FORMATION AND GLASSY PROPERTIES OF IRREVERSIBLY ADSORBED POLYMER NANOLAYERS

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Abstract

The growth of nanotechnology and increasing employment of polymer films in the energy, pharmaceutical, and sustainability sectors merit accurate characterization of polymers reduced to the nanometer size scale. However, an increased influence of interfaces due to the large surface-to-volume ratio inherent to these geometrically-confined systems can result in substantial deviations from bulk behavior.

Annealing a supported polymer film in the melt state, a common practice to relieve residual stresses and erase thermal history, can result in the growth of an irreversibly adsorbed layer. This layer of polymer chains physically adsorbed to the substrate interface has been shown to influence thin film properties such as diffusion, viscosity, and glass transition temperature ($T_g$). Understanding the implications of annealing on the properties of polymer films is essential in their proper selection and processing for applications. This dissertation examined the formation and glassy properties of irreversibly adsorbed nanolayers with regard to interfacial influences, composition, and confinement in an effort to better predict how annealing can impact the properties of films.

We used a fluorescence bilayer method to selectively label and measure the $T_g$ of polystyrene adsorbed layers and investigate the role of interfacial competition in determining their $T_g$. Comparing exposed and buried adsorbed layers revealed that the free surface strongly influenced $T_g$ at short annealing times ($t_{ads}$), while chain adsorption dictated $T_g$ at long $t_{ads}$. 
Abstract

We then synthesized a series of homopolymers and random copolymers of styrene and methyl methacrylate and evaluated the growth and structure of their adsorbed layers. Composition-based trends in adsorbed layer plateau thickness, growth kinetics, and sensitivity to leaching solvent were used to propose a mechanism for copolymer adsorption, explaining how different segment-substrate interaction strengths in a single chain mitigate adsorption in random copolymers.

Finally, we compared the adsorption kinetics of thick and thin films of poly(tert butylstyrene) (PtBS) to reveal an elevated effective annealing temperature ($T_{\text{eff}}$) in thin films that was used to determine $T_g$ at the substrate. The relationship between adsorption kinetics and $T_{\text{eff}}$ enabled development of a general method for predicting adsorbed layer thickness in confined films for any annealing time and temperature.
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<tr>
<th>Acronym</th>
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<tbody>
<tr>
<td>1D</td>
<td>One-dimensional</td>
</tr>
<tr>
<td>2D</td>
<td>Two-dimensional</td>
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<tr>
<td>3D</td>
<td>Three-dimensional</td>
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<tr>
<td>AFM</td>
<td>Atomic force microscopy</td>
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<tr>
<td>BCP</td>
<td>Block copolymer</td>
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<tr>
<td>BDS</td>
<td>Broadband dielectric spectroscopy</td>
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<tr>
<td>BLS</td>
<td>Brillouin light scattering</td>
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<tr>
<td>BPD</td>
<td>1,10-bis(1-pyrene)decane</td>
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<tr>
<td>BPO</td>
<td>Benzoyl peroxide</td>
</tr>
<tr>
<td>CD</td>
<td>Capacitive dilatometry</td>
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<tr>
<td>CRR</td>
<td>Cooperatively rearranging region</td>
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<td>DMA</td>
<td>Dynamic mechanical analysis</td>
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<td>DRI</td>
<td>Differential refractive index</td>
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<td>DRS</td>
<td>Dielectric relaxation spectroscopy</td>
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<td>DSC</td>
<td>Differential scanning calorimetry or differential scanning calorimeter</td>
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<tr>
<td>FFT</td>
<td>Finite Fourier Transforms</td>
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<td>FRP</td>
<td>Free radical polymerization</td>
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<td>FTIR</td>
<td>Fourier transform infrared spectroscopy</td>
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<td>FVHD</td>
<td>Free volume holes diffusion</td>
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<td>P4MS</td>
<td>Poly(4-methylstyrene)</td>
</tr>
<tr>
<td>PALS</td>
<td>Positron annihilation lifetime spectroscopy</td>
</tr>
<tr>
<td>PC</td>
<td>Polycarbonate</td>
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<tr>
<td>PEO</td>
<td>Poly(ethylene oxide)</td>
</tr>
<tr>
<td>PET</td>
<td>Poly(ethylene terephthalate)</td>
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<td>Poly(methyl methacrylate)</td>
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<tr>
<td>PS</td>
<td>Polystyrene</td>
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<tr>
<td>PS-$b$-PMMA</td>
<td>Polystyrene-$block$-Poly(methyl methacrylate)</td>
</tr>
<tr>
<td>PSD</td>
<td>Polarization state detector</td>
</tr>
<tr>
<td>PSG</td>
<td>Polarization state generator</td>
</tr>
<tr>
<td>P($S$-$r$-MMA)</td>
<td>Poly(styrene-$random$-methylmethacrylate)</td>
</tr>
<tr>
<td>PtBS</td>
<td>Poly(tert-butylstyrene)</td>
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<td>RML</td>
<td>Reduced mobility layer</td>
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<tr>
<td>Acronym</td>
<td>Full Form</td>
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<td>S</td>
<td>Styrene</td>
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<td>Silicon</td>
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<td>Size exclusion chromatography</td>
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<tr>
<td>TC1</td>
<td>4-tricyanovinyl-([\text{N-(2-hydroxyethyl)-N-ethyl}])aniline</td>
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<td>Ultraviolet-visible</td>
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<tr>
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<td>Vogel-Fulcher-Tammann</td>
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<tr>
<td>WLF</td>
<td>Williams-Landel-Ferry</td>
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Chapter 1

Introduction

1.1 Dissertation Objective

The rapid expansion of polymer chemistries and composite materials has revolutionized a variety of industries, ranging from automotive\textsuperscript{1,2} and packaging\textsuperscript{3} to biomedical.\textsuperscript{4} The exceptional properties of these highly-tunable materials, including high strength-to-weight ratio, ease and diversity in processing, chemical resistance, and flexibility, ensure an ever-expanding breadth of applications.\textsuperscript{5} As technology moves to increasingly smaller sizes, demand for the incorporation of polymers into nanoscale devices continues to grow. Polymer thin films have been used as lithography photoresists for semiconductor manufacturing,\textsuperscript{6–8} advanced membranes for separations,\textsuperscript{9–11} biomaterial coatings,\textsuperscript{12} and in organic thin film transistors.\textsuperscript{13}

Research over the past 30 years has revealed that the dynamic, mechanical, and thermal properties of polymers confined to nanometer dimensions can differ substantially from their macroscopic values.\textsuperscript{14–16} For example, the glass transition temperature ($T_g$), at which polymers undergo a dramatic change between rubbery and glassy behavior, can vary tens of degrees from bulk. The accurate prediction of properties of polymers at the nanoscale is essential for their appropriate selection and incorporation into applications. The need to evaluate polymers in these confined geometries has motivated the development of new characterization techniques with enhanced sensitivity and precision.

One such technique, fluorescence spectroscopy, used location-specific measurements of $T_g$ to demonstrate that a competition of interfacial influences, enhanced
in nanoscale geometries due to large surface-to-volume ratios, was largely responsible for deviations from bulk behavior. Ellison and Torkelson showed that in a polystyrene (PS) thin film supported on a silica substrate, enhanced mobility and reduced $T_g$ at the polymer-air interface dominated over bulk $T_g$ at the substrate (dictated by weak polymer-substrate interactions) to depress average film $T_g$. Measurements of $T_g$ at the substrate and free surface of films of a series of poly(n-methacrylates) provided additional evidence that a film’s average $T_g$ reflected a balance between $T_g$ at its interfaces. Furthermore, positive deviations from bulk $T_g$ occurred in thin films when polymer-substrate interactions were strong enough to overcome the free-surface effect. Trends revealed in these studies suggested that the magnitude and direction of $T_g$ deviations could be predicted for a given polymer film based on its thickness and polymer-substrate pairing.

However, recent findings have indicated that film processing can also impact the properties of thin films. Melt-state annealing is common in the preparation of thin films to remove solvent, stresses, and thermal history, but it is not often accounted for in the determination of film properties. Even in cases of weak polymer-substrate interaction, such as polystyrene on silicon, this critical step can lead to the physical adsorption of polymer chains on to the substrate. Many simultaneous interactions with the substrate stabilize these chains against desorption, making them essentially irreversibly adsorbed. A resulting irreversibly adsorbed layer grows in thickness with annealing time and can be isolated by solvent leaching. The growth of this adsorbed layer has been closely correlated with changes in thin film properties, such as $T_g$ and viscosity, with annealing. However, the study of irreversible adsorption has been limited to simple
Chapter 1

model systems, and little is known about how it proceeds with different polymers and annealing conditions.

This dissertation seeks to broaden the understanding of irreversible adsorption in order to better anticipate how annealing impacts the behavior of a wide variety of polymer films. Specifically, we introduce complexities in the form of film geometry and polymer composition and evaluate their impacts on adsorbed layer growth and \( T_g \). In order to accomplish this, we synthesized polymers of controlled composition and molecular weight and annealed their films above \( T_g \) to promote irreversible adsorption. Adsorbed layers were isolated from films after set annealing times by solvent leaching and were measured in terms of thickness and morphology by spectroscopic ellipsometry and atomic force microscopy (AFM). \( T_g \) of select adsorbed layers were also measured by fluorescence spectroscopy. These measurements were compiled to trace the growth and \( T_g \) of adsorbed layers as impacted by the presence of a free surface, compositional heterogeneity, and film thickness.

1.2 Dissertation Organization

This introductory chapter provides motivation, context, and orientation for this dissertation. The next three chapters include background on fundamental concepts and previous work necessary for the understanding of this thesis work. Chapter 2 introduces amorphous polymers, the glass transition, and how properties can change when polymers are confined to nanoscale dimensions. Chapter 3 describes the irreversible adsorption of polymer chains to a substrate during melt-state annealing, its origins in theory and solution studies, and its ability to impact the properties of thin films. Chapter 4 presents the basic physics of the fluorescence characterization technique used in this dissertation.
Chapter 1

to measure adsorbed layer $T_g$. Prior contributions of this technique to the characterization of nanoscale polymers and evaluation of interfacial influences are also reviewed. We published much of this chapter as a review article in *Macromolecular Chemistry and Physics.* 23 Chapter 5 provides an overview of the major experimental techniques employed in the following results chapters of this dissertation. It includes descriptions of spectroscopic ellipsometry, AFM, and fluorescence, as well as an evaluation of the protocol for the creation and isolation of irreversibly adsorbed layers.

Chapter 6 presents our experimental investigation of the influence of a free surface on irreversibly adsorbed layer $T_g$. It describes our synthesis of pyrene-labeled PS as well as our evaluation of the growth of its adsorbed layers. The chapter then discusses the use of fluorescence to conduct location-specific $T_g$ measurements of exposed and buried adsorbed layers. We compare these measurements in order to evaluate how the free surface and adsorption at the substrate compete to influence adsorbed layer $T_g$ at different stages of its growth. Results are quantified using the Free Volume Holes Diffusion (FVHD) model, relating adsorbed layer $T_g$ to the escape of internal free volume at interfaces. The work described in this chapter was published in *Macromolecules.* 24

Chapter 7 discusses how compositional heterogeneity and different polymer-substrate interactions impact the irreversible adsorption of random copolymers. It describes our synthesis and characterization of a series of poly(styrene-random-methylmethacrylate) copolymers with different compositions. Trends in adsorbed layer plateau thickness, growth kinetics, and sensitivity to annealing temperature and leaching solvent are discussed with regard to polymer composition and polymer-substrate interactions. We use these results to propose a mechanism for copolymer adsorption that
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explains how the combination of different segment-substrate interaction strengths in a single chain creates a barrier for copolymer adsorption. Finally, we discuss our attempts to use copolymer adsorbed layers as neutral substrates for block copolymer alignment. Some of this work was recently accepted for publication in *Soft Matter*.

Chapter 8 examines irreversible adsorption in confined films and how deviations in film $T_g$ at the substrate interface can impact adsorbed layer growth. It discusses our efforts to connect differences in adsorption kinetics observed in poly(tert-butylstyrene) (PtBS) thin films with their dramatic deviations in $T_g$ under confinement. We discuss how relationships between adsorption kinetics and effective annealing temperature can be used to predict the extent of adsorbed layer growth in films of various thicknesses for a given annealing protocol (time and temperature). The chapter closes with a description of our efforts to synthesize pyrene-labeled PtBS for use in fluorescence measurements.

A summary of this dissertation is presented in Chapter 9, along with recommendations for future work to extend the generality of irreversible adsorption. Appendices follow Chapter 9, and include a list of publications (Appendix A), descriptions of polymers synthesized (Appendix B), and calculations for the FVHD model used to interpret data in Chapter 6 (Appendix C).
1.3 References


Chapter 2

The Glass Transition in Amorphous Polymers and the Effects of Geometric Confinement

The next three chapters are intended to provide background in the fundamental concepts of relevance to this dissertation. This chapter begins with a brief introduction to polymer structure and composition. It then discusses the glass transition phenomena in bulk polymer systems. Focus then shifts to how the glass transition behavior of polymers changes upon geometric confinement. Particular attention is given to the importance of interfacial influences in determining polymer properties at the nanoscale. The role of interfaces is then expanded upon in Chapters 3 and 4.

2.1 Polymer Structure and Composition

A polymer is a chain-like molecule that consists of many individual repeat units, or monomers, that are connected to each other by covalent bonds. The long-chain nature of these macromolecules gives them the unique chemical and physical properties mentioned in Chapter 1. Controlling the length and architecture of polymer chains, along with the identity and arrangement of their monomer units, enables the tuning of numerous macroscopic properties over a wide range.

The number of repeat units in a polymer chain is referred to as the degree of polymerization, $N$. Each polymer is comprised of a distribution of chains of different lengths, so its molecular weight ($M$) is represented by an average value that can be calculated either by dividing the total number of repeat units by the total number of chains ($M_n$), or by weighting chain contributions proportionally to the length of the chain.
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$(M_w)$. The dispersity, $D$, defined as the ratio of $M_w$ to $M_N$, provides a measure of the breadth of the distribution. While this dissertation will only focus on linear polymers, in which all the monomer units form a single one-dimensional chain, polymers can have different chain architectures as well, including branched, ring, and crosslinked networks.

Macromolecules are often in the range of nanometers in size, which depends on chain conformation as well as length. Chain conformations are impacted by both polymer chemistry and interactions with the surrounding environment. Ideal polymer chains do not factor in intermolecular forces or polymer-solvent interactions and model polymer conformations are similar to random walks, where steps of equal length are made independent of previous steps. There are several models to describe ideal chains, imposing various levels of constraints on their conformations, which all seek to relate chain length, $N$, to end-to-end distance. This distance is often translated to a radius of gyration ($R_g$), or the average distance of each monomer from the polymer’s center of gravity. This value is roughly depicted relative to a polymer chain in Figure 2.1. The exact relationship between $N$ and $R_g$ for ideal chains depends on monomer size, backbone stiffness, and architecture, but it generally follows the following scaling for linear polymers:

$$R_g = \frac{bN^{1/2}}{\sqrt{6}}$$  \hspace{1cm} (2.1)

where $b$ is a segmental Kuhn length that reflects monomer length and chain rigidity. $R_g$ can be measured by several scattering techniques, and its scaling with $N^{1/2}$ (and it follows $M^{1/2}$) is consistent with experiments.¹

Real chain conformations are further impacted by their environment and the balance between monomer-monomer and solvent-monomer interactions. Solvents are
classified for each polymer based on how they impact the chain conformation. In melts and in $\theta$-conditions (specific solvents and temperatures), intermolecular forces are shielded either by other monomers or the solvent, enabling the chain to adopt ideal conformations. Good solvents induce swelling in the polymer, increasing $R_g$ due to effective repulsions between monomers (preference for the solvent). Poor solvents cause polymer chains to collapse to smaller configurations because monomers prefer to interact with each other rather than the solvent.

Polymers consisting of only one type of monomer are called homopolymers, while those that combine two or more chemically distinct monomers are referred to as heteropolymers. The arrangement of monomers within heteropolymers dictates their classification. This dissertation will focus primarily on homopolymers, with Chapter 7 introducing two types of copolymers (heteropolymers consisting of two distinct monomers): random and block. Random copolymers are statistical copolymers consisting of different monomers randomly arranged throughout the chain. They are considered statistical copolymers because their arrangement results from monomer spatial distribution and preferential addition during polymerization. In a block copolymer, monomers are arranged in long segments of like composition, resembling homopolymers connected by a covalent bond. Generalized depictions of a homopolymer, random copolymer, and bulk copolymer are given in Figure 2.1. Several textbooks provide detailed references on the physics of bulk polymers.\textsuperscript{2,3}
Figure 2.1 Schematic of polymer physical and chemical structure. (Top) The size of a polymer chain, made up of many covalently-linked monomers, is often described by its radius of gyration ($R_g$), which is the average distance of any repeat unit from the chain’s center of gravity. (Bottom) The different composition classes of polymers included in this dissertation, with chemically distinct repeat units “A” (blue) and “B” (red). Both copolymers are depicted with symmetric molar composition.
2.2 The Glass Transition

The glass transition occurs when a liquid, super-cooled below its crystallization temperature, falls out of equilibrium and is kinetically arrested in an amorphous state. Unlike a crystalline solid, this non-equilibrium amorphous phase has no long-range order and structurally resembles a liquid. Kinetic trapping, or the “freezing in” of molecular structure, occurs when the cooling rate (i.e., experimental timescale) is faster than the rate of molecular rearrangement (i.e., relaxation timescale). As such, an increase in experimental cooling rate increases the temperature at which the glass transition is observed ($T_g$). In principle, any material should be able to form a glass with sufficiently high cooling rates. However, these rates are often prohibitively high for small molecules that readily crystallize. At the macroscale, this transition is accompanied by a many-orders-of-magnitude increase in a material’s viscosity and a change from rubbery or liquid-like behavior to the solid-like behavior of a glass.

The dramatic change in material properties accompanying the glass transition makes $T_g$ an important classifying thermal property of amorphous materials. Many polymers, including all those used in this dissertation, are completely amorphous and do not undergo crystallization. However, $T_g$ still strongly impacts semi-crystalline polymers, which all possess a significant amorphous fraction due to packing frustration preventing the complete incorporation of chains into a crystal lattice. As such, the performance and resulting selection of all polymers for applications are strongly impacted by their $T_g$. For example, applications that require a flexible, rubbery polymer should seek one with a $T_g$ below its use temperature; this could be polyisoprene or polybutadiene at room temperature. By contrast, polymers that are desired to be hard should be used at
temperatures below their $T_g$, where they exist in a glassy state. Polystyrene (PS) and poly(methyl methacrylate) (PMMA) are both glassy at room temperature. Polymer $T_g$ is impacted by free volume, attractive forces between molecules, and the incorporation of plasticizers or copolymers, as well as intramolecular factors such as internal chain mobility, chain stiffness, and chain length.\textsuperscript{2}

The glass transition is still a major area of research and a conclusive theoretical explanation has yet to reach consensus in the field. Major causes for difficulty in describing it theoretically lie in the fact that it possesses characteristics of both a thermodynamic and kinetic transition.

### 2.2.1 Glass Transition Thermodynamics

Figure 2.2 illustrates the glass transition as it is often depicted thermodynamically: a change in the slope of a thermal property proportional to the derivative of free energy, such as specific volume or enthalpy, against temperature. The glass transition resembles a second-order phase transition, because it also presents as a gradual step change in a second-order derivative of the free energy (such as heat capacity or thermal expansion coefficient). However, since it designates the transition from an equilibrium state to a non-equilibrium state, rather than between two equilibrium states, it is not a true thermodynamic phase transition. This is further supported by the dependence of $T_g$ on experimental cooling rate.\textsuperscript{5}

The $T_g$ in bulk polymer systems can be measured thermodynamically or pseudo-thermodynamically, based on changes in thermodynamic properties or properties that reflect thermodynamic properties, respectively. The most common thermodynamic measurement technique is differential scanning calorimetry (DSC), which measures $T_g$ as

\textsuperscript{5}
Figure 2.2. Illustration of the glass transition (shown in blue) and physical aging (shown in red) on a plot of specific volume or enthalpy against temperature. $T_g$ is the temperature at which a liquid, super-cooled below its melting temperature ($T_m$) falls out of equilibrium and into a glassy state. Physical aging is the gradual relaxation of a glass towards equilibrium when annealed at a temperature below $T_g$. 
Chapter 2

a step change in heat capacity or heat flow with temperature and is described further in Chapter 5. Volume dilatometry, used in many classical papers on the glass transition, measures $T_g$ as a change in the temperature-dependence of molar volume. Pseudo-thermodynamic measurement techniques that measure volume indirectly include ellipsometry (measures thickness), capacitive dilatometry (capacitance), and fluorescence (fluorescence intensity); they will be described in Section 2.3 and Chapter 3.

2.2.2 Glass Transition Dynamics

Despite commonalities with thermodynamic phase transitions, the glass transition is a kinetic phenomenon that occurs when molecules are unable to relax during the experimental timescale. As such, $T_g$ is closely tied to chain mobility and relaxation events. Due to their long-chain nature, polymers undergo many different motions and relaxations at different length scales and corresponding timescales. $T_g$ is most commonly associated with segmental relaxation and cooperative movement, which are referred to as $\alpha$-relaxation dynamics in amorphous polymers. These dynamics can be represented by a relaxation distribution function $r(t)$, that follows the Kohlrausch-Williams-Watt (KWW) form

$$r(t) = e^{-(t/\tau)^{\beta}} \quad (2.2)$$

where $\tau$ is a characteristic relaxation time and $\beta$ is the stretching exponent associated with the breadth of the relaxation time distribution.

Well above $T_g$, these characteristic relaxation times follow Arrhenius temperature dependence. However, kinetic trapping that occurs when $T_g$ is approached from the melt increases the energy barrier for segmental motion and leads to a dramatic increase in the time needed for relaxations to take place. The resulting increased temperature
sensitivity of relaxation times near $T_g$ is referred to as “super-Arrhenius” behavior, and it can be described by the Vogel-Fulcher-Tammann (VFT) equation:\textsuperscript{5}

$$\tau = \tau_0 e^{\left(\frac{B}{T - T_0}\right)} \quad (2.3)$$

where $\tau_0$ is a pre-exponential factor, $B$ is the Vogel activation energy, and $T_0$ is the Vogel temperature. This equation also holds for measurements of viscosity near $T_g$ and is mathematically equivalent to the Williams-Landel-Ferry (WLF) equation used to describe the time-temperature superposition of polymer mechanical properties.\textsuperscript{13} Figure 2.3 illustrates the dramatic increase in relaxation time and viscosity ($\eta$) near $T_g$. Convention defines $T_g$ as the temperature where $\tau = 100$ s and $\eta = 10^{13}$ Pa.\textsuperscript{4,5} The temperature-dependence of relaxation time is consistent with the dependence of calorimetric $T_g$ on cooling rate, further illustrating connections between $T_g$ measured thermally and dynamics in bulk systems.

$\alpha$-relaxation dynamics can be measured experimentally by a variety of techniques, including dynamic mechanical analysis (DMA)\textsuperscript{14} and dielectric spectroscopy\textsuperscript{15,16} (referred to as dielectric relaxation spectroscopy, DRS, and broadband dielectric spectroscopy, BDS). Temperature sweeps in isochronal conditions show peaks in viscous contributions, such as loss modulus ($G''$ in DMA) and dielectric loss ($\varepsilon''$ in DRS), corresponding to $\alpha$-relaxation. The temperature at which these peaks occur is referred to as $T_\alpha$ and is equal to $T_g$ (for a fixed cooling rate) at a measurement frequency of 1 mHz, (corresponding to relaxation times of 100 s).\textsuperscript{17} Alternatively, isothermal experiments show peaks in $G''$ and $\varepsilon''$ at frequencies corresponding to characteristic relaxation times, which can be input into Equation 2.3 and extrapolated to determine $T_g = T(\tau = 100$ s).\textsuperscript{18}
Figure 2.3 Schematic of dynamics near the glass transition, which can be described by Equation 2.3. $T_g$ is defined dynamically as the temperature upon cooling at which a glass-former’s relaxation time ($\tau$) slows to 100 s or its viscosity ($\eta$) increases to $10^{13}$ P.
addition to dynamic $T_g$, these measurements can be used to characterize the relaxation time distribution function, following Equation 2.2.

### 2.2.3 Theories of the Glass Transition

The dual thermodynamic and kinetic characteristics of the glass transition have made it difficult to describe theoretically. Another complication is illustrated in Figure 2.2. The extrapolated liquid line has a steeper slope than the crystalline line, implying that if a super-cooled liquid were cooled infinitely slowly, it could cross below the crystalline line and reach zero entropy before the temperature reaches absolute zero. Given that the crystalline state must have a lower configurational entropy, this causes a theoretical inconsistency referred to as the Kauzmann paradox. Resolution of the Kauzmann paradox provides another complexity in arriving at a unifying explanation of the glass transition. Several classical theories describing the glass transition exist, though none have been universally accepted. Three of these theories: (1) Gibbs-DiMarzio, (2) Free Volume, and (3) Adam-Gibbs will be briefly described below.

The Gibbs-DiMarzio Theory predicted that if a glass was cooled infinitely slowly, it would reach an equilibrium state with configurational entropy equal to that of a crystal and undergo a true thermodynamic phase transition at temperature $T_2$. In order to determine an expression for conformational entropy necessary for their calculations, Gibbs and DiMarzio developed a partition function based on a Flory-Huggins lattice model. This model described the number of chain conformations accessible to polymers of length $N$ on a lattice with a specific number of vacancy sites. The size of the lattice, reflecting temperature, determined the concentration of vacancies and thus the number of configurations. Since their calculations were all derived from a polymer lattice, this
theory only applied to polymeric glass-formers. Despite its successful prediction of $M$, composition, plasticization, and crosslinking impacts on $T_g$,\textsuperscript{20} the inability of the Gibbs-DiMarzio Theory to describe small molecule glass-formers or provide a value for $T_2$ limited its generality and adoption.

The free-volume interpretation of the glass transition has developed over time through several key contributions relating a material’s temperature-dependent relaxation dynamics (such as viscosity and segmental mobility) to the presence and quantity of free volume. In amorphous polymers, free volume results from chain packing frustration and is defined as the difference between the total volume of polymer and the volume occupied by polymer chains. The collection of holes, or voids, comprising free volume enables molecules to rearrange by filling voids and creating new voids in the vacated space. The relationship between mobility and free volume, developed by Doolittle for small-molecule glass formers,\textsuperscript{21} was extended to polymers by Williams, Landel, and Ferry in their WLF equation:\textsuperscript{13}

$$\log a_T = \frac{-B}{2.303 f_0} \left[ \frac{T-T_0}{f_0/\alpha_f + (T-T_0)} \right] = \frac{-C_1(T-T_0)}{C_2(T-T_0)}$$  \hspace{1cm} (2.4)

where $a_T$ is a shift factor for time-dependent properties (such as relaxation time and viscosity), $T$ is temperature, $T_0$ is a reference temperature (usually taken as $T_g$), $f_0$ is the fraction of free volume at $T_0$, $\alpha_f$ is the expansion coefficient of free volume, $B$ is a constant taken to be 1, and $C_1$ and $C_2$ are empirical constants. They fit this relation to experimental viscosity data for a wide variety of polymeric and small-molecule glass-formers and determined “universal” values for $C_1$ and $C_2$. These values, with $T_0$ set to $T_g$, enabled the determination of $f_0 = 0.025$, defining the fraction of free volume at which polymer chain mobility is sufficiently restricted to initiate the glass transition. The WLF
equation has been used extensively to relate the time and temperature-dependent viscoelastic properties of polymers, and it also accounts for the 3-5 K change in $T_g$ observed for each decade in experimental cooling rate. Williams, Landel, and Ferry also predicted that $\log(a_T)$ (corresponding to viscosity, relaxation time, etc.) becomes infinite at approximately 50 K below $T_g$, thus the Kauzmann temperature is not reached for kinetic reasons. The relationship between free volume and the glass transition has been employed as a foundation for the Free-Volume Holes Diffusion (FVHD) Model that will be described in more detail in Section 2.3.4.

Adam-Gibbs Theory attempted to resolve differences in the previous two theories by incorporating both kinetic and thermodynamic arguments in its description of the glass transition and resolution of the Kauzmann paradox. Most notably, this theory described the presence of cooperatively rearranging regions (CRRs): sub-volumes of the glass-forming material that can move cooperatively without requiring the rearrangement of surrounding sub-volumes. These CRRs were a collection of molecules in a small-molecule glass former, or a collection of polymer chain segments in a polymeric glass former. The collective motion of molecules or segments within CRRs contributed to the molecular mobility of a glass-forming material. The average size of each CRR was proposed to grow as temperature decreased toward $T_g$ by incorporating more molecules or segments, resulting in a loss of configurational entropy due to the increased cooperative motion. Adam and Gibbs combined this description of segmental mobility with the WLF equation to determine the temperature for the underlying thermodynamic transition proposed by Gibbs and DiMarzio. Their resulting empirical relation $T_g/T_2 =$
1.30 ± 8.4% was in good agreement with the temperature at which the WLF equation predicted a divergence in \( \log(a_T) \).\(^{22}\)

### 2.2.4 Physical Aging

As intrinsically out-of-equilibrium materials, glasses gradually approach thermodynamic equilibrium below \( T_g \) in a process referred to as physical aging or structural relaxation.\(^{23}\) This process manifests as the slow rearrangement of molecules towards more efficient packing, and changes in the thermodynamic properties with time. For example, a decrease in specific volume with time\(^{24}\) is shown in red in Figure 2.2. Changes in these properties also result in time-dependent mechanical and optical properties, making accounting for physical aging critical in determining the use and applications of polymer glasses, particularly over extended time periods. The rate of physical aging is governed by two accelerating factors: (1) stronger thermodynamic driving forces at lower temperatures, and (2) faster mobility at higher temperatures.\(^{25}\) These competing effects result in a peak in the rate of physical aging\(^{26}\) at a certain temperature, which is often described relative to \( T_g \).

Physical aging in bulk systems is often measured by monitoring changes the thermodynamic properties of volume (via dilatometry) or enthalpy (via DSC) with time.\(^{27}\) Upon sufficient aging at a given temperature, these properties will plateau to their equilibrium values (corresponding to the extrapolated liquid line). The time to reach this plateau as well as the change in volume or enthalpy required to reach it are used to quantify the rate of aging and structure of a glass, respectively.\(^{28}\) The fictive temperature \( (T_f) \) is the temperature at which a glassy line from an aged glass would intersect the extrapolated liquid line. It also describes the structure of a glass and can be thought of as
the liquid-state temperature kinetically trapped into the glass. Physical aging can also be measured dynamically via DRS.

2.3 Properties of Polymers under Nanoscale Confinement

Recent advances in polymer nanotechnology for applications in renewable energy, electronics, and healthcare drive improved characterization of nanoscale polymer systems. This geometric confinement, or the restriction of one or more dimensions to less than ~100 nanometers, greatly increases a polymer’s surface-to-volume ratio and reduces the overall dimensions to the order of molecular size (e.g., $R_g$). Over the past few decades, there has been substantial investigation into the deviation from macroscopic-scale, or bulk, properties observed in polymers when confined to the nanoscale. Researchers have observed dramatic changes in the $T_g$, physical aging, mobility, fragility, diffusion, viscosity, elastic modulus, and rubbery stiffening, with very few exceptions. The magnitude and direction of these deviations, as well as the confinement length scale necessary to induce changes, varies for specific polymer systems. These deviations have largely been attributed to the strong influence of surrounding interfaces due to large surface-to-volume ratios. Understanding the origin of these changes in behavior and being able to predict their deviations from bulk systems are essential to enabling polymer nanotechnology. Although this dissertation focuses mainly on one-dimensional (1D) confinement in the form of thin films (with thickness as the confining dimension), 2D (e.g., rods) and 3D (e.g., nanoparticles) confined systems have also been studied. Polymer films are further subdivided by the number of free (i.e., air) interfaces; films with two are “free-
Chapter 2

standing”, with one are “supported”, and with none are “capped”. These geometries are depicted in Figure 2.4a.

Confined geometries pose challenges to existing characterization techniques due to sensitivity limits and sample geometry requirements. These limitations have led to the development of new approaches, adapted to conducting nanometer-scale measurements. This section describes both techniques that have enabled the study of polymer properties restricted to the nanoscale as well as observed deviations of these properties from bulk.

In Section 2.2, we described the glass transition in bulk systems as having thermodynamic and kinetic signatures that are closely related. However, conflicting measurements of these properties at the nanoscale suggest a separation in $T_g$ measured thermodynamically and dynamically with the onset of confinement. While several attempts to resolve these differences have been made, a conclusive explanation has not been found. As such, they are described separately here as $T_g$ and segmental mobility and dynamics.

2.3.1 The Glass Transition Temperature ($T_g$)

The first observation of a size-dependent effect on $T_g$ was reported by Jackson and McKenna when they measured a depressed calorimetric $T_g$ in ortho-terphenyl confined to nanopores. This size-dependence of $T_g$ was extended in 1994 to polymer thin films in a seminal work by Keddie, Jones, and Corey. Ellipsometry allowed for the measurement of small changes in film thickness (effectively volume) with temperature and enabled determination of $T_g$ pseudo-thermodynamically. They observed a reduction in the $T_g$ of PS films supported on silicon (Si) with decreasing film thickness, down to ~20 K below bulk in ~15-nm-thick films. The deviations from bulk, starting at ~40 nm,
Figure 2.4 (A) Depiction of polymer thin film geometries, with the polymer film in blue and substrate in dark grey. (B) Glass transition temperature ($T_g$) of supported polystyrene thin films as a function of film thickness ($h$) compiled from different measurement techniques. Republished with permission of Taylor and Francis, from Ref.\textsuperscript{11} Permission conveyed through Copyright Clearance Center, Inc.
were much larger than those previously observed for small molecules, suggesting that the long-chain nature of polymers magnified the influence of confinement on the glass transition. Keddie et al. fit their thickness-dependent $T_g$ data to the function:

$$T_g(h) = T_g(\text{bulk}) \left[1 - \left(\frac{A}{h}\right)^\delta\right]$$

(2.5)

where $h$ is film thickness, $A$ is a characteristic length ($= 3.2 \text{ nm} \pm 0.6 \text{ nm}$), and $\delta$ is an exponent ($= 1.8 \pm 0.2$). The $M$-independence of $A$ suggested that their observed deviations in $T_g$ were not due to perturbations to chain size with confinement. Rather, they concluded that the deviations were due to the strong influence of a liquid-like layer at the polymer-air (free) interface that grew in proportion to the film with decreasing $h$.

The same technique was used to measure the $T_g$ of supported PMMA thin films. In contrast to the behavior of PS, PMMA films increased in $T_g$ with decreasing $h$ when supported on Si. This positive deviation from bulk $T_g$ was attributed to stronger substrate interactions from hydrogen bonding with the native-oxide layer on the Si. Measurements of PMMA supported on gold showed a negative $T_g$ deviation with decreasing $h$, indicating that both the free surface and polymer-substrate interactions contribute to the direction and magnitude of changes in $T_g$ with geometric confinement.

The balance of interfacial influences continued to be a leading hypothesis for confined $T_g$ behavior in polymer thin films for much of the next decade, and additional techniques were adapted to achieve further insight. Figure 2.4b illustrates the widely-observed decrease in PS $T_g$ when supported by several different substrates (including aluminum, hydrogen-passivated Si, and Si with a native oxide layer), as measured by a variety of techniques. The common results, despite different substrates emphasized the
dominance of the free surface influence over weak interactions at the substrate in determining \( T_g \) of this commonly-investigated model system.

Interest in the free-surface effect on \( T_g \) grew when Brillouin light scattering (BLS)\(^{44,54,77}\) and transmission ellipsometry\(^{41,51,78}\) enabled the measurement of free-standing thin film \( T_g \). These techniques detect \( T_g \) as a change in temperature-dependence of longitudinal phonon frequency\(^{79}\) and film thickness,\(^{78}\) respectively. The presence of two free surfaces, and hence a lack of substrate interactions, enhanced negative \( T_g \) deviations beyond those measured in supported films. The \( T_g \) of \( \sim 40 \)-nm-thick freestanding films of PS and PMMA measured 55 K\(^{78}\) and 15 K\(^{41}\) below their respective bulk values. This persistent difference in the magnitude of their deviations, even in an unsupported geometry, suggested that the relative strength of substrate interactions could not be entirely responsible for the difference in their confinement behavior. The correlation between these larger deviations and the increased number of free surfaces was confirmed in a study by Baumchen et al. where freestanding PS films were measured before and after their placement onto substrates.\(^{51}\) The latter measurements had much smaller \( T_g \) reductions with respect to bulk, in line with those reported for supported films directly spin-coated atop substrates.

Deviations in free-standing film \( T_g \) exhibited a dependence on \( M_W \) that was not present for supported films.\(^{77,78}\) An increase in the magnitude of \( T_g \) deviation with increasing \( M_W \) was only observed at high molecular weights (\( >380 \) kg/mol) and was attributed to chain conformation effects.\(^{78}\) However, the reason for its absence in supported films is still not understood. Recent work by Pye and Roth provided evidence of a second, stronger, \( M_W \)-independent \( T_g \) at high temperatures in freestanding high \( M_W \)
films, suggesting multiple mechanisms for propagation of the free surface’s influence into films.\textsuperscript{80,81}

Even with signal-strength limitations, we note that several studies used conventional DSC to measure $T_g$ of stacked ultrathin polymer films, remarkably finding similar behavior to free-standing films.\textsuperscript{82–85} These experiments involved stacking dozens, and in some cases hundreds, of films in order to achieve adequate signal. The recent development of nanocalorimetry, or Flash DSC, has enabled nanoscale measurements of the calorimetric $T_g$ with cooling rates spanning several decades. Using a Flash DSC, Gao \textit{et al.} measured $T_g$ of single ultrathin PS films supported on oil as well as on a rigid substrate and found them in agreement with those of supported PS on silicon.\textsuperscript{86} Shamim \textit{et al.} employed a similar technique to measure $T_g$ of polycarbonate (PC), and they also observed a reduction in $T_g$ depression with increasing cooling rate.\textsuperscript{49} Positron annihilation lifetime spectroscopy (PALS),\textsuperscript{87} and neutron reflectivity\textsuperscript{88,89} have also been used to characterize thin film $T_g$, as measured pseudo-thermodynamically by changes in the temperature-dependence of positronium lifetime (reflects volume) and thickness, respectively.

Understanding and predicting confined polymer $T_g$ is critical to advancing the application of polymers in nanotechnology. Interest in this field has produced a multitude of research, and several studies and review articles provide additional details on the subject.\textsuperscript{35,38,42,46,47,74} Although the majority of the experimental studies described above attribute confined $T_g$ behavior to strong interfacial influences, they relied on model fitting and indirect measurements of local $T_g$ to support their conclusions.\textsuperscript{36,44,90} Simulation and theoretical work also showed strong evidence of interfacial effects on $T_g$.\textsuperscript{91–93} Prior to the
development of fluorescence techniques, to be described in Chapter 3, confinement studies were limited to measurements of $T_g$ averaged across films, thus lacking the ability to provide direct, location-specific measurements.

2.3.2 Segmental Mobility and Dynamics

Studies of segmental dynamics under confinement have focused on the free surface, with multiple experiments illustrating the presence of a liquid-like layer with enhanced mobility at the free surface of PS and other polymers. The thickness of this layer has been observed to increase when heating a film toward $T_g$, with a maximum thickness between 3 and 10 nm, depending on the polymer. Interestingly, this is much thinner than the 30 - 40 nm length scale over which deviations in average film $T_g$ are observed in supported PS. Several additional methods have been used to probe polymer chain motion under confinement such as dewetting, hole growth, nanoembedding, and various surface relaxation techniques. These studies, either by probing the free-surface or averaging dynamics across the whole polymer film, have shown enhanced mobility and a broadening of dynamics in free-surface layers propagating several nanometers into the polymer film. The length-scale and magnitude of enhanced surface mobility varied depending on polymer, experimental temperature, and measurement technique.

Measurements of average polymer segmental dynamics in thin films have been conducted largely by BDS. Although $T_\alpha$ is closely associated with $T_g$ in bulk polymers, its confined values were constant or decreased only slightly in thin films, while $T_g$ decreased significantly. These differences between $T_\alpha$ and $T_g$ were largely attributed to sample artifacts from insufficient equilibration. However,
techniques are being developed to measure $T_g$ by both pseudo-thermodynamic and dynamic means in samples prepared identically. Capacitive dilatometry and DRS can measure $T_g$ and $\alpha$-relaxation dynamics in the same sample by probing different frequencies, eliminating contributions to the results from sample preparation. Measurements of PS nanospheres with different diameters showed the expected $T_g$ decrease with confinement when measured by capacitive dilatometry, but no change in $T_\alpha$ was observed with confinement.\textsuperscript{112} Sharp and Forrest also measured samples in identical geometries by DRS and ellipsometry, finding a strong divergence in $T_g$ and $T_\alpha$ for isotactic PMMA films.\textsuperscript{110} These direct comparisons suggested a real separation of $T_g$ and segmental dynamics in confinement, which has been addressed in several reviews.\textsuperscript{35,40,108}

### 2.3.3 Physical Aging

Physical aging has also been shown to deviate from bulk behavior upon confinement, and the requirement that physical aging occurs below $T_g$ suggests that physical aging under confinement would be impacted by deviations in confined $T_g$. The relationship between these two properties at the nanoscale is an ongoing area of research, and a substantial body of work exists examining the effects of confinement on physical aging of polymer thin films.\textsuperscript{25,26,55,56,113,114} Similar to $T_g$ measurements, conventional tools for characterizing physical aging in bulk samples have limitations in nanoscale characterization due to their lack of sensitivity and accessibility. Koh and Simon made an important distinction between the time to reach equilibrium, $\tau_e$, and aging rate as methods to quantify physical aging.\textsuperscript{83} These two different methods are both used in the literature to describe physical aging under confinement, so attention should be given to which method is employed.\textsuperscript{29}
Kawana et al. used small changes in film thickness with temperature (measured via ellipsometry) to derive thermal expansivity overshoots, which quantified the degree of physical aging, for PS films of different thickness aged at 343 K and 353 K for up to 7 days. They observed smaller overshoots in thinner films, which indicated a decrease in the extent of physical aging with increased confinement. However, these expansivity overshoots were still observed in 18-nm films after aging at the predicted confined $T_g$ (~353 K), suggesting that some portion of the films were still glassy. They attributed the presence of physical aging in these films to heterogeneous behavior where a ~10-nm liquid-like layer at the free interface was above the $T_g$, but the remainder of the film remained glassy and underwent bulk-like physical aging. This two-layer model was substantiated by the absence of a detectable overshoot in 10-nm-thick films (i.e., they were all liquid-like) and a thickness-independent overshoot temperature in thicker films. However, direct measurement of this mobile layer was not possible via ellipsometry.

Calorimetric measurements of confined PS films also supported deviations in physical aging due to reduced $T_g$. Although mass requirements prevented measurements of single ultrathin films via conventional DSC, Koh and Simon used this technique to measure confined structural relaxation in stacked PS thin films. They reported faster $\tau_e$ but slower physical aging rates in thin films compared to bulk when annealed at identical temperatures. However, annealing films relative to their confined $T_g$s yielded slightly longer $\tau_e$ in confined films and similar aging rates to bulk. This suggested that deviations in physical aging of ultrathin films were solely an effect of their reduced $T_g$, and equilibrium was reached faster in thinner films due to their increased mobility resulting from the proximity of aging temperature to confined $T_g$. Boucher et al. also measured
faster $\tau_e$ in confined PS films by a similar technique.\textsuperscript{115} Nanocalorimetry shows promise for characterizing single ultrathin films, but it has thus far mostly been used to expand the range of aging times and temperatures of structural recovery measurements in films for which thickness was greater than 1 $\mu$m.\textsuperscript{116,117} Very recent work by Koh and Simon examined aging in a single 20-nm-thick PS film and found faster aging rates, shorter $\tau_e$, and a broader distribution of relaxation times compared to bulk.\textsuperscript{118} The examination of a wider range of thicknesses would elucidate thickness-dependent trends.

Despite this initial evidence of a link, the relationship between physical aging and $T_g$ at the nanoscale remains unclear. Pye \textit{et al.} studied the thickness- and temperature-dependent aging of supported PS films via ellipsometry, calculating aging rate by plotting normalized film thickness against log aging time.\textsuperscript{26} They also observed a decrease in aging rate with film thickness at the temperature of peak bulk aging rate. However, measuring confined film aging rates at different temperatures showed not just a shift due to reductions in $T_g$, but that confined films had consistently lower aging rates at a range of temperatures. Comparisons between length scales of gradients in mobility and $T_g$\textsuperscript{119} led to the conclusion that while aging and $T_g$ under confinement derived from a similar mechanism, aging was not simply reflective of the shift in $T_g$.

While researchers largely report suppressed physical aging in supported thin films,\textsuperscript{26,83,113} free-standing films—characterized by transmission ellipsometry,\textsuperscript{114} PALS,\textsuperscript{120} and gas permeativity\textsuperscript{121,122}—have been widely observed to exhibit enhanced physical aging over large length scales.\textsuperscript{121–123} However, work by Pye and Roth suggested that this behavior, in films thicker than 200 nm, was likely due to thickness-dependent
stresses imposed on each sample by a difference between its thermal expansivity and that of the sample holder.\textsuperscript{114}

Physical aging in nanocomposites, where a polymer matrix is confined between nanoparticles with interparticle spacing on the order of ~100 nm, has also been studied extensively by DSC.\textsuperscript{29,124–126} \(\tau_e\) was found to increase relative to neat polymer with increasing surface-to-volume ratio of nanoparticle fillers (\textit{i.e.}, internal interface within the nanocomposite), regardless of the interaction strength between polymer and nanoparticles.\textsuperscript{127} However, accompanying measurements of nanocomposite segmental mobility by BDS showed no deviation from bulk.\textsuperscript{124,126} This suggested a separation of structural relaxation and segmental mobility under confinement, similar to that previously discussed for \(T_g\),\textsuperscript{40} which was rationalized by the Free Volume Holes Diffusion model.\textsuperscript{125,126}

The difference in film thickness for which deviations from bulk \(T_g\) and physical aging behavior are measured in thin films is an ongoing area of research. As with \(T_g\), layer models have been used extensively to interpret observed deviations in rates and extents of physical aging.\textsuperscript{26,113} However, direct measurement of these properties has been limited and correlation between fitted thickness and index of refraction limit aging rate measurements on films with thickness below 30 nm via ellipsometry.\textsuperscript{26}

\textbf{2.3.4 Free Volume Holes Diffusion Model}

Not all deviations in film properties upon confinement can be explained by the influence of interfaces. Namely, negative deviations from bulk \(T_g\) and physical aging rates in capped films and nanocomposites suggested an increase in mobility relative to bulk without the presence of a free interface.\textsuperscript{128,129} These deviations could be due to an
excess of free volume within confined samples resulting from heightened chain packing frustrations. Adaptations have been made to the Free Volume Holes Diffusion (FVHD) model, originally developed to describe physical aging in bulk poly(vinyl acetate),\cite{130} in order to explain how an excess in free volume can lead to lower $T_g$ in capped films and higher physical aging rates in nanocomposites.\cite{7,29,127,129} Here, we describe how FVHD predicts $T_g$.

With roots in free volume theory, this model predicts equilibrium existing when free volume holes present in a glass-former are able to diffuse out to interfaces on the timescale of the experiment. The diffusion of these free volume holes can be described by the equation:\cite{128}

$$\langle x^2 \rangle = 2D(T)t$$

where $\langle x^2 \rangle$ is the mean squared displacement of free volume holes in one dimension, $D(T)$ is the temperature-dependent diffusion coefficient of free volume holes, and $t$ is time. An expression for $D(T)$ in PS was derived from a combination of VFT and Arrhenius relationships.\cite{131}

$T_g$ was defined for a given cooling rate as the temperature at which $\langle x^2 \rangle$ was equal to the relevant sample length scale. This corresponded to the temperature below which free volume holes diffuse less than $\langle x^2 \rangle$ and could therefore no longer escape the sample to achieve equilibrium. The relationship between $T_g$ and the diffusion of free-volume holes was expressed as:\cite{128}

$$L^2 = 2D(T_g)q^{-1}$$

where $L$ is the relevant length scale of the sample, $q$ is the experimental cooling rate, and $D(T_g)$ is the free volume diffusion coefficient at $T_g$. Equation 2.7 could then be used in
combination with the $D(T)$ relationship to give $T_g$. Given that this length scale, or required diffusion distance reflects film thickness, it is intuitive that the system would stay in equilibrium longer, leading to a reduction in $T_g$ with decreasing film thickness. This model has also been used to describe the effects of irreversible adsorption on thin film $T_g$\textsuperscript{128,132} (which will be discussed in Chapter 4) and the experimental results in Chapter 6 of this dissertation.

2.4 Looking Forward

As discussed in Section 2.3, deviations in $T_g$, mobility, and physical aging have been attributed to the influence of interfaces. Both the free surface and polymer-substrate interface contribute toward this observed behavior. However, the strength of this correlation would be greatly improved by the direct measurement of $T_g$ and physical aging rate at the interfaces and at different locations within films in order to quantify the extent of perturbation. These measurements would enable a comparison of length scales crucial to understanding the relationship between $T_g$ and segmental mobility and predicting the behavior of polymers at the nanoscale. A fluorescence technique able to conduct these measurements is described in Chapter 3, along with its resulting contributions to the field.
Chapter 2

2.5 References


Chapter 2


Chapter 2


58. Marvin, M. D., Lang, R. J. & Simmons, D. S. Nanoconfinement effects on the


Chapter 3

A Fluorescence Technique to Characterize Confined Systems

As described in Chapter 2, the thermal and mechanical properties of confined polymers have been observed to deviate substantially from bulk properties, making them a subject of extensive investigation over the past few decades.\textsuperscript{1-3} Although the influence of interfaces was postulated as a major cause of deviations in behavior under confinement, it was not directly demonstrated until the development of a fluorescence characterization technique that enabled location-specific measurement of polymer properties with nanometer resolution. While fluorescence had been used extensively to characterize bulk properties of polymers, including $T_g$\textsuperscript{4-6} and polymerization conversion,\textsuperscript{6} it proved particularly well-suited to study polymers at the nanoscale.

Here, we describe the development and application of this fluorescence technique to investigate the behavior of confined polymers as well as the insights it has provided into how surfaces and interfaces can induce dramatic modifications in key material properties.\textsuperscript{7,8} Specific methods for data collection and analysis are discussed in Chapter 5. This chapter first gives an introduction to the physics of fluorescence, then it describes specific studies that have employed fluorescence to study confined systems, ranging from homopolymer thin films to nano-structured systems.

3.1 Introduction to Fluorescence

When a molecule absorbs energy via light, an electron is excited to a higher energy state, returning to the ground state through either radiative or non-radiative
deactivation. This cycle combines three photophysical processes: absorption, luminescence, and non-radiative decay.\textsuperscript{9} Fluorescence is a type of luminescent process in which the excited-state electron returns to the ground state by emitting a photon (\textit{i.e.}, light). As shown in a simplified Jablonski diagram in Figure 3.1a, absorption of energy by a molecule promotes one of its electrons to one of several vibrational levels \((v_m)\) of the excited state \((S_1)\), from which the electron undergoes internal conversions to return to the lowest excited vibrational state \((S_1v_0)\). From this energy level, the molecule can return the excited-state electron to the ground state \((S_0)\) through emission of a photon (fluorescence) or by non-radiative deactivation in the form of rotational and vibrational motion. These competing deactivation pathways enable fluorescing molecules (\textit{i.e.}, fluorophores) to probe the properties of their surrounding environments due to the sensitivity of non-radiative motion to density changes in the polymer matrix.\textsuperscript{8}

Fluorescence spectroscopy excites fluorophores with light at a specific wavelength and records the emitted light with a photodetector. Transitions between different energy levels during deactivation correspond to the emission of photons at different wavelengths. Collecting these photons gives a characteristic spectrum for each fluorophore, as shown in Figure 3.1b, with the intensity of the spectrum reflecting the number of photons emitted at each wavelength. This fluorescence emission spectrum occurs at longer wavelengths than its corresponding absorption spectrum due to the loss of energy through internal conversion.

Kinetically, the rate equation for unimolecular fluorescence can be described as

\[
\frac{d[M^*]}{dt} = I_0 - (k_f + k_i)[M^*] \tag{3.1}
\]

where \([M^*]\) is the concentration of excited molecules, \(I_0\) is a constant reflective of the
Figure 3.1. (A) Simplified Jablonski diagram illustrates fluorescence as an energy deactivation pathway competing with internal conversion (vibrational or rotational motion resulting in heat loss). (B) Photons corresponding to specific energy levels and wavelengths combine to form a fluorescence emission spectrum. Reprinted from Ref.\textsuperscript{10}
instrumental properties, and $k_f$ and $k_i$ are the rates of fluorescence and non-radiative deactivation, respectively.\(^9\) Fluorescence can be measured through steady-state or transient experiments, the former of which are employed in this thesis and are described in Chapter 5. Steady-state measurements are time-averaged over the fluorophore’s fluorescence lifetime. They use a continuous light source (e.g., a xenon lamp) to excite a sample and collect fluorescence spectra at photostationary conditions. This allows for the assumption that $d[M^*]/dt = 0$, thus the steady-state fluorescence intensity ($I_F$) at a particular wavelength can be described as

$$I_F = k_f [M^*] = I_0 \frac{k_f}{(k_f + k_i)} = I_0 \varphi_f$$  \hspace{1cm} (3.2)

where $\varphi_f$ is the quantum efficiency.\(^9\) This equation clearly illustrates the dependence of fluorescence intensity on relative rates of fluorescence and non-radiative deactivation.

Transient, or fluorescence lifetime, measurements use a pulsed light source and collect emitted intensity as a function of time. Equation 3.1 still applies to these measurements, without the assumption that $d[M^*]/dt = 0$. The fluorescence intensity as a function of time can then be expressed as

$$I_F(t) = k_f M_0 A_1 e^{-(k_f+k_i)t} = F_0 e^{-(k_f+k_i)t}$$  \hspace{1cm} (3.3)

where $A_1$ and $F_0$ are constants.\(^9\) The fluorescence lifetime ($\tau_F$) can be defined as

$$\tau_F = \frac{1}{(k_f + k_i)}$$  \hspace{1cm} (3.4)

Transient measurements are advantageous over steady-state measurements, as they are less sensitive to instrumental background.\(^9\)

The selection of fluorophores, or dyes, is important in designing a fluorescence experiment, and the wide variety of fluorescing molecules available enables their
optimization for each experimental system and technique. A molecule’s quantum yield, defined as the number of photons emitted via fluorescence relative to the number absorbed, is one of the most important factors in its selection. High quantum yield improves measurement sensitivity and reduces the necessary concentration of dye, thus enabling minimal perturbation to polymer matrices. Fluorophores sensitive to minute changes in the density of their surrounding matrix have been used to measure $T_g$ \cite{8,11,12} and physical aging, \cite{13,14} while those with high degrees of anisotropy are desired for dye rotation experiments. \cite{15-17} Dye pairs can also be incorporated into samples as electron donors and acceptors for energy transfer experiments. \cite{18} While these extrinsic fluorophores reflect the properties of their matrices, intrinsic fluorescence measurements of the matrix can also be conducted, \cite{19} eliminating the need to incorporate probes. However, not all matrices intrinsically fluoresce (conjugated bonds are usually needed), and intrinsic signals are often weaker than those of extrinsic probes.

### 3.2 Fluorescence to Measure $T_g$ and Physical Aging in Confined Systems

Fluorescence provides several advantages for characterizing polymers at the nanoscale. The tradeoff between fluorescence and non-radiative energy deactivation enables probing properties of the surrounding polymer matrix. Its high sensitivity gives strong signals relative to the amount of fluorophores, enabling measurements at low concentrations, reflective of an unperturbed matrix. This sensitivity is also ideal for measuring nanoscale samples that do not meet the size or mass requirements of other techniques. The use of extrinsic fluorophores also provides the opportunity for location-specific measurements. Since fluorescence signal is effectively only collected from dye molecules, the location or substructure probed by measurements can be controlled
through the selective placement of dye-labeled polymer within a sample. Finally, the instrumentation required to conduct these measurements is readily accessible, and experiments can be conducted in-house.

These advantages have enabled its large contribution to the understanding of how properties are impacted by the substrate and free surface in confined systems. A select subset of measurements enabled by fluorescence is represented in Figure 3.2. This technique has been applied to study single-component thin films in both supported \(^7,^8,^11,^13,^19-^23\) (Figure 3.2a) and freestanding \(^24,^25\) (Figure 3.2b) geometries, nanocomposites \(^23,^26\) (Figure 3.2i), patterned \(^27\) (Figure 3.2j), and nano-structured films such as irreversibly adsorbed layers \(^28\) (Figure 3.2k) and brushes \(^29\) (Figure 3.2l). It has also enabled the examination of polymer-polymer interfaces \(^30-^32\) (Figure 3.2g) and phase separation \(^33\) (Figure 3.2h) in multicomponent systems. The next section provides an overview of fluorescence’s contribution to the understanding of single-polymer systems, showcasing its ability to probe \(T_g\) and physical aging radiating from interfaces and in nano-structured films.

### 3.2.1 Polymer Thin Films

Torkelson and coworkers pioneered the application of fluorescence to study confined thin films, illustrating its ability to contribute to the field through the measurement of \(T_g\) as a function of film thickness for several polymer systems. \(^7,^11\) Its accuracy was confirmed by comparison of data with published thickness-dependent \(T_g\) measurements \(^34\) and the \(T_g\) (onset) of bulk samples measured by DSC. \(^7,^8\) Due to the versatility of this technique, they were also able to measure how small modifications to polymer repeat units, \(^21\) incorporation of plasticizers, \(^22,^23\) and polymer-substrate
Figure 3.2. Different geometries that have been probed via fluorescence: (A) supported films,7,8,11,13,19–23,35,36 (B) free-standing films,24,25 (C) capped films,26 (D) substrate layer,8,12,13 (E) free-surface layer,8,12,13,25 (F) multilayer films,8,12,13,25 (G) polymer-polymer interfaces,30,31 (H) micelles,33 (I) nanocomposites,23,26 (J) patterned films,27 (K) irreversibly adsorbed layers,28 and (L) grafted brushes.37 Fluorescently-labeled or doped polymer is shown in green against neat polymer layers. Arrows indicate dimensions that can be adjusted. Reprinted from Ref.10.
interactions\textsuperscript{12,26} impacted confined $T_g$. They observed an increase in the breadth of the transition in polystyrene (PS) thin films, which was studied in more detail and compared to ellipsometric measurements.\textsuperscript{38} This study suggested that fluorescence measurements may slightly overweigh contributions from the free surface in measuring average $T_g$ of supported films, while ellipsometry might slightly under-weigh the same contributions. This discrepancy likely accounted for the $\sim 4$ K larger reduction in average PS film $T_g$ measured by fluorescence.\textsuperscript{38}

The $T_g$ of PS films were also measured by intrinsic fluorescence (emission peaks originated from the interaction of phenyl rings in PS rather than a probe molecule) and proved consistent with extrinsic fluorescence studies.\textsuperscript{19} This supported the argument that the low concentration of fluorescent dye molecule did not impact the measured $T_g$ and thus only probed properties of the polymer matrix. These intrinsic measurements were also used to measure $T_g$ in P(S-r-MMA) thin films, and found that random copolymers exhibited confinement behavior intermediate to their component homopolymers.\textsuperscript{19} This result proved to be in good agreement with ellipsometric measurements of $T_g$ in similar copolymer systems\textsuperscript{39} and demonstrated the ability of fluorescence to probe polymers with heterogeneous composition.

As outlined in Chapter 2, interfaces have long been thought to play a strong role in determining deviations from bulk $T_g$,\textsuperscript{34,40,41} and several layer models have been proposed to describe $T_g$ and dynamics in thin films.\textsuperscript{34,41–43} While some techniques, such as gold nanoembedding,\textsuperscript{44–46} were able to probe mobility and dynamics at the free surface, equivalent measurements of surface $T_g$ were lacking. Fluorescence was able to
address this need, with location-specific measurements enabled by the covalent attachment of pyrene-based fluorophores to polymers.

In 2003, Ellison and Torkelson used fluorescence to provide the first direct measurement of interfacial $T_g$ in supported PS films. In placing a 14-nm-thick layer of fluorescently-labeled PS atop a 270-nm-thick neat PS film, they selectively probed $T_g$ at the free surface and observed a 32 K depression from bulk. By contrast, an identical 14-nm-thick labeled layer sandwiched between two 270-nm-thick neat layers reported bulk $T_g$. Comparison of the $T_g$ of these two labeled layers demonstrated the difference in $T_g$ of the free surface layer from bulk and verified their ability to produce multilayer films with continuous properties (i.e., that behaved as one film). They measured $T_g$ throughout the PS film by carefully controlling the thickness of surface- and substrate-adjacent layers (and thus the distance of the labeled layer from each respective interface), as depicted in Figure 3.2d-f. These location-specific measurements exposed a gradient in $T_g$, with the magnitude of its deviation from bulk decreasing gradually from 32 K at the free surface to 0 K 30 - 40 nm from the free surface. Bulk $T_g$ was measured at the substrate in films over 40 nm thick. This gradient reflected both free surface and substrate influences, and below ~50 nm these interfaces began to compete. Figure 3.3 shows that in this range, $T_g$ at the free surface increased until it aligned with average film $T_g$ at ~30 nm. Subsequent measurements near the substrate demonstrated that its $T_g$ also changed to maintain a continuous gradient throughout the film. In films thinner than ~ 25 nm, the $T_g$ gradient was suppressed and replaced by a single film $T_g$ that reflected both substrate and free-surface contributions.
This pivotal study provided clear evidence that the thickness-dependence of $T_g$ in supported PS films resulted from the competition of a strongly-depressed $T_g$ at the free surface and bulk $T_g$ at the substrate. In films < 40 nm, the free surface dominated over the weak substrate interactions, resulting in negative deviations in $T_g$. Extension of these multilayer experiments to a series of methacrylates demonstrated the generality of competing interfaces dictating thin film $T_g$ in supported films. In PMMA, a 10 K positive deviation from bulk $T_g$ at the substrate (due to strong polymer-substrate interactions) dominated over a 7 K negative deviation at the free surface to display positive deviations in average film $T_g$. Thus, fluorescence presented confined $T_g$ in supported thin films as the result of the relative strength of the free surface and substrate influences.

Kim et al. employed the same multi-layer film technique to measure free surface $T_g$ in free-standing PS films. However, they modified fluorescence measurements slightly using a self-referencing technique, which was able to measure thickness-dependent free-standing film $T_g$ in good agreement with previously-reported trends. They found that the $T_g$ of the free-surface layer in a free-standing film was identical to that in a supported film when films were several hundreds of nanometers thick. However, in free-standing films thinner than ~56 nm, the free-surface $T_g$ decreased further. They attributed this additional $T_g$ depression to the influence of the opposing free surface penetrating through the film, and the film thickness at its onset coincided with the length scale at which the free-surface $T_g$ in supported films increased due to competition from its substrate interface. The $T_g$ gradient was also suppressed in free-standing films below ~56 nm, roughly twice the thickness reported for supported films. This combination of
Figure 3.3. $T_g$ of a 14-nm-thick free-surface layer increases in ultrathin PS films below 50 nm to make a complete gradient in $T_g$. Inset: Schematic of the multi-layer film geometry used to measure free surface $T_g$. Total film thickness, $h$, was controlled by the thickness of the neat PS underlayer, while thickness of the fluorescently-labeled surface layer (where $T_g$ was measured) remained constant. Reprinted with permission from Macmillan Publishers Ltd: Nature Materials Ref.\textsuperscript{8}, Copyright 2003.
free-surface effects extended the generality of $T_g$ gradients and combined interfacial influences$^{8,12}$ to films with symmetric interfaces and could explain the larger $T_g$ depression seen in free-standing films.$^2$

Their multilayer study was also able to provide evidence against one of the major theories for the molecular weight dependence of $T_g$ in free-standing films. De Gennes’ sliding motion mechanism states that free volume is transported along polymer chains extending from the free surface into the interior of the film.$^{48}$ Molecular weight (i.e., chain length) would thereby dictate the distance the free volume was transported and the magnitude of $T_g$ depression within films. Kim et al. used stacked films to eliminate the possibility of polymer chains extending from the free interface to the interior of the film. They recovered trends in $T_g$ depression with molecular weight$^{47}$ in the interior layers of these films, demonstrating that chain bridging was not responsible.$^{25}$

Chapter 2 explained that the rate of physical aging at a given temperature increases with chain mobility and thermodynamic driving force towards equilibrium. Chain mobility increases with aging temperature ($T_{aging}$), but the thermodynamic driving force decreases as aging temperature increases toward $T_g$. The resulting close relationship between aging rate and $T_g$ had been used to explain aging rates in confined systems,$^{49}$ but fluorescence demonstrated how interfaces separately impact $T_g$ and physical aging rate. By measuring the change in fluorescence intensity as a function of aging time, Priestley et al. isolated aging rates at the labeled free surface, center, and substrate interface in poly (methyl methacrylate) (PMMA) thin films.$^{13}$ At 305 K, aging was fastest in the center of the film and slowest at the substrate interface, with a suppressed aging rate also observed at the free surface. Elevated local $T_g$ at the substrate and reduced $T_g$ at the free surface in
Figure 3.4 Physical aging rates of PMMA at 305 K are perturbed by the free surface and substrate interface, with bulk rates recovered by 250 nm from either interface. Physical aging rates and length scales are based on fluorescence multilayer film experiments. From Ref.\textsuperscript{13} Reprinted with permission from AAAS.
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PMMA films$^{12}$ were used to interpret these results. Slower aging rates at the interfaces were attributed to (1) restricted mobility at the substrate from hydrogen bonding, and (2) reduced thermodynamic driving force at the free surface due to depressed local $T_g$. Increasing $T_{aging}$ to 348 and 388 K led to heightened mobility and faster aging at the substrate but slower aging at the free surface due to decreased $T_g - T_{aging}$. Interestingly, despite these connections between local aging rate and $T_g$, physical aging rate was perturbed over much larger distances than $T_g$.\textsuperscript{8,12} Figure 3.4 illustrates the gradient in aging rate, with deviations from bulk extending 200 nm from either interface.\textsuperscript{13} This separation of interfacial influences on $T_g$ and physical aging rate provided valuable insight into their respective length scales.

3.2.2 Nanocomposites

In order to measure the effects of confinement on polymers comprising a nanocomposite matrix, Rittigstein et al. used doubly-supported, or capped, fluorescently-labeled films (i.e. sandwiched between two substrates, see Figure 3.2c) to create model nanocomposites, with film thickness representing interparticle spacing.\textsuperscript{26} They observed positive perturbations in the average $T_g$ of PMMA and P2VP films measuring hundreds of nanometers thick. These measurements demonstrated the ability of two substrate interfaces with favorable interactions to combine to strongly increase $T_g$, reminiscent of the combined effect of symmetric interfaces in free-standing PS films.\textsuperscript{25} Separate measurements of aging rates in nanocomposites with varying polymer-nanoparticle interaction strength led to the conclusion that increased concentration of nanoparticles in a polymer matrix with favorable interactions can suppress physical aging rates substantially.\textsuperscript{50} This was consistent with the work of Priestley et al. on PMMA supported
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films. It is important to note that, similar to ellipsometry, fluorescence measures physical aging rate rather than equilibration time, which was described in Chapter 2 to decrease with increased confinement and nanoparticle loading in nanocomposites.

3.2.3 Nano-structured Films

Advances in lithography have enabled the expansion of using polymers for patterning, and incorporation into devices. These non-uniform films have a larger free surface area than their flat counterparts. Given the large impact of the free surface and resulting deviations from bulk properties, characterizing these structures and accounting for this difference in geometry (where the xy plane is no longer infinite) is an important step prior to their application. These complex, nano-structured systems provide another challenge to measuring polymer properties under confinement. Ellipsometry, capillary dilatometry, and X-ray reflectivity require relatively flat, continuous films to accurately measure $T_g$. DSC has been used to study 2D-confined (where two dimensions are restricted to the nanoscale) polymer systems through anodized aluminum oxide template-supported nanorods and nanotubes, but the ability to change sample geometry and interfacial interactions were somewhat limited by template constraints. Additionally, these techniques do not enable location-specific measurements in the presence of a free surface without costly and time-intensive scattering and reflectivity studies. Fluorescence has been employed to study both complex geometries and multiple interfaces using only in-house bench-top instruments.

Work by Mundra et al. on patterned PMMA films supported on silica investigated the impact of patterning and resulting 2D confinement on $T_g$. They used electron beam lithography to remove sections of the polymer films down to the substrate, leaving long
strips or “lines” of polymer confined by two dimensions (Figure 3.2j). Smaller line width (corresponding to the width of polymer film strips remaining after etching across the substrate) resulted in increasing fraction of free surface to substrate interaction and significant $T_g$ depression from bulk. This is in contrast to the positive deviation expected in PMMA thin films due to strong interactions with the substrate, indicating domination of the free surface influence due to the larger exposed area. Without fluorescence, this detailed comparison of the free surface influence to that of the substrate in nano-patterned films would not be possible.

Polymer brushes, created by chemically grafting one end of a polymer chain to the substrate, are often used to modify substrates and increase the compatibility of nanocomposite fillers with polymer matrices. When incorporated in these geometries, they serve as another nanostructure that challenges bench-top technologies. The $T_g$ of isolated brushes and their effect on overall polymer films was studied by ellipsometry, but in-situ measurements of brush $T_g$ had not been measured prior to Lan and Torkelson’s study of densely grafted brush layers. They were able to measure average brush $T_g$ within a polymer film (Figure 3.2l) as well as at specific locations from the substrate within the brushes. In contrast to the reduction in $T_g$ observed for PS supported films below ~40 nm, they saw invariant average brush $T_g$ down to ~11 nm. However, they measured a dramatic gradient in the $T_g$ of chain segments within the brush layer, ranging from 36 K above bulk $T_g$ near the substrate to 14 K below bulk $T_g$ near the free surface. Finally, through bilayer experiments, they were able to measure the influence of brush thickness on overlayer $T_g$ and overlayer thickness on brush $T_g$. This study directly illustrated how fluorescence can complement confinement studies done by ellipsometry.
and contribute additional insight through targeted measurements of specific components that cannot be otherwise easily isolated.
3.3 References


Chapter 4

Irreversible Adsorption

Chapters 2 and 3 emphasized the important role that interfaces play in determining the properties of polymers confined to nanoscale dimensions. This chapter focuses on a specific substrate effect that recently has been shown to influence the properties of thin films through melt-state annealing.

4.1 Introduction

Irreversible adsorption is the physical adsorption of polymer chains to a non-repulsive substrate, and it can occur atop substrates in contact with polymer solutions or melts. Adsorption occurs when attractive forces between the substrate and adsorbing species present enthalpic gains that outweigh entropic penalties imposed by restrictions to molecular conformation and mobility.\(^1\) Even in cases of weak polymer-substrate interaction strength, the long-chain nature of polymers enables many individual contact points per molecule that combine to create a high energetic boundary for desorption, making the adsorption of polymers effectively irreversible. In a given system, adsorbed chains combine to form an irreversibly adsorbed layer at the substrate, which grows in thickness with time annealed or exposed to solution until it eventually plateaus. Although polymer adsorption has a variety of technologically-relevant applications,\(^2-4\) this chapter focuses on its ability to perturb properties of thin films as a result of annealing during their processing.

The growth and characterization of adsorbed layers has been studied for decades, initially as a way to evaluate the structure of polymer chains in contact with a substrate.
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Theoretical and experimental investigations of polymer adsorption from solution and melts combine to provide a fundamental understanding of adsorbed layer formation. In the next two sections, we discuss key findings relevant to the structure and growth of adsorbed layers as well as their kinetics and preferential adsorption. The chapter then describes experimental evidence of the ability of physically-adsorbed polymer layers to impact the properties of polymers in confined geometries. It ends with a brief summary of the background chapters and opportunities for extension.

4.2 Adsorbed Layer Structure and Growth

Johnson and Granick conducted a series of experiments on the adsorption of poly(methyl methacrylate) (PMMA) from a carbon tetrachloride solution to determine if its irreversibility originated solely from the combined attractive force of many binding sites.\(^5\) Using Fourier transform infrared spectroscopy (FTIR) in an attenuated total reflection mode, they were able to identify and quantify adsorbed species as well as the bound fraction of carbonyl groups from shifts in the corresponding FTIR peak. They observed very slow and minimal exchange of PMMA (many carbonyls per chain) but rapid desorption of stearic acid (short aliphatic chains containing one carbonyl group each) when adsorbed layers were exposed to a PMMA solution. The stability of PMMA adsorbed layers relative to those of stearic acid confirmed that the irreversible adsorption of PMMA was due to the many binding sites at thermal equilibrium rather than the attachment strength of individual bonds with the substrate. Although both molecules were attached to the substrate via their carbonyl groups, many desorption events needed to occur simultaneously for entire PMMA chains to desorb. This desorption was achieved
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when ethyl acetate displaced the hydrogen-bonded carbonyl groups, further emphasizing that individual contact points were reversibly adsorbed.

Theoretical studies on the configuration of polymer chains adsorbed onto a surface from solution are abundant.\textsuperscript{6–11} Despite some differences in assumptions and methodology, these studies collectively describe adsorbed polymer chains to be composed of three main conformations: trains, loops, and tails; these are depicted in Figure 4.1a. Trains are sequences of chain segments in contact with the substrate. Loops are sequences of unattached segments that are bounded by attached segments. Tails are detached chain ends that are only attached to the substrate on one side. These configurations were used to interpret calculated concentration and density profiles as a function of system parameters, such as solution concentration (extending to unity for melt systems), chain length, polymer-solvent, and polymer-substrate interactions.\textsuperscript{6,12} Early theories stated that polymers in equilibrium conformations in contact with a hard, non-interacting wall would follow random walk statistics and have $N^{1/2}$ contacts with the wall.\textsuperscript{9,13–16} However, these theories made some simplifying assumptions that did not account for tail contributions and interactions of the polymer with the solvent and substrate.\textsuperscript{17} Scheutjens and Fleer later accounted for these factors and found that long tails contributed the most to adsorbed layer thickness, which was still proportional to $N^{1/2}$.\textsuperscript{12} The agreement of their results with simplified scaling arguments suggested that molecular weight played a larger role in determining equilibrium adsorbed thickness than polymer-substrate interactions. The same theoretical scaling of adsorbed layer thickness with $N$ was determined for melt systems by increasing the polymer fraction in solution to unity.\textsuperscript{8}
Figure 4.1. Irreversibly adsorbed layers consist of chains that form tail, loop, and train conformations and can be divided into two sub-layers. (A) Schematic of chain conformations. (B) Tightly-bound flattened sublayers of PS (170 kg/mol) adsorbed layers are isolated via extensive solvent leaching. Adsorbed layer thickness is shown as a function of desorption time (with sample immersed in toluene). Inset shows architecture of adsorbed layers, with tightly-bond flattened layers in blue and loosely-bound layers in red. Reprinted Figure 4.1b with permission from Ref.\textsuperscript{18}. Copyright 2012 by the American Physical Society.
While theory argued that adsorbing chains will equilibrate on a substrate surface in random walk conformations that minimize free energy, experimental and simulation studies suggested that kinetics prevent achievement of equilibrium chain conformations.\textsuperscript{5,19} Instead, adsorbed chain conformations were found to depend strongly on adsorption time.\textsuperscript{18,20,21} Experimental investigations linking adsorbed layer growth and structure are described below. Studies made this connection through examinations of the thickness at which adsorbed layers plateau (sometimes referred to as the “equilibrium” thickness\textsuperscript{22,23}) as well as the conformations adopted by subsets of adsorbed chains.

Several experimental studies have examined the scaling of plateau thickness with $N$ for melt adsorption, using the methodology proposed by Guiselin\textsuperscript{8} to isolate adsorbed layers from films through solvent leaching prior to their characterization. Durning et al. studied the adsorption of PMMA onto quartz and observed $h_{\text{dry}} \sim N^{0.47\pm0.05}$, with $h_{\text{dry}}$ being the plateau thickness for adsorbed layers after long annealing.\textsuperscript{22} This scaling was consistent with theory, but measurements on adsorbed layers swollen by a good solvent suggested less long loops were present than predicted theoretically.\textsuperscript{12} This result suggested that equilibrium thickness of the adsorbed layer was not sufficient to elucidate chain conformation. Fujii et al.\textsuperscript{23} examined polystyrene (PS) adsorbed layers on both hydrogen-passivated silicon and silicon with a native oxide layer and observed $h_{\text{dry}} \sim R_g$ for both systems over a wide range of molecular weights, consistent with random-walk statistics. The scaling factor was larger for the PS-Si system, indicating that stronger polymer-substrate interactions result in thicker adsorbed layers for PS.

Schneider et al. used infrared (IR) dichroism to probe the influence of available binding sites at the substrate on PMMA chain orientation when adsorbing from
Early adsorbing chains were more anisotropic than later adsorbing chains, and they spread parallel to the substrate to maximize contact and minimize free energy. They observed a bimodal attachment landscape with peaks at high bound fraction, corresponding to early-bound chains, and low bound fraction, corresponding to late-adsorbing chains. They suggested that more concentrated solutions and melts would not follow this same landscape due to the impingement timescale being comparable to that of the spreading of individual chains.

Contrary to the predictions of Schneider et al., irreversibly adsorbed layers grown in the melt also exhibit a bimodal distribution of chain configurations, consisting of a tightly bound “flattened” sublayer and loosely bound sublayer. These distinct layers, depicted in the Figure 4.1b inset, have been experimentally observed in-situ by Koga and coworkers via X-Ray and neutron reflectivity measurements. The flattened sublayer was found consistently ~20% higher in density than the loosely-bound adsorbed component, which exhibited bulk-like density. Extensive solvent leaching, on the order of 120 days, enabled the isolation of the tightly-bound flattened layer by utilizing the difference in desorption energy between the two layers originating from the difference in the number of contact points. The gradual isolation of this flattened sublayer with desorption time is shown in Figure 4.1b. In their initial study, Gin et al. assumed that the extended (parallel to the substrate) conformations of chains in the flattened sublayer originated from early-stage adsorption in the absence of surface coverage limitations. The loosely bound sublayer was then composed of late-adsorbing chains that formed more trains and loops as a result of limited surface binding availability. The denser, flattened sublayer was seen to be molecular-weight independent, consistent with self-consistent
field theory predictions that claimed average loop size for isolated chains adsorbed on a surface should be independent of chain length.\textsuperscript{12} However, the entire adsorbed layer followed the $R_g$ scaling observed by Fujii \textit{et al.},\textsuperscript{23} due to contributions from the loosely bound chains.

Flattened sublayers were later studied extensively in terms of their growth with annealing time,\textsuperscript{24} chain conformations,\textsuperscript{25,26} and polymer-substrate interactions.\textsuperscript{24} It was found that isolation of the PS flattened layer could be accelerated by the use of chloroform rather than toluene as a leaching solvent. The surface morphologies of flattened sublayers were studied by atomic force microscopy (AFM), and it was determined that they formed heterogeneous structures, with polymer surface coverage increasing with segment-substrate interaction strength. These flattened layers were also analyzed in terms of their growth kinetics, which are discussed in the next section.

### 4.3 Kinetics and Preferential Adsorption

As mentioned above, chain conformation and adsorption kinetics are closely linked in irreversible adsorption. Experimental studies of polymer adsorption from solution have provided many insights that have been used to interpret the growth of adsorbed layers from polymer melts. Studies have shown that adsorbed layers grow via a two-stage process, with faster growth and more elongated chain conformations at early stages transitioning to slower growth with less contact points per chain once growth is limited by surface coverage. However, quantitative descriptions of their growth kinetics and dependence on polymer selection and experimental conditions are still an area of open research. While secondary growth is almost exclusively fit to a logarithmic function, early-stage growth has been described as both power-law and linear.
Rotella et al. employed a combination of dielectric relaxation spectroscopy (DRS) and second harmonic generation to elucidate the adsorption kinetics of PS from the melt.\textsuperscript{20} Chain immobilization due to irreversible adsorption at the substrate during melt state annealing had previously been seen to cause a drop in the dielectric strength, $\Delta \varepsilon$, of films with annealing time.\textsuperscript{27,28} In their study, Rotella et al. divided the drop in $\Delta \varepsilon$ into two distinct regimes: early, power-law decay and later logarithmic decay, which corresponded to different phases in adsorption.\textsuperscript{20} DRS measurements were compared with second harmonic generation data, which provided a measurement of dye orientation in the film. They observed a gradual change in the orientation of dye molecules (and thereby polymer chains) into configurations parallel to the substrate with increased annealing time. In the logarithmic growth regime, there was a marked increase in the concentration of chains oriented perpendicular to the substrate. They rationalized these findings into a model for chain adsorption at the substrate. At short times, adsorbing chains adopted flattened configurations to minimize free energy in the absence of surface coverage limitations. At later times, with much of the surface covered with adsorbed chains, chains could only adsorb by diffusing through the existing layer and finding “holes” in the surface. These chains were more likely to adsorb in a perpendicular configuration, also implying more tails and loops.

Jiang et al. also used power law growth to describe the early growth of both the flattened sublayer and the entire adsorbed layer (composed of both loosely-bound and flattened sublayers) of PS.\textsuperscript{24} Thickness measurements as a function of annealing time revealed that the two sublayers grew simultaneously. This was in contrast to their initial hypothesis that early-adsorbing chains exclusively formed the flattened sublayer\textsuperscript{18} and led
to the conclusion that adsorption was a competition between loosely binding chains and the “zipping down” of tightly-binding chains.\textsuperscript{24,25} Flattened layers of PS, PMMA, and poly (2-vinyl pyridine) (P2VP) were compared, and it was determined that increasing polymer-substrate interaction strength led to thicker flattened sublayers as well as slower kinetics, consistent with simulations.\textsuperscript{1} They attributed the slower kinetics to the tightly-bound chains rapidly covering the surface and thus providing a kinetic barrier to further adsorption.

Later investigations into adsorbed layer growth kinetics of PS on Si by Housmans et al. proposed that this two-stage adsorption process was comprised of linear growth at short times and logarithmic growth at longer annealing times:\textsuperscript{29}

\[
h_{\text{ads}}(t_{\text{ads}}) = \begin{cases} h_{t_{\text{ads}}=0} + vt_{\text{ads}} & t_{\text{ads}} < t_{\text{cross}} \\ h_{\text{cross}} + \Pi \log t_{\text{ads}}/t_{\text{cross}} & t_{\text{ads}} > t_{\text{cross}} \end{cases}
\]  

(4.1)

where \( h_{\text{ads}} \) is the thickness of the adsorbed layer at annealing time \( t_{\text{ads}} \), \( v \) and \( \Pi \) are linear and logarithmic growth rates, \( h_0 \) is the thickness of the adsorbed layer at \( t_{\text{ads}} = 0 \), \( t_{\text{cross}} \) is the crossover time from linear to logarithmic growth, and \( h_{\text{cross}} \) is the adsorbed layer thickness at \( t_{\text{ads}} = t_{\text{cross}} \). They used this model to analyze kinetic parameters as a function of annealing temperature and PS molecular weight, finding that the thickness of the adsorbed layer at any time during adsorption (not just at equilibrium) was proportional to \( R_s \). They also determined that \( t_{\text{cross}} \) was \( M_w \)-independent, implying that the onset of logarithmic growth was determined by surface coverage, not chain length. They reported an increase in linear and logarithmic adsorption rates with molecular weight, which are shown in Figure 4.2.
Figure 4.2 Dependence of PS adsorbed layer growth parameters, described in Equation 4.1, on $M_w$ and annealing temperature. Reprinted (adapted) with permission from Ref. [29]. Copyright 2014 American Chemical Society.
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Experiments were expanded to include more complex systems, investigating how preferential adsorption controlled adsorption in disperse and compositionally heterogeneous systems. Santore and coworkers observed transport-limited adsorption rates of poly (ethylene oxide) (PEO) onto silica from a phosphate buffer solution, resulting in adsorption rates inversely proportional to molecular weight. While smaller molecular weight PEO adsorbed faster than larger molecular weight (shown in Curves 1 and 2, respectively in Figure 4.3a) the larger molecular weight was seen to displace the smaller molecular weight, due to its larger attractive potential (from more simultaneous attractive sites) leading to preferential adsorption. The desorption of 33 kg/mol PEO is shown by Curve 3, with the total adsorbed amount shown by Curve 4. Interestingly, this preference reverses in adsorption from the melt. Instead of being driven by enthalpy gains (as in solution), preferential adsorption is dictated by the larger entropic penalty incurred with adsorption of chains with higher $M$. However, the long $M$ chains are only partially displaced in melt adsorption, unlike the complete desorption of low $M$ chains observed in solution.

In addition to the number of potential contact points, individual strength of those contacts (polymer-substrate interactions) also led to preferential adsorption. Johnson and Granick found that PMMA, with an individual contact strength of ~4 $kT$, was seen to adsorb much more favorably than PS (~1 $kT$) when introduced simultaneously to a substrate, as the many individual polymer segments combine to give large differences in overall chain affinity for the substrate. Furthermore, when PS was allowed to adsorb onto a Si substrate which was then exposed to a dilute concentration of PMMA, rapid desorption of PS was introduced. The rate of desorption was found to be inversely
Figure 4.3 Preferential adsorption from solution induces desorption in systems with weaker polymer-substrate interactions. (A) Molecular weight influences amount of polymer adsorbed per area \( (\Gamma) \): Uncompetitive adsorption of 33 kg/mol (curve 1) and 120 kg/mol (curve 2) PEO, competitive adsorption of 33kg/mol PEO (curve 3), total surface coverage in competitive adsorption (curve 4). Reprinted (adapted) with permission from Ref. 30. Copyright 1998 American Chemical Society. (B) Chemistry: PMMA (open circles) adsorbs more readily than PS (closed circles) and will displace it. (Diamonds) mass adsorbed per area \( (\Gamma) \) of PMMA segments H-bonded to the surface. Reprinted figure with permission from Ref. 34. Copyright 1993 by the American Physical Society.
proportional with PMMA solution concentration, as desorption required the diffusion of
long PS chains through a strongly-adsorbing front of PMMA chains. Figure 4.3b shows
the desorption of PS (filled circles) after an adsorbed layer was put in contact with a
PMMA solution (open circles).

4.4 Impacts of Adsorption on the Physical Properties of Polymer Films

Irreversible adsorption has been shown to influence a variety of film properties,
including thermal expansion, \(^\text{36}\) crystallinity, \(^\text{37-39}\) mobility, \(^\text{27,40-42}\) viscosity, \(^\text{43}\) and \(T_g\). \(^\text{44-46}\) The field is growing rapidly, but here we limit our discussion to the areas that have
received the most attention: dynamics (including segmental dynamics, dynamic \(T_g\) and
viscosity) and thermodynamic \(T_g\).

4.4.1 Dynamics

Early experimental evidence of the ability of an adsorbed layer to influence film
properties was given by DRS measurements of dielectric strength, or the amount of
mobile chains contributing to \(\alpha\)-dynamics. \(^\text{28,47}\) These experiments reported the presence
of a dead layer of zero mobility and an intermediate reduced mobility layer (RML) in
proximity to the substrate that accounted for an increased dynamic \(T_g\) relative to bulk in
sufficiently confined films. The RML, containing both adsorbed and unadsorbed chains,
was proposed as a transition layer between chains completely adsorbed and immobile at
the substrate and bulk properties sufficiently far from the interface, similar to the rigid
amorphous fraction in semi-crystalline polymers. \(^\text{47}\) The thickness of this layer was seen
to vary with the strength of interaction with the substrate. \(^\text{28}\) Poly (ethylene terephthalate)
(PET), which forms very strong, chemical bonds with an alumina substrate, was proposed
to form a RML up to 20-nm-thick, while those formed by polymers interacting with the substrate by physical bonds were much thinner. Although chemical adsorption is not the focus of this study, it provides a meaningful comparison and context for physical adsorption studies.

Rotella et al. also used DRS with labeled PS to probe segmental mobility in the proximity of a substrate interface in capped films. By measuring the dielectric responses of films upon slow heating and cooling, they probed the effects of slow and long annealing, respectively. They observed a significant decrease in the peak height of the dielectric loss ($\varepsilon''$) upon annealing, indicating a reduction in segmental dynamics. This change in dynamics was quantified in terms of $\Delta \varepsilon$. Figure 4.4a shows the behavior of $\Delta \varepsilon$ with film thickness in different geometries. No change in $\Delta \varepsilon$ of a labeled layer sandwiched in the center of a film (geometry 2) confirmed that the decrease in chain mobility seen in proximity to the interfaces originated from chain pinning at the substrate. Interestingly, the dynamic $T_g$, shown in Figure 4.4b and determined from the temperature dependence of the segmental mobility (as described in Section 2.2.2), showed negative deviations from bulk near the interfaces on heating. This was attributed to an excess of free volume due to chain packing frustration at short annealing times. Films showed positive deviations in $T_g$ upon cooling, indicating additional adsorption with longer annealing time removed this excess free volume.

The existence of an irreversibly adsorbed layer has also been shown to impact the viscosity of confined PS films. Using X-ray photon correlation spectroscopy and gold nanoparticle markers, Koga et al. measured diffusion coefficients of nanoparticles embedded within polymer films using different incident angles to focus on the surface
Figure 4.4 Changes in dynamic film properties upon short (heating) and long (cooling) annealing. Film geometries and heating/cooling measurements are indicated on the right and are indicated by marker color and fill, respectively. (A) Dielectric strength, $\Delta \varepsilon$, decreases with film thickness upon short and long annealing in proximity to substrates. (B) Dynamic $T_g$ decreases with film thickness after short annealing due to chain packing frustration, but it increases after long annealing due to additional adsorption and a decrease in free volume. Insets show projected $\Delta \varepsilon$ and $T_g$ profiles within films upon heating (red) and cooling (blue) Reprinted (adapted) with permission from Ref.27. Copyright 2010 American Chemical Society.
layer and center of the film. These local measurements of diffusion coefficient were then used to calculate polymer viscosities. In a series of films ranging from 32 to 235 nm thick, they observed the ability of a ~7 nm adsorbed layer to influence viscosity up to 60 nm from the substrate. The increase in viscosity radiating from the adsorbed layer was even able to suppress mobility at the free surface of a 32-nm-thick film, making it two orders of magnitude slower than at the surface of bulk films.

4.4.2 Glass Transition Temperature ($T_g$)

In a pivotal study, Napolitano and Wübbenhorst performed a series of experiments using dielectric spectroscopy to relate $\Delta \varepsilon$ to the growth of a PS adsorbed layer with annealing time. They measured the $T_g$ of these adsorbed layers via capacitive dilatometry (CD) and saw an overlap with the reduction in chain mobility (indicated by $\Delta \varepsilon$), as shown in Figure 4.5a. The gradual increase in $T_g$ and decrease in mobility with annealing extended to spin-coated thin films and corresponded to the gradual pinning of additional points of adsorbed chains as they proceeded toward equilibrium conformations.

They used these trends to propose three stages in the adsorption process, based on a dimensionless parameter $t^*$, which was the ratio between annealing time and a characteristic timescale of adsorption. At early annealing times, when $t^* \ll 1$, chain adsorption was limited by initial adsorption and chain frustration. This resulted in excess free volume at the substrate, which explained the negative deviation from bulk $T_g$ in Figure 4.5b as well as the dynamic $T_g$ measured by Rotella et al. at $t^* \sim 1$, chains filled vacant sites at the substrate and conformations rearranged. After long annealing times, when $t^* \gg 1$, adsorption reached a new steady state where the surface
Figure 4.5. (A) Correlation between the $T_g$ of PS adsorbed layers measured via capacitive dilatometry (stars) with the growth of an irreversibly adsorbed layer and change in dielectric strength (normalized trace shown by solid line). Reprinted by permission from Springer: Nature Communications Ref.44, Copyright 2011 (B) Correlation between the $T_g$ and normalized free volume, $\zeta^N$, in PS adsorbed layers. Inset shows deviations in $T_g$ as a function of adsorbed layer thickness. Reprinted (adapted) from Ref.45 Copyright 2012 American Chemical Society.
was saturated and the adsorbed layer thickness was proportional to the polymer’s $R_g$. These adsorption regimes were experimentally supported by a measured gradual reduction in faster relaxation times.\(^{44}\)

In a later study, Napolitano et al. sought to confirm the dependence of $T_g$ and $\Delta \varepsilon$ on the presence of excess free volume trapped by chain frustration at the substrate.\(^{45}\) They employed a molding-like approach to measure free volume at the interface by allowing dielectric probe molecules to diffuse into adsorbed layers at different states of growth. The amount of free volume was quantified through the dielectric response of the probe molecules, reflective of their ability to rotate. As shown in Figure 4.5b, the amount of free volume decreased with increasing adsorbed layer $T_g$, supporting the claim that interfacial free volume contributes to $T_g$ deviations under confinement. These results were then compared to free volume calculated from inputting $T_g$ data into the FVHD model (described in Section 2.3.4) and were found in good agreement.\(^{46}\)

We note that $T_g$ in these studies was measured via CD, a pseudo-thermodynamic technique which relies on the proportionality between film capacitance and thickness to determine $T_g$ as the sudden change in thermal expansivity between the liquid and glassy states.\(^{44}\) As mentioned in Chapter 2, this technique allows for a direct comparison between dilatometric (thermodynamic) $T_g$ and dynamics of the adsorbed layer. The overlap between $\Delta \varepsilon$ and thermodynamic $T_g$ (Figure 4.5a), combined with FVHD arguments, is promising for understanding the relationship between dynamics and $T_g$ under confinement.\(^{49,50}\)
4.5 Opportunities for Extension

Chapter 2 described how the $T_g$, dynamics, and physical aging of polymers in confined geometries can vary substantially from their bulk properties. Understanding how these deviations change with polymer chemistry, geometry, and interfacial interactions is critical for increasing the deployment of polymer thin film technologies. Chapter 3 discussed how the development of a fluorescence technique enabled direct measurement of $T_g$ and physical aging at precise locations within thin films. These studies greatly extended appreciation for how both the free surface and substrate interface compete to influence the properties of confined systems. This chapter showed that melt-state annealing can impact polymer thin film dynamics and $T_g$ through the growth of an irreversibly adsorbed layer on the substrate. The importance of understanding the impacts of irreversible adsorption on film properties has prompted additional investigations during the timeframe of this dissertation, and they will be discussed in Chapters 7, and 8.

There is ample opportunity to expand the understanding of irreversible adsorption beyond theoretical investigations of model systems and introduce variables relevant to thin films under confinement. Characterization techniques have limited adsorbed layer $T_g$ measurements to capped geometries, preventing examination of the role of a free surface on adsorbed layer $T_g$. Fluorescence provides an excellent means to study the $T_g$ of adsorbed layers and perturbations in film $T_g$ resulting from their growth. Its location specificity and lack of geometric constraints would enable in-situ measurements of adsorbed layers as well as an examination of free surface effects.

Adsorption from the melt has only been studied in homopolymer systems, with adsorbed layers isolated from films of constant thickness. Examining adsorption of
polymers with compositional heterogeneity and in thin films would further bridge the gap between theoretical studies of adsorption and its role in determining confinement behavior. The next three chapters describe our efforts to extend the generality of irreversible adsorption characterization through the thoughtful introduction of system complexities. We present three experimental investigations probing the influences of a free surface, compositional heterogeneity, and film geometry on the $T_g$ and growth of irreversibly adsorbed layers.
4.6 References


Chapter 4


Chapter 5

Experimental Methods and Analysis of Adsorbed Layer Formation Protocol

This chapter provides an overview of the primary experimental tools and methods utilized in this dissertation. Rather than focusing on the details of specific experimental protocols (which are given in each of the pertinent chapters), techniques are described with regard to their fundamental concepts, capabilities, and use in the field. However, general methodologies regarding the treatment of substrates and preparation of adsorbed layers are described here, as well as the specific instruments used throughout this dissertation. Methodologies and characterization techniques are organized by the objective for which they were employed and are divided into: polymer synthesis, bulk characterization of polymers, preparation of thin films and adsorbed layers, characterization of film thickness and morphology, and measurement of confined $T_g$. The results of several experiments evaluating adsorbed layer processing parameters are included in Section 5.3.

5.1 Polymer Synthesis via Free Radical Polymerization

All polymers used in this dissertation (with the exception of PS-$b$-PMMA used in Chapter 7 and PtBS-280 used in Section 5.3.3 and Chapter 8) were synthesized via free radical polymerization (FRP) without additional solvent. FRP is a robust form of chain-growth polymerization that is initiated by the generation of free radicals (unpaired electrons) and proceeds via their propagation along the growing polymer chain. These free radicals are reactive with oxygen, making it necessary to take steps to avoid
contamination. However, FRP remains less sensitive to atmospheric conditions than other chain growth polymerization methods,\(^1\) which enables synthesis of high molecular weight polymers with minimal specialized equipment. These reactions are also well suited for random copolymerization,\(^1\) utilized throughout this thesis and described more in section 5.1.2. Details on specific synthesis protocols can be found at the beginning of Chapters 6 for neat and labeled polystyrene (PS), 7 for PS, poly (methyl methacrylate) (PMMA), and P(S-r-MMA), and 8 for neat and labeled poly(tert-butyl styrene) (PtBS).

### 5.1.1 Reaction Kinetics and Molecular Weight Control

FRP is governed by the relative rates of initiation, propagation, and termination of free radical chains. Free radicals are usually generated by the thermal, redox, or photo decomposition of a chemical initiator incorporated into the monomer feed. These free radicals then react with surrounding monomer, propagating chain addition until terminated by combination (where two radical chains combine) or disproportionation (where one radical chain steals a proton from another) events. Chain termination occurs independently of chain length, resulting in a distribution of chain lengths with relatively high \(D\) above 1.5. A detailed explanation of FRP kinetics can be found in Ref.\(^1\) A simplified version, including relationships employed in developing the synthesis schemes used to make the polymers in this dissertation, is given here.

From kinetic arguments, the instantaneous reaction rate, \(r_p\), can be defined as:

\[
r_p = k_p \sqrt{\frac{k_d f [I]}{k_t}} [M] \tag{5.1}
\]

where \(k_p\), \(k_t\), and \(k_d\) are temperature-dependent constants of propagation, termination, and decomposition for the reacting monomer (\(k_p\) and \(k_t\)) and initiator (\(k_d\)). \(f\) is the fraction of
generated radicals that initiate chain growth, and \([I]\) and \([M]\) are the instantaneous concentrations of initiator and monomer. By approximating the consumption of initiator at a given temperature as an exponential decline,\(^1\) one can estimate the degree of conversion \((\frac{[M]_0 - [M]}{[M]_0})\) as a function of time.

Chain length is largely dictated by kinetics, and the number-average chain length, \(x_n\), can be related to initiator and monomer concentrations by the following equation:\(^1\)

\[
x_n = \frac{k_p [M]}{\zeta (f_k d k_t)^{1/2} [I]^{1/2}}
\]  
(5.2a)

where \(\zeta\) describes the relative rates of termination due to combination and disproportionation, defined as:

\[
\zeta = \frac{k_{tc} + 2k_{td}}{k_{tc} + k_{td}}
\]  
(5.2b)

where \(k_{tc}\) and \(k_{td}\) are the constants of termination by combination and disproportionation, respectively. Polystyrene is terminated entirely by combination, while PMMA and other methacrylates are terminated by both disproportionation and combination. The relative contribution of combination to termination, \(\Pi_c\), is temperature sensitive\(^2\) and can be used to determine \(\zeta\) for given reaction conditions. Values for temperature-dependent rate constants for styrene (S), methyl methacrylate (MMA), and benzoyl peroxide (BPO) are given in Table 5.1 and are valid from 313 – 353 K. \(T\) is temperature in Kelvin. \(R\) is the ideal gas constant in J/mol·K.

### Table 5.1 Free radical polymerization constants

<table>
<thead>
<tr>
<th>Source</th>
<th>(k_p)</th>
<th>(k_t)</th>
<th>(\Pi_c)</th>
<th>(k_d)</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>S</td>
<td>(2.16 \times 10^7 e^{-32470/RT})</td>
<td>(1.30 \times 10^7 e^{-8920/RT})</td>
<td>-</td>
<td>-</td>
<td>3</td>
</tr>
<tr>
<td>MMA</td>
<td>(4.77 \times 10^7 e^{-3762/RT})</td>
<td>(6.58 \times 10^{10} e^{-2536/T})</td>
<td>(1.66 \times 10^{-2} e^{-1160/T})</td>
<td>-</td>
<td>2</td>
</tr>
<tr>
<td>BPO</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>(2.9 \times 10^{13} e^{-121400/RT})</td>
<td>3</td>
</tr>
</tbody>
</table>
While these theoretical calculations provide a starting point for determining feed concentrations of monomer and initiator, there is often some deviation in results due to experimental conditions and impurities. For a given monomer, initiator, and temperature, one can therefore simplify Equation 5.2a to a scaling relationship between the initiator concentration and molecular weight:

\[ x_n = \frac{c}{\sqrt[I]} \]  (5.3)

where \( C \) is a constant that can be determined for a given monomer, initiator, and reaction conditions. Note that \( x_n \) represents the average number of monomer units per chain, so it is reflective of number-average molecular weight \( (M_n) \) in the disperse polymers created by this polymerization method. Equations 5.2a and 5.3 are based on instantaneous concentrations of monomer and initiator and will change as the reaction proceeds. However, keeping reactions at low conversion allows for their use in estimating \( M_n \) from feed concentrations.

### 5.1.2 Random Copolymerization

As mentioned in Chapter 2, random, or statistical, copolymers are polymers that consist of two or more distinct monomers incorporated randomly along the polymer chain. The composition of a copolymer made via FRP is determined by the relative concentration of monomers available to add to the chain and their preference to react with the end radical. This relationship can be described by the copolymerization equation:\(^1\)

\[ F_1 = \frac{r_1f_1^2 + f_1f_2}{r_1f_1^2 + 2f_1f_2 + r_2f_2^2} \]  (5.4)

where \( F_1 \) is the instantaneous molar fraction of monomer 1 in the polymer, \( f_1 \) and \( f_2 \) are instantaneous molar fractions of monomer 1 and monomer 2 in the monomer feed, and \( r_1 \)
and $r_2$ are reactivity ratios of the two monomers (indicating their preference for binding to like or different monomers). As with Equation 5.2, this relationship is based on instantaneous values and will evolve with reaction time. Initial monomer feed composition can make a good approximation when low extent of conversion is maintained. It is also important to maintain low conversion to avoid compositional drift that can lead to compositional heterogeneity within a polymer batch.

Copolymerization also impacts reaction kinetics and resulting chain length. The termination constant, $k_t$, was found to be approximately:

$$k_t = f_1 k_{t1} + f_2 k_{t2}$$

(5.5)

where $k_{t1}$ and $k_{t2}$ are termination constants for monomers 1 and 2. However, two main models exist for prediction of propagation kinetics in copolymers.\(^5\,^6\) The older, simpler description is the Terminal model, which predicts radical propagation is only influenced by the last monomer unit on the chain, giving the overall propagation constant of the random polymerization:\(^5\)

$$k_p = \frac{r_1 f_1^2 + 2 f_1 f_2 + r_2 f_2^2}{(r_1 f_1 k_{11}) + (r_2 f_2 k_{22})}$$

(5.6a)

where $k_{11}$ and $k_{22}$ are values of $k_p(T)$ for each monomer (e.g. $k_{11}$ is the rate constant corresponding to a chain radical ending in monomer 1 adding monomer 1). Adjustments to the Terminal model were made in the Penultimate model,\(^7\) which accounts for the second-to-last monomer on the radical chain also impacting kinetics. This model made the following modifications to Equation 5.6a, replacing:\(^6\)

$$r_i \text{ and } r_2 \text{ with } \bar{r}_i = r'_i \left( \frac{f_i r_i + f_j}{f_i r_i + f_j} \right)$$

(5.6b)

$$k_{ij} \text{ and } k_{22} \text{ with } \bar{k}_{ii} = k_{ili} \left( \frac{r_i f_i + f_j}{r_i f_i + f_j} \right)$$

(5.6c)
where \( i \neq j \) and \( i,j = 1 \) or \( 2 \), \( k_{iii} \) is the homopolymer propagation rate, \( r'_i \) is another reactivity ratio corresponding to \( k_{ji}/k_{ij} \), and \( s_i \) is the rate constant ratio of homo-propagations \( k_{ji}/k_{ij} \). Coote et al. found \( s_1 \) and \( s_2 \) to be 0.6014 and 0.3615 for methyl methacrylate and styrene, respectively at 330 K.\(^6\) It was also estimated that \( r_1 = r'_1 \) thereby giving \( \bar{r}_1 = r_1 \).\(^6\)

Copolymerization reaction constants were determined from Equations 5.5 and 5.6 and used in Equation 5.2a, along with total monomer concentration, to determine initial estimates for initiator concentration in determining copolymer \( M_N \). As these reaction kinetics were strongly dependent on monomer feed composition as well as initiator concentration, it was especially important to have an accurate prediction capability.

### 5.2 Bulk Polymer Characterization

#### 5.2.1 Composition Measurement by \(^1\)H-NMR Spectroscopy

Nuclear Magnetic Resonance (NMR) Spectroscopy probes a material’s chemical structure through the measurement of local magnetic fields surrounding its atomic nuclei. Proton NMR (\(^1\)H-NMR) targets a molecule’s hydrogen atoms as a means for its identification. In small molecules, each chemically-unique hydrogen atom produces a sharp peak at a characteristic frequency, reflective of its functional group. The location and intensity of these peaks allow for identification of chemical structure. In polymers, these peaks are much broader due to the extensive repeat units within each macromolecule. In both cases, integration of the spectral peaks enables determination of the number of hydrogen atoms pertaining to each peak. Comparing the identity and number of these hydrogens allows for the determination of polymer composition. This will be described in more detail in Chapter 7. NMR also indicates the presence of residual
small molecule solvents and unreacted monomer by sharp peaks at characteristic frequencies.  

The chemical compositions for all synthesized and purchased polymers were confirmed by $^1$H-NMR from ~5 mg/mL samples in deuterated chloroform (CDCl$_3$). These experiments were conducted on a Bruker Avance III 500 MHz spectrometer available at the Princeton University NMR Center in the Department of Chemistry.

### 5.2.2 Molecular Weight Measurement by Size Exclusion Chromatography

Size Exclusion Chromatography (SEC), also known as Gel Permeation Chromatography (GPC) when using an organic solvent mobile phase, is an experimental technique used to determine the molecular weight and dispersity of polymers. In GPC, a dilute polymer solution is passed through a column of tightly-packed beads with well-controlled pore sizes. This porous stationary phase retains polymer chains for different times based on their size in solution, which is related to their molecular weight. Larger chains will not fit into many pores in the column, passing through more directly and eluting quickly, while smaller chains will explore more of the pores within the columns before they are eluted. Thus, polymer chains of different sizes (lengths) will elute at different times, effectively separating polymer chains by size.

Various detectors are attached to measure and characterize the eluted materials. Differential refractometry detects differences in index of refraction between the sample and solvent, enabling plots of sample concentration (proportional to the difference in refractive index) vs. elution time. These plots can then be compared to a calibration curve (often PS standards) to determine relative molecular weight and dispersity. Light
scattering can be used to obtain an absolute $M_w$ measurement in combination with the solution’s $dn/dc$ (change in solution refractive index with concentration).

Molecular weight and $D$ for the polymers in this dissertation were determined by SEC in tetrahydrofuran (THF) relative to PS standards. The Register lab kindly provided the use of their system, which uses a Waters 515 high pressure liquid chromatography (HPLC) pump connected to two 30 cm Agilent PLGel mixed C columns at 308 K and is equipped with detectors to measure differential refractive index (DRI) (Wyatt OptiLab T-PEX) and light scattering (miniDAWN TREOS) operating at 658 nm and 298 K. $M_w$ for PS and $D$ were determined from DRI while $M_w$ for PMMA, P(S-r-MMA), and PtBS were measured by light scattering using their $dn/dc$ values. Details of molecular weight measured for the polymers synthesized for this dissertation are included at the beginning of the relevant chapters and in Appendix B.

5.2.3 $T_g$ Measurement by Differential Scanning Calorimetry

Differential scanning calorimetry (DSC) is a characterization tool used to measure thermal transitions in a material. These transitions (such as melting, crystallization, and $T_g$) are indicated by changes in heat flow to the sample over a scanned temperature range. These measurements are taken at constant pressure, allowing heat flow to also be represented as heat capacity, $C_p$. A representative diagram is shown in Figure 5.1. First-order thermodynamic transitions such as melting and crystallization are shown by peaks in the heat flow or $C_p$, while second-order (or pseudo-second-order) transitions, such as $T_g$, are shown by a step change. Here, endothermic transitions are represented as positive changes in heat flow, indicating heat flow into the sample required for the transition. A differential scanning calorimeter measures heat flow to a sample by comparing it to a
Figure 5.1. Representative diagram of a differential scanning calorimetry (DSC) scan. Phase transitions are indicated by changes in heat flow or heat capacity ($C_p$) with temperature. The glass transition causes a step change in the heat flow or $C_p$. Crystallization shows a negative peak in the heat flow due to its exothermic nature. Melting, an endothermic transition, is represented by a peak in the heat flow.
Chapter 5

reference. Samples are placed in crimped aluminum pans, and references are often identical pans that remain empty. Heat flux DSC (used by TA Instruments and Mettler Toledo) places both a sample and reference pan in a shared furnace in which temperature is controlled and can be cycled over the range of interest. Heat flow is quantified by comparing temperatures of the sample and reference as the surrounding furnace is heated and cooled.

Measurements of bulk $T_g$ for polymers studied in this dissertation were conducted on a TA Instruments Q2000 DSC on second heating after cooling at rates selected to match fluorescence measurements. The first heating and isothermal holding above $T_g$ allowed for the removal of sample thermal history and control of cooling rate. This method of measurement is often used to measure bulk $T_g$ in the fluorescence literature.\textsuperscript{9-11}

5.2.4 Labeling Content Measurement by UV-Vis Spectroscopy

Ultraviolet-visible (UV-Vis) spectroscopy allows for the measurement of concentration via the Beer-Lambert Law, which describes the proportionality between a solution’s absorbance and its concentration of an absorbing species:

$$A = \varepsilon cl$$  \hspace{1cm} (5.7)

where $A$ is the solution absorbance, $\varepsilon$ is the molar extinction coefficient of the absorbing material, $c$ is the concentration of the absorbing material, and $L$ is the instrumental path length. Creating a calibration curve from solutions of known concentration allows for the determination of unknown concentration in a solution from its absorbance.

Fluorescence labeling amount was determined for covalently-labeled polymers included in this dissertation by measuring the absorbance of a solution of labeled polymer
in toluene and comparing it to a pyrenebutyl-methacrylate calibration curve, on an Agilent Technologies Cary 5000 UV-Vis-NIR Spectrophotometer.

5.3 Film and Adsorbed Layer Preparation

This section describes the steps involved in the preparation of films and adsorbed layers prior to their characterization and how they vary in the literature. It also includes several experimental investigations of parameters relevant in determining adsorbed layer thickness \( h_{\text{ads}} \). It is important to note that growth of the adsorbed layer of a given polymer with annealing time \( t_{\text{ads}} \) is mapped through the creation of many samples, each isolated via solvent leaching after a specific \( t_{\text{ads}} \) and providing a single time point. Thus, time-dependent behavior is measured through the compilation of isolated time points rather than continued measurement of a single sample. Throughout this dissertation, adsorbed layers will be referred to by the annealing time required to make them. For example, an adsorbed layer produced after annealing a 200-nm spin-coated film for 8 hours at 423 K and then washing it in solvent is an 8-h adsorbed layer. This classification will persist regardless of further treatment.

5.3.1 Substrate Treatment and Characterization

All substrates for adsorbed layer studies were treated with piranha solution in order to better standardize the interacting surface by removing any impurities and creating a fresh native oxide layer. Polished <100> silicon wafers, purchased from University Wafer, were divided into substrates measuring approximately 1 cm\(^2\) then immersed in a piranha solution (70:30 by volume concentrated sulfuric acid to 35 wt % hydrogen peroxide \( \text{H}_2\text{O}_2 \) in water) at 363 K for 1 hour. It was important to monitor
H₂O₂ concentration periodically, as it decreases over time and leads to a less effective reaction. They were then rinsed with copious amounts of deionized water and dried with nitrogen.

The thickness of each substrate’s native oxide layer was measured via ellipsometry (see Section 5.4.1) before use. The thickness of the native oxide layer was typically between 1.5 and 2 nm thick, with variation within each piranha-treated batch less than 0.05 nm. In the thickness range of relevance to adsorbed layers (1-10 nm), distinguishing between layers with similar refractive index becomes difficult via ellipsometry, and film thickness and native oxide thickness can become coupled. Independently measuring and fixing the native oxide layer thickness avoided this issue. This additional measurement step also allowed for a screening of substrates. Those with particularly thick native oxide layers, or that did not conform to the Complete Ease model (see Section 5.3.1) with a MSE > 3.0 were discarded and not used for adsorbed layer experiments. Generally, this treatment process greatly improved the uniformity of adsorbed layer measurements.

Bulk overlayer films for bilayer experiments were spin-coated on mica substrates that were not piranha-treated or pre-characterized, due to the fact that they would later be floated to a new “substrate” (see Chapter 6). Their thickness was determined by spin-coating an identical film on Si for measurement.

5.3.2 Spin-coating Films

Polymer thin films can be prepared in a variety of ways, including spin-coating, flow-coating, drop-casting, and MAPLE deposition, among others. The films used in this dissertation were largely prepared via spin-coating, due to its ability to rapidly
produce films of controlled and uniform thickness. In this ubiquitous technique, a solution of polymer in a volatile solvent is placed on a horizontally rotating disk, which is then spun at precise rates to control film thickness. Film formation takes place in two stages: (1) centrifugal forces induced by spinning spread the solution and discard excess polymer and solvent, and (2) remaining solvent evaporates. The physics of spin-coating are well summarized by Hall, Underhill and Torkelson as a combination of rheology and solvent evaporation.\(^{15}\) They use a variety of solvent and polymer solutions to evaluate the relationship governing the thickness of films prepared under specific process parameters, proposed by Bornside, Macosko, and Scriven:\(^{16}\)

\[
h_f = (1 - x^0) \left[ \frac{3\eta_0}{2\rho\omega^2} \right] \kappa (x^0 - x_{1\infty}) \left( \frac{1}{3} \right)
\]

(5.8)

where \(h_f\) is the final film thickness, \(\eta_0\) is the initial solution viscosity, \(\kappa\) is the mass transfer coefficient, \(\rho\) is the initial solution density, \(\omega\) is the spin speed, and \(x^0\) and \(x_{1\infty}\) are the initial and equilibrium solvent mass fraction, respectively. This relation incorporates changes in film thickness due both to solution flow and solvent evaporation. They found good agreement with this model and they published data sets of film thickness obtained from spin-coating PS and PMMA with different solution concentrations, solvents, and spin speeds.\(^{15}\) These empirical relationships were used extensively in initial experiments to determine the polymer solution concentration and spin speed needed to produce films of desired thicknesses. As differences in polymer molecular weight greatly influence these relationships (through changes in the solution viscosity), calibration data sets were developed for each individual polymer as needed. Although the vast majority of solvent evaporates during the spin-coating process, any remainder is removed, along with residual stresses via thermal annealing of the spin-coated films.
While it has been shown that chain dimensions are unperturbed parallel to the substrate in spin-coated thin films, spin-coating could still alter chain conformations in ways that could impact their likelihood of adsorption. In order to verify that adsorption was not enhanced or otherwise influenced by spin-coating, we compared the thickness of adsorbed layers grown in films that were either spin-coated (at 1000 rpm) or drop-casted (drops of solution were allowed to dry in air). Both sets of films were made from a 2 wt % solution of IPS-240 ($M_w = 240$ kg/mol; synthesized following the same procedure as IPS-155, described in Chapter 6) in toluene. Figure 5.2a shows very similar adsorbed layer growth between both casting methods. The dashed line is a fit of the spin-coated adsorbed layer thickness to a saturated exponential of the form:  

$$h_{ads}(t_{ads}) = h_0 + \Delta h \left( 1 - e^{-t_{ads}/t_{cross}} \right)$$  

(5.9a)

where $t_{cross}$ is a characteristic adsorption time and $h_0$ is adsorbed layer thickness at $t_{ads} = 0$ h. Plateau thickness ($h_p$) can then be calculated as  

$$h_p = h_0 + \Delta h$$  

(5.9b)

This equation has been used approximate adsorbed layer growth, and $t_{cross}$ is used to determine the transition from linear to logarithmic growth in Chapters 7 and 8. Close alignment in $h_{ads}$ between spin-coated and drop-casted adsorbed layers showed that spin-coating did not cause or enhance adsorption by altering the amount of polymer-substrate contacts or chain conformations.

5.3.3 Annealing Polymer Films

In order to promote the growth of irreversibly adsorbed layers, spin-coated films are annealed for various times at specific temperatures ($T_{ann}$). Literature reports
Figure 5.2 Processing effects on adsorbed layer thickness. (A) Comparison of $h_{ads}$ from spin-coated (triangles) or drop-casted (circles) films of PS-240; dotted green line is a fit of spin-coated data to Equation 5.9a. (B) Thickness of 5-h PS-109 adsorbed layers isolated by soaking the annealed film in toluene, sonicating it in toluene, or spin-coating toluene on top of it. (C) Impact of soaking time on adsorbed layer thickness of 27-h /PS-155 adsorbed layers. (D) Thickness of adsorbed layers of different polymers, isolated after 3 h of annealing at various temperatures. Lines indicate $h_{ads}$ in films that were not annealed above room temperature (~295 K); arrows indicate bulk $T_g$ for each polymer, as indicated by color.
occasionally involve a pre-annealing step in order to avoid complications involving residual solvent or stresses induced by spin-coating.\textsuperscript{19,21,22} However, the exact nature and presence of this pre-annealing step varies between reports.\textsuperscript{20,22–25} In order to simplify the relationship between annealing time and adsorption, a pre-annealing step was not included in the work of this dissertation.

Additionally, little explanation has been given for the temperature chosen other than ensuring melt behavior. The majority of early work in this area studied films annealed at approximately 50 K above bulk $T_g$.\textsuperscript{20,21,24,26,27} In the work of Jiang et al., they increased the relative annealing temperature of P2VP thin films to account for the strong hydrogen-bonding interactions between P2VP and the substrate.\textsuperscript{24} This is the only study for which confinement effects on $T_g$ of the spin-coated film are accounted for in terms of $T_{ann}$ in the preparation of adsorbed layers. As mentioned in Chapter 3, kinetic investigations revealed that an increase in $T_{ann}$ can significantly increase the rate of adsorbed layer growth.\textsuperscript{22,28}

It is not clear at what $T_{ann}$ adsorption begins to influence film properties. Determination of an onset temperature would reveal the lowest annealing temperature at which adsorption should be accounted for in thin film preparation. Figure 5.2d plots $h_{ads}$ after 3 h of annealing against $T_{ann}$ for PS-109, PMMA-119, and PtBS-280. PS and PMMA synthesis details are given at the beginning of Chapter 7. PtBS-280 was purchased from Polymer Source and used as received. It was measured by SEC to have a $M_W = 280$ kg/mol and $D = 1.18$. Lines indicate $h_{ads,0}$, the residual thickness measured without annealing above room temperature ($\sim$295 K). PMMA-119 had a much thicker $h_{ads,0}$, attributed to its stronger interaction with the substrate.\textsuperscript{29} While PS-109 and
PMMA-119 showed minimal adsorption (compared to \( h_{\text{ads}, 0} \)) below their respective \( T_g \) (indicated by arrows), PtBS-280 showed signs of adsorption as low as 40 K below its \( T_g \) in both thick and “thin” films. We note that 230-nm-thick films show average \( T_g \) deviations of \( \sim 5 \) K from bulk,\(^{10}\) but they formed adsorbed layers with \( h_{\text{ads}} \) consistent with that of 880-nm-thick films in the temperature range where they overlapped and extended the range to create a complete picture. The impacts of annealing temperature on specific polymers and copolymers are discussed further in Chapters 7 and 8.

Unless otherwise noted, films in this dissertation were annealed at bulk \( T_g + 45 \) K, under 10\(^{-2} \) torr vacuum, in temperature-controlled ovens.

### 5.3.4 Isolating Irreversibly Adsorbed Layers

As described in Chapter 3, Guiselin proposed that adsorbed layers could be isolated from films after annealing by thorough washing with a good solvent.\(^ {30} \) Solvent leaching has since been employed to isolate irreversibly adsorbed layers from their host film prior to their characterization.\(^ {21,22,31,32} \) Napolitano and Wübbenhorst and Fujii et al. washed films in toluene for 3 cycles (each consisting of rinsing and soaking films for 10 minutes in fresh toluene), totaling 30 minutes.\(^ {21,25} \) Koga and coworkers used 5 washing cycles, totaling 50 minutes, to isolate their adsorbed layers.\(^ {20,24} \) Unni et al. soaked films for much longer times with very controlled steps and a variety of solvents, but their reports of substantial dewetting of PS after long annealing, even with toluene,\(^ {31} \) were different than commonly found. Finally, as described in Chapter 3, extensive leaching has been employed to further desorb the “loosely bound fraction” within adsorbed layers, isolating a flattened sublayer.\(^ {20,24} \) This leaching procedure was intended to separate the adsorbed layer further, rather than removing only unadsorbed polymer chains.
Figure 5.2b compares the thickness of 5-h adsorbed layers of PS-109 when isolated by different methods. 200-nm-thick films were washed either by soaking in toluene for 30 minutes (following our standard procedure), sonicating in toluene for 30 minutes, or by spin-coating toluene on top of the film at 4000 rpm. Sonicating reduced $h_{ads}$ by $40 \pm 29\%$ relative to soaking. Some of this effect could be due to mild heating of the solvent introduced by sonicating. Alternatively, spin-coating toluene onto the film left a 14-nm-thick residual layer, likely resulting in part from rapid evaporation of solvent. This comparison showed that while the precise $h_{ads}$ depends on how unadsorbed chains are removed and therefore should be kept constant in experiments, the presence of an adsorbed layer is unaltered.

Unless otherwise noted, in this dissertation annealed films (after cooling for several hours and often overnight) were rinsed with a good solvent and soaked in fresh solvent for ten minutes. This rinsing and soaking cycle was repeated twice more to thoroughly remove any unadsorbed chains, for a total of three wash cycles and 30 minutes of soaking. The impact of longer soaking on $h_{ads}$ was also investigated by increasing the amount of washing cycles (for up to a total of 60 minutes soaking in toluene) on 27-h adsorbed layers of lPS-155. Figure 5.2c shows that $h_{ads}$ after various washing times did not change within error. Koga *et al.* reported desorption of loosely-bound PS chains after ~100 days of soaking in toluene, but as stated previously, this pertained to a secondary isolation of a distinct sublayer. The fact that no change in $h_{ads}$ occurred up to 1 h indicated isolation of a stable adsorbed layer.
5.4 Film and Adsorbed Layer Characterization: Thickness and Morphology

Measurements of adsorbed layer thickness were largely conducted by ellipsometry due to the relative ease and efficiency of measurement combined with its sensitivity to differences in sample thickness. This technique relies largely on fitting models to measurements of changes in light polarization induced by the sample. Different models were developed for each polymer from thicker films of the same polymer. To ensure these model fits accurately reported thickness, sample thicknesses were spot-checked with atomic force microscopy (AFM) measurements. These techniques are described below and enabled rapid and accurate measurements of film thickness. AFM also provided the ability to characterize adsorbed layer morphology, shown in Chapter 6 for PS.

5.4.1 Spectroscopic Ellipsometry

Ellipsometry is an optical characterization tool that uses changes in the polarization of light induced by a sample to determine its optical and physical properties. An ellipsometer shines linearly polarized light on a sample and detects and characterizes the elliptically polarized light that reflects off. These light wave transformations are depicted in Figure 5.3a. Arrows labeled p and s indicate the direction of linearly polarized light waves sent to the sample at incidence angle $\Phi$.

The transformation from linear to elliptical polarization is due to changes in the amplitudes and phase of $p$ and $s$ light waves upon contact with the sample. The magnitude of these changes, determined by the nature of the sample, is quantified by two parameters $\Delta$ and $\Psi$, defined as:
Figure 5.3 Ellipsometry enables the characterization of film thickness and optical constants by measuring changes in polarized light induced by the sample. (A) Transformation of light in an ellipsometry measurement, where linearly polarized light with $p$- and $s$- components becomes elliptically polarized after interaction with the sample induces changes in amplitudes and phase of the reflected $p$- and $s$- polarizations. (B) Schematic of an ellipsometer, where light is sent from the source through a polarization state generator (PSG) to create well-defined linearly polarized light. This light is then reflected off the sample, and the reflected light is collected by the polarization state detector (PSD) to measure the changes in polarization. In spectroscopic ellipsometry, these changes in polarization are measured as a function of wavelength. This figure was adapted from Ref \textsuperscript{33} with permission.
where $\delta_1$ and $\delta_2$ are the differences in phase between $p$ and $s$ waves before and after reflection, respectively. $R_p$ and $R_s$ are the real components of the total reflection coefficients of $p$ and $s$ waves, which are the ratios of the amplitudes of each reflected wave to the incoming wave and incorporate the sample’s index of refraction. These two parameters combine to describe and quantify the changes in light polarization, where $\Delta$ is reflective of the change in phase and $\Psi$ is reflective of the change in wave amplitude.

Modern ellipsometers collect modulated intensity measurements that are then transformed to these parameters as a function of wavelength. These data for $\Delta$ and $\Psi$ for a range of wavelengths are then fit to various models through regression analysis to determine sample characteristics. Older ellipsometers collect measurements at a single wavelength while spectroscopic ellipsometers, as used in this dissertation, improve measurement precision by collecting data at a wide range of wavelengths.

Ellipsometers consist of a system to produce controlled linearly polarized light and a system to detect elliptically polarized light, arranged on either side of a sample stage. A general schematic is shown in Figure 5.3b. The light production system consists of a light source (broad spectra for spectroscopic ellipsometers, laser for single-wavelength ellipsometers) and a polarization state generator (PSG) to produce and control linearly polarized light. The light detection system consists of a polarization state detector (PSD) and a light detector to characterize the elliptically polarized light reflected off the sample. The incidence angle at which light comes in contact with the sample can be controlled to optimize signal strength.
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Thicknesses of polymer films and adsorbed layers were determined using a Woollam M-2000 Spectroscopic Ellipsometer and fitting to a two-layer model consisting of native oxide and PS layers. The native oxide layer was fit to a silicon with native oxide model available in the library of the Complete Ease software package, which was used to analyze and fit data. As mentioned in Section 5.3.1, native oxide layer thickness was measured for each substrate prior to covering it with a polymer film. Its thickness was then fixed during adsorbed layer and film thickness measurements in order to avoid any correlation between its thickness and the thickness of the polymer film or adsorbed layer.

The Cauchy model, a dispersion equation used for transparent films, was used to fit the raw data and determine polymer film thickness. It is of the form:

\[ n(\lambda) = A + \frac{B}{\lambda^2} + \frac{C}{\lambda^4} \ldots \]  

(5.11)

where \( n \) is refractive index, \( \lambda \) is wavelength (in \( \mu \)m), and \( A, B, \) and \( C \) are fitting parameters. The absorbing components of the Cauchy equation were fixed at 0 and are not included here, as all polymers studied were transparent in the wavelengths studied (400-1600 nm). As separate measurements of \( n \) and film thickness become unreliable below ~ 10 nm,\(^{12}\) \( A, B, \) and \( C \) parameters were determined by averaging values obtained from fitting the model to measurements of several 200 nm films of each polymer. They were then fixed for all subsequent measurements of films and adsorbed layers. These parameters are listed in Table 5.2.

As expected, \( A \) parameters (the largest contribution to index of refraction) were reflective of composition for P(S-r-MMA) copolymers, lying between those of PS and PMMA. Homopolymer values are in line with literature reports.\(^{12,34}\) The ability of these model parameters to accurately determine adsorbed layer thickness was verified by
comparing ellipsometry thickness measurements to physical measurements by AFM (described in the next section). Comparisons between thickness measurements are given in Chapters 6 (IPS), 7 (P(S-r-MMA) and PMMA), and 8 (PtBS).

### Table 5.2 Cauchy parameters used to determine polymer film thickness

<table>
<thead>
<tr>
<th>Polymer</th>
<th>A</th>
<th>B</th>
<th>C</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>1.563</td>
<td>0.0083</td>
<td>0.003</td>
</tr>
<tr>
<td>P(S-r-MMA) (75:25)</td>
<td>1.545</td>
<td>0.0087</td>
<td>5x10^-5</td>
</tr>
<tr>
<td>P(S-r-MMA) (48:52)</td>
<td>1.524</td>
<td>0.0085</td>
<td>0</td>
</tr>
<tr>
<td>P(S-r-MMA) (27:73)</td>
<td>1.501</td>
<td>0.0069</td>
<td>1x10^-6</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.478</td>
<td>0.0055</td>
<td>0</td>
</tr>
<tr>
<td>PtBS</td>
<td>1.520</td>
<td>0.00523</td>
<td>0</td>
</tr>
</tbody>
</table>

### 5.4.2 Atomic Force Microscopy

AFM is a type of scanning probe microscopy that provides sub-nanometer resolution normal to a sample’s surface, enabling detailed characterization of its surface morphology. AFM images a surface through the use of a probe consisting of a flexible cantilever with a sharp (radius on the order of 10 nm) tip at its free end. This probe travels across a sample surface to create a raster 3-dimensional image based on the probe’s interaction with the sample surface. A laser is focused on the tip and is reflected back to a position-sensitive photodetector that can sense deflections in cantilever position. A simplified diagram of major AFM components is depicted in Figure 5.4.

AFM can be operated in contact or non-contact mode, depending on the desired level of surface interaction with the tip. Intermittent contact or “tapping” mode is a type of non-contact mode frequently used for characterizing soft materials to avoid damage to the sample and adhesion of material to the tip.\(^{35}\) In this mode, the cantilever oscillates freely at a specific frequency and amplitude across the top of a sample. When the tip is in
Figure 5.4 Schematic of the active components of an atomic force microscope (AFM) indicating how reflection of a laser beam off of the cantilever is collected by a photodetector that can sense displacement of the cantilever due to changes in the sample surface morphology. Data from the photodetector is entered into a control loop feedback mechanism that enables adjustments in the height of the sample stage or cantilever support corresponding to cantilever displacement. These adjustments are then transformed into height profiles. Image reproduced from Ref. 36
contact with the sample surface, the amplitude of these oscillations is dampened. A control loop feedback mechanism prompts the AFM to raise or lower the cantilever support or sample stage (depending on the instrument) in order to maintain a set amplitude (a user-defined fraction of the free amplitude). This set amplitude effectively corresponds to a certain distance, $z_c$, between the oscillating cantilever and sample surface features. Changes to the height of the cantilever support or sample stage needed to maintain $z_c$ are achieved by sending a specific voltage to piezoelectric scanners that swell or shrink proportional to the applied voltage and its polarity. The distance of the shift in height necessary to maintain the set amplitude and $z_c$ ($\Delta z$) is then translated to give a sample height profile across the xy plane. Several feedback parameters can be tuned to control the precision of the image collected. The main parameters adjusted are: amplitude set point (controls the amount of force with which the tip comes in contact with the sample and $z_c$) and integral gain (controls how quickly deviations in amplitude from the set point are corrected to maintain $z_c$ after a perturbation).

Due to its extreme sensitivity, AFM can also distinguish between the modulus of different materials.\textsuperscript{37} This is of particular use in gaining contrast in multicomponent systems such as phase-separated block copolymers and polymer blends, the former of which will briefly be discussed in Chapter 7. More capabilities of AFM are described in several review articles.\textsuperscript{38,39}

All AFM images presented in this dissertation were collected using an Asylum Research MFP-3D-SA Atomic Force Microscope in non-contact mode. The AFM probes were silicon with force constants $= 11 \text{ - } 54 \text{ N/m}$ and resonance frequencies $= 200 \text{ - } 400 \text{ kHz}$. All images were taken at room temperature with 512 x 512 pixel resolution and
analyzed using Gwyddion software, a scanning probe microscopy data analysis tool, to determine morphology and film thickness.

### 5.5 Measurement of $T_g$ via Fluorescence

Chapter 4 described how fluorescence techniques have been employed to gain insight into location-specific properties of nanoconfined polymer systems. This section describes in more detail how measurements of $T_g$ are conducted by relying on the ability of extrinsic fluorescent probes to detect changes in the density of their surrounding polymer matrix. Generally, these probes are derivatives of pyrene or 4-tricyanovinyl-[N-(2-hydroxyethyl)-N-ethyl]aniline (TC1) dyes; a representative form of pyrene is shown in the inset of Figure 5.4a. As mentioned in Chapter 4, these probes rely on a tradeoff between fluorescence emission and non-radiative energy dissipation through molecular motion to characterize their environment. Pyrene’s non-radiative deactivation largely occurs via vibrational motion of the probe, while TC1 has a significant rotational motion component. The temperature-dependence of their fluorescence response has been observed to be sensitive to $T_g$ due to relative changes in the density and rigidity of the polymer matrix above and below $T_g$. At higher temperatures, increased mobility and reduced density in the polymer matrix allows for a larger fraction of the probe’s energy to be dissipated via motion—resulting in lower fluorescence intensity. Figure 5.5a displays the difference in emission intensity of pyrene with a 100 K difference in temperature.

Both of these fluorophores can be incorporated into a polymer matrix by doping or labeling at dilute concentrations, to avoid plasticization or perturbation of the polymer. Slight modification of the dye is required to label the polymer chain by covalently
Figure 5.5 (A) Pyrene fluorescence emission spectrum in a 350 nm thick polystyrene film at 298 K (thin curve) and 398 K (bold curve). Data have been normalized by the maximum intensity of the spectrum at 298 K. Also shown is the molecular structure of pyrene. This figure was reprinted from Ref.\textsuperscript{41} with permission from Springer. (B) Fluorescence intensity measurements of 545 nm- (squares) and 17 nm- (diamonds) thick pyrene-labeled PS films plotted against temperature. Reprinted by permission from Macmillan Publishers Ltd: Nature Materials Ref.\textsuperscript{11}, copyright 2003.
attaching the probe. While the key molecular structure of a given dye is not altered, it is linked to a methacrylate monomer via a short carbon chain. The length of this linker chain, typically methyl or butyl, depends on the dye and technique used.\textsuperscript{11,42,43} Dye-labeled monomers are then incorporated at low concentrations (< 1 mol\%) relative to neat monomer in FRP reactions to produce labeled polymer.\textsuperscript{11,40} While both doping and labeling enable average \( T_g \) measurements in thin films, fluorescently-labeled polymer has a significant advantage: it can be combined with unlabeled, neat, polymer to study site-specific phenomena, providing precise control of label location. Synthesis of pyrene-labeled PS is detailed in Chapter 6.

Samples are prepared on quartz substrates that are specifically chosen to not transmit light at the wavelengths of interest (depending on the fluorophore) so as not to interfere with the fluorescence emission spectra. Measurement of \( T_g \) requires the combination of a spectrofluorometer with a front-facing sample collection setting and a temperature-controlled sample holder. A broad spectrum light source, such as a Xenon lamp, and a monochromator allow for excitation of a sample at a desired wavelength, with the specificity of wavelength and intensity of light controlled with a bandpass filter. A scanning monochromator and photodetector collect the fluorescing light intensity at each wavelength over a desired range, producing a spectrum. Steady-state fluorescence measurements are conducted by collecting spectra upon cooling, after holding the films well above \( T_g \) to erase any thermal history. Excitation wavelength and the wavelength range for emission spectra collection depend on the probe used, noting that probes modified for labeling require different settings than their doped counterparts.
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The precise method for determining $T_g$ from these spectra depends on the system and sample geometry. For supported films, either peak intensity$^{11}$ or integrated spectra intensity$^{10}$ is plotted against temperature. An example of peak intensity data is shown in Figure 5.5b for labeled PS films. For all systems, distinct slopes pertaining to the rubbery and glassy regions are fit to the intensity data with their intersection being $T_g$. These slopes reflect the difference in the temperature-dependence of probe mobility due to changes in the density of the polymer matrix.$^{44}$ While $T_g$ measured by peak intensity and integration are found to be in good agreement within experimental error,$^{10}$ integration is reflective of total quantum yield and is considered a more robust approach.$^{45}$ This method has also been slightly adapted to measure $T_g$ of free-standing films through self-referencing fluorescence$^{43,46}$ and unlabeled films through intrinsic fluorescence.$^{47}$ Details of these adaptations are not of particular relevance to this dissertation and are not included here, but an overview of these and other fluorescence techniques was recently published for the reader’s reference.$^{48}$

All fluorescence measurements in this dissertation were conducted on a Horiba Scientific Fluorolog-3 spectrofluorometer in a front facing geometry. Sample temperature was controlled by an Instec HCS302 hot and cold stage attached to an Instec mK2000 Temperature Controller with LN2-P (liquid nitrogen pump) attachment. Details on fluorescence experimental procedures used for this dissertation are given in Chapters 6 and 8.
5.6 References


Chapter 6

Measurement of Glass Transition Temperature in Exposed and Buried Adsorbed Polymer Nanolayers

6.1 Introduction

Thin polymer films in contact with a substrate serve as the enabling material for a range of emerging technologies, including nanoimprint and block copolymer lithography for microelectronics, membranes for efficient separations and drug delivery, and semiconductors for organic solar cells and electronics. In these applications, the polymer thin film is often prepared by solution-casting directly atop the substrate. After initial film formation, annealing the polymer film in the melt state is often a critical step in production to remove excess solvent, relax residual stresses and thermal history induced during casting, and—in the case of block copolymer films—induce self-assembly. As described previously, monomer-substrate interactions on the order of $k_B T$ can lead to the formation of an irreversibly adsorbed polymer nanolayer during prolonged melt-state annealing. The long-chain nature of macromolecules, whereby multiple interaction sites exist, stabilizes this adsorbed nanolayer against desorption. Though the nature of polymer adsorption onto surfaces from solutions has been well-established, adsorption from the melt state is still being studied in terms of its mechanism, structure, and influence on thin film properties.

Recent work has focused on examining a connection between the development of irreversibly adsorbed nanolayers during melt-state annealing and the well-documented significant deviations from bulk physical properties in ultrathin polymer films.
Several studies have demonstrated a correlation between the growth of an irreversibly adsorbed nanolayer and deviations in thin film properties from the bulk, including glass transition temperature \((T_g)\), viscosity,\textsuperscript{26} dynamics,\textsuperscript{24} and diffusion.\textsuperscript{25} Additionally, these adsorbed layers have been studied in terms of their stability.\textsuperscript{35} In particular, it was shown that the \(T_g\) in polystyrene (PS) thin films could be controlled solely by adjusting the annealing time and temperature, which influenced the development of an adsorbed nanolayer.\textsuperscript{12} The current understanding of irreversibly adsorbed nanolayer properties (including \(T_g\)) has been obtained by performing studies on the exposed nanolayer (\(i.e.,\) after the removal of unadsorbed polymer) in a capped geometry.\textsuperscript{12} Unfortunately, experimental challenges have prevented the analysis of adsorbed nanolayer properties buried within the thin film (\(i.e.,\) in-situ analysis) and the examination of interfacial influences. As a result, understanding the critical role that the formation of adsorbed nanolayers plays in determining the properties of ultrathin polymer films remains a fundamental challenge.

This challenge was addressed by employing a unique fluorescence bilayer method to directly measure \(T_g\) of the irreversibly adsorbed polymer nanolayer. The study was undertaken using PS, a model polymer for which \(T_g\) in the thin film geometry has been thoroughly investigated.\textsuperscript{8,27,36,37} The PS adsorbed nanolayer, covalently labeled with a fluorescing dye molecule capable of reporting polymer \(T_g\),\textsuperscript{36} was isolated (\(i.e.,\) exposed) at different stages of growth and incorporated (\(i.e.,\) buried) into a bulk polymer film. By performing measurements on both the exposed and buried adsorbed nanolayer geometries, we were also able to examine the influence of the free surface on the nanolayer \(T_g\). Our results revealed a suppression of the free surface influence and
increased deviation of $T_g$ in submerged adsorbed layers with longer annealing. The development of these trends was attributed to increased chain adsorption at the substrate interface. Furthermore, bilayer-annealing studies showed a marked increase in the timescale of bulk $T_g$ recovery with enhanced degrees of adsorption. These findings expand the understanding of how irreversible adsorption contributes to thin film $T_g$ through the examination of interfacial effects. An appreciation for this relationship enables prediction of the impacts of melt-state annealing on technologically-relevant polymer thin film properties.

**6.2 Materials and Methods**

The fluorescent probe incorporated into labeled PS, pyrenebutyl-methacrylate, is shown in the Figure 6.1 inset. It was synthesized in batches following a procedure developed in and used by the Torkelson laboratory at Northwestern University.\(^{36}\) 1-pyrenebutanol (purchased from Sigma-Aldrich) was reacted with methacryloyl chloride (Sigma-Aldrich) via an esterification reaction in tetrahydrofuran (THF) (Sigma-Aldrich). This reaction proceeded slowly under nitrogen, with a methacryloyl chloride solution (3.42 mL in 20 mL THF) being added dropwise, over the course of approximately 1 h, to a 1-pyrenebutanol solution (2.55 g in 100 mL THF with 5 mL tri-ethyl amine) immersed in a dry ice and acetone bath. The reaction was allowed to come to ambient temperature while stirring overnight, then the THF was evaporated off. The reactants were dissolved in toluene before byproducts were separated out into a saturated solution of sodium bicarbonate in water. The products were retained in a dark yellow toluene phase, toluene was evaporated, and they were further purified by recrystallization in ethanol (Fisher Scientific). The chemical composition for synthesized pyrenebutyl-methacrylate was
Figure 6.1. $^1$H-NMR spectrum for synthesized pyrenebutyl-methacrylate. Residual solvent (CDCl$_3$) appears at 7.26 ppm and water appears at 1.59 ppm. Peaks are integrated and correspond to protons indicated by labels on inset chemical structure.
confirmed from its \(^1\)H-NMR spectrum in deuterated chloroform (CDCl\(_3\)), as shown in Figure 6.1.

Pyrene-labeled PS (lPS-155) \((M_w = 155 \text{ kg/mol}; D = 1.9)\) was synthesized by bulk free radical polymerization of styrene (Sigma-Aldrich) with 0.16 mol\% pyrenebutyl-methacrylate at 348 K under nitrogen with benzoyl peroxide (BPO) as the initiator. Afterwards, the polymer was dissolved in toluene (Fisher Chemical) and precipitated in methanol (Fisher Chemical) three times to remove any excess monomer. Unlabeled PS (PS-116) \((M_w = 116 \text{ kg/mol}; D = 1.9)\) was synthesized and characterized similarly without the addition of pyrenebutyl-methacrylate. Similar synthesis routes were followed to achieve identical end functionality and comparable dispersity for both polymers. The removal of monomer and solvent was confirmed, along with polymer composition via \(^1\)H-NMR. Their molecular weights were determined via SEC, and labelling content for lPS-155 was determined by UV-vis spectroscopy to be 0.2 mol \%, as described in Chapter 5.

lPS-155 was then used to create adsorbed layers, following the procedure outlined in Chapter 5. 200-nm-thick lPS-155 films were annealed at 423 K for different times \((t_{ads})\) before washing 3 cycles in toluene. Figure 6.2 shows that the fluorescence intensity of the toluene soaking solutions decreased below that of pure toluene after two soaks, indicating three soaking cycles were sufficient to remove unadsorbed lPS-155. This was consistent with the experiments described in Chapter 5 that showed no change in adsorbed layer thickness of lPS-155 with additional washing time.

In order to prepare bilayer films for buried adsorbed layer measurements, 400-nm-thick PS-116 overlayers were spin-coated from a toluene solution onto mica and
Figure 6.2. (A) Fluorescence spectra of subsequent soaking solutions for an 8-h irreversibly adsorbed layer compared to that of toluene. (B) Integrated fluorescence intensity of soaking solutions for 8-h irreversibly adsorbed layers. Error bars (smaller than data points) represent ± 1 standard deviation of the integrated fluorescence intensity of soaking solutions from identically prepared films.
annealed above \( T_g \) to remove residual solvent and stresses. These unlabeled bulk films were then floated onto previously-prepared \( lPS-155 \) adsorbed layers in a bath of deionized water. After drying thoroughly, the stacked films were annealed at 393 K for 20 minutes in order to remove wrinkles induced during floating and create a consolidated bilayer film. This consolidation temperature and annealing time were both considerably less than those used to make the adsorbed nanolayer, thus ensuring minimal modification of the adsorbed amount during consolidation. Consolidation steps were therefore not counted towards bilayer annealing time. Bilayer films at this stage are referred to as containing buried, or submerged, adsorbed layers of \( t_{ads} \) (shown in Figure 6.7). Several of these bilayer films were later annealed further at 423 K under vacuum for bilayer annealing time \( t_{Bann} \) (shown in Figure 6.8), where \( t_{Bann} = 0 \) is the state at which bilayer films are consolidated but not further annealed. These further annealed bilayer systems are referred to by both \( t_{ads} \) and \( t_{Bann} \). Hence, a 6-h irreversibly adsorbed layer (\( t_{ads} = 6 \)) that has been capped with PS-116, consolidated, and further annealed for 2 h is referred to as a 6-h bilayer system with \( t_{Bann} = 2 \).

Fluorescence measurements of \( T_g \) were conducted following the pseudo-thermodynamic approach\(^{38-40} \) described in Chapter 5. A Horiba Scientific Fluorolog-3 Spectrofluorometer was employed to measure \( T_g \) of the nanolayers. Samples were excited at \( \lambda = 340 \) nm (with 3.8 nm bandpass) and emission spectra were collected from \( \lambda = 350 \) to 500 nm. The fluorescence emission spectra of \( lPS-155 \) adsorbed layers were obtained upon cooling from 413 K to 303 K in 5 K increments, after initially holding samples at 413 K for 20 minutes to remove thermal history. To ensure equilibration and isothermal
measurements, films were stabilized for five minutes at each temperature prior to collecting spectra; this resulted in an effective average cooling rate of 1 K/min.

The spectra were integrated, and normalized integrated intensities were plotted as a function of temperature. $T_g$ was identified as the intersection of linear fits to the rubbery and glassy regimes. These fits were determined from at least four data points at each of the extreme ends of the temperature range. Data points were included moving inward to ensure $R^2 > 0.99$. Once this condition was no longer reached, due largely to changes in the curvature related to the glass transition, data points were no longer included in determining linear fits. An example of the fluorescence spectra and integrated data collected is shown in Figure 6.5a for a 10-h /PS-155 adsorbed layer.

### 6.3 Growth of Adsorbed Nanolayers

In recognition of structure-property relationships inherent to adsorbed layers,\textsuperscript{12,41} an understanding of their surface topography and thickness at different stages of development is essential to relating trends in $T_g$ and interfacial influences to their growth. Figure 6.3 shows AFM topological images of exposed /PS-155 adsorbed layers created by annealing films for different times. In agreement with prior literature studies, a smooth nanolayer was observed after a critical $t_{ads}$.\textsuperscript{11} In line with the work of Bal et al. on the stability of the PS adsorbed layer,\textsuperscript{35} adsorbed layers isolated after less than 2 h annealing (corresponding to a thickness of $3.1 \pm 0.2$ nm) were unstable and spinodally dewetted immediately after rinsing, as recognizable by the characteristic pattern shown in Figure 6.3. Due to this dewetting, adsorbed layers formed after less than 2 h of annealing have an enhanced surface area; the implications of this on $T_g$ will be discussed later.
Figure 6.3. 5x5μm AFM surface topography images of /PS-155 irreversibly adsorbed layers annealed for different times: (A) 0.5 h (5 nm height scale), (B) 1 h (5 nm height scale), (C) 2 h (2 nm height scale), and (D) 4 h (2 nm height scale). White lines indicate the section of the image represented by the inset profiles.
Adsorbed layer growth has been shown to be dependent on both polymer molecular weight and annealing temperature. The thickness of the irreversibly adsorbed nanolayer ($h_{\text{ads}}$) for both lPS-155 and neat PS-116 as a function of adsorption time is shown in Figure 6.4. Films were annealed on silicon and thickness measurements were obtained by ellipsometry. For films annealed less than 2 h, in which incomplete nanolayers were formed, the average film thickness was determined by averaging the thickness across the film, to match average thicknesses reported by ellipsometry. Within experimental error, the growth rates of the adsorbed nanolayers for both the labeled and neat PS were identical and followed a trend consistent with the literature—with small differences due to their respective molecular weights.

The dotted lines in Figure 6.4 indicate the plateau thickness ($h_p$) for each polymer, representing the average thickness of adsorbed layers after leveling out at $t_{\text{ads}} = 6$ h. The $R_g$ of labeled and neat PS used in this investigation were calculated according to the correlation reported by Fetters et al. for PS in cyclohexane at 308 K (theta solvent and temperature):

$$R_g = 2.42 \times 10^{-2} M^{0.512}$$

(6.1)

where $M$ is molecular weight. Using the weight-average molecular weights measured by SEC, $R_g$ was 11.0 and 9.5 nm for lPS-155 and PS-116, respectively. Dividing $h_p$ by $R_g$ for each polymer gave scaling factors of $0.49 \pm 0.05$ and $0.55 \pm 0.03$ for lPS-155 and PS-116, respectively. These scaling factors were within error of each other and in agreement with the scaling relationship $h_p = 0.47R_g$ reported by Fujii et al. for PS adsorbed layers on SiO$_x$. The growth profiles presented in Figure 6.4 confirm that the pyrenebutyl methacrylate labels on lPS-155 did not alter its adsorbed layer growth kinetics or $h_p$. 
Figure 6.4. Adsorbed layer thickness measured via ellipsometry as a function of $t_{ads}$ for labeled PS (lPS-155) and neat PS (PS-116) on silicon. Thicknesses of lPS-155 adsorbed layers on silica substrates (green circles) were measured via AFM. Error bars represent ± 1 standard deviation of $h_{ads}$ for multiple samples. Lines show $h_p$ for each polymer, obtained by averaging adsorbed layer thicknesses after 6 h of annealing at 423 K.
Also plotted in Figure 6.4 are $h_{ads}$ for select nanolayers grown on silica for which film thickness was measured via AFM. The thicknesses of these adsorbed layers were within error of corresponding thicknesses on silicon, indicating no discernible difference between the influences of the two substrates on irreversibly adsorbed nanolayer formation.

6.4 $T_g$ of Exposed Adsorbed Layers

Once the growth and development of these adsorbed layers were characterized, the fluorescence of PS-155 was exploited to measure their $T_g$ via fluorescence spectroscopy.\textsuperscript{36,44,45} Figure 6.5a plots the normalized integrated fluorescence intensity as a function of temperature for a 10-h exposed irreversibly adsorbed nanolayer. Linear fits of the fluorescence data at high and low temperatures (corresponding to rubbery and glassy regimes, respectively) intersect at 363 K. This intersection has been previously shown to be an accurate measurement of $T_g$ in bulk and confined polymers.\textsuperscript{36,44,45} Hence, $T_g$ for the 10-h adsorbed nanolayer was determined to be 363 K. The inset in Figure 6.5a shows the temperature-dependent fluorescence spectra for this 5.5-nm-thick adsorbed nanolayer.

The fluorescence technique was used to determine the $T_g$ of the exposed adsorbed nanolayers as a function of $t_{ads}$. The results are presented in Figure 6.5b and are represented by blue diamonds. At $t_{ads} = 1$ h, $T_g$ was reduced by $30 \pm 4$ K compared to the bulk. Upon continued annealing up to $t_{ads} = 6$ h, $T_g$ of the adsorbed nanolayer gradually increased to $362 \pm 3$ K, a $17 \pm 3$ K reduction from bulk $T_g$. Interestingly, the magnitude of the $T_g$ deviations reported for the adsorbed nanolayers were less dramatic than those of spin-coated films. For instance, $T_g - T_g(\text{bulk}) \approx -30$ K for 1.5-nm-thick adsorbed
Figure 6.5. (A) The temperature dependence of fluorescence intensity for a 10-h irreversibly adsorbed layer; solid lines are linear fits to the high and low temperature data. Inset shows temperature dependence of its spectra. (B) Exposed adsorbed layer $T_g$ at different $t_{ads}$ as measured by fluorescence (diamonds) and as reported for capped adsorbed layers by Napolitano and Wübbenhorst\textsuperscript{12} (squares), shifted to match respective $T_g$(bulk) values. Error bars on fluorescence data correspond to ± 1 standard deviation of $T_g$ for multiple samples. The dashed line illustrates $T_g$ predicted by FVHD with fitting parameters $(A_{free}/A_{total})_{max} = 0.55$ and $a = 0.0083$ h$^{-1}$. 
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nanolayers and 15-nm-thick spin-cast films.\textsuperscript{36} Hence, the adsorbed nanolayers had a greater $T_g$ in comparison to spin cast films of comparable thickness. This difference is even more noteworthy when one considers that the 1.5-nm-thick adsorbed layer was not homogenous but textured, and hence, exposed to additional free surfaces which are considered to be a key requirement to observe a $T_g$ reduction in confined polymer systems.\textsuperscript{46} This elevation of $T_g$ in the adsorbed nanolayers was likely due to the immobilization of the chains at the substrate from irreversible adsorption, which is reminiscent of how the rigid amorphous fraction in semi-crystalline polymers possesses a higher $T_g$ due to chain immobilization.\textsuperscript{47,48}

Further annealing films beyond 6 h resulted in no change in adsorbed layer $T_g$, within error. The $T_g$ and thickness of the irreversibly adsorbed layer show strikingly similar development, with 6 h also being the approximate time at which $h_{ads}$ ceased to increase. To demonstrate this connection, Figure 6.6 plots adsorbed layer $T_g$ against $h_{ads}$. A positive correlation between the two parameters was observed, consistent with correlations between $T_g$ and adsorbed layer growth in capped films.\textsuperscript{12}

Also plotted in Figure 6.5b (squares) are the only previous $T_g$ measurements of irreversibly adsorbed PS nanolayers, reported by Napolitano and Wübbenhorst.\textsuperscript{12} Here, PS ($M = 97$ kg/mol) adsorbed layers were sandwiched between two aluminum substrates with no free surface present. The initial reduction in adsorbed layer $T_g$ was attributed to additional free volume resulting from packing frustration during low-density chain adsorption, and the increase in $T_g$ of the adsorbed layers upon annealing was ascribed to the gradual densification of chains at the substrate. $T_g$ of these capped irreversibly adsorbed nanolayers completely recovered (and exceeded) bulk $T_g$. In our system,
Figure 6.6. Exposed adsorbed layer $T_g$ (as measured by fluorescence) plotted against adsorbed layer thickness (as measured by ellipsometry). The dotted line serves as a guide to the eye. Error bars represent ±1 standard deviation in thickness and $T_g$ measurements for multiple films.
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$T_g$(bulk) was never recovered—a striking difference in behavior that highlights the key role of the free surface in modifying adsorbed nanolayer $T_g$.

This large influence of the free surface on confined $T_g$ is consistent with a multitude of studies reporting negative $T_g$ deviations in the presence of a free surface. However, similar adsorbed layer growth as reported previously suggested that free volume also contributed to adsorbed layer $T_g$ in the presence of a free surface. These comparisons with supported films and capped adsorbed layers suggested that the $T_g$ behavior observed in the exposed PS adsorbed layer was due to competition between the influences of chain adsorption and free volume at the substrate and enhanced mobility at the free interface.

6.5 $T_g$ of Buried Adsorbed Nanolayers

A better understanding of the origins of $T_g$ depression in the exposed adsorbed layer was gained by removing any competing free surface effects and studying buried layer dynamics. Fabrication of bilayer films, in which only the adsorbed nanolayer was labeled with the fluorescent dye molecule capable of reporting $T_g$, enabled in-situ analysis of the adsorbed layer. Figure 6.7 compares the $T_g$ of the adsorbed nanolayer in the exposed and buried-layer geometries as a function of $t_{ads}$, where again $t_{ads}$ represents the annealing time directly after spin casting used to grow the adsorbed nanolayer. The insets in Figure 6.7 illustrate these two different geometries: the exposed nanolayer and the bilayer film consisting of the labeled adsorbed nanolayer and neat PS overlayer. Placement of the overlayer film atop the adsorbed nanolayer resulted in the effective removal of the free surface, and therefore, the bilayer geometry could be considered as an effective model for in-situ analysis of the adsorbed nanolayer $T_g$.  

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Figure 6.7. Irreversibly adsorbed layer $T_g$ with and without a free surface as a function of $t_{ads}$. Error bars represent ± 1 standard deviation of $T_g$ for multiple samples. Insets illustrate exposed and buried adsorbed layer geometries. Lines show $T_g$ predicted by FVHD for exposed and submerged adsorbed layers. Predictions for submerged adsorbed layers shown are with fitting parameter $(A_{free}/A_{total})_{min} = 0.05$ and $h_{ads}$ as measured (dash dot) and set at 5.4 nm (solid) to account for swelling.
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At shorter $t_{ads}$, there was a dramatic difference in $T_g$ of the exposed and buried nanolayers. Removal of the free surface at $t_{ads} = 1$ h resulted in a near complete recovery of bulk $T_g$ within the adsorbed nanolayers. This recovery was likely due to relatively loose binding of the adsorbed nanolayer formed at short $t_{ads}$ that could be effectively infiltrated with the overlayer film. By contrast, covering the adsorbed nanolayer formed at $t_{ads} > 6$ h had a minor effect on its $T_g$. The fact that $T_g$ of the adsorbed nanolayer was unchanged with and without the overlayer film suggested a gradual decrease in the influence of the free surface on the buried nanolayer $T_g$ with increasing degree of adsorption. While placement of the PS-116 overlayer atop these adsorbed nanolayers resulted in the removal of the free surface, we argue that free volume present due to chain packing frustration could not effectively escape the nanolayer. This was in part because nanolayers formed at long annealing times were tightly bound to the substrate, thus preventing inter-diffusion of chains and interchange of dynamics between the two layers.

Since prior work suggested an increase in adsorption density and decrease in free volume within adsorbed layers at longer adsorption times,$^{22,41,49}$ it is reasonable to deduce that strong chain adsorption likely reduces the influence of the free surface on nanolayer $T_g$. Hence, excess free volume resulting from chain packing frustration within the adsorbed layer exerts a stronger influence on nanolayer $T_g$ than the free surface in the long-anneal regime. This will be expanded upon in Section 6.7.

6.6 $T_g$ as a Function of Annealing Time of Bilayer Films

In order to promote chain interpenetration and the recovery of bulk dynamics, consolidated bilayer films were systematically annealed at 423 K under $10^{-2}$ torr vacuum. $T_g$ of the buried adsorbed layer was then measured as a function of bilayer annealing time.
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Figure 6.8 plots the $T_g$ of the submerged adsorbed layer as a function of $t_{Bann}$. The adsorbed nanolayer incorporated into each bilayer film in panels A, B, and C, was originally prepared by $t_{ads}=4, 6, \text{ and } 10$ h of respective annealing. Annealing each bilayer system at 423 K resulted in an increase in adsorbed layer $T_g$ as a function of $t_{Bann}$ and eventual recovery of bulk $T_g$. Strikingly, the critical bilayer annealing time required for the attainment of bulk $T_g$ ($t_{Bann}^*$), was dependent on $t_{ads}$ (i.e., the original annealing time used to grow the adsorbed nanolayer). To obtain $t_{Bann}^*$, each curve in Figure 6.8a-c was fit to an exponential function of the form:

$$T_g = A \cdot e^{-\frac{t_{Bann}}{\tau}} + T_g(\text{bulk})$$  \hspace{1cm} (6.2)

where the fitted prefactor $A$ ($< 0$) represents the initial deviation from $T_g(\text{bulk})$ after consolidating the bilayer and $\tau$ represents an intrinsic timescale of the $T_g$ recovery process. Fitted values of $A$ were all within error of $t_{Bann} = 0$ measurement. The intersection of these fits with $T_g(\text{bulk}) - 1$ K (to account for error in $T_g(\text{bulk})$ and avoid effect of asymptotes) was then used to determine the recovery time, $t_{Bann}^*$. Figure 6.8d, plots $t_{Bann}^*$ as a function $t_{ads}$, confirming that $t_{Bann}^*$ was strongly influenced by $t_{ads}$ with the 4-h adsorbed layer requiring the least amount of bilayer annealing to recover bulk $T_g$.

It can also be deduced that total annealing time ($t_{ads} + t_{Bann}$) did not determine recovery of bulk $T_g$, but rather the conformation and degree of adsorption within the adsorbed layer prior to its incorporation into a bilayer film.

The timescale for bulk $T_g$ recovery, $t_{Bann}^*$ should not be interpreted as the time for complete interpenetration of the upper layer within the adsorbed nanolayer. The apparent diffusion coefficients, based on the use of $t_{Bann}^*$, were of order $10^{-10}$ cm$^2$/s, as predicted
Figure 6.8. Recovery of bulk $T_g$ in (A) 4-h, (B) 6-h, and (C) 10-h irreversibly adsorbed layers when annealed in the bilayer geometry, as measured by fluorescence. Error bars represent ± 1 standard deviation of $T_g$ for multiple samples. (D) Bulk $T_g$ recovery time as a function of $t_{ads}$. Errors are propagated from exponential fit parameters. Solid lines in panels A - C show $T_g$ predicted by FVHD.
by the scaling argument:

\[ D \sim \frac{h_{ads}^2}{t_{Bann}^*} \] (6.3)

These estimated apparent diffusion coefficients were much higher values than would be expected for polymers of similar molecular weight. The difference in timescales suggests that chain interdiffusion was not entirely responsible for the recovery of bulk \( T_g \). Previous studies have shown that interfacial influences on \( T_g \) penetrate length scales greater than chain interpenetration, but the apparent dependence of these interfacial influences on degree of chain adsorption warrants further explanation.

Two sets of experiments were performed in order to verify that these bilayer annealing experiments did not result in any adsorption of the bulk overlayer, desorption of the irreversibly adsorbed underlayer, or chain exchange between the two layers. To confirm that additional adsorption of the \( PPS-155 \) adsorbed layer or neat \( PS-116 \) overlayer was not responsible for observed bulk \( T_g \) recovery, bilayer films were soaked in toluene for 8 h to thoroughly remove unadsorbed chains before remeasuring \( T_g \). As seen in Figure 6.9a and 6.9b, no significant change in \( T_g \) of the adsorbed layers, within error, took place prior to bulk \( T_g \) recovery for the 4 and 6-h bilayer systems, indicating an absence of additional adsorption. In films annealed longer than \( t_{Bann}^* \), increased scatter led to uncertainty in the accuracy of \( T_g \) measurements and prevented confident reports of \( T_g \). However, the increase in \( T_g \) toward \( T_g(\text{bulk}) \) commenced much sooner than \( t_{Bann}^* \). The relative availability of interface at lower adsorption times would make additional adsorption or desorption more likely at lower \( t_{ads} \), in the 4 and 6-h systems.

In order to investigate if chain exchange (desorption of a labeled chain paired with adsorption of a neat chain) occurred during bilayer annealing, the fluorescence
content of the rinsing and soaking solutions were analyzed to detect desorption of lPS-155. Desorption would be indicated by a fluorescence response of the toluene soaking solutions resulting from desorbed lPS-155. Again, more desorption would be expected in loosely bound adsorbed layers characteristic of low $t_{ads}$. A 2-h bilayer system, which recovered bulk $T_g$ almost immediately, was therefore examined. Figure 6.9c shows overlays of the spectra of toluene soaking solutions before and after soaking the bilayer films for 8 h to remove the bulk overlayer. Minimal change in the fluorescence response is detected, with no trends present. One would expect a higher fluorescence response to correlate with longer $t_{Bann}$ in the presence of chain exchange. Minimal fluorescence response and lack of trends combined to indicate a lack of chain exchange or lPS-155 desorption.

### 6.7 Interpretation by Free Volume Holes Diffusion Model

Deviations in $T_g$ of irreversibly adsorbed layers from bulk have been attributed to the presence of excess free volume and its gradual displacement at longer $t_{ads}$ due to an increased degree of chain adsorption at the substrate. The amount of free volume at the substrate interface has been quantified in capped adsorbed layers using the Free Volume Holes Diffusion (FVHD) Model, which defines a relationship between the diffusion of free volume out of a film and the $T_g$.\textsuperscript{49,53} Equation 2.7 was adapted to our system and gave:

$$\left(\frac{h_{eff}}{2}\right)^2 = 2D(T_g)q^{-1}$$  \hspace{1cm} (6.4)

where, $h_{eff}$ is an effective length scale of the adsorbed layers, $D(T_g)$ is the diffusion coefficient of free volume holes at adsorbed layer $T_g$, and $q$ is the experimental cooling
Figure 6.9. Minimal evidence of additional chain adsorption and exchange is observed during bilayer annealing. Change in irreversibly adsorbed layer $T_g$ after conducting bilayer annealing experiments and rewashing to remove the bulk overlayers (post-wash $T_g$) from initial exposed irreversibly adsorbed layer $T_g$ (original $T_g$) for (A) 4-h and (B) 6-h irreversibly adsorbed layers as a function of bilayer annealing time ($t_{Bann}$). Shaded areas indicate when $T_g$(bulk) is recovered for each system ($t_{Bann}^*$), reported as the lower error limit in Figure 6.8d. Error bars represent ± 1 standard deviation of $T_g$ from multiple samples with the same annealing conditions. (C) Fluorescence spectra for the toluene soaking solutions used to remove neat PS-116 overlayers as a function of bilayer annealing time for a 2-h irreversibly adsorbed bilayer system. The spectrum for a toluene blank is shown in red.
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rate. It is important to note that this effective length scale was not equal to $h_{ads}$, although it was related. Rather, $h_{eff}$ reflected the thickness of the adsorbed layer as well as the relative free interface, described below. Comparing adsorbed layer $T_g$ at long adsorption times ($t_{ads} > 6 \text{ h}$) to the diffusion coefficient of free volume holes in a bulk PS matrix$^{49,53}$ revealed $D(T_g)_{ads} = D(T_g)_{bulk}/343$: a two order-of-magnitude difference, consistent with the literature.$^{54}$ Details on FVHD calculations are outlined in Appendix C. The model allowed for the prediction of how $T_g$ changed with $t_{ads}$, employing the relationship between the diffusion of free volume holes within adsorbed layers and the amount of “free interface” (free volume present at the free surface and substrate interface), $A_{free}$, available as a sink for said holes. Incorporating a linear decrease in the fractional free interface with adsorption time, as consistent with previous studies,$^{41}$ its progression was described using the equation:

$$\frac{A_{free}}{A_{total}} = \left(\frac{A_{free}}{A_{total}}\right)_{max} - a \cdot t_{ann} \quad (6.5)$$

where $A_{free}/A_{total}$ is the fractional free interface, $a \approx 0.01 \text{ h}^{-1}$ is the rate of free interface filling, and $(A_{free}/A_{total})_{max}$ is the maximum amount of free interface—achieved at $t_{ads} = 0$. Equations 6.4 and 6.5 were then evaluated using measured $h_{ads}$ and optimizing fitting parameters to obtain $T_g$ values. Figure 6.5b shows $T_g$ predicted by FVHD overlaying experimental $T_g$. Close agreement of the data suggested that the reduced ability of free volume to diffuse to sinks at the substrate and free surface with $t_{ads}$ was a plausible explanation for measured trends. It is worth remarking that applying the FVHD Model required adjusting the parameter $(A_{free}/A_{total})_{max}$ to give $(A_{free}/A_{total})_{max} = 0.55$ for exposed adsorbed layers. Given the boundary condition $(A_{free}/A_{total}) = 0.5$ (assuming all free interface was at the free surface) at long adsorption time, it follows that at $t_{ads} = 0$, the
substrate interface provided a source of free volume that was about one tenth as strong as that being provided by the free surface. This result was in the same order as that found in Ref. 49, where the FVHD was applied to \( T_g \) depression data of Alumina-capped PS films.

Following similar logic, the FVHD model was used to describe both removing the free surface (Figure 6.7) and bilayer annealing experiments (Figure 6.8). Figure 6.8 shows that the FVHD model was not consistent with measured \( T_g \) of submerged adsorbed layers when using \( h_{\text{eff}} \) derived from measured values of \( h_{\text{ads}} \), likely due to swelling of the submerged adsorbed layers resulting from some interpenetration of the two layers. In order to account for this swelling, \( h_{\text{ads}} \) was fixed at the average plateau thickness (\( h_p = 5.4 \) nm), thereby approximately representing a decrease in the amount of swelling to zero at \( t_{\text{ads}} = 6 \) h, when no interpenetration was expected. This modification, also pictured in Figure 6.7, resulted in much better agreement between the model and experimental \( T_g \).

The FVHD fits to Figure 6.8 reflected the recovery of bulk \( T_g \) with bilayer annealing. Curves in the fits approaching \( t_{\text{Bann}}^* \) resulted from the combination of VFT and Arrhenius components to \( D(T) \) in the model.\(^{48} \) At \( t_{\text{Bann}}^* \) the fit was truncated due to diverging \( h_{\text{eff}} \) when \( (A_{\text{free}}/A_{\text{total}}) \) approached zero (see Appendix C). Despite qualitative agreement between FVHHD predictions and experimental data, differences in the recovery of \( T_g(\text{bulk}) \) indicated additional levels of complexity in the system. For one, the FVHD model assumes that \( D_{\text{ads}}(T_g) \) was consistent for all degrees of chain adsorption and is independent of the molecular weight of the polymer matrix. Additionally, in the \( T_g(\text{bulk}) \) recovery experiments it is likely that some degree of chain interdiffusion, suggested by the swelling of the submerged adsorbed layer predicted by FVHD (Figure 6.7), also contributed to the rate of recovery.
6.8 Conclusions

This chapter examined the glassy dynamics of the buried irreversibly adsorbed nanolayer within PS thin films by selectively labeling adsorbed layers at different stages of development within bilayer films and employing fluorescence to measure their $T_g$. This approach enabled the first investigation of the influence of a free surface on adsorbed layer $T_g$. Measurements of $T_g$ as a function of annealing time revealed a competition of interfaces and how the free surface largely influences adsorbed layer $T_g$ at short $t_{ads}$, but its influence was diminished with increased degree of adsorption at longer $t_{ads}$. Further examination of bulk $T_g$ recovery through bilayer annealing experiments indicated that an increased degree of chain adsorption extended the time for bulk $T_g$ recovery. This investigation of the influence of interfaces and free volume diffusion on irreversibly adsorbed layer $T_g$ serves as a foundation to further the understanding of the interplay between processing, structure, and dynamics in polymers confined to the nanoscale.
6.9 References


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Chapter 7

Polymer-Substrate Interactions in the Irreversible Adsorption of Random Copolymers

7.1 Introduction

As described previously, interfacial influences dictate the magnitude, direction, and onset of observed deviations from bulk behavior with film thickness, and they vary depending on polymer composition$^{1-3}$ and interaction strength with supporting substrates.$^{4,5}$ Polystyrene (PS), which weakly interacts with a silicon substrate, exhibits large negative deviations from its bulk $T_g$ in films with thickness below 40 nm$^{6,7}$ due to enhanced mobility at the free surface.$^{8,9}$ Alternatively, silicon substrates have hydrogen-bonding interactions with poly(methyl methacrylate) (PMMA) films that create positive deviations in film $T_g$ with reduced thickness, below a critical value.$^5$ However, eliminating the potential for hydrogen bonding, by removing or coating the substrate, allows the free surface effect to dominate, resulting in negative deviations in $T_g$ for PMMA.$^{4,10}$

Random copolymers exhibit thickness-dependent $T_g$ intermediate to their respective homopolymers,$^{3,11}$ which allows for the control of thin film $T_g$ by tuning composition. Park et al. observed random copolymer confinement behavior reflective of composition by ellipsometry.$^{11}$ Poly(styrene-random-methylmethacrylate) (P(S-r-MMA)) with a majority S component showed negative deviations from bulk $T_g$, and the magnitude of these deviations decreased with higher MMA content. They described these deviations with a parallel-type additive interaction parameter, in which the polymer
component with lower substrate interaction strength (styrene) dominated confinement behavior. They found this relation held for P2VP-co-PS as well. Mundra et al. also measured a composition-dependent confinement effect in P(S-r-MMA) by intrinsic fluorescence, showing a more evenly-balanced influence from component polymers.\(^3\)

Chapters 4 and 6 described how, in addition to its role in erasing thermal history, annealing above \(T_g\) can result in the growth of an irreversibly adsorbed nanolayer,\(^{12–18}\) which has been closely associated with deviations from bulk behavior in thin films.\(^{16,19–22}\) In Chapter 6, we used a fluorescence bilayer technique to selectively measure \(T_g\) of exposed and buried PS adsorbed layers.\(^{19}\) These geometries enabled isolation of the impact of the free surface on adsorbed layer \(T_g\) and revealed that it was suppressed at later stages of growth due to stronger chain adsorption at the substrate dominating over free surface effects. Perez-de-Eulate et al. further demonstrated the ability of irreversible adsorption to largely erase a dramatic free surface effect\(^2\) through the recovery of bulk \(T_g\) in poly(tert-butylstyrene) (PtBS) thin films with extended annealing.\(^{20}\)

Understanding the mechanism and kinetics of adsorbed layer growth gives insight into how annealing can impact confined polymer properties. Adsorbed nanolayers have been experimentally characterized in terms of thickness,\(^{16,19,23}\) density,\(^{17,18}\) surface topography,\(^{17,19}\) and \(T_g.\)\(^{16,19,24}\) These measurements enabled elucidation of their equilibrium thickness,\(^{19,25–27}\) architecture,\(^{17,18}\) and growth mechanism.\(^{17,23,27,28}\) With increased annealing time, adsorbed layers gradually thicken toward a quasi-equilibrium, or plateau, thickness.\(^{25}\) Experiments and simulations on homopolymer systems have shown that this thickness \((h_p)\) scales with chain length and following random walk statistics,\(^{25,26}\) with the scaling factor depending on polymer-substrate interactions.\(^{25,27}\)
As described in Chapter 4, chains adsorb in a combination of trains, loops, and tails. Koga and coworkers focused on the characterization of adsorbed chain conformations resulting from different stages of growth and identified two distinct sublayers: a tightly-bound, dense “flattened layer” and a “loosely-bound layer”. Jiang et al. studied the growth of flattened layers further, observing an increase in $h_p$ with increasing polymer-substrate interaction strength.

The growth of adsorbed layers from the melt state is commonly believed to follow two kinetic regimes: fast growth at short times, corresponding to chains pinning to a largely uncovered substrate, and slow surface-coverage limited growth at long times, as chains adsorb through initially attached chains and rearrange. Jiang et al. further described the fast growth regime at early stages of adsorption as a race between zipping down of tightly-bound chains and diffusion-limited adsorption of loosely bound chains. This two-stage mechanism is consistent with the bimodal growth reported for chains adsorbing from solution. Housmans et al. found both these stages to be dependent on annealing temperature ($T_{ann}$) and polymer molecular weight.

Simavilla et al. later proposed that $T_{ann}$ impacts the growth of homopolymer adsorbed layers through two distinct contributions: thermal fluctuations of the polymer chain (influences adsorption rate) and polymer-substrate interaction strength (influences $h_p$). Changes in chain fluctuation with temperature are represented by the polymer’s thermal activation energy of segmental motion ($E_a$), which Simavilla et al. related to adsorption rate by an observed Arrhenius temperature dependence. Individual segmental interaction energy with the substrate was reported to be on the order of $\sim k_BT$, consistent with findings in adsorption from solution studies. Simavilla et al. argued that for a
given polymer, energetic contributions from molecular motion (i.e., $E_a$) were much larger than those of polymer-substrate interactions, and therefore $T_{ann}$ should have a much larger impact on kinetics than on $h_p$. They demonstrated that $h_p$ did not change significantly with $T_{ann}$ for several homopolymer systems.

Despite the well-established influence of polymer-substrate interactions and the growing appreciation for the role of irreversible adsorption in determining confined film properties, considerable investigation is still needed into how these influences are interrelated. While there has been limited work examining polymer-substrate interactions as related to homopolymer adsorption, there has been no examination of how different polymer-substrate interactions combine in the growth of random copolymer adsorbed layers. Extending the study of irreversible adsorption to polymers with heterogeneous compositions is critical in determining its generality and application to more complex systems.

In this chapter, we study model systems of PS, PMMA, and P(S-r-MMA) spanning the full range of composition. This set of polymers is advantageous fundamentally because it allows for the comparison between two different polymer-substrate interactions: Van der Waals in the case of PS and hydrogen bonding in the case of PMMA. Additionally, P(S-r-MMA) brushes are often used to modify substrates for PS-b-PMMA block copolymer films, which are of particular interest in lithography. Through the use of this polymer series, we investigate the impact of specific polymer-substrate interactions on adsorbed layer growth and how they compete in the irreversible adsorption of random copolymers. We find that, unlike with their $T_g$ confinement behavior (also strongly tied to interfacial interactions), the growth metrics of P(S-r-
MMA) adsorbed layers are not intermediate to those of PS and PMMA. Rather, \( h_p \) is dictated by the degree of compositional heterogeneity and adsorption kinetics are heavily biased towards those of PMMA. We then utilize selective desorption to quantify polymer-substrate interactions in P(S-\( r \)-MMA). These interactions correlate well with composition, suggesting non-preferential adsorption of individual segments. These results form the foundation of our proposed copolymer adsorption mechanism, in which differences in adsorption density and polymer-substrate attraction combine to create a barrier to growth with increasing compositional heterogeneity. We finally present our attempts to use P(S-\( r \)-MMA) adsorbed layers to create neutral substrates for PS-\( b \)-PMMA thin films.

### 7.2 Experimental Methods

#### 7.2.1 Synthesis and Characterization of P(S-\( r \)-MMA)

Polymers used in this study were synthesized via free radical polymerization of styrene (S) and methyl methacrylate (MMA), both purchased from Sigma-Aldrich. Inhibitors were removed by running these monomers through a column packed with aluminum oxide prior to their use. Relative feed ratios of S and MMA were selected for desired copolymer composition, using reactivity ratios of 0.49 for both S and MMA.\(^{35}\) Reactions were conducted without additional solvent at 348 K under nitrogen with precise concentrations of benzoyl peroxide (Sigma-Aldrich) initiator to control molecular weight. Copolymer chain compositional uniformity was maintained by restricting the reactions to <15% conversion to avoid drift, and it was confirmed by comparing the composition of polymers synthesized with different reaction times. Synthesized polymers
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were dissolved in toluene (Fisher Chemical) and precipitated in methanol (Fisher Chemical) three to four times to remove unreacted monomer, as confirmed by $^1$H-NMR.

Table 7.1 summarizes the characterization data obtained for polymers in this study. Copolymers are referred to by their molar composition (X:Y) where X is the mol % S and Y is the mol % MMA. Composition was determined from $^1$H-NMR spectra by comparing integrated areas of the aromatic (6-8 ppm) and aliphatic (0-4 ppm) portions of the spectrum, shown in Figure 7.1, in a system of equations:

\begin{align}
5x_S &= kA_{Ar} \quad (7.1a) \\
3x_S + 6x_{MMA} &= kA_{Al} \quad (7.1b) \\
x_S + x_{MMA} &= 1 \quad (7.1c)
\end{align}

where $x_S$ and $x_{MMA}$ are the molar fractions of styrene and methyl methacrylate in the polymer, respectively, $A_{Ar}$ and $A_{Al}$ are the integrated areas of the aromatic and aliphatic regions, and $k$ is a multiplication factor to account for the absolute intensity.

Molecular weight was measured via Size Exclusion Chromatography in tetrahydrofuran (THF) against PS standards. Weight average molecular weight ($M_W$) was determined for each polymer from light scattering data analyzed using composition-weighted $dn/dc$ values; homopolymer values were 0.0818 mL/g for PMMA-119$^{37}$ and 0.189 mL/g for PS-109.$^{38}$ Dispersity, $D$, was determined from differential refractive index data and used to calculate $M_N$. The $M_W$ of all polymers were within 10 % of 108 kg/mol in order to reduce the effect of molecular weight on our results. $T_g$ was determined by Differential Scanning Calorimetry (DSC) on a TA Instruments Q2000 DSC, measured as the onset of $T_g$ upon second heating at 10 K/min after cooling at 2.5 K/min. $R_g$ for PS-109 and PMMA-119 were determined from empirical relations.$^{19,39,40}$
Figure 7.1. $^1$H-NMR spectra of the polymers described in Table 7.1, arranged from the top down in order of increasing styrene content. Integrated intensities of the aromatic and aliphatic regions were used to calculate their compositions. The spectra were normalized by their residual solvent peak at 7.26 ppm for CDCl$_3$. 


### Table 7.1. Specifications for synthesized PS, PMMA, and P(S-r-MMA).

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Mole Fraction MMA, $x_{\text{MMA}}$</th>
<th>$w_{\text{MMA}}$</th>
<th>$M_w$ (kg/mol)</th>
<th>$D$</th>
<th>$T_g$ (K)</th>
<th>$R_g$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-119</td>
<td>1</td>
<td>1</td>
<td>119</td>
<td>2.2</td>
<td>393</td>
<td>9.2</td>
</tr>
<tr>
<td>P(S-r-MMA) (27:73)</td>
<td>0.73</td>
<td>0.72</td>
<td>105</td>
<td>2.0</td>
<td>385</td>
<td></td>
</tr>
<tr>
<td>P(S-r-MMA) (48:52)</td>
<td>0.52</td>
<td>0.51</td>
<td>109</td>
<td>2.0</td>
<td>377</td>
<td></td>
</tr>
<tr>
<td>P(S-r-MMA) (75:25)</td>
<td>0.25</td>
<td>0.24</td>
<td>99</td>
<td>1.7</td>
<td>376</td>
<td></td>
</tr>
<tr>
<td>PS-109</td>
<td>0</td>
<td>0</td>
<td>109</td>
<td>1.8</td>
<td>378</td>
<td>9.2</td>
</tr>
</tbody>
</table>

### 7.2.2 Adsorbed Layer Preparation and Measurement

Polymer films 200 ± 20 nm thick were spin-coated from dilute toluene solution onto piranha-treated silicon (wafers were immersed in 70:30 H$_2$SO$_4$:H$_2$O$_2$ for ~30 minutes and rinsed with deionized H$_2$O). Films were then annealed at a given temperature ($T_{\text{ann}}$) under 10$^{-2}$ torr vacuum for set lengths of time ($t_{\text{ads}}$) to promote the growth of adsorbed layers. When annealing films relative to their bulk $T_g$, $T_{\text{ann}}$ was: 423 K for PS-109, P(S-r-MMA) (75:25), and P(S-r-MMA) (48:52); 430 K for P(S-r-MMA) (27:73); and 438 K for PMMA-119. Those temperatures will be referred to as $T_g + 45$ K throughout the remainder of the text. Adsorbed layers were then isolated through a series of three rinsing and 10-minute soaking steps in a good solvent (toluene, unless specified otherwise in Section 7.7). Fresh solvent was used for each step. These isolated adsorbed layers were then dried overnight at room temperature under vacuum to remove any residual solvent before characterization.

All adsorbed layer characterization was conducted at room temperature. Adsorbed layer thickness was determined using ellipsometry, as described in Section 5.4.1. Each sample was measured at a 65° angle at 3 different locations near the center of the film, each 0.3 cm apart and fit to a Cauchy model. The ability of this model to accurately report adsorbed layer thickness was verified by comparisons with AFM measurements.
Figure 7.2. Comparison of adsorbed layer thickness, $h_{\text{ads}}$, for different polymers measured via AFM and ellipsometry. y-error bars and x-error bars at thicknesses >3 nm correspond to the standard deviation of 3 thickness measurements at different locations on the same sample. x-error bars below 3 nm in thickness correspond to the standard deviation calculated from the full-width-half-maximum of the height distribution curve of dewetted AFM images, assuming a Gaussian distribution.
shown in Figure 7.2. We note that, as with /PS-155 in Chapter 6, adsorbed layers thinner than approximately 3 nm dewetted prior to measurement. However, the thickness measured by ellipsometry averaged over the film, and we believe essentially reports the thickness of the film prior to dewetting. Good agreement with AFM measurements, with thickness determined as the peak in the height distribution, confirmed this assumption.

7.2.3 Calculating Solubility Parameters

Hildebrand and Hansen solubility parameters for P(S-r-MMA) were determined from volume-fraction weighted averages of PS and PMMA parameters. Volume fractions of S and MMA were calculated by the following equation:

$$\varphi_1 = \frac{x_1 \bar{V}_1}{x_1 \bar{V}_1 + (1-x_1) \bar{V}_2}$$

(7.2)

where $\varphi_1$ and $x_1$ are the volume and molar fractions of component 1, respectively, and $\bar{V}_1$ and $\bar{V}_2$ are the molar volumes of each component. Molar volumes for PS and PMMA were derived from a group contribution method, in which der Waals volumes ($V_w$, assigned from group contributions) were related to $\bar{V}$ using an empirical relationship: $\bar{V}/V_w = 1.60 \pm 0.045$. Calculated molar volumes, volume fractions, and solubility parameters for polymers, combined with those used for solvents, are listed in Table 7.2. Hansen Solubility parameters were taken from Ref. Hildebrand solubility parameters for solvents were taken from Ref. and for polymers from Ref.

The root-mean-squared difference between solubility parameters was used to compare solubility between polymers and solvents. Hansen solubility parameters (HSP) use a 3D lattice to determine solubility from three contributions. Relative solubility is given by the Hansen diameter, $R_a$, which was calculated for each polymer-solvent pair from the established relation.
\[ R_a^2 = 4(\delta_{D,1} - \delta_{D,2})^2 + (\delta_{P,1} - \delta_{P,2})^2 + (\delta_{H,1} - \delta_{H,2})^2 \]  

(7.3)

where \( \delta_D \), \( \delta_P \), and \( \delta_H \) are the dispersive, polar, and hydrogen bonding contributions of the HSP, respectively, and numbered subscripts designate the two components.

Table 7.2. Solubility parameters of polymers and solvents.

<table>
<thead>
<tr>
<th>Solubility Parameters (MPa(^{1/2}))</th>
<th>Hildebrand</th>
<th>Hansen</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>( V_w )</td>
<td>( V_g )</td>
</tr>
<tr>
<td>PS</td>
<td>62.83</td>
<td>99.0</td>
</tr>
<tr>
<td>P(S-r-MMA) (75:25)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(S-r-MMA) (48:52)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>P(S-r-MMA) (27:73)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>PMMA</td>
<td>56.93</td>
<td>86.5</td>
</tr>
<tr>
<td>Toluene</td>
<td>18.2</td>
<td></td>
</tr>
<tr>
<td>THF</td>
<td>18.6</td>
<td></td>
</tr>
<tr>
<td>Chloroform</td>
<td>19</td>
<td></td>
</tr>
</tbody>
</table>

7.3 Bulk and Confined \( T_g \) of P(S-r-MMA)

The copolymers synthesized for this investigation exhibited an asymmetric trend in bulk \( T_g \) with composition, as shown by the orange circles in Figure 7.3. P(S-r-MMA) exhibited \( T_g \) within 2 K of PS until its MMA weight fraction, \( w_{\text{MMA}} \), increased above \( ~0.5 \). The \( T_g \) of copolymers with \( w_{\text{MMA}} > 0.5 \) increased rapidly and approximately linearly with \( w_{\text{MMA}} \) until reaching that of PMMA. This data set was supplemented by additional P(S-r-MMA) samples, synthesized via the same method with different monomer feed ratios, to clarify the trend with composition. P(S-r-MMA) is a known exception to the Fox equation,\(^{46}\) shown by the orange line in Figure 7.3, exhibiting a clear negative deviation. Other consistent data sets, taken from the literature, are shown by the green triangles\(^{11}\) and purple squares.\(^{47}\) This large deviation from the Fox equation has been
studied in greater detail elsewhere and was attributed to contributions from dyad and triad sequences along the copolymer chains. These sequences are particularly important in PMMA homopolymers, as tacticity has been shown to have a large impact on its bulk $T_g$ and confinement behavior. Despite the influence of these chain sequences on the $T_g$ of bulk P(S-r-MMA), they do not impact the $T_g$ of P(S-r-MMA) thin films, which reported $T_g$ deviations proportional to their composition. Dominated by interfacial influences rather than chain sequences, P(S-r-MMA) confined $T_g$ was attributed to the balance between S and MMA contributions to specific interactions at the substrate (Van der Waals for S and hydrogen-bonding from MMA) and free surface effects. 

Irreversible adsorption is also an interface-driven phenomena and thus should not be strongly impacted by the chain sequences that dictate bulk $T_g$. Changes in $T_g$ of PS and PtBS homopolymer films with annealing have been strongly correlated with the growth of adsorbed layers, but this has not been extended to systems with competing substrate interactions. Examining the irreversible adsorption of P(S-r-MMA) presents the opportunity to compare the impact of polymer-substrate interactions on adsorption and confined $T_g$ as well as infer how annealing could impact confinement behavior in copolymer thin films.

### 7.4 Composition Effects on Adsorbed Layer Plateau Thickness

As described previously, irreversible adsorption has been shown to progress with annealing time, and PS, P(S-r-MMA), and PMMA adsorbed layers followed the standard growth pattern. Figure 7.4 plots adsorbed layer thickness for each polymer as a function of $t_{ads}$ (i.e., the time annealed at $T_g + 45$ K prior to isolation by solvent leaching). The considerably thinner adsorbed layers made by the copolymers, reaching a minimum in
Figure 7.3. Glass transition temperatures of a series of P(S-r-MMA) polymers deviate from the Fox equation\textsuperscript{46} and show an asymmetric trend with composition. Polymers synthesized via free radical polymerization are shown in orange circles. Closed circles represent polymers used in this study; open circles are from additional polymers synthesized by the same method as described above, included to show a more complete composition trend. Literature values from Park \textit{et al.}\textsuperscript{11} (green triangles) and Zhang and Blum\textsuperscript{47} (purple squares) are included and also display an asymmetric trend.
P(S-\textit{r}-MMA) (48:52), were immediately evident and were quantified by \( h_p \). The differences in \( h_p \) between these polymers, despite similar \( M_W \), indicate a composition-driven effect. However, the decrease of \( h_p \) with increasing heterogeneity, indicated by the non-monotonic trend with composition shown in Figure 7.5a, provides an interesting contrast to the composition-dependent behavior of confined \( T_g \).\(^{3,11}\) This difference in behavior suggests that the close association of adsorption with \( T_g \) in homopolymers\(^{16,19,20}\) does not hold for copolymers and that copolymer \( h_p \) is impacted by additional factors that disrupt its direct increase with polymer-substrate interactions (\textit{i.e.} MMA content).\(^{27}\) To better evaluate and understand the composition-dependent adsorption behavior indicated by \( h_p \), we first compare the homopolymer extremes.

It is important to note that P(S-\textit{r}-MMA) (27:73) and PMMA-119 were annealed at higher absolute temperature to maintain the constant difference between \( T_{\text{ann}} \) and bulk \( T_g \). Johnson \textit{et al.} reported a temperature dependence of segmental interactions, stronger with MMA than PS,\(^{30}\) which might imply that this higher \( T_{\text{ann}} \) was solely responsible for the non-monotonic trend in \( h_p \). However, as indicated by the stars in Figure 7.5a, annealing P(S-\textit{r}-MMA) (27:73) and PMMA-119 at 423 K (the same \( T_{\text{ann}} \) as the other polymers) still showed an increase in \( h_p \) for \( x_{\text{MMA}} > 0.5 \), confirming that the non-monotonic trend was not simply due to different \( T_{\text{ann}} \).

Despite different interaction strengths with the substrate resulting from their mechanisms of interaction, PS-109 and PMMA-119 adsorbed layers have \( h_p \) values within error of each other (listed in Table 7.3). We calculated \( h_p \) as the average thickness after 15 h annealing time, and it was consistent with \( h_p \) estimated from Equation 5.9.\(^{28}\) While adsorption from the melt has been studied for both PS and PMMA, simultaneous
Figure 7.4. The growth of PS-109, P(S-r-MMA), and PMMA-119 irreversibly adsorbed layers at $T_g + 45$ K reveals a non-monotonic trend with composition. Thickness is measured by ellipsometry, and error bars represent ±1 standard deviation from the average thickness of replicate samples.
study for a direct comparison of their growth has been limited to their flattened sublayers.\textsuperscript{17} Experimentally, plateau thickness has been related to radius of gyration ($R_g$) of PS and degree of polymerization ($N$) of PMMA by the following scaling relationships:\textsuperscript{25,26}

$$h_p(PS) = \alpha R_g$$  \hfill (7.4)

$$h_p(PMMA) = \beta N^{1/2}$$  \hfill (7.5)

where $\alpha$ and $\beta$ are scaling constants. We calculated values of $\alpha$ and $\beta$ for PS-109 and PMMA-119 based on our experimental $h_p$ values and $R_g$ and $N$ derived from measured $M_W$ and $M_N$, respectively. $\alpha_{PS}$ was within error of that previously calculated for identically-synthesized PS,\textsuperscript{4,19} and $\beta_{PMMA}$ was within range of the $\beta = 0.21 \pm 0.05$ nm$^{-1}$ scaling reported by Durning \textit{et al.} for PMMA adsorbed layers.\textsuperscript{26} Not only were $\alpha_{PS}$ and $\beta_{PMMA}$, listed in Table 7.3, in line with those reported previously, but they were within error of calculated values of $\alpha_{PMMA}$ and $\beta_{PS}$, respectively. The similarities in $h_p$ and its scaling with $R_g$ and $N$ for PS-109 and PMMA-119 confirmed that chain length plays a larger role than polymer-substrate interactions in determining $h_p$ for homopolymers, consistent with theoretical arguments.\textsuperscript{26} $P(S-r\text{-MMA})$ adsorbed layers did not follow this chain-length controlled behavior. As shown in Table 7.3, their $\beta$ values were almost 50% lower than those of PS-109 and PMMA-119, indicating that the largely chemistry-independent scaling does not extend to copolymers. This discrepancy merited an examination of the homopolymers in search of behavior that was not captured by the comparison of their $h_p$ values.
Adsorbed layer architecture and chain conformation studies provided further insight into differences in PS-109 and PMMA-119 adsorbed layers, which were used to better understand copolymer behavior. Superimposing the structure of the tightly-bound flattened components reported by Jiang et al.\textsuperscript{17} onto our adsorbed layers, we inferred that the PMMA layer was likely comprised of a larger fraction of tightly adsorbed chains (i.e., a thicker flattened layer). Following this logic, PS-109 and PMMA-119 adsorbed layers reached similar $h_p$ for different reasons: PMMA-119 formed a denser adsorbed layer with more chains adsorbed, while PS-109 formed a looser adsorbed layer with increased formation of loop and tail structures. Simulations reported by Linse and Kallrot further supported this picture, with increasing polymer-substrate interaction strength yielding higher amounts of adsorbed chains and contact points per chain.\textsuperscript{51} Their bead-spring
model and Monte Carlo simulations also predicted a higher concentration of trains and a lower concentration of tails in polymer chains with higher interaction strength.

7.5 Effects of Composition on Growth Kinetics

Adsorption kinetics proved another useful metric by which to compare the impact of polymer-substrate interaction strength on irreversible adsorption of PS-109 and PMMA-119. While the secondary, slower adsorbed layer growth is generally accepted to proceed logarithmically,\textsuperscript{17,23} the initial, fast growth regime has been described to follow either a linear\textsuperscript{23,27,28} or power law\textsuperscript{17,18} function. Our data showed better agreement with linear growth at short times, following the model proposed by Housmans \textit{et al.},\textsuperscript{23,27} described by Equation 4.1. The kinetic parameters, determined by fitting Equation 4.1 to the data in Figure 7.4, are reported in Table 7.3. The linear growth rate ($v = 0.7$ nm/h) that we measured for PS-109 was 2-3 times higher than that reported by Housmans \textit{et al.} for monodisperse PS with the same $M_W$.\textsuperscript{23} We attribute this difference to dispersity effects, with longer chains in the distribution leading to faster adsorption. Although lower molecular weight chains are expected to preferentially adsorb in melt systems due to smaller entropic penalties,\textsuperscript{52,53} they would not exclude all high molecular weight chains. Regardless, the similar $M_W$ and $D$ of our polymers ensured that the derived growth rates were sufficient to compare polymer growth kinetics as a function of composition, without molecular weight effects.

Although the kinetics of PMMA adsorption from the melt have been studied less extensively, they follow a bimodal adsorption pattern from solution\textsuperscript{29} that is consistent with the two-stage mechanism proposed for melt adsorption of PS, and Equation 4.1 has been used to determine its linear growth rate.\textsuperscript{27} Adsorption rates, $v$ and $\Pi$, are plotted
Figure 7.5. (A) Plateau thickness, $h_p$, and (B) linear, $v$, and (C) logarithmic, $\Pi$, growth rates of PS-109, P(S-r-MMA), and PMMA-119 adsorbed layers created at $T_{\text{ann}} = T_g + 45$ K (open symbols) and $T_{\text{ann}} = 443$ K (closed symbols). Stars in A represent $h_p$ for P(S-r-MMA) (73:27) and PMMA-119 created at $T_{\text{ann}} = 423$ K. $h_p$ was calculated by averaging $h_{\text{ads}}(t_{\text{ads}} > 15$ h).
against composition as the open symbols in Figure 7.5b and c. The slower adsorption of PMMA-119 relative to PS-109 is consistent with both simulation and experimental results. Both Linse and Kallrot’s bead-spring model and the study of flattened layers by Jiang et al. argued that chains with stronger substrate interaction adsorb more tightly to the substrate, serving as a kinetic barrier to additional adsorption and thereby slowing growth.

As with plateau thickness, the kinetic trends observed for homopolymers could not be directly applied to copolymers, and adsorption rate did not slow with increased MMA content. However, while \( h_p \) increased symmetrically with increasing compositional homogeneity, kinetics indicated a more biased trend. Apart from \( P(S-r-MMA) \) (48:52), the other copolymers were both within error of PMMA-119’s linear growth rate, and polymers with \( x_{MMA} > 0.5 \) displayed logarithmic growth rates within error of PMMA-119. These kinetic commonalities between \( P(S-r-MMA) \) and PMMA suggest a similar growth mechanism and a shared kinetic barrier.

### 7.6 Sensitivity to Annealing Temperature

Comparison of adsorbed layer growth at multiple annealing temperatures provided a means to elucidate the relative temperature-sensitivity of \( h_p \) and kinetics, which enabled the isolation of different contributions to adsorption: relative polymer-substrate interaction strength and activation energy of segmental motion. Films were all annealed at 443 K (well above \( T_g \) of all polymers) prior to adsorbed layer isolation. Figure 7.6 illustrates the changes in the resulting adsorbed layer growth patterns, with corresponding \( h_p \) and kinetic parameters represented by the solid symbols in Figure 7.5. The change in annealing temperature (\( \Delta T_{ann} \)) varied for each polymer, depending on its
Chapter 7

$T_g$, and is indicated in the Figure 7.6 caption. It is clear that an increase in $T_{ann}$ led to an overall increase in adsorption kinetics, consistent with previous studies on PS.\textsuperscript{23} Interestingly, copolymer adsorbed layers also exhibited an increase in $h_p$, which is contrary to the results of Simavilla \textit{et al.} for homopolymers.\textsuperscript{27}

As indicated in Figure 7.5a, plateau thicknesses of PS-109 and PMMA-119 did not show large changes with $T_{ann}$, reflecting the expected behavior for weakly-temperature dependent polymer-substrate interaction strength ($\sim k_B T$).\textsuperscript{23,27} By contrast, P(S-$r$-MMA) showed significant increases in $h_p$, reaching scaling values within error of $\beta_{PS}$ and $\beta_{PMMA}$. This change in copolymer $h_p$ with $T_{ann}$ indicates a different governing mechanism for copolymer growth where small increases in segmental interaction strength with the substrate can impact $h_p$. Annealing copolymers up to 60 h at $T_g + 45$ K did not show an increase in adsorbed layer thickness to within range of their $h_p$ at 443 K, confirming that the low $h_p$ observed at 423 K was not due to slow kinetics masking a later plateau.

Increasing $T_{ann}$ resulted in an overall increase in linear growth rate, with homopolymers exhibiting the largest degree of change. While the increases in $\nu$ were approximately equal for PS-109 and PMMA-119, $\Delta T_{ann}$ was 20 K for PS-109 and only 5 K for PMMA-119. The increased temperature sensitivity of $\nu$ in PMMA was consistent with its higher $E_a$ relative to PS\textsuperscript{27,54} and corresponds to a larger increase in molecular motion with temperature, following Arrhenius kinetics.\textsuperscript{23,27} The linear growth rate of P(S-$r$-MMA) adsorbed layers increased with MMA content, despite a decreasing $\Delta T_{ann}$, indicating an increase in $E_a$ and temperature-sensitivity with MMA content. Logarithmic growth rates stayed approximately constant with $\Delta T_{ann}$ in PS-109 and S-rich copolymers,
Figure 7.6. Adsorbed layer growth after annealing films at 443 K (solid markers) reveals composition-dependent changes from those annealed at $T_g + 45$ K. Thickness plateaus for $T_g + 45$ K adsorbed layers are shown by the lines for comparison. (A) PS-109, $\Delta T_{ann} = 20$ K; (B) P(S-r-MMA) (75:25), $\Delta T_{ann} = 20$ K; (C) P(S-r-MMA) (48:52), $\Delta T_{ann} = 20$ K; (D) P(S-r-MMA) (27:73), $\Delta T_{ann} = 13$ K; (E) PMMA-119, $\Delta T_{ann} = 5$ K. PS-109, P(S-r-MMA) (75:25), and (48:52) were annealed much longer at $T_g + 45$ (open symbols) and showed no change in $h_p$. 
and they decreased in PMMA-119 and MMA-rich copolymers. We attribute this to the accelerated linear growth of MMA-rich polymers quickly filling surface sites and reducing opportunities for chain diffusion and/or rearrangement, thereby slowing $\Pi$.

7.7 Interfacial Interactions Probed by Solvent Leaching

As mentioned in Chapter 4, irreversibly adsorbed layers of PMMA created from solution can be removed given the appropriate choice of solvent.\textsuperscript{31} While the effect of leaching with different solvents on adsorption from the melt has been studied with regard to PS adsorbed layer architecture\textsuperscript{17,18} and substrate-solvent interactions,\textsuperscript{55} solvents have not been used to completely desorb these layers.

7.7.1 Impacts of Polymer-Solvent Solubility on Adsorbed Layer Thickness

In order to evaluate the role of polymer-solvent solubility on the above results, we examined the effect of washing annealed PS-109 and PMMA-119 films with tetrahydrofuran (THF). Although both toluene and THF are good solvents for PS and PMMA, polarity introduced by PMMA and THF relative to purely hydrocarbon PS and toluene require that Hansen, rather than Hildebrand, solubility parameters be used to compare these polymer-solvent pairings. HSPs take into account dispersive, polar, and hydrogen-bonding contributions to more accurately describe solubility. As described in Section 7.2.3, these contributions combine to give a Hansen Distance, $R_a$, with smaller distances indicating heightened compatibility.\textsuperscript{45} Relative compatibilities between polymers and solvents are shown in Table 7.4. Listed solvents are toluene (T), THF, and chloroform (C). Displayed values are the square of the differences between matching solubility parameters for each polymer-solvent pair. Smaller numbers indicate a larger
degree of solubility. \( p \) and \( s \) subscripts indicate polymer and solvent parameters, respectively. Lighter shading indicates a smaller difference in solubility parameters, or higher compatibility. Hildebrand parameters indicate PS is more compatible with both toluene and THF, but comparing \( R_a \) values reveals that THF is a better solvent for PMMA, and toluene is a better solvent for PS.

Table 7.4. Comparison of solubility parameters between polymers and solvents.

<table>
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<tr>
<th></th>
<th>Hildebrand</th>
<th>Hansen</th>
</tr>
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<tr>
<td></td>
<td>(( \delta_r - \delta_p ))^2</td>
<td>(( \delta_{D,s} - \delta_{D,p} ))^2</td>
</tr>
<tr>
<td></td>
<td>T</td>
<td>THF</td>
</tr>
<tr>
<td>PS</td>
<td>0.64</td>
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<tr>
<td>P(S-r-MMA) (75:25)</td>
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<td>P(S-r-MMA) (48:52)</td>
<td>0.90</td>
<td>0.30</td>
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<tr>
<td>P(S-r-MMA) (27:73)</td>
<td>1.02</td>
<td>0.37</td>
</tr>
<tr>
<td>PMMA</td>
<td>1.21</td>
<td>0.49</td>
</tr>
</tbody>
</table>

Figure 7.7a compares the growth of PS and PMMA adsorbed layers, isolated by washing with THF. PS (circles) maintained the same adsorption behavior when washed with THF as with toluene (Figure 7.4). This stability against desorption differed from the work of Unni et al., which found that strong interactions between polar solvents and silicon substrates led to the dewetting of PS adsorbed layers after only 3 min of soaking.\(^{55}\) Despite its stronger interactions with the substrate,\(^{30}\) PMMA (squares) was completely removed when washed with THF.\(^{1}\) By contrast, PMMA adsorbed layers behaved very similarly to PS when washed with toluene (Figure 7.4), revealing a substantial sensitivity to washing solvent. Their different mechanisms of adsorption and strength of interactions
with the substrate, emphasized earlier in this chapter, combined with differences in solubility imply that the desorption behavior of PS and PMMA are governed by a combination of polymer-substrate and polymer-solvent relationships. The relative stability of PS adsorbed layers confirms that the solvent is not simply displacing weaker bonds at the substrate, suggesting that PMMA desorption was either driven by increased solubility between the polymer and solvent, or interference by the hydrogen-bonding solvent in existing polymer-substrate interactions.

In order to confirm that these effects were due to competition of polymer-substrate and polymer-solvent hydrogen-bonding interactions during washing rather than chain configurations resulting from exposure of polymers to different solvents, we compared the effects of different spin-coating solvents on PS and PMMA adsorbed layers. The thicknesses of PS and PMMA adsorbed layers spin-coated from different solvents and exposed with toluene are displayed in Figure 7.7b. Adsorbed layer thicknesses were largely within error for both PS and PMMA films. While there was a decrease in adsorbed layer thickness in PMMA films when washing with chloroform and THF, it was still much less dramatic than that observed when washing films with different solvents. The absence of this effect when washing adsorbed layers further emphasized the role of annealing in the adsorption of PS. There was difficulty in obtaining spin-coated films of PS from a THF solution due to the substrate’s strong preference for THF dominating over its weak interactions with PS, resulting in a dewetted film.\textsuperscript{56} This experiment made it clear that competition between the solvent and substrate during washing is impacting desorption behavior in PMMA, much more than solvent effects on chain conformations.
Figure 7.7. (A) PMMA adsorbed layers completely desorb when isolated with THF, while the thickness of PS adsorbed layers are largely unaltered by a different washing solvent. Adsorbed layers were created by annealing films relative to $T_g$. Error bars represent ±1 standard deviation from the average thickness of replicate samples. (B) Adsorbed layers made from spin-coating films of (top) PS and (bottom) PMMA with different solvents and washing with toluene shows that washing solvent has a larger influence on adsorbed layer thickness than spin-coating solvent.
The desorption of PMMA in THF was likely due to interference of the hydrogen-bonding solvent with the hydrogen bonds between the polymer and substrate, as was shown with PMMA and ethyl acetate by Johnson and Granick.\textsuperscript{31} This hypothesis was supported by the individual contributions of the HSPs, which revealed that the lower $R_a$ between PMMA and THF was driven by similarities in the hydrogen bonding contributions ($\delta_H$). However, despite closer alignment of $\delta_{H,\text{chloroform}}$ with $\delta_{H,\text{PS}}$, PS showed negligible change in $h_{ads}$ when washed with chloroform while PMMA was completely desorbed (Figure 7.8a and e). This decoupling between desorption behavior and polymer-solvent interactions, emphasized the importance of the presence of hydrogen bonding at the substrate. Washing with chloroform confirmed that PMMA desorption resulted from both polymer-solvent and polymer-substrate interactions: it was more soluble in THF and chloroform than toluene (polymer-solvent), and it adsorbed to the substrate via hydrogen bonding\textsuperscript{31} (polymer-substrate), which was interfered with by hydrogen-bonding solvents. However, similar preferences in $R_a$ and the degree of hydrogen bonding at the substrate prevented separation of the role of these interactions in homopolymers.

Expanding our study of polymer-solvent interactions to P(S-\textit{r}-MMA) enabled the separation of these effects due to a decoupling of solubility and composition. Solubility ($R_a$) described polymer-solvent interactions while composition ($x_{\text{MMA}}$) described polymer-substrate interactions through potential for hydrogen bonding. Figure 7.8a-e shows $h_{ads}$ of all polymers when washed with toluene, THF, or chloroform after annealing for select times at $T_g + 45$ K. Interestingly, copolymers exhibited partial desorption of their
Figure 7.8. Higher MMA content resulted in a larger loss of $h_{ads}$ when films annealed at $T_g + 45$ K were washed with THF or chloroform compared to toluene. (A-E) Thicknesses of copolymer adsorbed layers washed with different solvents. (F) Change in $h_{ads}$ from toluene for a given annealing time is calculated as the difference between THF-washed thickness and toluene-washed thickness as a % of the toluene-washed thickness. $(h_{ads,THF}-h_{ads,Toluene})/h_{ads,Toluene} \times 100$ (G) Change in $h_{ads}$ when washing with chloroform; also includes data from annealing films 3 h at 443K.
adsorbed layers, as indicated by a decrease in—but not complete loss of—$h_{ads}$ when washed with THF and chloroform compared to toluene.

This change in $h_{ads}$ with washing solvent is quantified in Figures 7.8f and g as a percent change from the thickness of toluene-washed adsorbed layers. Both THF and chloroform cause increased desorption (indicated by a large decrease in relative $h_{ads}$) with increasing MMA content. Also plotted in Figures 7.8f and g are normalized $R_a$ (dotted line) and $x_{MMA}$ (dashed line). Their alignment with desorption data enabled evaluation of polymer-solvent and polymer-substrate contributions, respectively. For copolymers washed with THF, as with homopolymers, it is clear that $R_a$ was in line with the data and was driven by $\delta_H$. However, chloroform again provided the ability to separate polymer-solvent and polymer-substrate interactions through the deviations in $R_a$ and $x_{MMA}$ shown in Figure 7.8g. Although chloroform was more compatible with P(S-\(r\)-MMA) (48:52) and (27:73), the polymers showed less change in $h_{ads}$ with solvent than PMMA, instead following $x_{MMA}$. This behavior indicated that the degree of hydrogen bonding with the substrate, and its interference by a hydrogen-bonding solvent, played a larger role in adsorbed layer desorption than polymer-solvent solubility. We therefore conclude that, despite its higher compatibility with PS, toluene’s lack of hydrogen-bonding tendencies prevents polymer-solvent interactions from largely impacting $h_{ads}$ in all polymers studied here.

### 7.7.2 Quantifying Specific Segment-Substrate Interactions in P(S-\(r\)-MMA)

Guiselin predicted,\(^57\) and it has been supported experimentally,\(^23\) that for a given polymer, $h_{ads}$ is directly proportional to the number of individual contacts with the substrate, both scaling with $N^{1/2}$. As such, the relative change in copolymer $h_{ads}$ when
washed with different solvents reflects a similar change in the relative number of individual contacts with the substrate. It follows that studying the partial desorption of copolymer adsorbed layers in hydrogen-bonding solvents can be used to gain valuable insight into polymer-substrate interactions. Extending homopolymer desorption behavior to copolymers allowed for the assumption that all MMA contacts desorbed and all S segments remained adsorbed onto the substrate. By this logic, a relative loss in $h_{ads}$ is a direct measure of the composition of adsorbed segments, or the ratio of hydrogen bonding (with MMA) to Van der Waals interactions (with S). The correlation between relative $h_{ads}$ and $x_{MMA}$ in Figure 7.8f and g implied that the fraction of desorbing MMA segments is equal to $x_{MMA}$; therefore, adsorbing segments in P(S-$r$-MMA) are not dominated by the stronger hydrogen-bonding interactions of MMA with the substrate. Similar behavior when annealing films at 443 K for 3 h (shown in Figure 7.8g) suggests this preference does not change with $T_{ann}$, at least at short annealing times.

This impartial adsorption of S and MMA contacts was different than what would be expected from preferential adsorption experiments of PMMA and PS homopolymers adsorbing from solution. Recall from its reference in Chapter 4 that PMMA completely displaced PS due to stronger interaction strength with the substrate. However, this effect was largely due to the magnified difference in attraction by the combination of many segments along polymer chains. In random copolymers, different interaction strengths are combined in the same chain, preventing large differences in attraction strength between chains. The proximity of S and MMA along the copolymer chains also prevents significant segregation of groups at the substrate.
Chapter 7

Although desorption data follows the composition lines well for both THF and chloroform, deviations evolve with adsorption time. Negative deviations from the composition line at $t_{ads} = 3$ h suggest either a slight preference of MMA at the substrate or some desorption of S contacts. Positive deviations at $t_{ads} = 15$ h could suggest an increase in the relative number of S-substrate interactions, with longer annealing times. However, as it would require as much as an 85% preference for S over MMA at the substrate to account for the magnitude of deviation shown in Figure 7.8f and g, this is unlikely to be the major cause. Alternatively, positive deviations could indicate an increased stability of MMA-substrate interactions due to tighter overall chain adsorption. Johnson et al.$^{30}$ reported slower desorption of PS adsorbed layers with increasing $M$ of PMMA in solution due to the PMMA effectively trapping PS chains at the substrate. Similarly, more copolymer contacts and tighter chain configurations at longer annealing times could prevent the complete desorption of MMA by trapping it at the substrate.

7.8 Proposed P(S-r-MMA) Adsorption Mechanism

P(S-r-MMA) possesses characteristics of both PS and PMMA, which manifest as intermediate $T_g$ in bulk systems as well as confined $T_g$ in thin films. However, as shown above, these shared characteristics do not translate directly to adsorbed layer thickness. The illustrations in Figure 7.9 depict proposed differences in PS and PMMA adsorbed layer chain configuration that combine in their random copolymers. Consistent with experimental observations and simulation results,$^{17,51}$ PS (top) adsorbs loosely due to its relatively weak interaction with the substrate. This loose adsorption results in an adsorbed layer with a higher concentration of loops and tails compared to that of PMMA.
Figure 7.9. Diagram of proposed differences between PS, PMMA, and P(S-r-MMA) adsorbed layers. PS exhibits looser adsorption, with more loops and tails. PMMA has tighter chain adsorption, but also many loosely-adsorbed chains with only a few contact points. P(S-r-MMA) has tighter bound chains than PS, giving it less large loops and tails, but it also does not have the loosely-bound chains in gaps in the tightly bound layer that PMMA has.
(bottom), which has more tightly adsorbed chains in the form of trains due to stronger polymer-substrate interactions.

In a P(S-r-MMA) adsorbed layer (center), these tendencies for strong and weak chain adsorption from MMA and S contributions combine to increase packing frustration and prevent additional chain adsorption. The stronger MMA interactions dominate close to the substrate, leading to tighter densely adsorbed chains that increase the barrier for additional adsorption, slowing kinetics consistent with the similarities in kinetics with PMMA. Chain packing frustration from different interaction strengths at the substrate could also contribute to kinetic barriers. Simultaneously, the S fraction contributes toward weaker average segmental attraction to the substrate, which, combined with a thicker flattened layer, does not allow many chains to penetrate to the surface and loosely adsorb. With limited adsorption of loosely-bound chains, P(S-r-MMA) adsorbed layers would not greatly exceed the thickness of their flattened layer and form thinner adsorbed layers than their homopolymer components. In PMMA, individual segments have interactions strong enough to diffuse through denser, tightly-bound chains to adsorb. In PS, weaker-adsorbing chains are less encumbered by the flattened layer, and chains form more loops and tail configurations. This competition between tight and loose chain adsorption increases with increasing compositional heterogeneity. Unbalanced compositions in P(S-r-MMA) (27:73) and (75:25) allowed MMA and S units to dominate the adsorption mechanism, respectively, resulting in larger \( h_p \). However, the nearly symmetric composition of P(S-r-MMA) (48:52) led to the most dramatic competition of influences and was thinner accordingly. Solvent leaching experiments supported the idea that competition of polymer-substrate interactions dictated chain configurations and \( h_{ads} \).
by revealing that individual interactions with the substrate mirrored P(S-\(r\)-MMA) composition without preference for stronger MMA interactions.

Finally, the temperature-sensitivity of copolymer adsorption is consistent with this proposed mechanism. The large change in copolymer \(h_p\) at elevated \(T_{\text{ann}}\) indicated a change in polymer-substrate interaction strength and supports the idea of limited loosely bound chain adsorption. In copolymers, this small increase in \(\sim k_B T\) interactions allows for the penetration of additional chains through the tightly-bound layer to bind with the substrate. However, the fact that P(S-\(r\)-MMA) (27:73) did not show a change in \(h_p\) when created at \(T_{\text{ann}} = 423\) K implies that a sufficiently high \(T_{\text{ann}}\) is needed to overcome the barrier to adsorption imposed by tightly bound chains. The relatively small change in copolymer \(v\) demonstrated that the thermal fluctuation of chains played a less important role in limiting adsorption than interaction energy with the substrate.

### 7.9 P(S-\(r\)-MMA) Irreversibly Adsorbed Layers as Neutral Substrates

As mentioned at the beginning of this chapter, random copolymers are sometimes used to create neutral substrates for block copolymer (BCP) thin films. Due to their blocky chemistries, BCPs will separate into different microphases, with domains rich in each component, depending on the length and ratio of their blocks. For example, asymmetric BCPs will form sphere or cylinder domains with their minority component, while symmetric BCPs will form lamellar microdomains. Neutral substrates can be created by end-grafting, crosslinking, or side-grafting random copolymers to the substrate, and they promote perpendicular orientation of BCP microdomains to the substrate.\(^{58}\) Perpendicularly-oriented, or “standing” domains can then be used as templates for lithography or other applications requiring precise nanoscale patterning.\(^{34}\)
These applications have made creation of neutral substrates the focus of a significant research effort.\textsuperscript{33,34,58–60}

Two key design factors come into play when using neutral substrates to orient BCP microdomains perpendicular to the substrate in thin films: surface energy and commensurability. Surface energy dictates which blocks prefer the substrate or air interfaces, and neutral interfaces are achieved when its surface energy is equally attractive for both blocks. Lamellae-forming PS-\textit{b}-PMMA is a common system for which to create neutral substrates because a relatively weak bias at the air interface means orientation is largely controlled by substrate interactions. Commensurability is related to how bulk domain spacing ($L_0$) is impacted by a confining geometry, such as film thickness. For a typical system consisting of a BCP thin film atop a random copolymer brush, surface energy and commensurability are controlled, respectively, through composition of the random copolymer brush and thickness of the BCP film.

Here, we describe our work to tailor P(S-\textit{r}-MMA) adsorbed layer composition and annealing conditions to achieve neutral substrates, as indicated by orienting PS-\textit{b}-PMMA films into standing lamellae. We sought to create neutral substrates with P(S-\textit{r}-MMA) adsorbed layers, both to present a direct application of copolymer adsorbed layers and to glean additional information about their structure, by comparing them to chemically-grafted neutral substrates. Although this study ultimately proved unsuccessful, we provide our methods and experimental challenges encountered in the event that this potential application of irreversibly adsorbed layers becomes of renewed interest.
7.9.1 Synthesis of P(S-r-MMA) to Neutralize Substrates

Synthesis of P(S-r-MMA) for substrate modification has been studied extensively, and composition ranges required to achieve neutral substrates depend on the BCP microstructure (dictated by its composition and molecular weight) and the method of attaching the random copolymer to the substrate.\textsuperscript{58} For our physically-bound adsorbed layers, we targeted a composition range of $0.66 \leq x_s \leq 0.74$ to match the neutral range demonstrated by Pujari \textit{et al.}\textsuperscript{33} for side-grafted P(S-r-MMA). By incorporating grafting groups at low concentrations throughout the copolymer chains, side-grafted brushes should form loop, train, and tail chain conformations, similar to adsorbed layers. We also wanted molecular weights similar to 104 kg/mol, the total chain length of the lamellae-forming PS-$b$-PMMA we sought to orient. PS-$b$-PMMA (49:51) was purchased from Polymer Source, and it was confirmed to have symmetric composition ($x_s = 0.49$) by $^1$H-NMR. Following the same synthesis and characterization methods as described in Section 7.2.1, we synthesized several copolymers near the neutral range, with those used in this study described in Table 7.5. Compositions for all polymers were determined by $^1$H-NMR and are indicated in their name by the same convention used previously; molecular weight and dispersity were determined via SEC. P(S-r-MMA) (58:42) was synthesized to be just outside the range in order to probe differences in the limits of the neutral range for adsorbed layers compared to chemically-grafted brushes.

Table 7.5 P(S-r-MMA) synthesized for the creation of neutral substrates.

<table>
<thead>
<tr>
<th>P(S-r-MMA)</th>
<th>$M_W$ (kg/mol)</th>
<th>$D$</th>
</tr>
</thead>
<tbody>
<tr>
<td>(58:42)</td>
<td>120</td>
<td>2.2</td>
</tr>
<tr>
<td>(67:33)</td>
<td>121</td>
<td>2.0</td>
</tr>
<tr>
<td>(69:31)</td>
<td>110</td>
<td>1.7</td>
</tr>
</tbody>
</table>
7.9.2 Commensurability

There are certain commensurate thicknesses, expressed in terms of $L_0$, at which stable BCP film formation is achieved. These thicknesses depend on BCP chemistry and microphase structure, and for lamellae-forming PS-$b$-PMMA exist at $(m + \frac{1}{2})L_0$, where $m$ is an integer.\cite{61} Even on neutral substrates, PS-$b$-PMMA prefers to orient parallel to the substrate due to a slight preference of the PS block for the air interface. When attempting to create standing structures in thin films, one should make films with incommensurate thicknesses in order to frustrate the bulk microstructure and encourage adoption of a perpendicular orientation. Previous studies have targeted films with thicknesses of $\sim 0.6$-$0.7L_0$.\cite{33,60} In order to determine an approximate $L_0$ for PS-$b$-PMMA (49:51), we fitted reported literature values\cite{33,59,61} to the $L_0 \sim M^{2/3}$ scaling expected for lamellae-formers, giving $L_0 = 45 \pm 3$ nm.

7.9.3 Results

We spin-coated $26 \pm 3$ nm-thick (as confirmed by AFM) BCP films atop isolated adsorbed layers of P(S-$r$-MMA) (58:42), (67:33), and (69:31). Adsorbed layers, prepared and measured as described in Section 7.2.2, ranged from 3-5 nm thick, depending on annealing time (5-20h). Spin-coating toluene onto adsorbed layers decreased $h_{ads}$ by less than 0.5 nm, confirming that adsorbed layers were not removed during spin-coating of the BCP films. PS-$b$-PMMA films were also spin-coated directly onto piranha-treated Si as control samples. The presence of $44 \pm 8$ nm-thick regions near the edges of the PS-$b$-PMMA films enabled evaluation of multiple thicknesses in each sample. Films were all annealed at 443 K for 2 h to encourage microphase separation and domain orientation. They were then imaged via phase-contrast AFM to determine lamellar orientation for
each film. Standing lamellae present as “lines” in an AFM image, while lamellae oriented parallel to the substrate appear as a featureless surface. Microphase separation was consistently seen in the ~44 nm region of each sample, even in samples without any adsorbed layer on the substrate. No features were observed in the thinner regions, initially designed to frustrate commensurability. Figure 7.10a and b show representative AFM images for 26 nm and 44 nm regions of PS-b-PMMA films on piranha-treated Si (control). Films spin-coated on P(S-r-MMA) adsorbed layers showed identical behavior, regardless of adsorbed layer composition.

$L_\theta$ was measured experimentally by conducting Finite Fourier Transforms (FFT) of phase images using Image J software. Figure 7.10c is a 2D-FFT of Figure 7.10b, with the ring indicating a clear characteristic length scale. This length scale is also presented as a peak in the 1D FFT (Figure 7.10d), which was transformed into real space (Figure 7.10e) and taken to be $L_\theta$. Averaging over all films gave $L_\theta$ (experimental) = 58 ± 3 nm, which was ~10 nm larger than $L_\theta$ predicted by scaling arguments. This domain spacing was consistent with the thicker regions of the spin-coated films being incommensurate. However, it did not explain why there was no variation in film behavior with underlayer composition (including the control).

In order to eliminate the possibility of the lack of substrate-specific behavior being a result of insufficient annealing (i.e. domains kinetically trapped in an out-of-equilibrium state), we annealed the films further at 443 K overnight. The same sample as shown in Figure 7.10a and b was imaged after this additional annealing, and is presented in Figure 7.10h and i. Zoomed-in sections, shown in Figure 7.10f and g confirm the presence of short lines and dots. These structures are more characteristic of cylinder-
Figure 7.10. 2x2 μm AFM phase image of (A) ~26 nm film and (B) ~44 nm film of PS-b-PMMA spin-coated on a silicon substrate with no adsorbed layer (control) and annealed for 2h at 443 K taken at 512x512 pixel resolution with 3° and 4° resolution in phase, respectively. (C) 2D FFT of B, showing clear length scale with corresponding (D) 1D-FFT (from averaging radially across C) and (E) Real space profile, showing $L_0$ at ~60 nm. (F) and (G) are sections of H and I, respectively, zoomed-in to show line and dot patterns present. (H) and (I) are 5x5 μm AFM phase images of the same films as (A) and (B), respectively after overnight annealing at 443 K.
forming systems.\textsuperscript{60} However, the symmetric composition of PS-\textit{b}-PMMA (49:51) indicated that only lamellae should be formed.

The creation of neutral substrates with physically-bound irreversibly adsorbed layers remains an interesting conceptual investigation. However, persistent experimental anomalies in the form of questionable PS-\textit{b}-PMMA microphase behavior and a lack of dependence on substrate treatment presented significant doubts to the ability of our system to produce accurate and meaningful results. As such, this study was not pursued further, and P(S-\textit{r}-MMA) preferential adsorption at the substrate was investigated via solvent leaching, as described in Section 7.6.

7.10 Conclusions

Through the examination of adsorbed layer growth in PS, PMMA, and a series of their random copolymers, we gained a clearer picture of how different polymer-substrate interactions combine to influence irreversible adsorption in systems with compositional heterogeneity. Our results revealed that the irreversible adsorption of P(S-\textit{r}-MMA) faces additional barriers to growth than either of its component homopolymers and is not intermediate to their two behaviors. This differed substantially from the blended properties usually displayed by random copolymers, which extend to their confined \(T_g\) behavior.\textsuperscript{3,11} Kinetic analysis confirmed that tightly binding chains dictate copolymer adsorption rates, as in PMMA. Annealing at a higher temperature increased kinetics and enabled the recovery of copolymer \(h_p\) scaling consistent with homopolymers. Using different solvents to isolate adsorbed layers suggested polymer-solvent interactions play a minimal role in determining \(h_{ads}\) when washing with toluene. However, these experiments also revealed a distinct sensitivity of MMA-containing polymers to
hydrogen-bonding solvents. The relative difference in $h_{ads}$ induced by washing with THF or chloroform provided a measure of hydrogen-bonding interactions at the substrate.

These insights provided a picture of P(S-r-MMA) adsorption where tighter adsorption and weaker average individual interaction strengths resulting from compositional heterogeneity combine to limit the adsorption of loosely-bound chains and give thinner adsorbed layers. P(S-r-MMA) formed denser tightly-bound layers at the substrate than PS, which served as a barrier to additional adsorption of chains with weaker average segment-substrate interactions than PMMA. Raising $T_{ann}$ increased the segmental attraction to the substrate sufficiently to overcome the growth barrier imposed by the tightly-bound layer and allowed for additional chains to be adsorbed. Despite kinetic similarities to PMMA, P(S-r-MMA) did not preferentially adsorb via MMA-substrate interactions, but with both MMA and S components, reflecting composition.

Differences between confined $T_g$ and adsorption trends suggest that relative polymer-substrate interactions are not sufficient to predict the adsorption behavior of copolymers. Their reduced degree of adsorption implies that P(S-r-MMA) films are less susceptible to annealing-induced property changes, providing copolymerization as a route to reducing annealing effects on thin film behavior.

**Notes**

† Tacticity-dependent confinement behavior has been attributed to the degree of hydrogen bonding with the substrate allowed by the relative proximity of carbonyl groups to the native oxide layer. From preliminary experiments and studies of spin-coated PMMA on Al, we expect tacticity also influences PMMA’s affinity for irreversible adsorption. The PMMA used here has a 4:37:59 isotactic:atactic:syndiotactic triad ratio, as determined by $^1$H-NMR, which is consistent with what is expected for PMMA synthesized via free radical polymerization in bulk.
\( \alpha_{es} \) calculated is higher than the \( \alpha = 0.47 \) reported by Fujii et al. for monodisperse PS.\textsuperscript{25} This difference is likely due to the broader distribution of chain lengths in our polymer not being fully captured by average \( R_g \) and disproportionately contributing to \( h_p \). Since \( h_p \) increases with molecular weight,\textsuperscript{25} it follows that longer chains likely increase \( h_p \), resulting in a larger \( \alpha \).

The initial thickness at \( t_{ads} = 0 \) (\( h_o \)) was fitted to the data and fell within error of experimentally-measured thicknesses without annealing.

THF left a thicker residue after soaking bare substrates, likely due to the presence of trace inhibitors. To account for this difference in residue, each solvent’s residual thickness on blank substrates was subtracted from adsorbed layer thickness measurements for comparison. Suspected variation in this residue between samples resulted in a few negative adsorbed layer thicknesses (in Figure 7.7)
7.11 References


Chapter 8

Irreversible Adsorption in Confined Films

8.1 Introduction

Chapters 6 and 7 have shown how free surfaces and polymer-substrate interactions can influence the \( T_g \) and growth of irreversibly adsorbed layers. Irreversible adsorption has been increasingly correlated with changes in polymer thin film properties with annealing in the melt state.\(^1\) However, the impact of confinement-induced property changes on adsorbed layer growth has not been well-studied. In measuring the development of adsorbed layers directly in confined systems, we aim to strengthen the connection between irreversible adsorption and the study of geometrically-confined polymers in order to anticipate how processing will alter thin film behavior. Accounting for irreversible adsorption resulting from processing will enable a better contextual understanding of how polymers behave at the nanoscale.

In a recent study, Perez-de-Eulate et al. measured a gradual increase in the \( T_g \) of supported poly(tert-butylstyrene) (PtBS) thin films with prolonged annealing.\(^2\) PtBS has been previously shown to exhibit a dramatic reduction in \( T_g \) with film thickness. However, larger changes in \( T_g \) with decreasing film thickness (\( h_{sc} \)) upon annealing effectively erased this substantial confinement effect, as shown in Figure 8.1a. Bulk \( T_g \) was recovered in films down to 40 nm thick after 12 hours of annealing at 453 K, and this recovery was attributed to suppression of the free surface effect due to the growth of an irreversibly adsorbed layer. Corresponding adsorbed layers, isolated from 200-nm-thick films after identical annealing conditions, were only 5-6 nm thick, demonstrating an
Figure 8.1. PtBS exhibits a dramatic reduction in $T_g$ upon confinement. (A) Recovery of bulk $T_g$ in PtBS thin films with annealing time, as measured by Perez-de-Eulate et al. via ellipsometry. Reprinted with permission from ref.\textsuperscript{2} Copyright 2017 American Chemical Society. (B) Fluorescence measurements of PtBS (diamonds), P4MS (circles), and PS (triangles) $T_g$. Solid line is a trace of Equation 2.5, fit to the data of Keddie \textit{et al.} for PS. Inset shows the repeat unit structure of PtBS. Reprinted with permission from ref.\textsuperscript{3} Copyright 2005 American Chemical Society.
ability to influence film $T_g$ over length scales far surpassing their thicknesses ($h_{ads}$). Although an increase in $T_g$ resulting from chain adsorption has been observed in capped films$^4$ and adsorbed layers$^5$ (with and without a free surface), this study reported the first complete recovery of bulk $T_g$ in supported thin films by melt-state annealing. In doing so, it introduced two major limitations in the connection between confined $T_g$ and irreversible adsorption that provided motivation for the work in this chapter: (1) adsorbed layers were isolated from bulk films without consideration of confinement effects on their growth, and (2) free-surface $T_g$ was not directly measured.

Although Perez-de-Eulate et al. measured the average $T_g$ of films ranging in thickness from 30 to 300 nm, adsorbed layers (to which changes in $T_g$ were attributed) were all grown in identical bulk films.$^2$ Their isolation from a separate system did not enable the direct connection between observed annealing-induced increases in thin film $T_g$ and adsorbed layer growth. Isolating adsorbed layers from bulk films is a common practice, employed widely in the literature as well as in Chapters 6 and 7. Changes in polymer diffusivity,$^6$ mobility,$^7$ and viscosity$^8$ in the proximity of a substrate, as well as deviations from bulk $T_g$ in thin films$^{2,4}$ have all been associated with the growth of irreversibly adsorbed layers by superimposing the growth patterns of adsorbed layers onto changes in the properties of thin films with annealing. While this practice enables a controlled study of irreversible adsorbed layer development and its dependence on thickness-independent factors (such as polymer-substrate interactions, molecular weight, and annealing temperature), it should not be applied directly to model adsorption in confined systems.
As mentioned in Chapter 3, fluorescence enables the measurement of nanoscale and location-specific $T_g$. Fluorescence studies on supported polystyrene (PS) films demonstrated direct competition between the free surface and substrate interfaces. The free surface was able to perturb $T_g$ up to 30 nm into thin films, and it depressed $T_g$ at the substrate in films thinner than 36 nm. Thus, the proximity of a free surface can alter behavior at the substrate, likely including adsorption, in sufficiently thin films. It follows that film thickness is a variable that influences irreversible adsorption and should not be ignored when studying the impacts of annealing on confined systems. Very recent work by Simavilla et al. sought to investigate the impact of confinement on adsorption by measuring the effect of $h_{sc}$ on adsorbed layer growth.\(^9\) They did not observe any changes in adsorption kinetics in PS films of different thicknesses at short times to indicate differences in adsorption mechanisms. However, they observed substantial decreases of almost 50% in plateau thickness ($h_p$), or equilibrium adsorbed amount, when isolated from films thinner than 5-10 times the polymer’s radius of gyration ($R_g$) and attributed this to changes in the polymer-substrate interaction strength imposed by nano-confinement.

Ellison et al. used fluorescence to measure the dramatic negative deviation from bulk $T_g$ in supported PtBS thin films for the first time.\(^3\) Its confined $T_g$ (diamonds) is compared to that of PS (line) and poly(4-methylstyrene) (P4MS) (circles) in Figure 8.1b. PtBS showed $T_g$ deviations in films ~ 300 nm thick, and its $T_g$ was 50 K below bulk at film thicknesses of ~20 nm. They attributed this substantially larger $T_g$ depression relative to PS to the addition of a bulky butyl side group (repeat unit structure of PtBS is shown in the figure inset), which increased the chain stiffness and substantially lowered
Chapter 8

the density of PtBS relative to PS. Fluorescence measurements were conducted on PtBS doped with 1,10-bis(1-pyrene)decane (BPD), which did not allow for determination of location-specific $T_g$.

While Perez-de-Eulate et al. claimed average film $T_g$ was a result of competition between free-surface and adsorption effects, they were similarly not able to isolate the free surface layer $T_g$. Suppression of the free-surface effect was determined by fitting a model to confined film $T_g$ data in order to determine a rheological temperature at the free surface ($R_s$). Far from providing a direct measurement, this method required simultaneous fitting of both $R_s$ and a length scale of $T_g$ perturbation ($\xi_0$). Conclusions were made based on correlation of changes in the fitting parameters with adsorbed layer thickness, regardless of determining physical values. They attributed the increase in free surface $T_g$ to restrictions to the diffusion of free volume imposed by adsorbed layers.

In light of its substantial confinement effects and their perturbations resulting from irreversible adsorption, a direct measurement of location-specific $T_g$ in PtBS would be particularly useful to determine free surface and substrate $T_g$. As mentioned above, $T_g$ at the substrate can be impacted when in close proximity to the free surface (i.e. in sufficiently thin films). The ability of average PtBS $T_g$ to be perturbed at much larger length scales than PS suggests a thicker threshold thickness for this free-surface effect to penetrate to the substrate and potentially impact adsorbed layer growth.

Continuing our efforts to expand the ability to predict adsorbed layer growth and its impacts on confined film behavior, this chapter addresses how irreversible adsorption is impacted by geometric confinement. It studies how adsorbed layers develop in films of different thickness, as $h_{sc}$ is a crucial parameter in predicting behavior of nanoscale
polymers for applications. This confined film adsorption study primarily focuses on PtBS, due to its dramatic thickness-dependent $T_g^{2,3}$ and response to annealing. Select measurements of PS and poly(methyl methacrylate) (PMMA) adsorbed layers are included for context. Initial attempts to fluorescently label PtBS and potential issues with measuring its $T_g$ via fluorescence are also presented.

### 8.2 Adsorbed Layer Growth Depends on Film Thickness

In order to evaluate if adsorbed layer growth was altered by confinement, we compared $h_{ads}$ isolated from films of varying thickness after a set annealing time, $t_{ads}$. Measuring $h_{ads}$ at a single $t_{ads}$ enabled the comparison of how a given annealing procedure impacted adsorption in films with different $h_{sc}$. Although the work of Simavilla et al. on $h_p$ revealed the maximum thickness of adsorbed layers formed in films, it could only be applied to films annealed to their plateau. Many thin film studies, anneal films for shorter, set times. It was therefore deemed more valuable to understand how $h_{ads}$ and resulting property changes after a given $t_{ads}$ depend on film thickness. Films of PS-109, PMMA-119, and PtBS-280 were spin-coated to thicknesses ranging from 12 to 900 nm and annealed for 8 h at ~45 K above each polymer’s bulk $T_g$ before soaking in toluene to reveal 8-h irreversibly adsorbed layers. Thicknesses of spin-coated films and adsorbed layers for all polymers were measured by spectroscopic ellipsometry. Figure 8.2a illustrates the ability to accurately measure PtBS-280 thickness by ellipsometry, as compared to select AFM images. This evidence was provided for PS and PMMA in Chapters 6 and 7.

Figure 8.2b plots $h_{ads}$ against $h_{sc}$ for the different polymers studied. PS-109 and PMMA-119 exhibited modest decreases in $h_{ads}$ with thinner $h_{sc}$, and $h_{ads}$ ranged from 4-6
Figure 8.2. Adsorbed layer thickness ($h_{\text{ads}}$) and relative adsorbed amount are dependent on film thickness ($h_{\text{sc}}$). (A) Comparison of PtBS-280 film and adsorbed layer thicknesses measured by AFM and ellipsometry. (B) 8-h adsorbed layer thickness as a function of spin-coated film thickness for PS-109 (circles), PMMA-119 (triangles), and PtBS-280 (squares). (C) Data from B plotted as the relative fraction of the film adsorbed ($h_{\text{ads}}/h_{\text{sc}}$) for a given film thickness.
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nm in thicker films to ~2 nm when $h_{sc} = 10$-20 nm. Although not equivalent, this was consistent with the decrease in $h_p$ and potential slowing of kinetics observed by Simavilla et al.\textsuperscript{9} for films with $h_{sc}$ below ~5-10 $R_g$. In films thicker than 150 nm (~15 $R_g$) minimal change in $h_{ads}$ indicated that differences in $h_{sc}$ played a minor role in the growth of irreversibly adsorbed layers when they were isolated from thicker films. Most studies, including those described in Chapters 6 and 7 fall above this threshold. By contrast, PtBS showed a much stronger dependence of $h_{ads}$ on film thickness. Figure 8.2b shows that its $h_{ads}$ increased from ~7 nm to ~13 nm as $h_{sc}$ decreased. In addition to a different trend in $h_{ads}$ with $h_{sc}$, PtBS adsorbed layers were considerably thicker than those of PS and PMMA. This can be partially accounted for by the larger $M_w$ of PtBS-280, accompanied by an $R_g$ of 14 ± 1 nm (based on relations between PtBS $R_g$, $M_w$, and $D$ developed from light scattering experiments).\textsuperscript{10} However, $h_{ads}$ is within error of $R_g$ in 8-h adsorbed layers isolated from the thinnest films of PtBS-280, while Chapter 7 showed that PS-109 and PMMA-119 plateau at ~0.5 $R_g$. The butyl group reduces PtBS bulk density by 10% relative to PS.\textsuperscript{3} Its bulky side groups could frustrate chain packing and cause PtBS chains to adopt more loop and tail configurations, forming lower density adsorbed layers with higher amounts of free volume.

In order to rationalize the ability of adsorbed layers to impact film properties, Figure 8.2c plots the relative adsorbed amount ($h_{ads}$/$h_{sc}$) as a function of $h_{sc}$. This perspective revealed that PS and PMMA films < 20 nm thick were composed of almost 20% adsorbed chains after 8 h of annealing, while bulk films were less than 2% adsorbed. This implies that even when absolute adsorbed layer thickness decreases with $h_{sc}$, irreversible adsorption has a much stronger impact on thinner films. Similarly, the 2-4 nm
change in absolute $h_{ads}$ when assuming bulk adsorption behavior translates to a much larger difference in relative fraction of the film adsorbed. It follows that $T_g$ would increase with annealing more significantly in thinner films, effectively suppressing negative deviations in $T_g$ with confinement. For example, 30-nm-thick films annealed for 8 h were almost 40% adsorbed, which roughly corresponded to a 30 K change in their $T_g$, as reported by Perez-de-Eulate et al.\textsuperscript{2} These results suggested thicker adsorbed layers in thinner films also contributed toward suppression of the confinement effect on $T_g$, rather than solely restrictions to free volume diffusion.

The increase in PtBS $h_{ads}$ with thinner $h_{sc}$ was postulated to result from its confinement behavior. As stated previously, PtBS $T_g$ decreases dramatically in thinner films, which could lead to a higher annealing temperature relative to its $T_g$ at the substrate. Increasing adsorption temperature has been shown to result in an increase in kinetics of adsorption,\textsuperscript{11,12} which would manifest as thicker $h_{ads}$ at a single $t_{ads}$. Differences in $h_{ads}$ with $h_{sc}$ could then be due to differences in kinetics induced by thickness-dependent deviations in substrate-adjacent $T_g$. While PMMA and PS both exhibit deviations from bulk $T_g$ at the substrate in sufficiently thin films,\textsuperscript{13,14} they exhibit milder changes in $T_g$ with film thickness. The next two sections describe our efforts to evaluate this hypothesis in terms of PtBS adsorption kinetics and confined $T_g$.

### 8.3 Acceleration of Adsorption Kinetics in PtBS Thin Films

The possibility that the increase in PtBS $h_{ads}$ with decreasing $h_{sc}$ was due to an underlying increase in kinetics was investigated by comparing adsorbed layer growth in a 50-nm-thick film with that in an 880-nm-thick film (well within “bulk” behavior). The growth profiles of adsorbed layers isolated after annealing thin and bulk films at both 463
and 443 K are shown in Figure 8.3a. It was clear that the adsorbed layers in 50-nm-thick films (open symbols) grew more quickly than those in corresponding 880-nm-thick films (closed symbols). Lines are fits of the data to Equation 5.9a, with parameters listed in Table 8.1. Adsorption kinetics studies have shown that \( h_p \) does not change with \( T_{ann} \) in homopolymers,\(^{12} \) so it was set equal in fitting. \( \Delta h \) was bounded to ensure \( h_p \) was within error of the 50-nm-thick film annealed at 463 K, which had the fastest growth and therefore was most likely to reach \( h_p \). \( t_{cross} \) decreased with decreasing \( h_{sc} \) for both \( T_{ann} \), supporting our hypothesis that the thicker 8-h adsorbed layers in thinner films was due to a manifestation of kinetics. This difference in adsorption kinetics between films with different \( h_{sc} \) annealed at the same temperature also emphasized the importance of proximity of \( T_{ann} \) to \( T_g \), not just as an absolute temperature.

Normalizing \( t_{ads} \) by \( t_{cross} \) resulted in the collapse of all film growth curves in Figure 8.3b, as expected for adsorbed layers created by annealing at different temperatures. We note that \( t_{cross} \) calculated from fits with unbounded \( \Delta h \), followed the same trend in \( t_{cross} \); these parameters are also listed in Table 8.1. It is likely that kinetics were too slow in some films to accurately capture \( h_p \) without adding constraints. Even though our 50-nm-thick films were \(~4R_g\), we saw no evidence of the decrease in \( h_p \) with film thickness compared to bulk.

### Table 8.1. Saturated exponential fit parameters for PtBS adsorption

<table>
<thead>
<tr>
<th>( h_{sc} ) (nm)</th>
<th>( T_{ann} ) (K)</th>
<th>( h_0 )</th>
<th>( \Delta h )</th>
<th>( t_{cross} )</th>
<th>( h_p ) (nm)</th>
<th>( h_0 )</th>
<th>( \Delta h )</th>
<th>( t_{cross} )</th>
<th>( h_p ) (nm)</th>
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</thead>
<tbody>
<tr>
<td>50</td>
<td>463</td>
<td>0 ±0.2</td>
<td>15.2 ±0.4</td>
<td>1.5 ±0.2</td>
<td>15.2 ±0.5</td>
<td>0 ±0.2</td>
<td>15.2 ±0.4</td>
<td>1.5 ±0.2</td>
<td>15.2 ±0.5</td>
</tr>
<tr>
<td></td>
<td>443</td>
<td>0 ±0.5</td>
<td>13.8 ±0.8</td>
<td>1.8 ±0.4</td>
<td>13.8 ±0.9</td>
<td>0 ±0.5</td>
<td>13.8 ±0.8</td>
<td>1.8 ±0.4</td>
<td>13.8 ±0.9</td>
</tr>
<tr>
<td>880</td>
<td>463</td>
<td>0.7 ± 0.5</td>
<td>13.1 ± 0.8</td>
<td>5.8 ±1.3</td>
<td>13.8 ±0.5</td>
<td>0.7 ±0.2</td>
<td>11.7 ±0.4</td>
<td>5.8 ±0.7</td>
<td>12.4 ±0.4</td>
</tr>
<tr>
<td></td>
<td>443</td>
<td>1 ± 0.7</td>
<td>11 ±3</td>
<td>27 ±16</td>
<td>12 ±3</td>
<td>0.7 ±0.4</td>
<td>6.5 ±0.5</td>
<td>5 ±1.2</td>
<td>7.2 ±0.6</td>
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</tbody>
</table>
Figure 8.3. Adsorbed layer growth kinetics in PtBS depend on original spin coated film thickness ($h_{sc}$). (A) Adsorbed layer growth is plotted as a function of annealing time at 463 K (navy squares) and 443 K (blue triangles) for 50-nm (open) and 880-nm-thick (closed) films. Solid lines are fits of Equation 5.9a to the data for 880-nm-thick films, and dotted lines are fits to the data for 50-nm-thick films. (B) Growth curves in A collapse when annealing time is normalized by $t_{cross}$. 
As in Chapter 7, \( t_{\text{cross}} \) was used to separate linear and logarithmic kinetic regimes, with corresponding growth rates calculated from fits of Equation 4.1 to the data. The resulting kinetic parameters are listed Table 8.2. Linear growth rates, \( v \), increased with \( T_{\text{ann}} \) and decreased with increasing \( h_{sc} \). Logarithmic growth rates, \( \Pi \), for all PtBS films were within error of each other. Simavilla et al. reported identical linear growth rates in 130, 235, and 325-nm-thick PS films, diverging only in the logarithmic growth regime.\(^9\)

It is clear from Figure 8.3a that our data does not follow this model, but the films studied here were much thinner, operating at \( h_{sc} \) where average film \( T_g \) is much less than \( T_g \) (bulk). The difference in our results could therefore be attributed to confinement effects dominating over any changes to polymer-substrate interactions in confined films of PtBS.

Table 8.2. Kinetic growth rates and \( T_{\text{eff}} \) for PtBS adsorbed layers

<table>
<thead>
<tr>
<th>( h_{sc} ) (nm)</th>
<th>( T_{\text{ann}} ) (K)</th>
<th>( h_0 ) (nm)</th>
<th>( v ) (nm/h)</th>
<th>( t_{\text{cross}} ) (h)</th>
<th>( h_c ) (nm)</th>
<th>( \Pi )</th>
<th>( T_{\text{eff}} )</th>
</tr>
</thead>
<tbody>
<tr>
<td>50</td>
<td>463</td>
<td>0.2</td>
<td>8.0 ±0.5</td>
<td>1.5</td>
<td>10.5 ± 0.6</td>
<td>4.8 ± 0.7</td>
<td>483</td>
</tr>
<tr>
<td>443</td>
<td></td>
<td></td>
<td>6.5 ± 0.7</td>
<td>1.8</td>
<td>9.2 ± 0.6</td>
<td>4.0 ± 0.6</td>
<td>479</td>
</tr>
<tr>
<td>880</td>
<td>463</td>
<td>0.6</td>
<td>1.7 ± 0.21</td>
<td>5.8</td>
<td>8.8 ± 0.5</td>
<td>4.5 ± 0.8</td>
<td>463</td>
</tr>
<tr>
<td>443</td>
<td></td>
<td></td>
<td>0.32 ± 0.05</td>
<td>27</td>
<td>7.05 ± 0.3</td>
<td>5 ± 1</td>
<td>443</td>
</tr>
</tbody>
</table>

Growth rates of adsorbed layers isolated from bulk films follow Arrhenius temperature dependence.\(^{11,12}\) Linear growth rates for adsorbed layer isolated from bulk films annealed at 443 and 463 K were compared to solve for activation energy using the relation:

\[
\ln \left( \frac{v_2}{v_1} \right) = \frac{E_a}{R(T_1-T_2)} \tag{8.1}
\]

where \( v \) is in nm/s, \( T \) is in K, \( R \) is the gas constant in J/mol·K, and \( E_a \) is activation energy in J/mol. \( E_a \) was found to be 142 ± 17 KJ/mol, which is in reasonable agreement with the
activation energy for segmental motion for PtBS used by Simavilla et al.\textsuperscript{12} This relation and value of $E_a$ were then used to determine an effective annealing temperature ($T_{\text{eff}}$) for confined films (\textit{i.e.}, the temperature at which a bulk film would need to be annealed to give the same adsorption kinetics). These temperatures are also listed in Table 8.2. $T_{\text{eff}}$ provided a quantitative measure of how the proximity of a free surface impacts polymer behavior at the substrate when annealing confined PtBS films.

8.4 Relationship between Confined $T_g$ and Adsorbed Layer Thickness

As stated above, only average $T_g$ values have been measured in PtBS films, and it was not known how far the effect of the free surface penetrated and how substrate-adjacent $T_g$ was altered. Confirmed by kinetic arguments above, increases in $h_{\text{ads}}$ above those isolated from bulk films were interpreted as the onset of deviations from bulk $T_g$ in PtBS adjacent to the substrate. The data set from Figure 8.2b was expanded to include additional annealing temperatures in Figure 8.4a and indicated that substrate-adjacent $T_g$ deviated from bulk $T_g$ at $h_{sc}$ below $\sim$200 nm in PtBS films annealed at 463, 443, and 423 K. The free surface was able to alter PtBS $T_g$ up to 200 nm away, compared to 30 nm in PS, providing evidence of the suspected stronger free-surface influence on PtBS thin films. This difference in strength of the free surface effect would also explain why $8-h_{\text{ads}}$ increased with decreasing $h_{sc}$ in PtBS and not PS.

In addition to demonstrating the distance over which $T_g$ was perturbed by the free surface, adsorption kinetic differences were used to quantify substrate-adjacent $T_g$ in PtBS thin films. Accelerated kinetics in 50-nm-thick films resulted from depressed $T_g$ at the substrate, which effectively increased the annealing temperature above that imposed
Figure 8.4. (A) Thickness of 8-h PtBS adsorbed layers isolated from films of different $h_{sc}$, annealed at 463 K, 443 K, and 423 K. (B) Dependence of $t_{cross}$ on $T_{eff}$. $A$ was fit to $(2 \pm 1) \times 10^{-15}$ h and $b$ was fit to $(6.1 \pm 0.1) \times 10^{-5}$ K$^{-1}$ (C) Data from A normalized by $t_{cross}$ calculated for each film, assuming $T_g$ at the substrate is equivalent to average $T_g$ ($h_{sc}$).
and felt by bulk films (i.e., $T_{an}$). It followed that the difference between $T_{eff}$ and $T_{an}$ was equal in magnitude to the depression of $T_g$ at the substrate interface from bulk $T_g$. $T_{eff}$ calculated above for 50-nm-thick films annealed at 463 and 443 K gave an average substrate-adjacent $T_g$ of 392 ± 11 K. This was within error of the average $T_g$ for 50-nm-thick supported films, determined to be 398 ± 3 K by fitting fluorescence and ellipsometry data$^{2,3}$ to Equation 2.5 (using parameters $A=2.5 \pm 0.3$ and $\delta=0.97$). $T_g$ of 50-nm-thick capped PtBS films was measured to be 409 K by capacitive dilatometry. Closer alignment with $T_g$ of supported films indicated the importance of the free surface influence in adsorption.

The similarity between $T_g$(substrate) and average film $T_g$ was consistent with the fluorescence study by Ellison et al., where they showed that for a given PS film, $T_g$ averaged over the film was closer to that at its substrate than at its free surface.$^{13}$ Below ~24 nm, a gradient in $T_g$ was no longer possible, making $T_g$ at the substrate and free surface identical and equal to average film $T_g$. Although unable to determine if a gradient in $T_g$ existed within the 50-nm-thick films, our combined results showed that substrate-adjacent $T_g$ gradually decreased in films below 200 nm thick and became within error of average $T_g$ at $h_{sc} = 50$ nm.

In Section 8.3, we demonstrated the ability to collapse adsorbed layer growth profiles in films of different thicknesses and annealing temperatures by normalizing $t_{ads}$ by each film’s $t_{cross}$. Plotting $t_{cross}$ as a function of $1/T_{eff}$ gave a clear exponential relationship, as seen in Figure 8.4b. This relationship could then be used to determine a film’s $t_{cross}$ based on its $T_{eff}$. As $T_{eff}$ reflects $T_g$ at the substrate, $t_{cross}$ can be determined for each $h_{sc}$ when $T_g$(substrate) is known. Assuming $T_g$ at the substrate was equal to average
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$T_g$, we normalized $t_{\text{ads}}$ (8 h) for each data point in Figure 8.4a by its $t_{\text{cross}}$ (calculated from $h_{\text{sc}}$). The resulting normalized adsorption curve, shifted in time and temperature, is displayed in Figure 8.4c. A rough fit of the data to Equation 5.9a is given by the dashed line, with $h_0 = 1.0 \pm 0.81 \text{ nm}$, $\Delta h = 12.9 \pm 0.87 \text{ nm}$, and $t_{\text{cross}} = 1.9 \pm 0.22 \text{ h}$.

This plot of normalized adsorbed layer growth enables the prediction of $h_{\text{ads}}$ for a film of any thickness at any annealing temperature as long as $T_g$ at the substrate interface is known. For example, a 30-nm-thick film of PtBS-280 annealed for 2 h at 453 K would be expected to grow an adsorbed layer 11 ± 3 nm thick, while a 500-nm-thick film annealed under the same conditions would have $h_{\text{ads}} = 2 \pm 8 \text{ nm}$. Additional data would improve the fit and reduce the error of the relationship between $T_{\text{eff}}$ and $t_{\text{cross}}$, and thus the robustness of its predictive capability. Determining the relationship between $t_{\text{cross}}$ and $T_{\text{eff}}$ from several adsorbed layer profiles would thus enable extensive mapping across annealing time, film thickness, and temperature. Different $T_{\text{eff}}$ could be achieved either by annealing bulk films at different $T_{\text{ann}}$ or annealing films of different $h_{\text{sc}}$ (when substrate $T_g$ deviates from bulk) at the same temperature. As supported film $T_g$ does not change with molecular weight and adsorption kinetics do, the relationship between $T_{\text{eff}}$ and $t_{\text{cross}}$ would need to be established for each molecular weight.

8.5 Measurements of Pyrene-labeled PtBS $T_g$ via Fluorescence

Despite its dramatic confinement behavior and its particular interest in recent studies of irreversible adsorption in PtBS, location-specific $T_g$ has not previously been measured in PtBS. Substrate-adjacent $T_g$ measurements could be used to confirm the relationship between $T_{\text{eff}}$ and $T_g(\text{substrate})$ as well as determine how the accelerated growth of adsorbed layers in confined films could change $T_g$ at the substrate during
annealing. Free surface $T_g$ measurements as a function of annealing time would provide a means to validate the claims made by Perez-de-Eulate et al. as explanation for large increases in PtBS thin film $T_g$ with annealing.$^2$ Multilayer film fluorescence experiments isolating the free surface and substrate-adjacent $T_g$ would be possible with the successful synthesis of fluorescently-labeled PtBS. Below we describe our efforts to synthesize pyrene-labeled PtBS and measure its $T_g$ via fluorescence.

8.5.1 Synthesis and Characterization of PtBS

Neat and pyrene-labeled PtBS were synthesized via free radical polymerization (FRP) for use in fluorescence measurements. Several batches of PtBS were synthesized to determine approximate dependencies of molecular weight and reaction rate on initiator concentration at 348 K. Following the relationship described in Equation 5.4, a constant value of $C \approx 100$ was found and used to determine the monomer and initiator feed ratios required to achieve desired molecular weights. Each polymer was precipitated from toluene solution into methanol ~7 times to remove excess monomer. Synthesized PtBS and $\text{lPtBS}$ were found to have $M_w$ of 381 and 382 kg/mol, with $D = 2.1$ and 2.0, respectively. These measurements were conducted with SEC, as described in Chapter 5, using a $dn/dc$ value of 0.140 mL/g to determine $M_w$ from light scattering data.$^{15}$ These polymers are referred to as PtBS-381 and $\text{lPtBS-382}$ in the remainder of this section. Bulk $T_g$ was taken to be $T_g$(onset) measured via DSC on second heating after cooling at 2.5 K/min: 419 K for PtBS-381 and 418 K for $\text{lPtBS-382}$.

Composition was verified using $^1$H-NMR, as described in Chapter 5. These spectra are shown in Figure 8.5, compared to PtBS-280 purchased from Polymer Source. All samples showed an approximately 3:1 ratio of aliphatic (0.5-2.5ppm) to aromatic
Figure 8.5. $^1$H-NMR spectra of purchased and synthesized PtBS used in this study: (A) PtBS-280 purchased from Polymer Source, (B) PtBS-381 synthesized by FRP, and (C) PtBS-382 synthesized by FRP. Inset in B shows repeat unit structure of PtBS with areas 1 and 2 pertaining to aliphatic and aromatic protons, respectively. The peaks pertaining to these groups are also labeled, with their integrated values shown at their bases.
(6.0-7.2 ppm) protons, consistent with the molecular structure of PtBS, pictured in the inset of Figure 8.5b. These spectra also indicated successful removal of the tert-butylstyrene (tBS) monomer (appears in the 3.0 to 5.5 ppm range). Residual toluene, appearing at 2.4 ppm, escaped during DSC measurement due to a pinhole in the hermetic lid and did not contribute towards bulk $T_g$. The label content of pyrenebutyl-methacrylate attached to $I_PtBS-382$ was found to be 0.27 mol % by absorbance measurements, following the method described in Chapter 5.

### 8.5.2 Fluorescence Measurements

Unfortunately, difficulties were encountered in measuring the $T_g$ of $I_PtBS-382$ via standard fluorescence techniques. While Ellison et al. were able to match $T_g$(DSC) by fluorescence measurements of PtBS doped with 1,10-bis(1-pyrene)decane (BPD), this was the first attempt to measure PtBS $T_g$ with a covalently labeled fluorescent dye. $T_g$ of $I_PtBS-382$ measured by fluorescence was consistently ~11 K below its $T_g$ onset (418 K) measured by DSC.

Several possible sources of this deviation were studied for their impact on measured $T_g$, including excitation wavelength, and labeled vs. doped samples. Films used for the measurements shown were annealed above bulk $T_g$ for > 24 h, showing no change in $T_g$ with additional annealing. This indicated that residual solvent plasticizer did not cause deviations from bulk $T_g$. Figure 8.6a plots integrated intensity as a function of excitation wavelength. Exciting near a peak in this plot increases the quantum yield of the dye and potentially impacts its sensitivity to $T_g$. Wavelengths at which $T_g$ was measured are indicated by solid circles. Fluorescence intensity-temperature plots for a drop-cast
Figure 8.6. Fluorescence characterization of /PtBS-382 bulk films with different excitation wavelengths. (A) Integrated fluorescence intensity of /PtBS-382 as a function of excitation wavelength. Maxima were found at 328 and 344 nm. Solid markers indicate excitation wavelengths examined for its influence on $T_g$. (B) Integrated fluorescence intensity temperature-dependence of a bulk /PtBS-382 film excited the wavelengths indicated by solid circles in A. The intersection of linear fits to the rubbery and glassy regimes (solid black lines) is $T_g$. All measurements of $T_g$ are within 3 K of 407 K.
PtBS film excited at these wavelengths are shown in Figure 8.6b. All indicated $T_g$ within 3 K of 407 K.

In addition to not being able to measure bulk $T_g$ accurately, we were unable to re-create the dramatic $T_g$ deviation from bulk $T_g$ that was demonstrated by Ellison et al. A 20-nm thick film, previously shown to differ by 50 K from bulk $T_g$, was only seen to exhibit a 7 K depression in $T_g$. Measurements of $T_g$ for a 20-nm-thick film and bulk film of /PtBS-382 are shown in Figure 8.7a. It is possible that this could be a result of reduced confinement effect with annealing (the film was annealed briefly above bulk $T_g$ prior to measurement). However, the extent to which no confinement effect is observed cannot be explained by the minimal annealing undergone, following the changes predicted by Napolitano et al. Figure 8.7b shows that we were able to reproduce measurements of bulk $T_g$ with BPD-doped PtBS-381. However, 20-nm-thick doped films still did not show a 50 K reduction in $T_g$. We note that the PtBS used by Ellison et al. had a lower bulk $T_g$ (403 K) than ours, likely due to its relatively low molecular weight ($M_N = 32$ kg/mol), high dispersity ($D = 3.31$), and proximity to the entanglement molecular weight for PtBS. This could potentially impact observed confinement effects on $T_g$. Average $T_g$ values from these measurements, along with those for /PtBS-382 are compared to a trace of the data of Ellison et al. in Figure 8.7c. This suggested that the problem was in the covalent labeling, rather than sample preparation or instrumental settings. There have been previous reports for adjusting dye chemistry and experimental approaches in specific systems. Either a different dye or a different linkage should be used in future attempts to measure location-specific $T_g$ of PtBS.
Figure 8.7 Comparison of $T_g$ for bulk and confined films of PtBS as measured by fluorescence. Films were excited at 342 nm. (A) $/\text{PtBS-382}$, (B) PtBS-381 doped with BPD. (D) Deviations from bulk $T_g$ compared to those reported in the literature.$^3$
8.6 Conclusions

Adsorbed layers make up a significantly larger fraction of thin films, enabling disproportionate changes in their behavior with annealing. Recent work by Perez-de-Eulate et al. correlated the annealing-induced suppression of PtBS’ dramatic $T_g$ depression upon confinement with the growth of an irreversibly adsorbed layer.\textsuperscript{2} We studied the irreversible adsorption of PtBS in thin films and presented evidence for an acceleration of adsorption kinetics in thinner films resulting from the increase in effective annealing temperature. Temperature dependencies of kinetic parameters were used to determine effective annealing temperatures and corresponding $T_g$ at the substrate. Kinetic differences in films as thick as 200 nm revealed the ability of a free surface to perturb $T_g$ over much larger distances in PtBS than in PS. Relations between adsorption crossover time and $T_{eff}$ enabled a time-temperature shift of $h_{ads}$ for 8-h adsorbed layers isolated from films of various thickness to create a single adsorbed layer growth curve, incorporating three different annealing temperatures. This normalized growth curve can be used to predict the thickness of an adsorbed layer growth in a film for a given film thickness, annealing time, and annealing temperature. The dramatic change in PtBS $T_g$ with confinement magnified the changes in adsorption kinetics with film thickness, but the methodology could be applied to any thin film system to determine what $h_{ads}$ would result from annealing films of a certain thickness at a given annealing time and temperature. This shows enormous potential for creating film annealing procedures to control and/or minimize adsorption impacts on thin film properties. Finally, further optimization of polymer labeling needs to be undertaken before location-specific $T_g$ can be measured in PtBS via fluorescence.
8.7 References


Chapter 9

Conclusions and Future Work

9.1 Dissertation Summary

Irreversible adsorption and its relevance in the processing and use of thin polymer films is gaining attention as increasing evidence of its ability to perturb film properties is published.\textsuperscript{1–4} A thorough understanding of how the growth of irreversibly adsorbed layers and resulting changes in thin film properties proceed with annealing is essential to the efficacy of polymer nanotechnology. With the rapid expansion of polymer chemistries and applications, the ability to predict the impact of processing on film properties should be expanded as broadly as possible. This dissertation used a combination of synthesis and characterization techniques to introduce complexities in terms of film geometry, polymer composition, and confinement to evaluate their impact on adsorption in order to make the connection between film processing and properties in a broader variety of systems.

Chapters 2 – 4 provided background on glassy properties under confinement, fluorescence, and irreversible adsorption. In doing so, they illustrated the need for location-specific characterization of adsorbed layers as well as an extension of the field to more complex systems. Chapter 5 described the primary techniques used to conduct the work presented in this dissertation. It included an evaluation of adsorbed layer preparation procedures, testing the sensitivity of adsorbed layer thickness ($h_{\text{ads}}$) to film casting method, washing time and method, and annealing temperature required for the onset of adsorption.
Chapter 9

In Chapter 6, we examined how a free surface influences the $T_g$ of polystyrene (PS) adsorbed layers by using a fluorescence technique to measure their $T_g$ in both exposed and buried geometries. Adsorbed layer $T_g$ had previously only been measured in a capped geometry, but the sensitivity and location-specificity of fluorescence enabled us to measure the $T_g$ of exposed (i.e., supported) adsorbed layers as a change in the temperature-dependence of fluorescence intensity of incorporated pyrene probes. Adsorbed layers were isolated from films of pyrene-labeled PS after different annealing times ($t_{ads}$). Their thicknesses and $T_g$s were measured and compiled to map the growth in $h_{ads}$ and increase in $T_g$ of the exposed PS adsorbed layer with $t_{ads}$. We found that, for a given $t_{ads}$ or $h_{ads}$, its $T_g$ was substantially lower than that of a capped adsorbed layer but higher than that of supported PS films, showcasing the influence of both the free surface and chain adsorption at the substrate, respectively. \(^5\) In order to separately evaluate these influences, we effectively removed the free surface by covering the labeled adsorbed layers with bulk films of neat PS and briefly annealing to create bilayer films. Submerged 1-h adsorbed layers regained bulk $T_g$, while 6-h adsorbed layer $T_g$ was unchanged when covered. Interpreting the difference in $T_g$ between the exposed and buried adsorbed layer as the influence of the free surface revealed a decreasing influence with $t_{ads}$. The difference became negligible after 6 hours, coinciding with the plateau in adsorbed layer thickness. Bulk $T_g$ was recovered in all adsorbed layers after additional annealing, but recovery time increased with $t_{ads}$ due to increased levels of chain adsorption. Good fits of the data to the Free Volume Holes Diffusion model indicated that the persistent deviations in adsorbed layer $T_g$ at longer $t_{ads}$ could be ascribed to excess free volume trapped by chain packing frustration at the substrate. This study demonstrated how chain
adsorption and the free surface compete to influence the $T_g$ of PS adsorbed layers. In doing so, it showed that the free surface effect—dominant in PS thin film studies—can be reduced with sufficient annealing.

Chapter 7 focused on chain adsorption at the substrate, using a series of homopolymers and random copolymers to study the effects of polymer-substrate interactions and copolymer composition on adsorbed layer growth. PS, poly(methyl methacrylate) (PMMA), and several P(S-r-MMA) copolymers were synthesized via free radical polymerization, and their adsorption behavior was compared. Measurements of $h_{ads}$ via ellipsometry revealed that P(S-r-MMA) did not show intermediate adsorption behavior to PS and PMMA, as seen with thin film $T_g$. This was different than expected, given the correlation between adsorbed layer growth and $T_g$ in PS. Rather, adsorbed layer plateau thickness ($h_p$) was a non-monotonic function of polymer composition, decreasing with increasing compositional heterogeneity. Copolymer kinetics were biased towards those of PMMA, indicating increased interaction strength created a similar kinetic barrier to adsorption. Solvent leaching experiments with hydrogen-bonding solvents provided further insight into polymer-substrate interactions. Comparisons between Hansen diameter ($R_a$, indicating polymer-solvent solubility), MMA mole fraction ($x_{MMA}$, indicating polymer-substrate interaction strength), and $h_{ads}$ suggested that the amount of hydrogen bonds with the substrate influenced desorption more than polymer-solvent solubility, and that polymer-solvent effects do not strongly impact $h_{ads}$ when washing with toluene. Selective desorption of MMA and the proportionality between the number of polymer-substrate adsorption sites and $h_{ads}$, enabled quantification of adsorption ratios between S and MMA contacts and revealed that copolymer interactions with the substrate
reflected their composition. Based on these trends in adsorbed layer growth and desorption, we proposed a mechanism for copolymer adsorption in which the combination of tight adsorption from the MMA component and weak attraction from the S component prevent gains in $h_{ads}$ from loosely bound chains. Increased $h_p$ of copolymers with annealing temperature indicated that a small increase in interaction strength was sufficient to allow more adsorption of loosely-bound chains. The chapter closed with a brief description of our efforts to use copolymer adsorbed layers to create neutral substrates for the alignment of PS-b-PMMA into standing lamellae. This study of copolymer adsorption shed light onto the competing adsorption mechanisms in P(S-r-MMA) and provided insights into how they combine to mitigate copolymer adsorption. It also revealed that interaction strength with the substrate is not sufficient to predict the growth of copolymer adsorbed layers.

Chapter 8 provided a shift from exclusively studying the growth and properties of adsorbed layers to focusing on how adsorption proceeds in confined thin films. We investigated how $h_{ads}$ was impacted by film thickness ($h_{sc}$) in order to better predict adsorbed layer presence and influence within thin films. At constant $t_{ads}$, poly(tert-butylstyrene) (PtBS) showed a marked increase in $h_{ads}$ as film thickness decreased, contrary to PS and PMMA. This behavior was shown to be the manifestation of differences in adsorption kinetics originating from thin films being annealed at higher temperatures relative to their depressed $T_g$. Kinetic analysis was used to determine the effective annealing temperature ($T_{eff}$) for confined PtBS films. This $T_{eff}$, which correlated with film kinetics, reflected deviations from bulk $T_g$ at the substrate. We determined that the free surface was able to influence $T_g$ over distances of ~ 200 nm in PtBS films,
displaying a much stronger effect than in PS.\textsuperscript{6} We also used the relationship between $T_{\text{eff}}$ and kinetics to collapse $h_{\text{ads}}$ measurements for 8-h adsorbed layers created at three different annealing temperatures, onto a single growth curve. This curve provided a means by which $h_{\text{ads}}$ can be predicted in films of any thickness, annealed for any $t_{\text{ads}}$ at any annealing temperature. The acceleration of adsorption in PtBS thin films revealed how $T_g$ under confinement is not only impacted by irreversible adsorption, but also influences the growth of adsorbed layers. Attempts to measure PtBS $T_g$ at the substrate via covalently-labeled PtBS and fluorescence were made. Unfortunately, consistent under-measurement of its bulk $T_g$ indicated that other fluorescence probes or linkages should be employed to obtain location-specific measurements of $T_g$.

By examining the influences of a free surface, compositional heterogeneity, and confinement on the growth and properties of adsorbed layers, this dissertation has furthered the understanding of irreversible adsorption and how it should be accounted for in the production and implementation of polymer thin films. Despite these advances, there is considerable room for further investigation and expansion upon the work of this dissertation. Several research directions with potential to strengthen the connection between irreversible adsorption and the behavior of polymers in confined geometries are discussed in the following section.

9.2 Recommendations for Future Work

9.2.1 $T_g$ Perturbations in Thin Films caused by Irreversible Adsorption

As illustrated in Chapter 8, PtBS is a particularly interesting polymer with which to study irreversible adsorption due to its dramatic confinement behavior and response to annealing. Connections between its confined $T_g$ and dependence of $h_{\text{ads}}$ on film thickness
emphasized the need for location-specific measurements of $T_g$ in PtBS—especially at the substrate. However, covalently labeled polymer is required to conduct these measurements via fluorescence, and pyrenebutyl-methacrylate does not accurately report bulk $T_g$. Synthesizing a labeled PtBS with which $T_g$ can be accurately measured is therefore a top priority. Other dyes that have been used to measure $T_g$ include 4-tricyanovinyl-(N-(2-hydroxyethyl)-N-ethyl)aniline (TC1),\(^7\) pyrenemethyl-methacrylate,\(^8\) and 1,10-bis(1-pyrene)decane (BPD).\(^9\) Once synthesized, labeled PtBS can be used in multilayer films to measure $T_g$ in layers adjacent to the free surface and substrate, similar to the work of Priestley \textit{et al.}\(^7\) These experiments would rapidly provide insight into the interfacial influences contributing to its large $T_g$ reduction under confinement. Determining the film thickness at which substrate-adjacent $T_g$ deviates from bulk would be particularly relevant for studying irreversible adsorption in thin films and would enable confirmation of the substrate-adjacent $T_g$ calculations presented in Chapter 8. Eventually, the $T_g$ of these layers should be measured as a function of annealing time. In doing so, a better understanding of how confined $T_g$ in PtBS influences, and is impacted by, the growth of irreversibly adsorbed layers will be gained.

\textbf{9.2.2 Impacts of Adsorption on Physical Aging}

Chapters 2 and 3 described how physical aging deviates from bulk behavior at the nanoscale and how fluorescence has been used to measure local aging rates in thin films. To our knowledge, there has been no investigation of how irreversible adsorption impacts aging rates in thin films; this is essential to evaluate how annealing can change the long-term performance of thin films. At a given aging temperature ($T_{\text{aging}}$), the rate of aging is influenced by both the distance of $T_{\text{aging}}$ from $T_g$ (determines the thermodynamic driving
force towards equilibrium) and chain mobility (determines the ability of chains to relax). As both $T_g$ and chain mobility have been shown to change with the growth of an irreversibly adsorbed layer, it follows that physical aging rate should similarly be impacted. Additionally, Priestley et al. showed that perturbations in aging rate extend much farther from interfaces than $T_g$—hundreds of nanometers in PMMA films.\textsuperscript{10} This length scale of perturbation implies that annealing films could cause a much larger impact on their aging rate than $T_g$. Measurements of average and location-specific aging rate in films as a function of $t_{ads}$ (prior to aging) would reveal valuable information about how irreversible adsorption could accelerate or slow property changes and densification that accompany structural relaxation.

### 9.2.3 Polymer-Substrate Interactions in Copolymer Adsorption

Chapter 7 used random copolymers with a moderate difference in polymer-substrate interactions, but extending this study to other copolymers presents additional opportunities to probe the role of compositional heterogeneity and polymer-substrate interactions in adsorption. Copolymers with similar polymer-substrate interaction mechanisms (\textit{i.e.}, Van der Waals or hydrogen-bonding interactions) could be used to separate contributions of compositional heterogeneity and differences in interaction strength as retardants in copolymer adsorption. This could be achieved with poly(styrene-
\textit{random}-\textit{a}-methylstyrene) (P(S-\textit{r-}aMS)) or poly(styrene-
\textit{random}-\textit{tert}-butylstyrene) (P(S-\textit{r-tBS}). Copolymers whose components exhibit larger differences interaction strength with the substrate, such as poly(styrene-
\textit{random}-\textit{2-vinilpyridine}) (P(S-\textit{r-2VP}), would provide the opportunity to see if a symmetric decrease in $h_p$ with composition is still present with a larger discrepancy, or if a stronger interacting segment would dominate,
shifting the minimum in $h_p$ to a different molar fraction. As P(S-\(r\)-2VP) $T_g$ confinement has been characterized,\textsuperscript{11} this would enable another comparison between random copolymer adsorption and confinement effects. These studies would determine if adsorption is consistently mitigated by degree of compositional heterogeneity, or to what extent specific copolymer pairings matter.

### 9.2.4 Mechanical Impacts of Adsorption in Nanocomposites

Nanocomposites present a much larger surface-to-volume ratio than thin films, which could serve to magnify their sensitivity to irreversible adsorption. As interparticle spacing is the relevant confinement dimension in nanocomposites, macroscopic samples can still exhibit confined behavior and therefore show effects of irreversible adsorption. Nanocomposites have many potential applications at the macroscale, and are of particular interest for their modified mechanical properties. Mechanical properties have been seen to change in response to confinement in thin films,\textsuperscript{12–15} but irreversible adsorption has not been accounted for in these systems. Nanocomposites also provide the opportunity to compare macroscale samples to location-specific measurements via fluorescence. A combination of macroscale and nanoscale measurements would enable detailed understanding of how irreversible adsorption can alter the properties of nanocomposite materials. As bulk characterization techniques are ubiquitous, and fluorescence has been used to measure $T_g$, physical aging, and mechanical response, this study could be extended to a variety of thermal and mechanical properties.
9.3 References


Appendix A

List of Publications


## List of Polymers Used in this Dissertation

<table>
<thead>
<tr>
<th>Polymer Name</th>
<th>Description</th>
<th>Molar Composition</th>
<th>$M_a$ (kg/mol)</th>
<th>$D$</th>
<th>$T_g$ (bulk) (K)</th>
<th>Source</th>
<th>Chapter(s) Used</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-109</td>
<td>Neat Polystyrene</td>
<td>$x_s=1$</td>
<td>109</td>
<td>1.8</td>
<td>378</td>
<td>Synthesized</td>
<td>5,7,8</td>
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<tr>
<td>PS-116</td>
<td>Neat Polystyrene</td>
<td>$x_s=1$</td>
<td>116</td>
<td>1.9</td>
<td>378</td>
<td>Synthesized</td>
<td>5,6</td>
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<tr>
<td>IPS-155</td>
<td>Pyrene-labeled Polystyrene</td>
<td>$x_s=0.16%$</td>
<td>155</td>
<td>1.9</td>
<td>379</td>
<td>Synthesized</td>
<td>5</td>
</tr>
<tr>
<td>IPS-240</td>
<td>Pyrene-labeled Polystyrene</td>
<td>$x_s=0.16%$</td>
<td>240</td>
<td>1.9</td>
<td>378</td>
<td>Synthesized</td>
<td>5,7,8</td>
</tr>
<tr>
<td>PMMA-119</td>
<td>Poly(methyl methacrylate) homopolymer</td>
<td>$x_s=0.25$</td>
<td>119</td>
<td>2.2</td>
<td>393</td>
<td>Synthesized</td>
<td>7</td>
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<tr>
<td>P(S-r-MMA) (75:25)</td>
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<td>1.7</td>
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<tr>
<td>P(S-r-MMA) (48:52)</td>
<td>Random copolymer of styrene and methyl methacrylate</td>
<td>$x_s=0.48$, $x_{PMMA}=0.52$</td>
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<tr>
<td>P(S-r-MMA) (27:73)</td>
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<td>$x_s=0.27$, $x_{PMMA}=0.73$</td>
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<td>P(S-r-MMA) (88:12)</td>
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<td>$x_s=0.58$, $x_{PMMA}=0.42$</td>
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<td>P(S-r-MMA) (67:33)</td>
<td>Random copolymer of styrene and methyl methacrylate</td>
<td>$x_s=0.67$, $x_{PMMA}=0.33$</td>
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<td>2.0</td>
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<td>Polymer Name</td>
<td>Description</td>
<td>$M_w$ (kg/mol)</td>
<td>$D$</td>
<td>Molar Composition</td>
<td>$T_g$ (bulk) (K)</td>
<td>Source</td>
<td>Chapter(s) Used</td>
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</tr>
<tr>
<td>P(S-(r)-MMA) (69:31)</td>
<td>Random copolymer of styrene and methyl methacrylate</td>
<td>110</td>
<td>1.7</td>
<td>$x_s=0.69$ $x_{MMA}=0.31$</td>
<td>375</td>
<td>Synthesized</td>
<td>7</td>
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<tr>
<td>PS-(b)-PMMA</td>
<td>Symmetric diblock copolymer of styrene and methyl methacrylate</td>
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<td></td>
<td>$x_s=0.49$ $x_{MMA}=0.51$</td>
<td></td>
<td>Polymer Source</td>
<td>7</td>
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<td>$x_{dBs}=1$</td>
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<td>Polymer Source</td>
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<td>381</td>
<td>2.1</td>
<td>$x_{dBs}=1$</td>
<td>419</td>
<td>Synthesized</td>
<td>8</td>
</tr>
<tr>
<td>iPtBS-382</td>
<td>Labeled poly(tert-butylstyrene)</td>
<td>382</td>
<td>2.0</td>
<td>0.27% pyrenebutyl-methacrylate</td>
<td>418</td>
<td>Synthesized</td>
<td>8</td>
</tr>
</tbody>
</table>
Appendix C

Free Volume Holes Diffusion Model Calculations

The Free Volume Holes Diffusion (FVHD) model is utilized in Chapter 6 to interpret how the $T_g$ of exposed and buried irreversibly adsorbed layers evolves with annealing time. A detailed description of calculations used in the model, incorporating data presented in Chapter 6, is provided here.

The temperature-dependent diffusion coefficient, $D(T)$, for free volume holes in bulk PS has been previously reported to follow the relationship

$$D(T) = D_0(VFT) \cdot e^{(-B/T_0)} + D_0(Arr) \cdot e^{(-E/kT)}$$

(C.1a)

where $D_0(VFT) = 302 \text{ cm}^2/\text{s}$, $B = 1000 \text{ K}$, $T_0 = 341 \text{ K}$, $D_0(Arr) = 1.80 \times 10^{15}$ cm$^2$/s, $E = 190 \text{ kJ/mol}$, and $k$ is the Boltzmann constant. Comparing $D(T)$ calculated at the average $T_g$ of long-annealed adsorbed layers (363 K) to that calculated at the average $T_g$ of bulk films (379 K), revealed that $D(T_{g\_ads}) = D(T_{g\_bulk})/343$. It follows from this relationship that $D_{ads}(T_g) = D_{bulk}(T_g)/343$. Therefore, for irreversibly adsorbed layers of polystyrene, as determined by the system studied in Chapter 6,

$$D_{ads}(T) = \frac{1}{343} \cdot \left( D_0(VFT) \cdot e^{(-B/T_0)} + D_0(Arr) \cdot e^{(-E/kT)} \right)$$

(C.1b)

Geometric arguments were used to relate the measured thickness of the irreversibly adsorbed layer to the free interface available as a sink for diffusing free volume. The thickness of the adsorbed nanolayer, is related to its interfacial area:

$$h_{ads} = \frac{2V}{A_{total}}$$

(C.2a)
where $h_{ads}$ is the thickness of the adsorbed nanolayer, $A_{total}$ is the area of both surfaces parallel to the substrate, and $V$ is the volume of the adsorbed layer. An effective thickness $h_{eff}$ is defined that corresponds to the amount of free interface, $A_{free}$:

$$h_{eff} = \frac{2V}{A_{free}} \quad (C.2b)$$

Holding volumes equal and rearranging 2a and 2b gives the relationship:

$$h_{eff} = h_{ads} \cdot \left(\frac{A_{free}}{A_{total}}\right)^{-1} \quad (C.3)$$

Measured values are used for $h_{ads}$, and $A_{free}/A_{total}$ can be calculated employing Equation 6.5 from the text,

$$\frac{A_{free}}{A_{total}} = \left(\frac{A_{free}}{A_{total}}\right)_{max} - a \cdot t_{ann} \quad (6.5)$$

Using the boundary conditions $(A_{free}/A_{total}) = 0.5$ at $t_{ads} = 6$ hours, corresponding to no free interface at the substrate and a complete free interface at the free surface, allows for the definition:

$$a = \frac{1}{6} \left[\left(\frac{A_{free}}{A_{total}}\right)_{max} - 0.5\right] \quad (C.4)$$

Thereby reducing the fitting parameters to one: $(A_{free}/A_{total})_{max}$. For a selected value of $(A_{free}/A_{total})_{max}$ (selection is explained later), $A_{free}/A_{total}$ can then be calculated from Equation 6.5 and input into Equation C.3 with measured $h_{ads}$ value to solve for $h_{eff}$.

After slight modifications to account for bulk behavior,² values of $h_{eff}$ (calculated from measured values of $h_{ads}$ and fitted parameter $(A_{free}/A_{total})_{max}$) were used in Equation 6.4 from Chapter 6:

$$\left(\frac{h_{eff}}{2}\right)^2 = 2D(T_g)q^{-1} \quad (6.4)$$
where $D(T_g)$ is the diffusion coefficient of free volume holes at $T_g$ and $q$ is the cooling rate. In order to determine the $T_g$ corresponding to calculated values of $D(T_g)$, and thus the $T_g$ predicted by the FVHD model, the temperature, $T$, was found to match $D(T_g)$ to $D_{ads}(T)$, calculated in Equation C.1b. Therefore, $T_g$(FVHD) is defined:

$$T_g(FVHD) = \{ T : D(T_g) = D_{ads}(T) \}$$

(C.5)

The equality can be interpreted as $T_g$(FVHD) is the temperature at which free volume holes have effectively diffused out of the film, given the assumed diffusion coefficient for free volume holes in adsorbed layers.

In order to determine a value for $(A_{free}/A_{total})_{max}$, many values of were used to calculate $T_g$(FVHD), which were then compared to $T_g$(fluor). The $(A_{free}/A_{total})_{max}$ value that provided the lowest mean squared error (MSE) was selected, a value of 0.55.

Calculations for buried adsorbed layer $T_g$ followed similar logic as for exposed layer $T_g$. However the fractional free surface as a function of original annealing time for capped films was described by:

$$\frac{A_{free}}{A_{total}} = \left( \frac{A_{free}}{A_{total}} \right)_{min} + b \cdot t_{ann}$$

(C.6)

where $(A_{free}/A_{total})_{min}$ is the amount of free interface at $t_{ads} = 0$, when maximum interpenetration of the top layer (complete coverage of the free surface) is expected. This value was determined by the initial condition of Equation C.4, with only the free interface from the substrate contributing, i.e. $(A_{free}/A_{total})_{min} = 0.05$. Less penetration is expected of the top layer with increased degree of adsorption until $A_{free}/A_{total} = 0.5$ at $t_{ads} = 6$ hours, when there is full coverage at the substrate and no interpenetration of the top bilayer. Using these conditions, $b = 0.075$ h$^{-1}$. Once again, the predicted values shown in the Chapter 6 were determined by defining $T_g$(FVHD) in accordance with Equation C.5.
Appendix C

Once again, the difference in derivation for FVHD model predictions for Figure 6.8a-c lies in the description of the fractional free volume changes with annealing time. This is described by the equation:

\[
\frac{A_{\text{free}}}{A_{\text{total}}} = \left(\frac{A_{\text{free}}}{A_{\text{total}}}\right)_{\text{max}} - c \cdot t_{\text{Bann}}
\]  

(C.7)

Where \(c\) is the rate of filling with bilayer annealing time and \(t_{\text{Bann}}\) is the bilayer annealing time. For each system (4, 6, and 10-hour irreversibly adsorbed layers), \((A_{\text{free}}/A_{\text{total}})_{\text{max}}\) is determined from the value of \((A_{\text{free}}/A_{\text{total}})\) for the corresponding \(t_{\text{ads}}\) in Figure 6.8. The other boundary condition is defined as \(A_{\text{free}}/A_{\text{total}} = 0\) when \(t_{\text{Bann}} = t_{\text{Bann}}^*\), where \(t_{\text{Bann}}^*\) is the \(T_g\)(bulk) recovery time. The determination of \(t_{\text{Bann}}^*\) was described in Chapter 6. Based on the boundary conditions, FVHD model fits to Figures 6.8a-c were established with no additional fitting parameters.

References
