle size to be more dependent on the PMMA block length since the PMMA composes the core of the micelle. However, when chain mobility is taken into account (primarily dependent on the PHEMA chain length) this finding is understandable. In the region of short PHEMA, the PMMA micellar core is pinned close to the surface. Our results, which are in excellent qualitative agreement with the predictions of Balazs and coworkers (figure 4.10), show a definite trend in the morphologies of the PHEMA-b-PMMA copolymer that range from flat (F) to “floating micelles” to “aggregating micelles” and finally to a bicontinuous phase (which we have seen so far to be “honeycomb”-like shaped).

Zhulina and Balazs predicted the transitions experimentally shown in our research. However, from their work it is not apparent whether the transitions from micellar to bicontinuous occur rapidly or gradually [26]. While separate categories of the individual phases appear in the AFM images quite clearly, the transitions were found to occur, however, very gradually as molecular weight was increased. Based on the AFM images, we were able to produce an approximate phase diagram (cf. Figure 4.12) based on the appearance of these phases. In the phase diagram, we have also included an M/BC (micellar/bicontinuous transitional) phase to demark a region in which micelles were partially aggregating. Several transitional lines are labeled in Figure 4.12. Their corresponding detailed AFM images, which clearly exhibit these transitions, are presented in Figures 4.13-4.16.
The transition labeled (a) is shown in figure 4.13. It represents the region of relatively short PHEMA and increasing PMMA blocks. Upon viewing the images sequentially from top left to bottom right we see a flat AFM image (F), two micellar images (M), two images in the aggregating micellar region (M/BC), and finally one that appears fully bicontinuous. The PHEMA block is small and so we believe that the confinement causes the transitions to occur sooner and have smaller features. Transition arrows (b) and (c) (Figures 4.14-4.15) exhibit similar patterns and transitions. Two main differences emerge. First there is an appearance of floating micelles (most clearly seen in figure 4.15), or micelles that are isolated and are located just beneath the surface of the PHEMA layer. Second, the structural features seen are enlarged. We believe that, due to the increased freedom, each PMMA chain is being tethered by a longer PHEMA bottom block. In other words, chains are allowed to aggregate to form micelles with larger micellar cores producing larger features. Also, due to increased chain freedom, micellar aggregation to produce a bicontinuous phase occurs more gradually over a longer range of polymer thicknesses. The last transitional line (d) (cf. Figure 4.16) depicts micelles formed from a relatively constant PMMA block thickness with increasing PHEMA thickness. Presumably, the increase in chain freedom causes these micelles to aggregate over a larger area thereby increasing micellar size.

Upon solvent treatment #2 (designed to collapse the bottom PHEMA block) a much different morphology was observed. Balazs predicted that upon collapsing the bottom block, the bottom block would form micellar cores while the top block would exhibit “flower-like” fingers protruding out from the micellar cores [26]. We believe that this is the type of morphology we observe in our samples. Balazs’ “flower-like” arrangement is seen as a
spongy morphology (cf. Figure 4.17), and it is only visible in intermediate regions of the sample. In regions with a short PHEMA block, the morphology appears fairly flat for all PMMA thicknesses. Upon increasing the PHEMA block, the spongy morphology becomes less visible giving away to larger order surface oscillations from the collapsed PHEMA.

In Figure 4.18 the transition from nearly flat to spongy is seen as we move along the wafer in the intermediate PMMA thickness (~12nm) region from short to long PHEMA block. The second image in Figure 4.18 exhibits the most clear spongy morphology and occurs at block thicknesses of 7-12nm for PMMA and 40-50nm for PHEMA. Continued increase in the PHEMA thickness brings about a mixed spongy/micellar structure seen in the last image in Figure 4.18.

4.3.2.2 Wettability studies of surface morphologies

Contact angle data can provide complementary information about the chemical nature of the topmost layer of polymer (< 1nm). Though certain error is associated with individual contact angle measurements, our experiments, which involve the acquisition of over 25 measurements per solvent exposure, reveal certain definite trends. It has to be stressed that high surface roughness can, at times, give artificially high or low readings based on the chemical nature of the surface. Specifically, a rough hydrophilic polymer surface (contact angle < 90°) may give artificially low readings whereas a more hydrophobic polymer surface (contact angle > 90°) may provide a high reading. To ensure this was not the case here, we measured surface roughness at each region on the sample. No significant increase in the surface roughness was detected on the areas of the samples corresponding to the transitional
regions between micellar and bicontinuous morphologies. Hence, surface roughness is not expected to greatly affect the differences in the contact angle data.

Clear differences in wettabilities were detected when comparing the surfaces exposed to different solvents (cf. Figures 4.19 and 4.20). Whereas the first solvent exposure procedure (collapse of the top PMMA block) produced contact angles varying from 50º to over 75º, the second exposure (collapse of the bottom PHEMA block) yielded a fairly homogeneous wettabilities ranging only from 65º to 75º.

Our results indicate that in the case of a tethered PHEMA-PMMA diblock layer exposed to selective solvent to collapse the top PMMA block, the measured contact angle increases with decreasing PMMA thickness. When correlated with the AFM data, this observation indicates that the areas most prone to rearrange (exposing the underlying PHEMA layer) are the areas with larger molecular weight PMMA block. In fact, in the regions of the substrate where we observe the clearest transition from micellar to bicontinuous we also observe a rapid decrease in the contact angle, which ranges from \( \approx 70^\circ \) to \( \approx 50^\circ \).

We hypothesize that, in the case of shorter PMMA (micellar region), the PMMA blocks remain in isolated micelles close to the surface and therefore affect the CA readings to indicate a PMMA surface. This hypothesis is in agreement with the theoretical prediction of Balazs and coworkers[26, 27]. In the case of longer PMMA (bicontinuous region), the interaction of the PMMA blocks to form the bicontinuous structure allows the PMMA phase to remain submerged in the PHEMA layer.
4.4 Studies of Grafted Triblock Copolymers

Structures more complex than diblock copolymers may be formed using our dipping method. These may involve ABC triblock copolymers. In order to carry out a complete investigation of the morphologies and surface behavior of surface-tethered ABC triblocks, one has to systematically vary four independent variables, i.e., the volume fractions of each block and the overall triblock brush thickness. In order to accomplish this, a few modifications to the existing sample preparation design have to be done. First, one has to switch from the orthogonal sample geometry to a triangular specimen arrangement. The new geometry would thus resemble classical ternary phase diagrams (drawn into regular or equilateral triangles) involving 3-component mixtures. In the conventional 3-component mixture cases, say XYZ, each corner of the triangle corresponds to the pure component (X or Y or Z), each side denotes the composition along a given binary alloy (XY, XZ and YZ), and any point inside the triangle marks the composition of the XYZ mixture. The relative proportion of every component of the mixture is given by the lengths on the perpendiculars drawn between the corner and the corresponding opposite side of the triangle. Our triblock copolymer system will be formed on such an equilateral triangle substrate. In order to add the effect of the fourth variable, i.e., the total length of the copolymer, several such triangular samples would have to be generated. There is no simple way to combine the effects of all four variables on a single sample. It has to be noted, however, that even with this “slight complication”, the suggested combinatorial sample design would still provide much improvement over the conventional “single specimen” approach, thus providing needed systematicity and speed of sample preparation and property screening.
As a proof of concept, we have generated, for the first time, such a surface-anchored triblock copolymer assembly with variable lengths of all three blocks. Rather than following the conventional approach of having the pure component positioned in each corner of the triangle, the block copolymers are organized such that each pure block occupies one of the edges of the sample and decreases smoothly as one moves in the direction perpendicular to the edge. The upper panel in Figure 4.21 depicts pictorially the intended sample design. First, a flat silicon substrate was cut into a triangular shape, and was decorated with BMPUS initiator. The sample was placed vertically into the dipping gradient chamber and PHEMA brushes with gradient in molecular weight were formed using the recipe detailed earlier. After the polymerization, the sample is thoroughly washed, rotated by 60° counterclockwise and molecular weight gradient PMMA brushes were grown from the existing PHEMA macroinitiators by again utilizing the dipping apparatus. After the second reaction, the sample was washed and again rotated by 60° counterclockwise, after which yet another molecular weight gradient of PDMAEMA was grown from the PMMA macroinitiator centers. The recipe for PDMAEMA used was exactly the same as for PMMA, except that MMA monomer was replaced with the same volumetric amount of DMAEMA monomer (see section 3.4.1). The surface growth rate was found to be nearly identical. We note that the thickness on selected areas on the sample was measured via VASE after each polymerization step. The bottom panel in Figure 4.21 shows thickness profiles for each block. The color variation denotes changes from $\approx 1$ to $\approx 30$ nm on the sample. As indicated by the data in Figure 4.21, the thicknesses of all blocks systematically vary in the three different directions, thus leading to gradual variations in compositions of the entire triblock copolymer. In order to address the effect of the block lengths, one would have to prepare several such specimens,
as discussed earlier in the text. Hence, while we are not in the position to make any detailed and systematic studies of the phase behavior of such triblock copolymer brushes, this single example illustrates the capability of the gradient-forming approach. It is our hope that in the near future this approach (or its variant) would be further developed and utilized to gain more insight into the phase behavior of complex and not yet fully understood systems, such as triblock copolymers.
4.5 References


Table 4.1: Solubility of PHEMA and PMMA polymers in various solvents

<table>
<thead>
<tr>
<th></th>
<th>Alcohols</th>
<th>Ketones</th>
<th>Toluene/THF</th>
<th>Water/DMF</th>
</tr>
</thead>
<tbody>
<tr>
<td>PHEMA</td>
<td>soluble</td>
<td>insoluble</td>
<td>insoluble</td>
<td>insoluble</td>
</tr>
<tr>
<td>PMMA</td>
<td>insoluble</td>
<td>soluble</td>
<td>soluble</td>
<td>insoluble</td>
</tr>
</tbody>
</table>

Table 4.2: Co-solvent system for polymerization of PHEMA from PMMA macroinitiator:

HEMA = 50.0ml (0.412mol)  
Methanol = 46.0ml (1.136mol)  
Water = 10.0ml (0.555mol)  
Acetone = 7.2ml (0.10mol)  
Bipyridine = 3.16g (2.02x10^{-2} moles)  
CuCl + CuCl₂ = BPY/2 = 10.0x10^{-3} mol  
CuCl / CuCl₂ = 5-30  
T = 25ºC
Figure 4.1a – Cartoon representation of Alternation Multiblock “Step” exhibiting all 6 multiblock layers on one sample.

Figure 4.1b – First alternating multiblock of PMMA-b-PHEMA. Growth rate of PHEMA multiblocks unchanged to within 5% thickness error. PMMA growth rate increases 25% after initial block formation indicating increased growth rate of PMMA blocks only when part of a copolymer with PHEMA.
Figure 4.2 – PMMA-b-PDMAEMA step multiblocks. Color represents top block. Green=PDMAEMA; blue=PMMA. Large decrease in growth rate of PMMA blocks after initial block. Very little change in PDMAEMA growth rate.
Figure 4.3 – Sample cartoon of diblock gradient making procedure. (A) Homopolymer gradient “macroinitiator” (B) Reimmersion of macroinitiator gradient to produce (C) copolymer gradient with constant length of second block. (D) Growth of second block gradient to create (E) diblock gradient of constant length and variable composition.
Figure 4.4 - PHEMA-b-PMMA diblock molecular weight gradients.
(a) Sample S1: Constant PMMA block on varying PHEMA (b) Sample S2: Compositional gradient in PHEMA/PMMA.

Reproduced from Tomlinson & Genzer, Chem. Comm., 12, 1350
Figure 4.5 - Sample S2 from above with DI water contact angle measurements along sample. Max CA followed by minimum CA as PMMA decreases. The “leveling off” effect (red box) is not an error in measurement and will be discussed in section 4.3.2.
Figure 4.6 – PHEMA-b-PtBA diblock gradient. Layer increases proportional to PHEMA content upon fluorination of the PHEMA.

Figure 4.7 – Contact angle data from Fluorinated PHEMA-b-PtBA before and after hydrolysis of PtBA to PAA. Smooth wettability gradient in CA is observed from ~78° to nearly 50°.
Figure 4.8 – PHEMA-b-PMMA orthogonal molecular weight gradient sample. (a) ellipsometric dry thickness of PHEMA gradient in X direction (b) PMMA (top block) gradient in Y direction (c) combined diblock gradient (d-f) Comparative ellipsometric measurements along specified lines from caption c.
Figure 4.9 – Actual orthogonal PHEMA-b-PMMA molecular weight gradient sample as described in previous figure.

Figure 4.10 – Diagram from Zhulina and Balasz showing phase predictions of tethered AB diblock layer exposed to theta solvent for A (bottom block) and poor solvent for B (top). Shows flat (I) micellar, continuous (BAB), and several micellar (M) phases.

*redrawn from Macromolecules 29, 8254 (1996)
Figure 4.11 - Morphology diagram of ethanol-quenched PHEMA-b-PMMA brushes based on atomic force microscopy (AFM) results revealing the existence of flat (F), micellar (M), and continuous (C) morphologies. The edge of each AFM scan is 0.4 μm long.
Figure 4.12 – Approximate phase diagram produced from AFM images. Flat (F), Micellar (M), and Bicontinuous (BC) regions are labeled. Transitional region (M/BC) was included due to the gradual aggregation of micelles to become bicontinuous as PMMA thickness increases. Lines (a)-(d) denote den transitions depicted by AFM images in Figures 4.13-4.16
Figure 4.13 - Transition (a) from Figure 4.12

Figure 4.14 - Transition (b) from Figure 4.12
Figure 4.15 - Transition (c) from Figure 4.12

Figure 4.16 - Transition (d) from Figure 4.12
Figure 4.17 – A similar continuous “spongy” morphology was observed over most of sample after solvent treatment to collapse bottom PHEMA block.
Figure 4.18 – Transition at intermediate PMMA thickness (~12nm) from short to long PHEMA. Spongy structure most visible in second slide at 47nm PHEMA.
Figure 4.19 – DI contact angle data taken after solvent treatment to collapse top PMMA block. Notice hydrophilic/hydrophobic transition corresponding with micellar to continuous regions.

Figure 4.20 – DI contact angle data taken after solvent treatment to collapse bottom PHEMA block. Hydrophobic CA found in all regions indicating PMMA close to surface.
Figure 4.21 – PHEMA-b-PMMA-b-PDMAEMA triangular triblock sample. Extension of the orthogonal diblock concept to include a third block produces a triangular triblock sample.
Chapter 5: Outlook

The chief goal of this Ph.D. Dissertation was to develop methodologies facilitating the formation of assemblies comprising grafted polymers on surfaces with gradually varying polymer properties (e.g. molecular weight, grafting density, or composition). We have shown that such assemblies are ideally suited to tackle several outstanding issues in the field of polymer brushes. We have addressed several phenomena pertaining to the formation and properties of surface-grafted polymer assemblies. Specifically, we have explored the kinetics of controlled/“living” polymerization in confined spaces and investigated the controlled character of the controlled/“living” polymerization on surfaces. We have also demonstrated how the molecular gradient weight approach can be utilized to form continuous compositional arrays of di- and tri- block copolymers on material surfaces.

The viability of many novel applications, including polymer electronics and responsive surfaces, relies on surface-grafted polymer assemblies. Polymer brush arrays with gradually varying properties, such as composition, molecular weight or grafting density, will be critically needed in the development of such devices. It is our hope that the assembly approaches developed during the course of this work, and the conclusions reached will be beneficial in the development of aforementioned applications.

5.1 Polymer Gradients in Electronic/Photonic Materials

In chapter 4 we outlined methodologies that enable fabrication of surface-grafted copolymer assemblies with variable composition and tailorable chemistries. While all work described here was based primarily on model flexible polymer chains, similar methods may
be employed to produce copolymers with conductive, semi-conductive, light-emitting or otherwise electrically active moieties. In fact, Zhao and coworkers have already synthesized photoactive liquid crystalline (LC) diblock copolymers via ATRP [1, 2]. They demonstrated that morphology and surrounding acid content affected the polymers LC qualities. Other researchers have found that polymer/copolymer morphology and preparation history greatly affects the optical properties of polymer films and the performance of organic light emitting diodes (OLED’s) [3]. It will be very tedious (if not almost impossible) to optimize the performance of such devices by utilizing the “discrete sample” approach. In Chapter 4 of this Dissertation we have shown that the film morphology of tethered diblocks can be tuned by varying the copolymer composition. By applying the gradient concept to electrically active or photoactive copolymers, it would be possible to pinpoint the right combinations of the materials characteristics required to obtain optimal device performance. For instance, an orthogonal copolymer gradient could be formed from light emitting conjugated polymers directly on a transparent anode and the film could be annealed or treated with selective solvent to produce a change in morphology. A thin metal film could be vapor-deposited onto the film surface and the entire sample would be ready to perform as an OLED. The performance characteristics could then be measured and subsequently optimized by measuring the intensity and wavelength of the light emitted as a function of position on the substrate.

As mentioned in Chapter 1, many applications for polymer films exist that require different monomers and different polymerization schemes. Although ATRP is the most widely used polymerization scheme for surface grafting, other polymerization schemes, such as ring opening metathesis polymerization (ROMP), are also being utilized successfully to
graft polymers to surfaces [4, 5]. In order to synthesize more conjugated conducting or semiconducting polymers, one would thus likely need to employ additional polymerization methods that are complementary to ATRP.

5.2 Polymer Gradients in Biomedical Applications

Several researchers have studied the ability of copolymer micelles in time-release drug applications [3]. By forming micelles from copolymers with hydrophilic/hydrophobic parts or even temperature/pH responsive parts one can encapsulate a drug, which may then be solubilized and transferred by ingestion or through the skin. We have demonstrated that grafted copolymer films exhibit micellar formation and that the micellar structure may be tuned by varying copolymer composition. Potential copolymers for drug release applications could be tethered in an orthogonal gradient formation, doped with an easily detectable drug, and subsequently collapsed into a micellar morphology. This sample could then be subjected to an aqueous solution resembling conditions within the body. By utilizing the gradient concept, one may screen for optimal combinations of the lengths of the copolymer blocks that would facilitate successful construction of such drug-delivering vehicles.

5.3 Polymer Gradients to Study Anti-fouling surfaces

In our previous research involving the study of protein deposition and cell growth on polymer layers we determined that compact brushes of PHEMA are capable of forming quite efficient anti-fouling coatings. Our new findings discussed in Chapter 4 indicate that PHEMA-b-PMMA brushes can form bicontinuous morphologies upon selective solvent exposure while exposing only the PHEMA surface. This phenomenon likely compacts the
PHEMA brush exposed to the surface since the hydrophobic PMMA top block is forced to
submerge underneath the PHEMA layer. Other research currently under way in the Genzer
group indicates that in addition to the chemistry, the surface topology may also be important
in the development of efficient anti-fouling surfaces. Hence, compacting of the PHEMA
brush could be exploited to produce particularly effective anti-fouling coatings for use on
ship hulls or in biomedical applications, where both chemistry and topology can be fine-
tuned in a single step by judiciously choosing the correct combination of the length of the
copolymer blocks.

5.4 Polymer Gradients in Polymer-Nanoparticle Composite Materials

Polymer nanoparticle composites have been recently utilized in many applications
ranging from high-efficiency solar cells [6, 7], catalysis [8], and sensor technologies [9], to
electroluminescent devices [10]. In these applications, nanoparticles made of gold, silver,
polymer, or semiconductor are introduced into a polymer matrix and the interaction between
the particles and the polymer enhances or produces a desired result. In some of these
experiments, based on a condensation reaction or electrochemical nucleation, the polymer
film itself was used to form the nanoparticles [11, 12]. Our group has recently demonstrated
that grafted polymer gradient assemblies are conveniently suited for screening the partition of
particles in polymer brushes as a function of the polymer molecular weight and grafting
density on the substrate [13]. Polymer and copolymer gradients could be further used in the
study of polymer nanoparticle composites comprising variable particle sizes. Brittain and
coworkers have already illustrated the concept of in situ nanoparticle formation by creating
silver nanoparticles on polymer brushes via a polycondensation reaction of a silver-
containing polyelectrolyte [11]. Since the size of nanoparticles greatly affects their characteristics (like absorption or catalytic activity), a gradient in particle size could help optimize particle size for specific applications.

5.5 Polymer Gradients in Studying Polymer Surface Growth

In Chapter 3 we demonstrated how polymer gradient geometries could be utilized to study kinetics of polymerization in confined geometries. Surface polymerization kinetics can be studied in more detail by varying system parameters, including solvent concentration, catalyst concentration, temperature, or pH. Diblock kinetics also can be comprehensively studied by creating orthogonal gradients of two blocks and measuring the growth rates of the second block from the first. We have discussed in Chapter 4 that the composition of the copolymer can affect the growth rate of the surface polymerization, presumably due to the increased or decreased solubility of the opposing blocks.

5.6 Conclusion

Our use of polymer gradients has contributed significantly to the understanding of surface-tethered polymer films. It is our hope that this combinatorial approach will be beneficial to other groups in making contributions in many relevant areas of research.
5.7 References


