Dynamic studies of nano-confined polymer thin films

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Boston University
DYNAMIC STUDIES OF NANO-CONFINED POLYMER THIN FILMS

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To see a world in a grain of sand, and a heaven in a wild flower.

— William Blake, Auguries of Innocence
To my wife, Xinlei,

and my parents, Jie and Xingguo.
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ABSTRACT

Polymer thin films with the film thickness \((h_0)\) below ~ 100 nm often exhibit physical properties different from the bulk counterparts. In order to make the best use of polymer thin films in applications, it is important to understand the physical origins of these deviations. In this dissertation, I will investigate how different factors influence dynamic properties of polymer thin films upon nano-confinement, including glass transition temperature \((T_g)\), effective viscosity \((\eta_{\text{eff}})\) and self-diffusion coefficient \((D)\).

The first part of this dissertation concerns the impacts of the molecular weight (MW) and tacticity on the \(T_g\)’s of nano-confined polymer films. Previous experiments showed that the \(T_g\) of polymer films could be depressed or increased as \(h_0\) decreases. While these observations are usually attributed to the effects of the interfaces, some experiments suggested that MW’s and tacticities might also play a role. To understand the effects of these factors, the \(T_g\)’s of silica-based poly(α-methyl styrene) (PaMS/SiOx) and poly(methyl methacrylate) (PMMA/SiOx) thin films were studied, and the results suggested that MW’s and tacticities influence \(T_g\) in nontrivial ways.

The second part concerns an effort to resolve the long-standing controversy about the correlation between different dynamics of polymer thin films upon nano-confinement. Firstly, I discuss the experimental results of \(T_g\), \(D\) and \(\eta_{\text{eff}}\) of poly(isobutyl methacrylate)
films supported by silica (PiBMA/SiOx). Both $T_g$ and $D$ were found to be independent of $h_0$, but $\eta_{\text{eff}}$ decreased with decreasing $h_0$. Since both $D$ and $\eta_{\text{eff}}$ describe transport phenomena known to depend on the local friction coefficient or equivalently the local viscosity, it is questionable why $D$ and $\eta_{\text{eff}}$ displayed seemingly inconsistent $h_0$ dependencies. We envisage the different $h_0$ dependencies to be caused by $T_g$, $D$ and $\eta_{\text{eff}}$ being different functions of the local $T_g$’s ($T_{g,i}$) or viscosities ($\eta_i$). By assuming a three-layer model, we were able to account for the experimental data and resolve the inconsistency. By extending the same ideas to the analogous data of silica-based polystyrene films (PS/SiOx), we found a resolution to the inconsistency regarding the effects of nano-confinement on the dynamics of polymer thin films.
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LIST OF ABBREVIATIONS

AFM .......................................................................................... Atomic Force Microscopy

$C_n$ .......................................................................................... Characteristic Ratio

$D$ .................................................................................................. Diffusivity

$M$ ................................................................................................. Mobility

$M_n$ ........................................................................... Number Averaged Molecular Weight

$M_w$ ........................................................................... Weight Averaged Molecular Weight

PiBMA ................................................................. Poly(isobutyl methacrylate)

PMMA ............................................................. Poly(methyl methacrylate)

PS ................................................................. Polystyrene

PSD ............................................................ Power Spectrum Density

PuMS ........................................................ Poly(α-methyl styrene)

$R_g$ .............................................................. Radius of Gyration

$T_g$ .......................................................... Glass Transition Temperature

$\gamma$ .......................................................... Surface Tension

$\eta$ ............................................................. Viscosity

$\eta_{\text{eff}}$ .......................................................... Effective Viscosity

$\zeta$ .......................................................... Friction Coefficient
CHAPTER 1

Introduction

1.1 Motivation for Studying Polymer Thin Films

Polymers are large molecules made by molecularly linking the monomer units. The large resultant molecular weight (MW) renders polymers unique properties such as toughness with light weight and viscoelasticity. In addition, when two or more chemically distinct monomers are used to form the polymer, distinctive and variable properties may be attained. These advantages, together with the relatively low-cost and abundance in variety, have made polymer the material of choice in a myriad of applications. The past several decades have witnessed a rapid growth in the application of polymer nanometer films as technologies are being developed to enable the manufacturing of smaller devices. As the film thickness is decreased, either in order to reduce the consumption of materials or to decrease the feature size of products, polymer thin films often exhibit physical properties different from the bulk counterparts [1-3]. The physical properties influenced by the nano-confinement effect include glass transition temperature ($T_g$) [4-37], self-diffusion coefficient ($D$) [38-43], effective viscosity ($\eta_{eff}$) [44-53], physical aging [54, 55], elastic modulus [56, 57], creep compliance [58], adhesion [59], etc. In order to make the best use of polymer thin films in applications, it is important to understand the physical origins of these deviations. To deepen the understanding, the goal of this work is to investigate how dynamic properties of polymer thin films could be affected by factors upon nano-confinement.
1.2 Outline of the Thesis

The thesis is organized as follows. Chapter 2 is an overview of polymer thin films, with an emphasis on the dynamic properties which deviate from the counterparts in the bulk under nano-confinement. The properties to be discussed include $T_g$, $D$ and $\eta_{\text{eff}}$. Chapter 3 is an overview of the ellipsometry technique used in this thesis work for film thickness and $T_g$ measurements. Chapter 4 is an overview of the atomic force microscopy technique used to measure the surface topography and thereby effective viscosity and equivalently total mobility of polymer thin films. Chapter 5 is an overview of the polymer thin film preparation methods employed. In Chapter 6 the effects of MW on the $T_g$ of poly(α-methyl styrene) (PαMS) films supported by silica are discussed. In Chapter 7 the effects of polymer tacticity on the $T_g$ of poly(methyl methacrylate) (PMMA) films supported by silica are discussed. In Chapter 8 the conflicting confinement effects on the $T_g$, $D$ and $\eta_{\text{eff}}$ of polymer films will be discussed. The discussions will be based on the results found of poly(isobutyl methacrylate) (PiBMA) and polystyrene (PS) thin films supported by silica, and how a three-layer model might provide a resolution to the apparent conflict.
CHAPTER 2
Overview of Polymer Thin Films

2.1 General Properties of Polymers

Polymers are macromolecules made by linking a number of repeating subunits (named “monomer”) through covalent bonds. The number of monomers, or the “degree of polymerization” as it is commonly used, can range from ~ 10 up to ~ 10000 for a typical polymer chain. Controlling the degree of polymerization during the chemical synthesis of a polymer is one of the commonly used methods to manipulate the physical properties of the polymers although other approaches are also common. For example, the molecular formulas of monomers influence the chemical and thereby many physical properties of polymers in countless ways. The chemical structures of polymer macromolecules also have impacts on the physical properties of polymers. The chain conformation can determine or affect the physical properties as well.

The molecular formulas of monomers predominantly determine the chemical properties of polymers and the related physical properties as discussed below. Because monomers are the fundamental building blocks of a polymer macromolecule, the chemical structure of the monomer governs many physical properties of the polymer most directly, including optical and electrical properties, surface tension, and melting point if applicable, etc. When the chemical structures of all the monomers incorporated in a polymer are identical, this polymer comprises only a single species of monomers and is called a homopolymer, e.g., polystyrene (PS), poly (α-methyl styrene) (PαMS),
poly(methyl methacrylate) (PMMA), poly(isobutyl methacrylate) (PiBMA). The corresponding chemical structures of PS, PMMA, PaMS, PiBMA are shown in Fig. 2.1, respectively. On the other hand, polymers containing a mixture of species of monomers are known as copolymer, e.g., PS-b-PMMA, a block copolymer which links PS and PMMA subunits by a covalent bond.

Figure 2.1: Structures of (a) PS, (b) PaMS, (c) PMMA and (d) PiBMA, the polymers utilized in this work.

Separately, how the monomers are arranged in a polymer may affect the architecture and tacticity of the polymer. The number of monomers contained in a polymer determines the MW of a polymer. The manners by which architecture, tacticity and MW of a polymer may affect its properties will be briefly discussed below.

The polymer architecture is the manner how a number of polymer branches are spatially arranged and connected to each other. There are numerous types of polymer architectures, and all the polymers used in this work belong to the simplest architecture – linear polymers. A linear polymer is a long chain formed by monomers. Shortly speaking, different polymers architectures can lead to different physical properties, such as $T_g$, solution viscosity, solubility, etc.

In addition to polymer architecture, experiments also showed that different MWs have significant impacts on the physical properties of polymers. The MW of a polymer is
its molar mass. The MW is typically expressed in two ways, the number averaged molecular weight ($M_n$) and the weight averaged molecular weight ($M_w$). Polydispersity index (PDI), which is numerically equal to the ratio of these two MWs, $M_w/M_n$, measures the distribution of MWs. Mathematically, PDI = 1 + ($\sigma/M_n$)$^2$, where $\sigma$ is the standard deviation of the MW distribution of a polymer specimen. Because numerous properties such as $T_g$ and $\eta_{\text{eff}}$ closely depend on MW, polymers with a narrow MW distribution are preferred in this thesis work. The polydispersity indices of all the polymers used are $\leq$ 1.10.

During the synthesis process of polymers, not only can the MW of a polymer be controlled the tacticity can sometimes be controlled, too. Tacticity defines the relative stereochemistry of adjacent chiral centers in the neighboring subunits within a polymer molecule. There are several different ways to quantify tacticity. A precise way to specify the different possible tacticities found in polymers (namely isotacticity, syndiotacticity and atacticity) is by the introduction of triads, namely sub-units of a polymer consisting of three consecutive monomer units. Figure 2.2 illustrates an isotactic triad (mm), a syndiotactic triad (rr) and a heterotactic triad (rm) for polypropylene. The mass fraction ratio (iso:hetero:syndio) of these three triads is a common quantitative measure of the tacticity of a polymer chain.
Figure 2.2: Three types of triads, isotactic triad (mm), syndiotactic triad (rr) and a heterotactic triad (rm) in a polypropylene molecule.

In addition to the chemical approaches as mentioned before, to manipulate the physical properties of polymers, a physical approach through altering chain conformation could be utilized. The chain conformation of a polymer is often manifested in the size of the polymer in space, which is commonly expressed by the radius of gyration ($R_g$). The $R_g$ of a polymer is defined to be the averaged root-mean-square distance of all the monomers from the center of mass. The size of a linear polymer, $R_g$, is related to the MW in a straight-forward way. In a melt of chemically identical chains, a linear polymer chain has a size

$$ R_g = b \left( \frac{N}{6} \right) = b \left( \frac{M_n}{6M_0} \right), $$  

(2.1)

where $N$ is the number of monomers, $b$ is the statistical segment length that for common polymers can be looked up from a handbook, $M_n$ is the number averaged molecular weight, and $M_0$ is the MW of the monomer. The $R_g$ of a polymer chain when in a solvent is altered by the quality of the solvent, which depends on the particular species of the polymer and solvent used along with the temperature, as described by Flory-Huggins solution theory on the thermodynamics of polymer solutions. Figure 2.3 illustrates how the size of a polymer is relevant to the polymer-solution interaction.
2.2 Dynamic Properties of Polymers

2.2.1. Glass Transition Temperature

Glass transition temperature $T_g$ corresponds to a temperature point when a polymer, on heating, undergoes a transition from an amorphous glassy state to a rubbery state that may subsequently begin to flow given adequate time. The reverse transition, called “vitrification”, is achieved by supercooling the polymer from the rubber state, bypassing crystallization, to the glassy state. During the vitrification, the viscosity of a polymer typically rises up rapidly to $10^{12}$ Pa·s upon past $T_g$. Despite the massive change of viscosity across the $T_g$, the glass transition is distinct from a phase transition [60]. As Fig. 2.4 illustrates, a glass transition is continuous in the first derivative of the volume and enthalpy with respect to temperature, in contrast to a discontinuity (at melting point $T_m$) in the first derivative for a crystallization process. In addition, Fig. 2.4 also shows that, the exact value of $T_g$ of a sample depends on the the cooling rate, namely that $T_g$ appears at a higher (lower) temperature, $T_{gb}$ ($T_{ba}$), for a higher (lower) rate of cooling. Because of this cooling rate dependence of $T_g$, the glass state is not a equilibrated state. In contrast, a
phase transition requires that the phases on either side of a transition must be in thermodynamic equilibrium. Basing on this comparison, the general consensus is that the glass transition involves kinetic effects and therefore is more than a simple phase transition [61].

**Figure 2.4:** $T_g$ can be defined by using the plot of volume (or enthalpy) against temperature. The exact value of $T_g$ depends on the cooling rate, so that there are two different $T_g$ ($T_{ga}$ and $T_{gb}$) acquired at different cooling rates (slower and faster, respectively).

Despite the complicated physical identification of the $T_g$ value mentioned above, glass transitions are easily found among materials. Many different species of materials can exhibit glass transitions, including polymers, colloidal particles, small organic molecules, ionic liquids, inorganic glasses [62], *etc.* The values of $T_g$ vary largely from species to species. In addition to the dependence of $T_g$ on the species of materials, even for the same species of polymers, *e.g.,* PMMA, the values of $T_g$ also depend on the MW.
As an example, when the MW decreases, the bulk $T_g$ of PMMA decreases (Fig. 2.5) [63]. As illustrated in Fig. 2.5, the MW dependence of $T_g$ can be fit to different curves by using different models. To understand the MW dependence of $T_g$, it is common to adapt the concept of free volume: a small fraction of the total volume of the liquid polymer is “free” to be used for molecular motion. When the polymer cools down, the density increases and the free volume decreases, eventually the motions of molecules slow down [62]. By assuming that most polymers have roughly the same free volume at the $T_g$, a lowering of $T_g$ can be predicted for lowering MW by the Fox and Flory model as follows:

$$T_g(M_n) = T_g(\infty) - \frac{C}{M_n}$$  \hspace{1cm} (2.2)
The constant $C$ is on the order of $10^4$-$10^5$ (K·g/mol), so $T_g(M_n)$ approaches to its long-chain limit $T_g(\infty)$ and becomes practically independent of $M_n$ when $M_n > 10^4$-$10^5$ (K·g/mol). In the Fox and Flory model, the $T_g(M_n)$ dependence is explained only in terms of a decrease in polymer free volume as $M_n$ increases, which may be caused by the fractional decrease of polymer chain ends in the sample that carries less free volume. As can be seen from the data of Fig. 2.5, this simple model only works well at relatively high MW ($>10^4$ (g/mol)), and the deviation at low MW ($<10^4$ (g/mol)) between the experimental $T_g$ data and the model line (Curve 1, red) is prominent (Fig 2.5). On the other hand, the Gibbs and DiMarzio model [64, 65] (Curve 3, blue), which also considers the effect of chain stiffness, is able to describe the $T_g$ data over the full range of $M_n$ studied. In the Gibbs and DiMarzio model, chain stiffness affects the $T_g$ through the flex energy, $\varepsilon$, namely the energy required to flex a chain segment on the main chain from the lowest energy orientation to a higher energy one [64, 65]. More specifically, it affects the $T_g$ through its influence on the relative probability a chain segment would adopt a higher energy orientation, which is proportional to the Boltzmann factor, $\exp[-\varepsilon/k_B T]$, where $k_B$ is Boltzmann's constant and $T$ is absolute temperature [64, 65]. When this probability is low enough (which occurs when either the temperature $T$ is low or flex energy $\varepsilon$ is high), the chain segments may become unable to explore all the available conformations, resulting in zero average configurational entropy and hence kinetic arrest as seen in the glass transition. On the basis of the Gibbs and DiMarzio model, the experimental $T_g$ data of PMMA in Fig. 2.5 can be interpreted as follows: At low $M_n$, the $T_g$ generally decreases due to availability of more free volume; Nevertheless, at low
enough temperatures, chain stiffness can adversely affect the probability of a chain adopting conformations different from that with the lowest energy. As a result, polymers with stiffer chains may attain zero configurational entropy (which is the criterion for the glass transition in the Gibbs and DiMarzio model) relatively independently of the free volume content, making the $T_g$ less dependent on $M_n$ than otherwise.

2.2.2 Diffusivity

The diffusive and random motion of a spherical particle of radius $R$ in a viscous liquid has been well investigated by scientists and some of the important relations discovered will be discussed as follows. By assuming each particle in the liquid experiencing the random collisions of the surrounding molecules and the viscous dissipation leading to a frictional force $\vec{f} = \zeta \vec{v}$, which is proportional to the velocity $\vec{v}$ with the friction coefficient $\zeta$ [62], the diffusivity (or diffusion coefficient) $D$ and the friction coefficient $\zeta$ are related through the Einstein relation:

$$D = \frac{k_B T}{\zeta}. \quad (2.3)$$

On the basis of Eq. (2.3), the time scale $\tau$ required for the particle to move a distance equal to its radius $R$ is given by

$$\tau \approx \frac{R^2}{D} \approx \frac{R^2 \zeta}{k_B T}. \quad (2.4)$$

Separately, the friction coefficient $\zeta$ can be further related to viscosity $\eta$ as given by Stokes law
\[ \zeta = 6\pi \eta R. \quad (2.5) \]

Combining Einstein relation (Eq. (2.3)) with Stokes law (Eq. (2.5)), the Stokes-Einstein relation is then found:

\[ D = \frac{k_B T}{6\pi \eta R}. \quad (2.6) \]

These important relations had been discovered before the development of polymer physics, but they reappeared in the same or similar formats when models for describing polymer dynamics were developed.

The simplest model to describe polymer dynamics is the Rouse Model. Rouse Model describes the dynamics of an ideal polymer chain consisting of \( N \) monomers in an unentangled melt, on condition that \( N \) is small so that \( M_n \) is smaller than \( M_e \), the MW for entanglement [62]. In the Rouse Model, each polymer chain is represented by \( N \) beads connected by springs, and each bead is only subjected to a random thermal force (Brownian force) and a frictional force (intramolecular force) with friction coefficient \( \zeta \) [62]. The total friction coefficient of the whole Rouse chain, \( \zeta_R \), is the sum of the contributions from \( N \) beads [62]:

\[ \zeta_R = N\zeta. \quad (2.7) \]

On the basis of Einstein relation (Eq. (2.3)), the corresponding diffusivity of the Rouse chain \( D_R \) is obtained [62]:

\[ D_R = \frac{k_B T}{N\zeta}. \quad (2.8) \]
By substituting the expression of $D_R$ from Eq. (2.8) into Eq. (2.4), the Rouse time $\tau_R$, which is the time required for a Rouse chain to diffuse a distance of the order of its size, is given by [62]

$$\tau_R \approx \frac{R^2}{D_R} = \frac{\zeta NR^2}{k_B T}. \quad (2.9)$$

The Rouse time $\tau_R$ is a significant parameter for describing polymer dynamics. We will revisit this expression of Rouse time $\tau_R$ in the following section about the viscosity of polymer chains.

### 2.2.3 Viscosity

In the Rouse Model, given that each chain is represented by $N$ beads connected by springs, there are in total $N$ modes associated with the chain’s motion, and the expression of the relaxation time $\tau_p$ associated with the $p$-th mode is given by [62]

$$\tau_p = \tau_0 \left( \frac{N}{p} \right)^2, \quad p = 1, 2, \ldots, N. \quad (2.10)$$

where $\tau_0$, called Kuhn monomer relaxation time, is given by [62]

$$\tau_0 \approx \frac{\zeta b^2}{k_B T}. \quad (2.11)$$

where $b$ is the Kuhn monomer length, and $\zeta$ is the monomer friction coefficient. As indicated by Eq. (2.10), each mode is associated to a relaxation time $\tau_p$, and the longest relaxation time ($p = 1$) is the Rouse time $\tau_R \approx \frac{\zeta NR^2}{k_B T}$ as defined previously in Eq. (2.9).

The Rouse time is the relaxation time over which the entire chain will diffuse a distance
equal to its size [62]. In addition, on time scales shorter than the Rouse time, the chain exhibits viscoelastic modes and contributes to the elastic modulus; on time scales longer than the Rouse time, the chain motion is simply diffusive [62]. By considering the situation after time \( t (\tau_0 < t < \tau_R) \), each of the modes contributes energy on the scale of \( k_B T \) to the elastic modulus \( \mu(t) \), which is given by [62]:

\[
\mu(t) \approx \frac{k_B T}{b^3} \left( \frac{t}{\tau_0} \right)^{1/2} \quad \text{for } \tau_0 < t < \tau_R.
\]  

(2.12)

The viscosity \( \eta \) can be obtained by integrating the elastic modulus \( \mu(t) \) over time \( t \) [62]:

\[
\eta = \int_0^\infty \mu(t) dt
\]

(2.13)

By substituting the expression of \( \mu(t) \) from Eq. (2.12) into Eq. (2.13), the Rouse viscosity is given by [62]

\[
\eta_R \approx \frac{\zeta}{b} N \propto M_n
\]

(2.14)

It should be mentioned that this linear relationship between viscosity \( \eta \) and \( M_n \), as shown in equation (2.13), is only valid for short polymer chains in an unentangled melt with relatively low \( M_n \) \((M_n < M_e)\). In the case of long polymer chains, the chain motion is topologically constrained by entanglements with nearby chains, under the condition that \( M_n \) is considerably larger than \( M_e \), the MW for entanglement. The entanglements restrict the polymer chain to a tube (Fig. 2.6), the center of which defines the primitive path of the chain. While small portions of the chain can fluctuate around the primitive path, the entire chain moves along the cube with snake-like motion.
The dynamics of this long chain along the confining tube can be expressed by the Reptation Model raised by de Gennes. In the Reptation Model, the chain can move along the tube by diffusion of small loops in the chain. The corresponding diffusivity, which is also called curvilinear diffusion coefficient and denoted by $D_c$ here, is simply the Rouse diffusion coefficient given by Eq. (2.8):

$$D_c = \frac{k_b T}{N \zeta}.$$  \hfill (2.15)

The relaxation time it takes for this chain to diffuse over the contour length of the primitive path $\langle L \rangle$, is the reptation time $\tau_{\text{rep}}$, as given by:

$$\tau_{\text{rep}} \approx \frac{\langle L \rangle^2}{D_c},$$  \hfill (2.16)

$$\langle L \rangle \approx \frac{b N}{\sqrt{N_e}}.$$  \hfill (2.17)
where $N_e$ is the number of Kuhn monomers per entanglement. By substituting Eq. (2.17) into Eq. (2.16), the reptation time $\tau_{\text{rep}}$ is given by

$$\tau_{\text{rep}} \approx \frac{b^2 N_e}{k_B T} \left( \frac{N}{N_e} \right)^3$$

(2.18)

In entangled polymer systems, the Reptation Model further predicts the important relation between viscosity $\eta$, diffusivity $D$, and $M_n$ as follows:

$$\eta \propto M_n^3,$$  

(2.19)

$$D \propto M_n^{-2}.$$  

(2.20)

This relation $\eta \propto M_n^3$ ($D \propto M_n^{-2}$) is a reasonable approximation of the actual observed relationship through experiments, $\eta \propto M_n^{3.4}$ ($D \propto M_n^{-2.3}$).

It should be also emphasized here that entangled polymers should be treated as a viscoelastic liquid, which has an almost constant modulus $\mu(t)$ over a wide range of time (or frequency) during a stress relaxation experiment. In contrast, unentangled polymers, which has a $\mu(t)$ with short-time decay (Eq. (2.12)), can be treated as a viscous liquid. Because there are prominent differences in the dynamics between unentangled and entangled polymers, a detailed discussion about the dynamics of unentangled and entangled polymer thin films is given in Chapter 4.3.

### 2.3 Deviations in Nano-confined Polymer Films

As the film thickness decreases, the polymer system may eventually reach a situation where the polymer chains can no longer maintain their most entropically favorable conformation as they do in the bulk state. Specifically, the chains will be confined in one
dimension when the film thickness becomes comparable to or less than the size, $R_g$, of the chain. This nano-confinement may influence physical properties of polymer thin films, including the $T_g$ [4-37], $D$ [38-43], $\eta_{\text{eff}}$ [44-53], etc. In addition, as the film thickness $h_0$ decreases, an increase of the interfacial-area-to-volume ratio may lead to enlarged effects on the measured properties from interfaces.

### 2.3.1 Glass Transition Temperature

Since Jackson and McKenna [66] discovered that the glass transition temperature, $T_g$, of o-terphenyl and benzyl alcohol, upon confinement in nano-porous glasses, can be visibly different from the bulk $T_g$, many other glass-formers [67, 68], notably polymeric thin films [69-92] had been found to exhibit similar and related phenomena. The first systematic measurements of $T_g$ for supported polymer thin films were performed in the early 1990’s by Keddie and coworkers on PS films [6, 7]. As shown in Fig 2.7, the $T_g$ of PS films supported by the native oxide of silicon is depressed as the film thickness $h_0$ decreases, and the $T_g(h_0)$ of PS appears to be independent of MW, with $M_w$ ranging from 120 to 2900 kg/mol [6, 7]. The thickness dependence $T_g(h_0)$ can be fit to an empirical equation of the form:

$$
T_g(h_0) = T_g(\infty) \left[ 1 - \left( \frac{A}{h_0} \right)^\delta \right]
$$

(2.21)

where $T_g(\infty) = 373.8$ K, the characteristic ratio $A = 3.2$ nm, and the exponential $\delta = 1.8$ for PS [7].
Figure 2.7: $T_g$ depression for thin PS films supported on the native oxide of silicon with $M_w = 120$ (○), 501 (◇), and 2900 kg/mol (△). Adapted from Reference [7].

If the observed $T_g$ reduction was a direct consequence of the conformation of the polymer chains upon confinement, then the onset of this $T_g$ reduction should be correlated to the typical size, $R_g$, of the polymer. Basing on their observation that the $T_g(h_0)$ (or more precisely, $T_g(h_0)/T_g(\infty)$) of PS films is independent of MW and $R_g$ ($M_n = 120$ to 3,000 kg/mol, and $R_g = 9.5$ to 46 nm), Keddie et al. concluded that the conformation of the polymer chains does not influence the $T_g$ reduction in any significant ways [6, 7]. Subsequent studies [93, 94] extending the measurement to PS films with lower MWs below the entanglement MW ($M_e \sim 17$ kg/mol for PS [95]) still found that the $T_g(h_0)/T_g(\infty)$ was independent of the MW. Because of these results, it had been perceived for some time that $T_g(h_0)/T_g(\infty)$ might not depend on MW.
Besides the ineffective influence to $T_g$ from the physical conformation of the polymer chains, the larger contribution from interfaces appears to be the dominant factor in the behavior of $T_g$. To explain the $T_g$ results of supported PS films, Keddie et al. proposed that variations in the $T_g(h_0)$ of polymer films might be caused by interfacial effects, and the $T_g$ depression of PS was attributed to enhanced mobility of chains near the free interface [6, 7]. This suggestion has found good consistency with many later experiments and thus been well adopted. For example, experiments measuring free standing PS films, where there was no supporting substrate and two free interfaces, showed that the $T_g$ is reduced more significantly than that for supported films where there was only one free interface [96, 97]. In addition, the thickness dependence of $T_g$ can be eliminated by capping the PS films and reduce the number of free interfaces [98, 99]. In all, these experimental results imply that the free interface makes the major contribution to the $T_g$ reduction in PS films.

While the effect of the free surface is important, the effect from the interface with the substrate could sometimes dominate. Keddie et al. [7] also found that the $T_g$ of polymer thin films under nano-confinement could be enlarged as the film thickness $h_0$ decreases, e.g., PMMA films supported by silicon covered with a native oxide layer. The $T_g$ enlargement was attributed to the strong hydrogen bonding between PMMA and the substrate, resulting in a low mobility of chain and a dominantly enlarged $T_g$ near the substrate surface.

As discussed above, the observations of $T_g$ confinement effect are usually attributed to the effects of the interfaces. However, some experiments suggested that
other factors, such as the MW and tacticity of polymers, might also play a role contributing to the deviation of $T_g$ from the bulk value. More recently, the Vogt group [100] found that the $T_g$ of atactic PMMA (a-PMMA) films supported by silica with number-average MWs, $M_n$, between 31.7 and 46 kg/mol could change from being enlarged to depressed if the polydispersity index of the polymer was increased sufficiently to include oligomers in the films. A subsequent experiment of Lan and Torkelson [101] found that for a-PMMA (and also poly(1-ethyl cyclopentyl methacrylate)) supported by silica with narrower MW distributions, the $T_g$ of the films with $M_n > 180$ kg/mol were enlarged - consistent with the original result of Grohens et al. [73] - but the $T_g$ of the films with $M_n < 4.5$ kg/mol were depressed - consistent with the aforementioned result of the Vogt group. To understand the effects of these emerging factors on $T_g$, including MW and tacticity, the thin film $T_g$ of PαMS and PMMA supported by silica were studied and the results will be discussed in Chapter 6 and 7.

### 2.3.2 Diffusivity

Since the $T_g$ measurements suggested that the mobility of polymer chains may be perturbed near interfaces, more direct measurements of probing polymer chain mobility through monitoring the diffusion process of polymers with fluorescent or isotopic labels were carried out by using various techniques, such as fluorescence recovery after patterned photobleaching (FRAPP) [102], secondary ion mass spectrometry [103], etc. On the basis of the experimental results, it turned out that $D$’s in silica-supported entangled PS thin films were reduced in both the in-plane (Fig. 2.8(a)) and out-of-plane
(Fig. 2.8(b)) directions by different factors [102, 103], consistent with simulation results [104, 105].

Figure 2.8: (a) In-plane (parallel to the interfaces) $D$ of entangled PS ($M_w = 38$ kg/mol) was reduced from the bulk $D$ when $h_0$ is smaller than $\sim 150$ nm ($\approx 50 R_g$). Adapted from Reference [102]. (b) Out-of-plane (vertical to the interfaces) $D$ of deuterated PS ($M_w = 90$ kg/mol) was reduced from the bulk $D$ when $h_0$ is smaller than $\sim 200$ nm ($\approx 25 R_g$). Adapted from Reference [103].

In addition to the thickness dependence of $D$, studies about the MW dependence of $D$ were carried out. Firstly, for the entangled polymer in a bulk state, the Reptation Model predicts that $D$ is scaled as $M_n^{-2}$ (Eq. (2.20)). Later refinements (e.g., tube length fluctuations) [62] revised the scaling to $D \sim M_n^{-2.3}$, which agrees better with experiment [106]. Secondly, the diffusion measurement of entangled PS films supported by native oxides of silicon showed that the MW dependence of $D$ deviates from that of bulk polymer ($D \sim M_n^{-2.3}$) in the vicinity of interfaces. For instance, within a distance of $\sim 4R_g$ from the air/polymer interface, the out-of-plane $D$ was found to scale as $M_n^{-2.5}$ [41]. On the other hand, near the polymer/substrate interface, the out-of-plane $D$ was found to
dramatically slow down and scaled as $M_n^{-1.5}$ within a distance up to $10R_g$ [103]. Basing on the results about the MW dependence of $D$ at different depths of the film, we can summarize that, influences from different interfaces lead to heterogeneity in polymer thin films, and the mobility of polymer chains in the vicinity of an interface could be quite different from the counterpart in the bulk. In the following section, finding of a similar heterogeneity in the mobility of polymer thin films will be discussed through the study of effective viscosity in polymer thin films.

2.3.3 Effective Viscosity

By way of dewetting experiments of PS thin films on glass slides, Reiter predicted that the viscosity of PS thin films should decrease from the bulk viscosity as the film thickness $h_0$ decreases, by directly relating the polymer viscosity to the dewetting velocity observed [107]. After that, more comprehensive viscosity studies of PS thin films supported by silica with a wide range of MW (from 2.4 to 2,300 kg/mol) were carried out by our group. The results are briefly summarized as follows.

In an experiment performed by former group members, unentangled PS thin films supported by silica with $M_w = 2.4$ kg/mol and thickness $h_0$ varying from 2.3 nm to 79 nm were systematically studied for the effective viscosity $\eta_{\text{eff}}$ versus temperature $T$. The result, $\eta_{\text{eff}}(h_0, T)$, is shown in Fig. 2.9(a) as a function of $T$ [45]. For analysis purposes in the thickness and temperature dependencies of $\eta_{\text{eff}}(h_0, T)$, the separate variables $h_0$ and $T$ in the function $\eta_{\text{eff}}(h_0, T)$ are set to certain values in turn, so that we can examine $\eta_{\text{eff}}(h_0)$ at a certain $T$ and $\eta_{\text{eff}}(T)$ at a certain $h_0$. 
First, one observes that at any given temperature $T$, the $\eta_{\text{eff}}$ of the films with thickness below $\sim$50 nm decreases with decreasing film thickness $h_0$ [45]. It is found in more recent studies by our group that the $\eta_{\text{eff}}$ reduction discovered therein is not limited to a low MW, but rather also found in higher MW’s up to 2,300 kg/mol [45, 48].

![Figure 2.9: (a) Effective viscosity $\eta_{\text{eff}}$ versus temperature $T$ with varying thickness $h_0$ for silica supported PS thin films with $M_w = 2.4$ kg/mol. The solid lines are the best fits to the VFT relation (Eq. (2.22)). (b) Kauzmann temperature $T_K$ from a fit of $\eta_{\text{eff}}$ to the VFT function. Adapted from [45].](image)

In addition to the thickness dependence of $\eta_{\text{eff}}$, the temperature dependence of $\eta_{\text{eff}}$ is also of interest. As illustrated in Fig. 2.9 (a), the temperature dependence of the $\eta_{\text{eff}}$ data at any given thickness $h_0$ could be described by the Vogel-Fulcher-Tammann (VFT) relation:

$$\eta(T) = \eta(\infty) \exp\left(\frac{B}{T - T_K}\right), \quad (2.22)$$

where the Kauzmann temperature, $T_K$, is the temperature at which the viscosity $\eta(T)$ approaches infinity, and $B$ is a constant. For PS, $T_K \approx T_g - 50K$ and $B = 1620 K$ [108].
Shown in Fig. 2.9(b) is the thickness dependence of $T_K$ found by fitting each group of $\eta_{\text{eff}}(T)$ in Fig. 2.9(a) to the VFT function [45]. Similarity found between the thickness dependence of $T_K$ and that of $T_g$ suggests a probable correlation between the discovered thickness-dependent depression of $\eta_{\text{eff}}$ and $T_g$ in PS thin films at $M_w = 2.4$ kg/mol (but this correlation turned out to be non-universal at high MW as discussed below) [45].

A more detailed analysis reveals that the viscosity data $\eta_{\text{eff}}(h_0, T)$ can be understood in a new light by considering the films to be a bilayer (Eq. (2.23)), consisting of a bulk-like layer at the bottom and a more mobile layer at the free surface [45]. Applying the no-slip condition at the substrate and layer interfaces, one finds the following expression for the total mobility, $M_{\text{tot}}$, of the bilayer films:

$$M_{\text{tot}} \approx \frac{h_0^3}{3\eta_{\text{bulk}}} + M_{\text{mobile}} \quad (2.23a)$$

and defining

$$\eta_{\text{eff}} \equiv \frac{h_0^3}{3M_{\text{tot}}} \quad (2.23b)$$

where $\eta_{\text{bulk}}$ represents the bulk viscosity, and the factors $\frac{h_0^3}{3\eta_{\text{bulk}}}$ and $M_{\text{mobile}}$ represent the contributions from the bulk-like bottom layer and the top mobile layer, respectively. Such a two-layer model is able to describe all of the $\eta_{\text{eff}}(h_0, T)$ data well [45]. Further analysis of the model fit result reveals that the thickness of the surface layer is no more than 2.3 nm.

A follow-up study of the $\eta_{\text{eff}}$ of PS films supported by silica (PS/SiOx) with a higher MW of 212 kg/mol [53] showed that the $\eta_{\text{eff}}$ also decreased with decreasing $h_0$ and the data could be fit to the two-layer model (Eq. (2.23)). However, the $T_K(h_0)$ dependence
obtained by fitting the $\eta_{\text{eff}}(T)$ data of different thickness disagreed with the $T_g(h_0)$ measurement found of the films.

In a later follow-up study, the $\eta_{\text{eff}}$ of PS/SiO$_x$ with a broad range of MW from 13.7 kg/mol (unentangled) to 2,300 kg/mol (entangled) was examined for $h_0 = 3$ to 20 nm and a fixed temperature of 120$^\circ$C. Detailed analysis of the data (shown in Fig. 2.10) revealed that the flow dynamics of the thin films with MW < $\sim$100 kg/mol was dominated by the surface mobility, but for the high-MW films (MW > $\sim$100 kg/mol) slippage at the substrate interface dominated. Moreover, the interfacial slippage was instigated by enhanced mobility at the free surface. In accordance, a new model was established to explain the $\eta_{\text{eff}}$ data. In contrast to the two-layer model (Eq. (2.23)), this new model (Eq. (2.24)) embracing both enhanced surface mobility and surface-promoted interfacial slippage was able to describe the thickness dependence of $\eta_{\text{eff}}$ data of PS/SiO$_x$ in the full range of MW studied [48]:

$$ M_{\text{tot}} \approx \frac{h_0^3}{3\eta_{\text{bulk}}} + M_{\text{mobile}} + \frac{h_0^2}{\xi} $$

(2.24)

where the third added term on the RHS accounts for slippage [48]. The parameter $\xi$ is the polymer-substrate friction coefficient and found to decrease with decreasing film thickness $h_0$ according to:

$$ \xi^{-1} = \xi_{\infty}^{-1}(1 + \alpha r) $$

(2.25)

where $r = \frac{M_{\text{mobile}}}{(h_0^3 / 3\eta_{\text{bulk}})}$ and $\alpha$ is a constant of the order unity [48].
Figure 2.10: MW dependence of $\eta_{\text{eff}}$ from PS/SiOx at 120°C, with varying film thickness from 3 to 20 nm, in contrast to the MW dependence of $\eta_{\text{bulk}}$. The dashed line denotes the bulk viscosity $\eta_{\text{bulk}}$. The dotted lines are fits to the two-layer model (Eq. (2.23)). The solid lines are fits to the model embracing both enhanced surface mobility and surface promoted interfacial slippage (Eq. (2.24)). Adapted from [48].
CHAPTER 3
Experimental Technique: Ellipsometry

3.1 Ellipsometry Setup

Ellipsometry is an optical technique for investigating the dielectric properties of thin films by polarized light. The basic setup of ellipsometry currently used is illustrated in Fig. 3.1. The working principle of ellipsometry can be described as follows: A light beam is firstly emitted from a light source. The light beam is then sent through a monochromator and a polarizer and then becomes polarized. After that, the polarized light is incident on the sample surface at an angle of incidence $\Phi$ and reflected from the surface. Because the polarization of the incident light changes during the interaction between the sample of interest and the light, the reflected light has a different polarization.

![Figure 3.1: Illustration of the setup of ellipsometry.](image)
from the incident light (Fig. 3.2). The reflected light then passes through another polarizer (the analyzer), and finally is focused onto the detector to generate a signal. In fact, the ellipsometer shown in Fig. 3.1 has been improved by incorporating compensators, which can delay the phase of one polarization axis with respect to another.

![Figure 3.2: Orientations of s- and p-polarization in an ellipsometric coordinate system. The polarization of the incident light changes during the interaction between the sample and the light, the reflected light has a different polarization from the incident light.](image)

By combining a rotatable compensator and a rotatable polarizer, elliptical polarization is attained by the incident beam in the ellipsometer, allowing one to measure the change in polarization with extreme accuracy by ellipsometry. The change in polarization is related to two quantities called the “ellipsometric angles”, namely the amplitude ratio $\Psi$ and the phase difference $\Delta$. Other fundamental physical properties can be modeled and extracted
from fitting the data of ellipsometric angles, $\Psi$ and $\Delta$, such as the film thickness and refractive index of thin films. For film thickness measurement, the resolution of ellipsometry is sub-nanometer, well below the diffraction limit of light, because ellipsometry exploits the phase information from the polarization change. In addition to its capability of precisely measuring polarization change, ellipsometry is an extremely surface sensitive technique. Therefore it is often utilized to determine structural information of multilayered samples, as well as the quality of interface between two materials. In all, ellipsometry is such a robust technique that it is widely used to measure material properties such as film thickness, composition, roughness, doping concentration, electrical conductivity, etc.

3.2 Ellipsometric Measurement and Analysis

As explained in the previous section, ellipsometry directly measures the change in polarization. In this section, we will explain how the ellipsometric angles, $\Psi$ and $\Delta$, are related to the polarization change, and how other physical properties are determined from $\Psi$ and $\Delta$ in general.

For an ellipsometric measurement, the polarization state of the light incident upon the sample can be decomposed into an s- and a p- component, where the s- component is perpendicular to the plane of incidence and parallel to the sample surface, and the p-component is parallel to the plane of incidence (Fig. 3.2). The Fresnel reflection
coefficients \( r_s \) and \( r_p \) (both are complex quantities), are defined to be the ratios of reflected to incident amplitudes of the s- and p- components, respectively. Ellipsometry measures the complex reflectance ratio, \( \rho \) (a complex quantity), which is the ratio of \( r_p \) over \( r_s \) and defined as follows:

\[
\rho = \frac{r_p}{r_s} = \tan(\Psi)e^{i\Delta} \tag{3.1}
\]

where \( \tan(\Psi) \) is the amplitude ratio of p- and s- components upon reflection, and \( \Delta \) is the phase shift upon reflection. Since ellipsometry is measuring the ratio of two values: \( r_p \) and \( r_s \) (rather than the absolute value of either), ellipsometric measurements can have high accuracy, with the resolution well below the diffraction limit.

After the data acquisition of \( \Psi \) and \( \Delta \), model analysis and fitting must be performed to extract other physical properties, because ellipsometry is an indirect method and the measured \( \Psi \) and \( \Delta \) cannot be converted directly into the dielectric constants of the sample. In most of the cases, to solve for unknown physical properties, a layer model must be assumed, which considers the dielectric function tensors and thickness parameters of all layers of the sample including the correct layer sequence. Using an iterative procedure (least-squares minimization), unknown dielectric constants and thickness parameters are varied, and the corresponding \( \Psi \) and \( \Delta \) values are calculated using the Fresnel equations. The calculated \( \Psi \) and \( \Delta \) values which match the experimental data best provide the dielectric constants and thickness parameters of the sample as a final solution.
For the $T_g$ measurement of polymer thin films, we employ a single-wavelength ellipsometer with a monochromatic laser source. In Chapter 3.3, we will show how the $T_g$ can be determined directly from the ellipsometric angles of $\Psi$ and/or $\Delta$ with very few assumptions. However, in order to determine the film thickness we need to impose additional assumptions about some dielectric functions, because the experimental output is restricted to one set of $\Psi$ and $\Delta$ values per measurement. On the other hand, a more robust setup, namely spectroscopic ellipsometry, can output more than one set of $\Psi$ and $\Delta$ values per measurement by performed ellipsometric measurement in a wide spectral range. By employing the spectroscopic ellipsometry, a complex dielectric function tensor in the corresponding spectral region can be obtained, which gives an access to a large number of fundamental physical properties. For instance, infrared spectroscopic ellipsometry can probe electronic, phonon and plasmon properties, which is, however, out of the scope of this thesis.

3.3 Determination of Glass Transition Temperature

In the work presented here, the $T_g$ measurement is conducted using a single-wavelength Stokes ellipsometer by Gaertner Scientific Corporation. This is a four-detector photopolarimeter ellipsometer with a fixed angle of incidence of 70 °C and a HeNe laser source at $\lambda = 633$ nm. A home-made sample stage equipped with a Peltier element connected to a temperature controller is used to control the sample temperature. In the $T_g$ measurement, the ellipsometric angles, $\Delta$ and $\Psi$, are measured as the sample temperature, $T$, is ramped down at a rate = 2 °C/min (Fig. 3.3(a)) [37]. At the glass transition, the
thermal expansion coefficient of the film changes abruptly. Assuming the ellipsometric angles to be proportional to the film thickness (which is expected to hold since the film thickness change should be only a few % given the typical thermal expansivity of polymer films to be of the order of $\sim 10^{-4}$ °C$^{-1}$ [71, 78]), the $T_g$ can be determined by plotting the first derivative of $\Delta$ or $\Psi$ versus $T$, then fitting the resulting curve to separate straight lines in the glassy and liquid states and identifying the mid-point of the transition region to be the $T_g$ (Fig. 3.3(b)) [37]. Figure 3.3 illustrates this $T_g$ measurement scheme on two different kinds of silica-supported PMMA samples, both with thicknesses of $\sim 30$ nm. We limited our study to films with thickness $\geq \sim 20$ nm as we found that the $T_g$ measurement became unreliable below this thickness [37].

**Figure 3.3:** (a) Two representative plots of ellipsometric angles, $\Delta$ and $\Psi$, as a function of temperature $T$. The data were taken from an a-PMMA2.5K/SiOx single-layer (gray) and an a-PMMA2.5K/s-PMMA2.5K/SiOx bi-layer film (black), with thicknesses of $\sim 30$ nm. (b) Illustration of how the $T_g$ of a film is determined in this experiment from the first derivative of an ellipsometric angle. The displayed data were based on the $\Delta(T)$ measurements shown in panel (a). In both panels, the data were shifted vertically for clarity. Adapted from Reference [37].
To calibrate the temperature $T$ of our measurement setup, small pieces of Gallium (melting temperature, $T_m = 29.7 \, ^\circ C$) and Indium ($T_m = 159.6 \, ^\circ C$) were placed on a silicon substrate, which was then put on top of the sample stage [109]. We observed when these specimens began to melt under an optical microscope as the set-point temperature was slowly increased past the melting points. This permitted us to relate the sample temperature with the set-point temperature at the two melting temperatures [109]. To decide how to interpolate between and extrapolate from these points, we undertook a second calibration procedure by attaching a thermocouple to the top of the sample stage with thermal grease. We found that the calibrations obtained by the two methods agreed within $0.7 \, ^\circ C$. Moreover, the sample temperature varied linearly with the set-point temperature throughout the temperature range examined [109].
CHAPTER 4

Experimental Technique: Atomic Force Microscopy

4.1 Atomic Force Microscopy Setup

Atomic Force Microscopy (AFM) is a scanning probe microscopy with the resolution on the order of fractions of a nanometer. AFM is widely used for applications with different purposes. Firstly, it is utilized to perform force measurement, namely measuring the force between the probe and the sample, as the separation in between varies. Secondly, the forces between the probe and the sample are used to manipulate the sample, such as scanning probe lithography and dip pen lithography. Thirdly, AFM is used for imaging, particularly surface topography, by monitoring the forces between the probe and the sample while the probe is scanned through different locations on the surface. Some other properties of the sample, which include mechanical and electric properties, can be measured simultaneously with the acquisition of surface topography imaging.

To image a sample, the AFM is commonly operated in two different imaging modes, contact and tapping modes. When the contact mode is used, the probe is brought into contact with the sample surface and scanned along an x-y grid. During the scanning process under contact mode, the z-position of the probe is continuously adjusted to ensure the probe-sample contact, so that the deflection of cantilever remains approximately the same. Because the contact-mode measurement can make irreversible changes to the sample surface, keeping the probe close enough to the sample surface for precision while preventing the probe from sticking to the surface presents a realistic request on AFM
techniques beyond the contact mode. Because of this realistic request, the tapping mode is invented and becomes frequently used, particularly for imaging soft materials. To be specific, the effective viscosity measurement of polymer thin films is conducted by operating AFM under tapping mode, which neither causes any damage to the polymer thin film nor interferes with the dynamics to be measured. As shown in Fig. 4.1, during the tapping mode operation, the oscillating probe is brought close to the sample surface, and the cantilever oscillation amplitude is maintained constant by an electronic feedback loop. As the cantilever gets close to a bump/pit on the sample surface, the damping force from the surface increases/decreases, and the probe’s oscillation amplitude decreases/increases. This change of the oscillation amplitude is then input to the feedback loop and the probe-sample separation is adjusted accordingly to maintain the constant amplitude of oscillation.

Figure 4.1: Schematic diagram of tapping-mode AFM using beam deflection detection.
4.2 Surface Topographic Measurement

Experimentally, we determine the dynamics of a polymer thin film by studying how its power spectral density (PSD) evolution with time upon annealing at a given measurement temperature. To determine the PSD, we first measure the surface topography of the films by using tapping-mode AFM. Then each topographic data (a 2-dimensional image) is converted into a PSD (a 1-dimensional array) [3, 110-112] by first being multiplied by a Welch function then Fourier-transformed [3, 110-112]. Afterward, the resulting two-dimensional Fourier spectrum is radial averaged to produce the one-dimensional PSD.

It is important to clarify that the present AFM measurement is fundamentally different from most other AFM measurements used for materials characterization [59, 61, 113-115]. In typical AFM measurements [61, 113], the AFM probe tip actively perturbs the specimen surface and thereafter monitors the dynamic response local to the film surface. Because the size of the probe tip is often quite small (typically <~10 nm), even a small probing force can translate into a large stress (e.g., for a force of 0.1 nN, the stress is ~1 MPa) that can result in nonlinear response for soft materials like polymer. But in our method, the AFM probe tip acts as a passive, benign monitor (through the use of light and high-frequency tapping) of the surface topography of the film as the film surface roughens spontaneously by thermal activation. Although our method measures the surface dynamics of the film (namely the dynamics by which the film surface evolves), it will become apparent in Chapter 4.3 that the measured dynamics arises from flow transport of all the materials in the film and so should reflect an overall dynamics. That
being said, one may still be able to infer information about the local dynamics at the free surface by applying a layer model to the measurement as discussed in Chapter 4.3.

It should also be clarified that the dynamics we measure can differ from that inferred from experiments involving capillary action of a solid substrate or wall, such as dewetting (more specifically, holes opening) or wicking of the polymer liquid into an empty capillary [116-120]. In contrast, our measurement is based on thermally activated surface dynamics, where the driving stress, \( \sigma \), (neglecting the conjoining pressure due to the interfacial potential) is due to gradient in the Laplace pressure, \( \Delta P \sim 2\gamma / R \), arising from undulations in the film surface. (Here, \( \gamma \approx 30 \text{ mN/m} \) is the surface tension and \( R \) is the local radius of curvature of the undulating film surface.) For undulations with amplitude \( \delta h \) and wavevector \( q \), \( R \sim 1/(q^2\delta h) \). Adopting the experimental condition, \( \delta h < 0.1h_0 \) (see below) and for \( h_0 = 10 \text{ nm} \), \( \sigma \sim \gamma \delta h q^2 < \sim 30 \text{ Pa} \). But in the experiments involving capillary action, the stress is provided by the polymer-substrate surface tension and given by \( \sigma = \gamma_s / h_0 \). As pointed out by Reiter [118], \( \gamma_s \sim 20 \) to 30 mN/m and so for \( h_0 \sim 10 \text{ nm} \), the stress is \( \sim 2 \) to 3 MPa and large enough to cause plastic deformation of thin films of common polymers such as PS. Indeed, spectacular phenomena had been observed in these experiments, including molecular layering of the precursor film of a polymer liquid spreading on a solid substrate [121] and formation of a highly asymmetric rim on the periphery of an enlarging hole in a viscoelastic (entangled) polymer film [118]. The latter should be contrasted with the relatively symmetric holes rims found in the counterpart films (in our measurement) when there is no capillary action – a condition
realized when the holes only appear as indentations, and have not grown deep enough to touch the substrate surface.

As we shall discuss in the next section, the dynamics we measure can be succinctly characterized by the effective viscosity of the film, $\eta_{\text{eff}}$ [122]. In general, the value of $\eta_{\text{eff}}$ varies with measurement time and does not reach the steady-state value until a sufficiently long time [3, 110-112]. In any given measurement, a priori we do not know how long it will take $\eta_{\text{eff}}$ to reach the steady-state value. To ensure that the steady-state value is reached, we continue the measurement until the measured $\eta_{\text{eff}}$ no longer change when the annealing time is lengthened four times or more. Because our analysis is based on linear approximations [123], measurements are only taken in the initial stage of roughening where the root-mean-square roughness is less than $0.1h_0$, where $h_0$ is the average film thickness.

4.3 Analysis for the Temporal Evolution of Power Spectral Density

4.3.1 Analysis for the Surface Dynamics of Newtonian Liquid Films

In this subsection, we shall discuss the model we developed to describe the surface dynamics of unentangled polymer films, which we treat as Newtonian liquids.

For a film possessing small undulations on the surface, the height profile can be written as $h(r) = h_0 + \delta h(r)$, where $h_0$ is the average film height, $r$ denotes positions in the plane of the film and $<\delta h(r)>_r = 0$. The presence of $\delta h(r)$, whether spontaneously [124-126] or artificially created [127-129], produces a spatially inhomogeneous excess
pressure according to $\Delta P(r) = -\gamma \nabla^2 \delta(h(r)) + dG(h_0)/dh$ \cite{111, 130}, where $\gamma$ is the surface tension and $G(h)$ the van der Waals potential of the film. Given this, the pressure gradient, $\nabla P$, is generally nonzero, causing the film fluid to flow, which in turn produces temporal variations in $\delta(h(r))$ and $P(r)$ (Here, $P(r) = P_{atm} + \Delta P(r)$, where $P_{atm}$ is the atmospheric pressure.) In the lubrication approximation, where the in-plane length scale of the undulations is much bigger than $h_0$, the unit-width, in-plane current is given by $j(r, t) = -M_{tot} \nabla P(r, t) + \xi(r, t)$ \cite{123}, where $M_{tot}$ denotes the mobility and $\xi(r, t)$ the conserved thermal noise. It should be remarked that inclusion of thermal noise in the treatment is essential for yielding good agreement with experiment \cite{131}.

By applying linear analysis, the following expression for the time-varying PSD, $A_q^2(t)$, was derived \cite{3, 51, 53, 122, 123, 132}:

$$A_q^2(t) = A_q^2(0) \exp(2\Gamma t) + \left[ \frac{k_B T}{d^2 G(h_0)/dh^2 + \gamma q^2} \right] \left( 1 - \exp(2\Gamma t) \right)$$  \hspace{1cm} (4.1a)

where

$$\Gamma(q) = -M_{tot} \left[ (d^2 G(h_0)/dh^2) q^2 + \gamma q^4 \right].$$  \hspace{1cm} (4.1b)

In here, $q$ is the wavevector and $q \equiv |q|$, $k_B$ is the Boltzmann constant, $T$ is absolute temperature. Figure 4.2 (a) and (b), respectively, shows a sequence of AFM images and corresponding PSDs we acquired from a representative low MW PS film. The solid lines represent the best fit to Eq. (4.1a) and (4.1b). As one can see, the model is able to describe the data well.
Figure 4.2: A representative sequence of AFM topographic images and power spectral density obtained in this study. The data was taken from a film with initial thickness, $h_0 = 4$ nm and $M_w = 2.4$ kg/mol annealed at 61 °C. (a) A subset of the AFM images. (b) The full set of power spectral, PSD, of the film at times (from bottom to top): 0, 15, 30, 60, 90, 210, 600, 1080, 2100, 3840 and 7200 s (open circles). The solid lines are the best fit to Eq. (4.1a). (Reproduced with permission from Ref. [133].)

If the no-slip boundary condition applies at the substrate surface and the film viscosity is homogeneous and given by $\eta$, one may derive that [123]

$$M_{\text{tot}} = \frac{h_0^3}{(3\eta)}.$$  

(4.2)
The mobility $M_{\text{tot}}$ defined here is analogous to the proportionality constant, $\pi R_0^4/(8\eta)$ found in the Poiseuille equation (i.e., $dV/dt = [\pi R_0^4/(8\eta)]VP$), which relates the fluid current engendered by a pressure gradient applied across a fluid-filled cylindrical pipe with radius $R_0$ and non-slipping wall [134]. One may observe that this mobility follows the pipe dimension to the power 4, but $M_{\text{tot}} \sim h_0^3$ in Eq. (4.2). The different power laws arise from the fact that the current considered in the Poiseuille equation is the volumetric fluid flow rate ($dV/dt$, m³/s) through the entire cross-section of the cylindrical conduit, but that considered in thin films ($j(r, t)$, m²/s) is the fluid flow rate per unit width of the film cross-section. Given the above expression of $M_{\text{tot}}$, it is common to define the effective viscosity as follows [122, 123]:

$$\eta_{\text{eff}} \equiv h_0^3/[3M_{\text{tot}}]. \quad (4.3)$$

In general, the dynamics and hence local viscosity in the film may not be uniform. In fact, more often than not the region near the polymer-air surface has lower apparent viscosity [135] than the rest of the films [122]. Assuming the mobility of the near-air surface to be $M_{\text{mobile}}$ and the viscosity of the rest of the film to be bulk-like and given by $\eta_{\text{bulk}}$, it has been shown that $M_{\text{tot}} \approx M_{\text{mobile}} + h_0^3/(3\eta_{\text{bulk}})$ for polymer films [133, 136, 137]. In the presence of dynamic heterogeneity as such, the value of $\eta_{\text{eff}}$ obtained from Eq. (4.3) would be an average viscosity, which explains the subscript “eff” attributed to the symbol $\eta_{\text{eff}}$. Experiments performed on thick ($h_0 \geq \sim 80$ nm) low-$M_w$ PS supported by silica (PS-SiOx) and PMMA supported by silica (PMMA-SiOx) had found good agreement between the measured $\eta_{\text{eff}}$ and bulk viscosity [132, 133, 138, 139]. These
agreements confirm the present method for viscosity measurement. In addition, they also indicate that any effects of enhanced surface mobility [127, 132, 133, 138, 139] or interfacial slippage are insignificant in these films.

### 4.3.2 Analysis for the Surface Dynamics of Viscoelastic Films

To develop a model to analyze the surface dynamics of entangled polymer films, which are viscoelastic, we use an adiabatic approximation as described in the following [123]. Figure 4.3 depicts a representative sequence of PSDs obtained from an entangled polymer film upon annealing above the $T_g$ from the as-cast state for various times $t$ as indicated in the figure legend (open symbols). After the first annealing time step (namely from $t = 0$ to 640 s, Fig. 4.3), the PSD shows an abrupt jump. This is understood to be caused by the glass-to-rubber transition, which we will not treat in our model. After this jump, there is a lengthy period of time of about 22400 s or 6.2 h where the PSDs show insignificant growth. Even though the PSDs show little growth in this time range, frame-to-frame comparison between the PSDs acquired by separate, in-situ measurements on a different film shows that the surface topography of the film was actually not stationary. This indicates that the film was in a quasi-steady state, undergoing equilibrium vibrations. We attribute the vibrations to the normal modes of the film in the rubbery elastic state. After $t = 22400$ s, the growth of the PSDs becomes apparent again (Fig. 4.3). Therefore, there are two dynamic processes with different time scales, corresponding to the fast vibrations associated with the initial “stagnant PSD regime” and the slow dynamic process associated with the later stage where the growth of the PSDs becomes
visible. Adopting an adiabatic approximation, we analyzed slow evolution of the film surface or PSD in the presence of the ensemble-averaged quasi-equilibrium fast vibrations [123]. We ascribe the slow evolution to the in-plane transport currents $\mathbf{j}(\mathbf{r}, t)$ caused by the local pressure gradient $\nabla P(\mathbf{r}, t)$ as discussed in the last section (Section 4.3.1). For the fast vibrations, we assume the energy of the modes to be $[3\mu_0/(2h_0^3q^2)]|u_q|^2$, in accord with that of the surface vibrations of an elastic film with wavevector $\mathbf{q}$, amplitude $u_q$, and shear modulus $\mu_0$ [140]. A linear calculation assuming lubrication approximation ($qh_0 \ll 1$) and stable films gives [123]:

$$A_q^2(t) = A_q^2(0) \exp(2\Gamma' t) + \left[\frac{k_B T}{d^2G(h_0)/dh^2 + \gamma q^2}\right](1 - \exp(2\Gamma' t)) \tag{4.4a}$$

where

$$\Gamma'(\mathbf{q}) = -M_{tot}q^2 \left[\left(\frac{d^2G(h_0)/dh^2}{d^2G(h_0)/dh^2 + \gamma q^2}\right)^{-1} + \left(\frac{3\mu_0}{h_0^2q^2}\right)^{-1}\right]^{-1}. \tag{4.4b}$$

The solid lines in Fig. 4.3 are model lines obtained by fitting the data to Eq. (4.4a) and (4.4b). As one can see, the model lines are able to simultaneously capture the stagnant PSD and subsequent PSD growth regimes, and also provide a good description to the data.
Figure 4.3: Power spectral density of a $h_0 = 3$ nm, $M_w = 115$ kg/mol PS film upon annealing at 115 °C for various times as shown in the legend (open circles). The solid lines are model lines obtained by fitting the data to Eq. (4.4a) and (4.4b), which gives $\eta_{eff,0} = h_0^3/(3M_{tot}) = 4.2 \times 10^8$ Pas and $\mu_0 = 10$ kPa. (Reproduced with permission from Ref. [51].)

On writing $M_{tot} = h_0^3/(3\eta_{eff,0})$ as in Eq. (4.3), where $\eta_{eff,0}$ denotes the effective viscosity of the film in the slow or growing PSD regime, we observe that the expression of $\Gamma'(q)$ in Eq. (4.4b) becomes identical to that derived by Safran and Klein [141] for a uniform Maxwell liquid film with no slip. This demonstrates consistency of our model with the Maxwell liquid model. However, we emphasize that in deriving Eq. (4.4a) and (4.4b), little assumption had been made and certainly no assumption had been made
about the dynamic homogeneity of the film, existence of slippage or even whether the
dynamics is caused by viscous flow. The only attribute we had assumed of the slow
dynamic process is the generic relation, \( j(r, t) = -M_{tot} \nabla P(r, t) \). As a result, the value of
\( M_{tot} \) or equivalently the steady-value of \( \eta_{eff} \) we measure should be open to interpretation.

As mentioned in Chapter 4.2, in each measurement we do not know beforehand
when the slow process is fully established and has reached the steady state. To ensure that
the steady state of the slow process has been reached, we continue the measurement until
further increase in the measurement time causes no change to the fitted value of \( M_{tot} \) and
hence \( \eta_{eff} \). To illustrate this, we fit the PSDs displayed in Fig. 4.3 one-by-one to Eq.
(4.1a) and (4.1b) and deduce \( \eta_{eff} \) then plot the result as a function of annealing time \( t \) in
Fig. 4.4 by the solid circles. There, one sees that \( \eta_{eff} \) establishes the steady-state value
after \( t > \sim 20000 \) s. The fact that the steady-state value found here (\( \sim 4 \times 10^8 \) Pas, Fig. 4.4)
is consistent with the value obtained above by fitting the PSD data in Fig. 4.3 directly to
Eq. (4.4a) and (4.4b) affirms our measurement protocol for determining the steady-state
\( \eta_{eff} \).
Figure 4.4: Values of $\eta_{\text{eff}}$ obtained by fitting the PSDs in Fig. 4.3 one-by-one to Eq. (4.1a) and (4.1b), plotted versus the annealing time, $t$. The dashed line is a plot of $\eta_{\text{eff}} = 2\mu_0 t$. (Reproduced with permission from Ref. [51].)

We summarize this subsection by recapitulating that we have derived Eq. (4.4a) and (4.4b), which are able to simultaneously describe the short-time stagnant and long-time growth regimes found in the time evolving PSDs. For the short-time (fast) dynamics, the model is assumed to be caused by the elastic normal modes of the films. For the long-time (slow) dynamic process, the only assumption the model makes is the relation, $j(r, t) = -M_{\text{tot}} \nabla P(r, t)$. With this, a steady-state effective viscosity may be defined as before, namely $\eta_{\text{eff,0}} \equiv h_0^3/(3M_{\text{tot}})$. In the case of thick PS-SiOx, a previous experiment [132] showed that the value of $\eta_{\text{eff,0}}$ is the same as the bulk viscosity of the polymer, indicating that dynamic inhomogeneity and slippage can be ignored in these films.
However, in cases where dynamic inhomogeneity or slippage cannot be ignored, $\eta_{\text{eff},0}$ is an effective viscosity and can depend on the film thickness in general. In such circumstances, further analysis of the $\eta_{\text{eff},0}(h_0)$ dependence would be necessary to pinpoint the origin of the slow process.
CHAPTER 5

Film Preparation

5.1 Preparation by Spin-casting

To properly study polymer thin films, we need to prepare contaminant-free polymer films with controllable film thickness $h_0$. In this work, the technique of spin-coat is used to produce a polymer nanometer film with a uniform film thickness. In addition to the requirement of uniform film thickness, a cleaning process is implemented to minimize the amount of contamination in the polymer samples as described below.

The substrates we use are single crystal (001) silicon wafers covered by either a native oxide or a 102 ± 2 nm thermal oxide layer, purchased from Si-Tech, Inc. Before use, the wafer is cut into 1 cm x 1 cm slides and cleaned in a mixture of sulfuric acid ($H_2SO_4$) and hydrogen peroxide ($H_2O_2$) in a 7:3 volume ratio, also known as piranha solution, at 130 °C for 20 min. The piranha solution produces free oxygen which can react with and remove organic contamination from the substrate surface. Then the substrate is thoroughly rinsed in deionized water and dried by 99.99% nitrogen gas. This is followed by further cleaning in oxygen plasma for 20 minutes, whereupon the slide is ready for use. It should be noted that hydroxyl groups (-OH) are produced on the substrate surface by both cleaning with piranha solution and with oxygen plasma.

After this cleaning process, the oxide layer thickness of the substrate is measured by ellipsometry, after which a polymer film is spin-coated onto the substrate. Most of the polymers used in this work are purchased from Polymer Source, Inc. (Montreal, Canada) or Scientific Polymer Product (Ontario, NY), with a typical polydispersity less than 1.10.
To make a polymer film, we dissolve the as-purchased polymer in solvent with various concentrations. Then we filter the solution through a polytetrafluoroethylene filter with nominal pore size of 0.1 μm before spin-coating it onto a cleaned substrate.

During spin-coating, several droplets of polymer solution are deposited on a substrate surface, which is then spun with a rotation speed from ~500 to ~4000 rpm for ~1 minute. The rapid spinning causes the solution to spread and dry into a solid film with a pretty uniform thickness. While this process is complex, the empirical relation between the film thickness $h_0$ and other adjustable parameters is given as follows [142]:

$$h_0 \propto C_0 \eta_0^\beta \omega^\alpha$$  

(5.1)

where $C_0$ is the initial polymer concentration, $\eta_0$ is the initial solution viscosity, and $\omega$ is the rotation speed. The value of $\alpha$ is −0.5, and $\beta$ has a typical value from 0.29 and 0.39 for polymer solutions [142]. Basing on this relation, a desire film thickness is achievable through adjusting the solution concentration and rotation speed through some experimentation.

### 5.2 Formation of Bi-layer Film

Rather than having the polymer film supported by a solid substrate, we can support the polymer film on a layer of polymer adsorbed to the substrate. Here, this system consisting of two layers of polymer is referred as a bi-layer film. In a bi-layer film, the layer of polymer adsorbed to the substrate is referred as the bottom layer, and the film supported by the bottom layer is the top layer. In this work, bi-layer films, consisting of PMMAs with similar MW but different tacticities, are used to determine relative sensitivity of
different PMMAs to the $T_g$ perturbations by different interfaces. To make the bi-layer films of PMMA, the PMMA used to make the bottom layer is first spun-cast onto the substrate to produce a film with thickness $h_0 > 4R_g$. In order to strengthen the adsorption process, this sample is then annealed at $> 20 \, ^\circ\text{C}$ above the bulk $T_g$ in vacuum for 10 h. During annealing, the carbonyl groups (C=O) in PMMAs interact with the hydroxyl groups (–OH) on the substrate surface, resulting in hydrogen bonds between the substrate and polymer. Furthermore, the existing hydrogen bonds lead to the anchoring of polymer macromolecules to the substrate. While the chains near the top of the film may not be part of the adsorbed layer, the film thickness $h_0$ must be large enough to avoid dewetting of the polymer during the annealing process.

After annealing, the un-adsorbed chained are removed by rinsing the sample thoroughly multiple times in a good solvent, after which it is soaked in a solvent bath for 5 minutes and dried with nitrogen. The residual thickness of the adsorbed polymer, $h_{\text{res}}$, is then measured by ellipsometry, and the process of rinsing, soaking and measuring is repeated until the $h_{\text{res}}$ does not change, when we conclude that only polymer chains that are adsorbed to the substrate remain. This residual layer made of adsorbed polymer serves as the bottom layer. Afterward, another layer of polymer is directly spun-cast onto it as the top layer.

Last but not least, it should be noted that, this way of making the bi-layer will produce a system similar to the athermal melt-brush systems used extensively in the study of autophobic dewetting, where the melt-brush systems comprise a layer of polymer melt spun-cast on top of an immobile, chemically identical polymer grafted
layers [143, 144]. According to Ferreira et al. [144], in cases where the polymer melt wets the grafted layer (which should also apply here), the width of the interface is of the order of the thickness of the grafted layer. Similarly, the polymer-polymer interface in a bi-layer film has a width of $-h_{\text{res}}$. For the method used here to make bi-layer films, the sample is thermally very stable with annealing and during measurement, although there is a trade-off that the polymer-polymer interface might be not as sharp as other methods, such as the floating method [27].
CHAPTER 6
Effects of Molecular Weight on the Glass Transition Temperature

6.1 Introduction

The question whether the MW could influence the $T_g$ of polymer thin films upon nano-confinement was firstly examined in the study of PS by Keddie et al. [6]. On the basis of their results (Fig. 2.7), no discernible variation was found in the thickness dependence of the $T_g$ of PS supported by silicon, namely $T_g(h_0)/T_g(\infty)$, as the MW was varied between 120 and 2,900 kg/mol, where the unperturbed radius of gyration $R_g$ was bigger than the smallest film thickness studied [6]. Subsequent studies [93, 94] extending the MW to below the entanglement MW, $M_e$, also did not observe any detectable influence of the MW on $T_g(h_0)/T_g(\infty)$. These results suggest that chain entanglement and physical confinement of the polymer chains in a small film thickness must not be essential to the mechanism responsible for the observed $T_g$ variations. Most theoretical accounts of the phenomenon relate it to a surface effect [6, 145-149]. For $T_g$ reduction, most researchers attribute it to a nanometer thick layer at the polymer-air interface with enhanced mobility and depressed $T_g$ [27, 29, 113, 122, 135]. For $T_g$ enlargement, it is attributed to an interfacial layer at the substrate surface with reduced chain mobility, whose effect dominates that of the surface mobile layer [150, 151]. Layer models based on these ideas have been developed and found to describe the experimental $T_g(h_0)/T_g(\infty)$ well [6, 7, 20, 23].
Recently, Dion et al. [100] noted that the MW invariance of \( T_g(h_0)/T_g(\infty) \) was not universal. Specifically, for atactic PMMA (a-PMMA) with \( M_n \) of 31.7 to 46 kg/mol, when the polydispersity index was increased from 1.8 to 2.6, the thin film \( T_g \) changed from being enlarged to being depressed with respect to the bulk value. The researchers thus concluded that silica-supported a-PMMA films with oligomeric components exhibited \( T_g \) depression, but \( T_g \) enlargement otherwise. In a more recent experiment, Lan and Torkelson [101] studied the \( T_g \) of silica-supported a-PMMA and poly(1-ethylcyclopentyl methacrylate) (PECPMA) films with narrower MW distributions on average, and found the same result as did by Dion et al. By using fluorescence labeling [101], they additionally found that the \( T_g \) near the polymer-air surface of the PECPMA films was depressed more at low \( M_n \) than at high \( M_n \), suggesting the phenomenon to originate from an increased perturbation to the \( T_g \) of the polymer surface with decreasing \( M_n \). On the other hand, our former group members [151] found that the \( T_g \) of silica-supported a-PMMA films with \( M_n = 2.5 \) kg/mol was higher than the bulk \( T_g \), in apparent inconsistency with the results of Lan and Torkelson [101] and Dion et al. [100].

In this experiment, we study the \( T_g \) of PaMS films supported by silica with \( M_n \) between 1.3 and 420 kg/mol. Previously, Paeng and Ediger [135] found no evidence of enhanced surface mobility in PaMS. On the other hand, Kim et al. [20] observed the \( T_g \) of silica-supported PaMS to be depressed relative to the bulk \( T_g \). We speculate that a near-surface region with enhanced mobility may be present in PaMS even though it was not detected in Ref. [135]. A support to this postulation is implicated in the observation of surface softening in PaMS by Karim and McKenna at temperatures 21 K or more
below the bulk $T_g$ [152]. The $M_n$’s of the PaMS films studied by Kim \textit{et al.} and Paeng \textit{et al.} were $\geq 23$ kg/mol [20, 135]. In light of previous results, one expects the $T_g$ of the PaMS films to depress by the same amount or more when the $M_n$ is decreased to 1.3 kg/mol. Instead, our experiments of PaMS films show that it becomes independent of film thickness. We tentatively explain this result in terms of simultaneous influences of chain stiffness and free volume on the $T_g$, as originally considered by Gibbs and DiMarzio [64, 65].

6.2 Experimental Results

Figure 6.1 and 6.2 respectively shows the change in the measured ellipsometric angle ($\Delta$) as a function of temperature $T$ for the 420 and 1.3 kg/mol PaMS films with different thicknesses. For clarity, the data of different thicknesses have been shifted vertically by various amounts. To make the data of the thinnest films more visible, the $\Delta$ versus $T$ scan is displayed in an expanded view in the inset of the respective figure. Evidently, all the data display two separate linear regions as described above. The $T_g$, as identified to be the intercept of the best fitted straight lines to the two regions, is shown by an $\uparrow$ arrow. We find that the position of the $T_g$ is reproducible between different runs within measurement uncertainties. From the positions of the $\uparrow$ arrows, it is apparent that the $T_g$ decreases with decreasing film thickness in the 420 kg/mol films, but it exhibits no detectable variation with film thickness in the 1.3 kg/mol films. These $T_g$ measurements, together with those
Figure 6.1: Plots of change in $\Delta$ versus temperature $T$ of the 420 kg/mol PaMS films with different thicknesses as indicated. The data have been shifted vertically for clarity. The inset shows a plot of $\Delta$ versus temperature for the 19 nm thick film. The black solid lines show the best linear fits to the data.

Figure 6.2: Plots of change in $\Delta$ versus temperature $T$ of the 1.3 kg/mol PaMS films with different thicknesses as indicated. The data have been shifted vertically for clarity. The inset shows a plot of $\Delta$ versus temperature for the 17 nm thick film. The black solid lines are the best linear fits to the data.
of the 20 kg/mol films, are shown in Fig. 6.3 as plots of \( T_g \) versus film thickness. As seen, the plots confirm the observations made above about the \( T_g \) of the 420 and 1.3 kg/mol films. For the 20 kg/mol films, the \( T_g \) exhibits a thickness dependence resembling that of the 420 kg/mol films. We have fitted the data of the 420 and 20 kg/mol films to the phenomenological model of Keddie et al. given by Eq. (2.21): \[ \frac{T_g(h)}{T_g(\infty)} = 1 - \left( \frac{A}{h_0} \right)^\delta \] [6]. The fitted values of \( T_g(\infty) \), \( A \), \( \delta \) are given in Table 6.1. In Table 6.1 we also list the \( T_g \) of the bulk polymers (\( T_{g,DSC} \)) obtained by using differential scanning calorimetry (DSC). As seen, \( T_{g,DSC} \) agrees reasonably well with the values of \( T_g(\infty) \) obtained in the fits. For the 1.3 kg/mol films, since no variation in the \( T_g \) is discernible, the data is fitted to a constant, interpreted to be \( T_g(\infty) \). The fitting result gives \( T_g = T_g(\infty) = 376 \pm 0.6 \) K.

![Figure 6.3](image_url)

**Figure 6.3:** The glass transition temperature \( (T_g) \) versus film thickness of the silica-supported PaMS thin films with various \( M_n \) of 1.3 and 20 and 420 kg/mol. While \( T_g \) depression is apparent in the films \( M_n = 20 \) and 420 kg/mol, no change in the \( T_g \) is discernible in the films with \( M_n = 1.3 \) kg/mol. The \( T_g \) data of the 20
and 420 kg/mol films are fitted to Eq. (2.21): 
\[
\frac{T_g(h_0)}{T_g(\infty)} = 1 - \left( \frac{A}{h_0} \right)^\delta
\]
That of the 1.3 kg/mol films is fitted to a horizontal straight line. The fitted results are represented by the solid lines. The inset shows the chemical structure of PaMS.

<table>
<thead>
<tr>
<th>$M_n$ (kg/mol)</th>
<th>$T_g(\infty)$ (K)</th>
<th>$A$ (nm)</th>
<th>$\delta$</th>
<th>$T_{g,DSC}$ (K)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1.3 kg/mol</td>
<td>376 ± 0.6 K</td>
<td>-</td>
<td>-</td>
<td>-</td>
</tr>
<tr>
<td>20 kg/mol</td>
<td>440 ± 0.5 K</td>
<td>5.7 ± 0.3 nm</td>
<td>3.2 ± 0.1</td>
<td>440 ± 5</td>
</tr>
<tr>
<td>420 kg/mol</td>
<td>445 ± 0.5 K</td>
<td>5.7 ± 0.3 nm</td>
<td>3.2 ± 0.1</td>
<td>444 ± 5</td>
</tr>
</tbody>
</table>

**Table 6.1:** Tabulated values of $T_g(\infty)$, $A$, $\delta$ and $T_{g,DSC}$ found in this experiment. $T_{g,DSC}$ data was obtained by using Differential Scanning Calorimetry (DSC) at a constant cooling rate of 10 K/min from a starting temperature at least 50 K above the $T_g$.

Shown in Fig. 6.4 is $T_g(h_0)/T_g(\infty)$, that is, the data of Fig. 6.3 upon normalization by $T_g(\infty)$, plotted versus film thickness $h_0$. As one can see, the results of the 20 and 420 kg/mol films essentially overlap, showing a depression with decreasing film thickness. This is in keeping with the result of Kim et al. [14]. On the other hand, the data of the 1.5 kg/mol films shows independence of the film thickness.
Figure 6.4: $T_g(h_0)/T_g(\infty)$ versus film thickness $h_0$ for the PaMS thin films with molecular weights, $M_n = 1.3$ and 20 and 420 kg/mol.

6.3 Proposed Chain Stiffness Effect on the Glass Transition Temperature of Polymer Films

Previous studies of silica-supported PS films [6, 93, 94] showed that the thickness dependence of $T_g(h_0)/T_g(\infty)$ was independent of the MW down to $M_n = 5$ kg/mol [15]. The different thickness dependences found here between the 1.5 kg/mol and the higher MW films warrant discussions.
As discussed above, Paeng and Ediger did not detect any enhanced surface mobility in PaMS [135]. While one plausible interpretation to Paeng et al.’s result is that there is no surface mobile layer in PaMS, we think that the opposite interpretation is also viable, i.e., a surface mobile layer actually exists, but for some unknown reasons, was not detected in the measurement of Paeng et al. This interpretation is also supported by some recent measurements we obtained. If one assumes that a surface mobile layer indeed exists in the PaMS films, and the \( T_g \) depression is caused by the \( T_g \) of this surface layer being lower than the \( T_g \) of the bulk polymer [27, 101], the present result implies that the \( T_g \) of the surface layer decreases less with decreasing \( M_n \) than the \( T_g \) of the bulk polymer does.

Cowie et al. [153] measured the \( T_g \) of PaMS bulk polymers at various \( M_n \) and found that the data of \( T_g \) versus \( M_n \) could fit well to the Fox and Flory model [154] provided \( M_n > 5 \) kg/mol. Below 5 kg/mol, it became weaker than that was predicted by the Fox and Flory model. On the other hand, the Gibbs and DiMarzio model [64, 65] was able to describe the data over the full range of \( M_n \). In the Fox and Flory model, the \( M_n \) dependence of \( T_g \) is explained only in terms of the increase in polymer free volume as \( M_n \) decreases, which could be attributed to the fractional increase of polymer chain ends in the sample that carries more free volume. In contrast, the Gibbs and DiMarzio model also considers chain stiffness, which affects the \( T_g \) through the flex energy, \( \varepsilon \), namely the energy required to flex a chain segment on the main chain from the lowest energy orientation to a higher energy one [64, 65]. More specifically, the chain stiffness affects the \( T_g \) through its influence on the relative probability a chain segment would adopt a
higher energy orientation, which is proportional to the Boltzmann factor, $\exp[-\varepsilon / k_B T]$, where $k_B$ is Boltzmann's constant and $T$ is absolute temperature [64, 65]. When this probability is low enough (which occurs when either the temperature $T$ is low or the flex energy $\varepsilon$ is high), the chain segments may become unable to explore all the available conformations, resulting in zero average configurational entropy and hence kinetic arrest as seen in the glass transition. But for this mechanism to pertain, it has to occur before the conventional mechanism of glass transition does, which is based on reduction of free volume with decreasing temperature [155]. In pragmatic terms, if $T_{g,\text{free-volume}}$ is the temperature where diminishment of free-volume alone would bring about kinetic arrest and $T_{g,\text{GD}}$ is the temperature where $\exp[-\varepsilon / k_B T]$ becomes small enough to cause the average configurational entropy to become zero. The condition for the Gibbs and DiMazio mechanism to pertain is that $T_{g,\text{GD}} > T_{g,\text{free-volume}}$. Because $T_{g,\text{free-volume}}$ is generally lower at lower $M_n$ [154], chain stiffness effect often emerges in the low $M_n$ regime as discussed above [153]. And when this happens, $T_g$ varies less with changes in $M_n$ than predicted by the Fox and Flory model (which accounts for the effect of free volume only) [154] because the aforementioned Boltzmann factor that governs the chain stiffness effect does not vary with $M_n$.

From the foregoing discussions, polymers with stiffer chains (and hence bigger $E$) should be more susceptible to the Gibbs and DiMarzio mechanism. On the basis of molecular structure, each PaMS monomer has a methyl side-group and a phenyl side-group simultaneously residing on a backbone carbon (see inset of Fig. 6.3), but in a PS monomer the methyl side-group is absent. Such a difference is expected to make the main
chain of PaMS more difficult to flex than the main chain of PS. Indeed, the $T_g(M_n)$ of PS has been found describable by the Fox and Flory model [154], but that of PaMS requires the Gibbs and DiMarzio model [153] as discussed above.

Now we return to the aforementioned observation that if the $T_g$ depression seen in the high-$M_n$ PaMS films is caused by a surface layer with lower $T_g$, our result (Fig. 6.4) implies that the $T_g$ of the surface layer decreases less with decreasing $M_n$ than the $T_g$ of the bulk polymer does. We contemplate that the free volume content at the air surface should be higher than that in the inner bulk. For one thing, the polymer–air interface is deformable as evident from the existence of dynamic surface capillary waves in the films [122]. This implies that the chain segments next to the air surface should find the neighboring sites to be only approximately half filled, with most of the other half (i.e., empty sites) being located in air. In the inner bulk, on the other hand, existing data suggests that they are more than 95% filled at the $T_g$ [153]. If the $T_g$ depression at the air surface [11, 27, 28, 101] is primarily caused by the higher free volume content therein, such a free-volume effect could lessen with decreasing $M_n$ in polymers with stiff chains like PaMS. According to Ref. [153], the $T_g(M_n)$ of the PaMS bulk polymer becomes practically independent of $M_n$ when $M_n$ is decreased below $\sim$2.5 kg/mol and the $T_g$ approaches a plateau value of $\sim$370 K. Because the thick-film $T_g$ measured here of the $M_n = 1.3$ kg/mol PaMS is close to this plateau value (Table 6.1), we ponder that the $T_g$ at the surface of this polymer may be about the same as the $T_g$ of the bulk polymer, which may render the thin films $T_g$ independent of the film thickness.
By using molecular dynamics simulations, Shavit and Riggleman investigated the influence of backbone rigidity on the thickness dependence $T_g(h_0)$ of polymer films [156]. In Fig. 4(a,b) of their paper [156], which compares the profiles of the structural relaxation time, $\tau_\alpha(h_0)$, in a free-standing film of fully flexible chains versus that of stiffer chains, we observe that the near-surface $\tau_\alpha$ of the film containing stiffer chains is less depressed from the bulk $\tau_\alpha$ than that of the film containing fully flexible chains. This is in keeping with the picture contemplated here for the PαMS films. However, the effect found by these workers is smaller. In their study [156], the degree of polymerization used was 500, corresponding to $M_n = 59$ kg/mol for PαMS. Since $T_g$ depression is observed here in PαMS films with $M_n \geq 20$ kg/mol (Fig. 6.3, 6.4), influence of chain stiffness effect on the surface $\tau_\alpha$ should be small, as observed in the simulations' result.

From the above discussions, bulk polymers exhibiting influence of chain stiffness on the $T_g$ may exhibit $M_n$ dependence in the thickness dependence, $T_g(h_0)$ of thin films. Besides PαMS, a-PMMA is another polymer that has been found to display $T_g(M_n)$ dependence described well by the Gibbs and DiMarzio model [63]. By measuring the dynamics of surface capillary waves in a-PMMA films supported by silica with $M_n = 2.5$ kg/mol, Li et al. [151] found that the substrate dominated the dynamics at temperatures above about $T_g + 28$ K. But at lower temperatures, the dynamics was dominated by the polymer–air interface. Li et al. also found that the $T_g$ of these films increased mildly by $\leq -5$ K when the film thickness was decreased to $\sim 20$ nm, indicating slight dominance of the substrate effect on the $T_g$. All these imply that the net effect, resulting from the tug of war between the polymer–air and –substrate interfaces that ultimately produces the
observed $T_g$ enlargement could be marginal. In fact, opposite trends had been reported [100, 101] for the $T_g(h_0)$ dependence of similar films with different tacticities that is difficult to be explained [101] in a straightforward manner by the known effects of tacticity on the thin film $T_g$ [18]. To resolve this seemingly contradiction, in Chapter 7 we contemplate that a more complicated competition between free volume, chain stiffness and tacticity may play a role in causing the different $M_n$ dependences seen by different groups in the $T_g$ of the PMMA films.

6.4 Conclusions

In conclusion, we have measured the $T_g$ of PaMS films supported by silica at various film thicknesses between 17 and 168 nm, and three different MWs of 1.3, 20 and 420 kg/mol. The $T_g$ measurements of the 20 and 420 kg/mol films, upon normalization by the asymptotic thick film $T_g$, essentially overlap, showing a monotonic depression with decreasing film thickness below ~100 nm. But the $T_g$ of the 1.3 kg/mol films displays no discernible dependence on film thickness. This is different from the thickness dependence of the $T_g$ of silica-supported PS films where no dependence on the MW had been found. We tentatively suggest the different result of the PaMS films to arise from their larger chain stiffness, which may cause the $T_g$ depression in the surface layer to lessen at low MWs. In polymers with stiff chains, the energy difference between different conformations may not be small compared to $kT_g$, the thermal energy at $T_g$. On cooling the polymer toward the $T_g$, the polymer chains may become less able to sample all the conformations available by the free volume, making the surface $T_g$ less responsive to free
volume change upon MW change. By lowering the MW, the $T_g$ (and accordingly $kT_g$) is lowered, making the effect of chain stiffness more important. As a result, the thin film $T_g$ may be depressed less at low MWs.
CHAPTER 7

Effects of Polymer Tacticity on the Glass Transition Temperature

7.1 Introduction

Recent studies of polymer films with various MWs found that, for polymers such as PMMA and PaMS, the $T_g(h_0)/T_g(\infty)$ could be dependent of MW. The Vogt group [100] found that the $T_g$ of a-PMMA films supported by silica (a-PMMA/SiOx) with $M_n$ between 31.7 and 46 kg/mol could change from being enlarged to depressed if the polydispersity index of the polymer was increased sufficiently to include oligomers in the films. A subsequent experiment of Lan and Torkelson [101] found that for a-PMMA supported by silica with narrower MW distributions, the $T_g$ of the films with $M_n > 180$ kg/mol were enlarged – consistent with the original result of Grohens et al. [73] – but the $T_g$ of the films with $M_n < 4.5$ kg/mol were depressed – consistent with the aforementioned result of the Vogt group. In a later experiment by our group [157], it was found that the $T_g$ of PaMS supported by silica with $M_n \geq 20$ kg/mol was depressed, but the $T_g$ of the films with $M_n = 1.3$ kg/mol was independent of the film thickness. These results of different groups show that there is no universal correlation between $\Delta T_g(h_0)$ ($\equiv T_g(h_0) - T_g(\infty)$) and the polymer MW when $\Delta T_g(h_0)$ exhibits dependence on the MW.

What we find surprising is the sensitivity of the noted MW dependence of $\Delta T_g(h_0)$ on the polymer tacticity in the case of PMMA supported by silica (PMMA/SiOx), which constitutes the motivation of this work. In an experiment by a former group member [151], the $T_g$ of PMMA/SiOx with $M_n = 2.5$ kg/mol and polydispersity index = 1.09 was
found to be enlarged, which ostensibly contradicts the result of Lan and Torkelson mentioned above [101]. A closer examination reveals that the syndiotacticity (s%) of the PMMAs used in different experiments were different. In the former [151], s% = 69% (iso:hetero:syndio = 7:24:69), but in Lan et al.’s [101] it was 59% (iso:hetero:syndio = 3:38:59). In the following, we detail a comprehensive investigation we undertook to understand the different results. In particular, we measured the $T_g$ of PMMA/SiOx with two different MW’s ($M_n = 2.5$ and ~50 kg/mol) and two different s%’s (= 56% and 69 or 79 %) similar to those studied in Refs. [101] and [151]. Besides the usual PMMA/SiOx single-layer films, we also studied bi-layer films containing PMMAs with similar MW but different s% supported by SiOx. The results enable us to identify which PMMA is more susceptible to $T_g$ perturbation by which interface (namely the free surface or substrate interface), and thereby envisage the physical underpinning of the variability of the $T_g$ of PMMA/SiOx with MW and tacticity.

7.2 Experimental Results

The PMMA polymers used in this work are different PMMAs with $M_n = 2.5$ (iso:hetero:syndio = 6:38:56 and 7:24:69), 47.3 (iso:hetero:syndio = 6:38:56) and 52 kg/mol (iso:hetero:syndio = 2:19:79) and polydispersity index less than 1.10. Typically, PMMAs with s% ≤ 59% were referred to as atatic (a-PMMA) [101, 158] and those with s% ≥ 80% syndiotactic (s-PMMA) [73, 74]. In this work, we relax the condition for the latter [73, 74] and refer to the PMMAs with s% ≥ 69% s-PMMA. So here are four types of PMMAs, which are respectively denoted as a-PMMA2.5K, s-PMMA2.5K, a-PMMA50K and s-PMMA50K.
We first discuss the result of the $M_n = 2.5$ kg/mol a- and s-PMMA single and bi-layer films (denote below by a-PMMA2.5K/SiOx, s-PMMA2.5K/SiOx, a-PMMA2.5K/s-PMMA2.5K/SiOx, and s-PMMA2.5K/a-PMMA2.5K/SiOx, respectively). Figure 7.1 shows the thickness dependence of the $T_g$ obtained. As one can see, the $T_g(h_0)$ of the single-layer s-PMMA2.5K films (solid triangles) are enlarged, with the change $\Delta T_g(h_0)$ reaching $\approx 2$ °C at $h_0 = 20$ nm. This result is consistent with the aforementioned published result of our group [151]. On the other hand, the $T_g$ of the single layer a-PMMA2.5K/SiOx films (solid squares) is depressed, which is qualitatively consistent with the result of Lan and Torkelson for a-PMMA3.3K/SiOx with $s\% = 59\%$ [101]. Taken together, our result of the 2.5 kg/mol single-layer films (solid symbols) show that the free surface dominates the $T_g$ of the a-PMMA2.5K/SiOx films, but the substrate surface dominates the $T_g$ of the s-PMMA2.5/SiOx films.

Next, we compare these data of the single-layer films with those of the bi-layer films (open symbols). First, one observes from the data of the a-PMMA/s-PMMA/SiOx bi-layer films (open squares) that on adding the s-PMMA bottom layer, the $\Delta T_g(h_0)$ of the a-PMMA layer changes dramatically from being negative before (solid squares) to zero after the s-PMMA addition. This clearly shows that the substrate perturbation to the $T_g$ of s-PMMA2.5K is stronger than the perturbations due to either surface to the $T_g$ of a-PMMA2.5K. At the same time, the $\Delta T_g(h_0)$ of the s-PMMA/a-PMMA/SiOx bi-layer films (open triangles) is essentially the same as that of the s-PMMA/SiOx single-layer films (solid triangles) within experimental uncertainty. Since the substrate surface
perturbs the \( T_g \) of s-PMMA2.5K more strongly than the free surface does the \( T_g \) of a-PMMA2.5K, the

![Figure 7.1: Change in \( T_g \) \((= T_g(h_0) - T_g(\infty))\) versus total film thickness, \( h_0 \), of the \( M_n = 2.5 \text{ kg/mol} \) a-PMMA and s-PMMA single-layer (solid symbols) and bi-layer films (open symbols). The solid curves are guides to the eye. Schematic representations of different films are shown by the drawings, where \( \text{a-PMMA2.5K} \) is labeled by “\( a \)” (white), \( \text{s-PMMA2.5K} \) by “\( s \)” (black) and the substrate is marked by diagonal stripes.](image-url)

The data of the s-PMMA single- and bi-layer films (open and solid triangles) could be explained if either (1) the (free) surface \( T_g \) of s-PMMA was enhanced relative to the bulk \( T_g \), and the effect of such \( T_g \) enhancement dominated the perturbations due to either the SiOx or the a-PMMA/SiOx substrates to the \( T_g \) of the upper s-PMMA layer or (2) there had been some replacement of the a-PMMA chains by the s-PMMA chains at the substrate surface during pre-annealing. We find the first explanation unlikely as we are unaware of any study showing that the free surface alone may induce an enhancement to
the surface $T_g$. On the other hand, the second explanation is quite probable given the strong effect noted of the SiOx substrate on the $T_g$ of s-PMMA and the somewhat thicker residual layer s-PMMA formed on SiOx than a-PMMA did (Table 7.1), which implies that s-PMMA interacts more strongly with the substrate than a-PMMA does [159]. This result is in keeping with an earlier finding that the fraction of carbonyls bonded to silica was slightly higher for s-PMMA than i-PMMA [74].

<table>
<thead>
<tr>
<th>Films</th>
<th>Average residual thickness, $h_{res}$, (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>a-PMMA2.5K/SiOx</td>
<td>0.3 ± 0.1</td>
</tr>
<tr>
<td>s-PMMA2.5K/SiOx</td>
<td>0.5 ± 0.1</td>
</tr>
<tr>
<td>a-PMMA47K/SiOx</td>
<td>1.1 ± 0.1</td>
</tr>
<tr>
<td>s-PMMA52K/SiOx</td>
<td>3.7 ± 0.2</td>
</tr>
</tbody>
</table>

Table 7.1: Average residual layer thickness of the PMMAs studied.

It is well known that the $T_g(h_0)$ of PMMA films supported by silica depends on the tacticity of the PMMA[73, 74]. According to the classic results of Keddie et al. [92] and Grohens et al. [73, 74] the $T_g$ is depressed for s-PMMA films, enhanced for a-PMMA films and significantly enhanced for i-PMMA films. The present result of the a-PMMA2.5K/SiOx films (Fig. 7.1), while in keeping with the results of the Vogt [100] and Torkelson groups [101], appears contradictory to the results of Keddie et al. and Grohens et al. A closer examination shows that the polymer MW studied in Fig. 7.1 ($M_n = 2.5$ kg/mol) is much lower than those studied by Keddie et al. and Grohens et al. ($\geq 30$ kg/mol) [73, 74, 92]. We thus performed analogous $T_g$ measurements on PMMA films with a higher $M_n$ of ~50 kg/mol.

Figure 7.2 shows the $T_g$ versus $h_0$ measurements of the $M_n \sim 50$ kg/mol films. For the single-layer films, we find that the $T_g$’s of the a-PMMA50K/SiOx are enhanced, but
those of the s-PMMA50K/SiOx are depressed, which are consistent with previous published results [73, 74, 92, 160]. With these findings, the signs of the $\Delta T_g(h_0)$ are reversed with respect to those of the 2.5 kg/mol films in Fig. 7.1. The possible reasons for this sign reversal will be discussed in Chapter 7.3. Now we focus on the remaining data of Fig. 7.2, namely the data obtained from the bi-layer films. For the a-PMMA/s-PMMA/SiOx films (open squares), insertion of the s-PMMA layer beneath the a-PMMA layer promotes the $T_g$ enhancement of the a-PMMA layer. Similarly, for the s-PMMA/a-PMMA/SiOx films (open triangles), insertion of the a-PMMA layer beneath the s-PMMA layer promotes the $T_g$ depression of the s-PMMA layer. These results indicate that the

Figure 7.2: Plots of $T_g(h_0) - T_g(\infty)$ versus total film thickness, $h_0$, of the $M_n \approx 50$ kg/mol a-PMMA and s-PMMA single-layer (solid symbols) and bi-layer films (open symbols). The solid curves are guides to the eye. Schematic representations of different films are shown by the drawings, where a-PMMA50K is labeled by “a” (white), s-PMMA50K by “s” (black) and the substrate is marked by diagonal stripes.
presence of s-PMMA next to the silica substrate enhances the $T_g$ of the films, in keeping with the results found in Fig. 7.1. Given this, to fully account for the result of Fig. 7.2 would require that the perturbations from the free surface, which are presumed to bring about depression of the surface $T_g$, are stronger in s-PMMA50K than in a-PMMA50K. This is ostensibly opposite to what we concluded above about the effect of the free surface on the 2.5 kg/mol films. In the next section, we shall address this and the other apparently contradictory observations, and more generally the possible reasons for the MW dependence revealed by Fig. 7.1 and 7.2 of the effects of the interfaces on the $\Delta T_g$ of the a- and s-PMMA films.

7.3 Proposed Effects of Polymer Tacticity on the Glass Transition Temperature of Polymer Films

First, we consider the reason why the surface $T_g$ of s-PMMA may be less depressed at $M_n = 2.5$ kg/mol than at $M_n \sim 50$ kg/mol. In a recent experiment [157], we observed a similar effect in PαMS supported by silica (PαMS/SiOx). There, we attributed the observation to flattening of the MW dependence of the $T_g$ of the PαMS bulk polymer at low MW as noted by Cowie et al. [153], which could imply that the $T_g$ of PαMS becomes less sensitive to changes in free volume at low MW. In other words, if depression of the surface $T_g$ is caused by augmentation of free volume at the free surface, the surface $T_g$ should be little modified from the bulk value at low MW. Cowie et al. [153] also found that the flattening of the $T_g$(MW) dependence of bulk PαMS could be accounted for by the model of Gibbs and DiMarzio [65] (or more precisely the original equation derived by Gibbs [64]). In the Gibbs and DiMarzio model, the glass transition is conjectured to be
caused by the average configurational entropy becoming equal to zero. Usually, such a zero-entropy state is brought about by a reduction of free volume upon cooling. But it could be promoted if the backbone of a polymer is sufficiently stiff to energetically restrict the polymer chains from exploring all the available configurations. At low enough temperatures, \( T \), where the energy difference between the higher and lower configurational energy states of a chain segment, \( \varepsilon \), is non-negligible compared to \( k_B T \), chain stiffness effect alone can be effective in suppressing any configurational variability and thus bringing about the zero-entropy state irrespective of the free volume content of the system. In corollary, the \( T_g \) of a polymer should saturate at a minimum value of the order of \( \sim \varepsilon / k_B \), explaining the flattening of the \( T_g(MW) \) of PaMS at low MW.

We contemplate that s-PMMA is stiffer than a-PMMA. By using FTIR spectroscopy, Grohens et al. [74] measured the relative populations of the lower- to higher-energy conformational states and thereby the value of \( \varepsilon \) in bulk and thin films of i-PMMA and s-PMMA. Their result shows that the value of \( \varepsilon \) is always higher for s-PMMA than for i-PMMA. Assuming that chain stiffness varies steadily with tacticity, this result would imply that the s-PMMA chains are stiffer than the a-PMMA chains. We have also collected the \( T_g(M_n) \) data of “atatic PMMA” and “syndiotactic PMMA” from Polymer Source, the supplier of our polymers, as well as those published by Beevers and White [63] on bulk PMMA with unspecified tacticity. It is noteworthy that Polymer Source classifies PMMA with \( s\% > 79\% \) as syndiotactic and apparently those with \( s\% < 79\% \) and \( i\% < \sim 10\% \) atactic. For ease of comparison, the \( T_g(M_n) \) data were normalized by the respective value of \( T_g(M_n = \infty) \) before plotted versus \( 1/M_n \) in Fig. 7.3. The data show
that the data of s-PMMA overlaps with that of Beevers et al., which fits well to Gibbs’ equation (dashed line, Fig. 7.3) and saturates toward a constant value of \( T_g(M_n)/T_g(M_n = \infty) \approx 0.86 \) at low \( M_n \); on the other hand, the data of a-PMMA fits better to Fox and Flory’s equation [154] and shows no clear tendency to saturate. There are, however, caveats with the data of Fig. 7.3. Most notably, they had been collected from PMMAs with a range of tacticities. Therefore, variations of the \( T_g \) with tacticity can contribute to the apparent \( M_n \) dependence seen in Fig. 7.3. In addition, although the \( T_g(M_n)/T_g(M_n = \infty) \) data of Beevers et al. (open circles, Fig. 7.3) agrees better with the supplier’s data for s-PMMA (open triangles, Fig. 7.3), their \( T_g(M_n = \infty) \) value actually agrees better with that of the supplier’s value for a-PMMA than for s-PMMA. With all the caveats noted, we

![Figure 7.3: Plots of \( T_g(M_n)/T_g(M_n = \infty) \) versus \( 10^5/M_n \) using the data of a-PMMA and s-PMMA (with \( s% > 79 \)) provided by our polymer supplier and the data of Beevers et al. [63] The normalization constant, \( T_g(M_n = \infty) \) is 386 K (\( i.e. \), 113 °C) for a-PMMA (supplier), 405 K (\( i.e. \), 132 °C) for s-PMMA (with \( s% > 79 \)).]
supplier), and 390 K (i.e., 117 °C) for the data of Beevers et al. The solid line is a fit to Fox and Flory’s relation [154] and the dashed line is the published fit to Gibbs’ equation [64] by Beevers et al.

however also perceive credibility of the data of Fig. 7.3. First, different data sets show the expected relative trends for the $T_g(M_n)$ dependence given that s-PMMA has a larger value for the conformational energy, $\varepsilon$, than a-PMMA does. In addition, the saturation value of $T_g(M_n) \approx 0.86 T_g(M_n = \infty)$ at low $M_n$ for the data of Beevers et al. (dashed line, Fig. 7.3) is approximately equal to $1.3 \varepsilon/k_B$ based on the value of $\varepsilon = 879$ cal/mol measured by Grohens et al. [74] for bulk s-PMMA. In contrast, the value of $\varepsilon/k_B$ for bulk a-PMMA is much lower, equal to 237 K (or -36 °C) [74], which would correspond to a saturation value of $T_g(M_n)/T_g(M_n = \infty) \approx 0.7$ in Fig. 7.3. Such a low saturation value corroborates with the data of a-PMMA in Fig. 7.3 showing no obvious tendency for saturation. Lastly, by using the bulk $T_g$ data reported above, one finds the value of $T_g(M_n)/T_g(M_n = \infty)$ to be 0.92 and 0.88 for, respectively, the a-PMMA2.5K and s-PMMA2.5K polymers studied here. These values fall well into the respective curves according to the norminated tacticities of these polymers. With the credibility of the data of Fig. 7.3 noted, we proceed to use this figure to account for the $\Delta T_g$ data of Fig. 7.1 and 7.2. Figure 7.3 shows that at $M_n = 2.5$ kg/mol, corresponding to $10^5/M_n = 40$ (kg/mol)$^{-1}$, the $T_g$ of s-PMMA should approach saturation, but that of a-PMMA not. Therefore, perturbations from the free-surface, if operative by free-volume augmentation, can cause depression of the surface $T_g$ in a-PMMA2.5K but not in s-PMMA2.5K. This, together with the stronger interactions s-PMMA has with the substrate than a-PMMA does, the data of Fig. 7.1 can be explained.
Now we address the sign reversal of the $\Delta T_g$’s in going between different MWs. First we address the sign reversal in the a-PMMA films. From Fig. 7.3, the $T_g(M_n)$ dependence of a-PMMA follows the Fox and Flory equation and does not show any tendency to saturate at low $M_n$, which is similar to the $T_g(M_n)$ dependence found of bulk PS [93]. As mentioned above, PS films show no MW dependence in the $T_g(h_0)/T_g(\infty)$ measurements [93], implying that perturbation from the free surface to $T_g(h_0)/T_g(\infty)$ is independent of MW. One may expect the same for a-PMMA since a-PMMA and PS exhibit similar $T_g(M_n)$ dependences. Henceforth, the sign change, from negative to positive, of the $\Delta T_g$ of the a-PMMA films in going from low to high MW must be caused by an increase in the polymer-substrate interaction with MW. We tentatively suggest this to be caused by a tendency of the polymer chains with statistically higher s% to segregate to the substrate surface. We expect this tendency to be higher with higher MW because first enthalpy gain per chain is higher at higher MW’s and secondly entropy factors, which tend to mix different components together, are more significant at lower MW’s. The idea that the tacticity of the PMMA chains being adsorbed to the substrate may influence the $\Delta T_g$ of the films is readily evident from the visibly different $\Delta T_g(h)$’s found above between the a-PMMA2.5K single- and bi-layer films. On the other hand, we notice that the $\Delta T_g(h_0)$ of the a-PMMA50K single-layer films is bigger than that of the a-PMMA2.5K/s-PMMA2.5K/SiOx bi-layer films. One possible reason for this observation is that the amount of perturbations the adsorbed layer can exercise on a film’s $T_g$ depends on its thickness, especially how it compares to the size of cooperativity at the glass transition. A study is underway to address this question.
Finally, we address the sign change of the $\Delta T_g$ of the s-PMMA films, which goes from positive to negative as the MW is increased from 2.5 to ~50 kg/mol. We believe that the main driver of this phenomenon is the saturation of the $T_g$ of s-PMMA with free volume change near $M_n = 2.5$ kg/mol (Fig. 7.3), which limits the surface $T_g$ of the s-PMMA2.5K from getting depressed, but not for the s-PMMA50K polymer. The facts that both the $T_g$’s of the a-PMMA50K single- and bi-layer films are enhanced while those of the s-PMMA50K films are depressed, and s-PMMA interacts more strongly with the substrate surface than a-PMMA does imply that perturbation from the free surface on the $T_g$ is stronger in the s-PMMA50K than in the a-PMMA50K polymer. Dhinojwala et al. [161] had found that the orientation order of the phenyl groups in PS supported by sapphire was higher at the interfaces. Higher structural order has been attributed to stronger glassy behaviors, namely slower rise in the alpha relaxation time or viscosity with cooling at the $T_g$ [162]. We ponder if the bigger depression in the surface $T_g$ implied in our result of the s-PMMA50K polymer relative to that of the a-PMMA50K polymer may be caused by the more regular microstructure of s-PMMA as that could enable better orientation order at the free surface. According to Ngai et al.’s coupling model description of glassy dynamics [145, 163-165], stronger glassy behavior corresponds to a smaller coupling parameter, $n$, which physically means weaker coupling between different simpler, one-molecule (primitive) relaxations, and better molecular orientation of polymer chains had been noted to corroborate with faster segmental dynamics [145]. Presumably any net orientation order at the surface tapers toward zero within roughly the same distance of the order of a monomer thickness [161]. Then reduction of the surface
$T_g$ should be stronger in s-PMMA than in a-PMMA, in keeping with the above observation.

The explanation presented above is probably not the only explanation that can account for the experimental observations. Some time ago, Ngai proposed an explanation for the different $\Delta T_g$’s found of the high-$M_w$ s-PMMA and i-PMMA films by using the coupling model [163]. It is not immediately obvious how it can be adapted to account for the MW and tacticity dependences found here of the $\Delta T_g$. It is hoped that presentation of the present ideas may stimulate further discussions.

Lastly, we should clarify that the effect propose above, relating the flattening of the $T_g(MW)$ dependence at low MW (Fig. 7.3) with suppression of reduction in the surface $T_g$, is different from the effect proposed by Zhang et al. [166] in explaining the lack of $T_g$ confinement effect found of cyclic PS (c-PS) supported by silicon down to $h_0 = 21$ nm. While the bulk $T_g$ of their polymer was also noted to be independent of MW (at $M_n = 3.4$ and 9.1 kg/mol), the workers attributed the flat $T_g(h_0)$ dependence to a speculated invariance of the molecular packing frustration at the free surface relative to that in the bulk polymer. Such invariance was inferred from the bulk fragility of a low-MW c-PS ($M_n = 4.6$ kg/mol) being similar to the limiting bulk fragility of linear PS in the $M_n \to \infty$ limit, and the assumption that fragility is a reflection of packing frustration [167].

7.4 Conclusions
A systematic study was performed on the thickness, \( h_0 \), dependence of the \( T_g \) of PMMA films supported by silica with two different MW (\( M_n = 2.5 \) and \( \sim 50 \) kg/mol) and syndiotacticities (s\%= 56\% for a-PMMA and 69 or 79\% for s-PMMA). Our result shows that the sign of \( \Delta T_g(h_0) \) is sensitive to both the MW and tacticity. To determine which interface (air or substrate) dominates in which of the four kinds of PMMA films studied, we constructed bi-layer films consisting of PMMAs with similar MW but different s\%. We find that while the sign of \( \Delta T_g(h_0) \) is consistent with the convention that it is governed by an interplay between two competing surface effects – namely, the free surface, which depresses the \( T_g \) and the substrate surface, which enhances it – the MW and tacticity modulate these effects in non-trivial ways. Specifically, our result implies that (1) the substrate effect on the \( T_g \) is stronger in s-PMMA than in a-PMMA and (2) at \( M_n = 50 \) kg/mol, the surface \( T_g \) of s-PMMA is depressed more from the bulk \( T_g \) than is that of a-PMMA, but at \( M_n = 2.5 \) kg/mol the effect of the free surface becomes ineffective in s-PMMA. We contemplate this ineffectiveness of the free surface to be brought about by the emergent effect of chain stiffness on the \( T_g \) of polymers as discussed by Gibbs and DiMarzio. In addition, preferential segregation of the statistically higher s\% polymer chains to the substrate surface in the a-PMMA films may also play a role.
CHAPTER 8

Conflicting Confinement Effects on the Glass Transition Temperature, Diffusivity and Effective Viscosity

8.1 Introduction

Nano-confined polymer films with thickness in the range of ~1–100 nm often exhibit physical properties different from the bulk. These include the $T_g$ \[89, 93, 168-171\], elastic modulus \[56, 57, 172, 173\], $D$ \[102, 103, 174, 175\], $\eta_{\text{eff}}$ \[133, 151, 176-178\], and so on. While many of these observations can be rationalized by assuming that the free surface causes the local dynamics to speed up and the substrate surface causes the local dynamics to slow down, some observations remain unexplainable. A long-standing question concerns the inconsistent thickness dependences demonstrated by the $T_g$ \[93, 94\] and $D$ \[102, 103\] of PS/SiOx. Specifically, both the $T_g(h_0)$ and $D(h_0)$ of these films exhibit reductions with decreasing $h_0$. Straightforward interpretation of the $T_g(h_0)$ would suggest that the dynamics of the films are dominated by the free surface, but that of $D(h_0)$ would imply that the substrate surface dominates. Given that the glass transition involves cooperative, local motions of the chain segments \[155, 170, 179, 180\] while $D$ involves large-scale translational motions of the whole chains, it is thus perceivable that the $T_g$ and $D$ may exhibit different thickness dependencies. But recent studies found that the effective viscosity $\eta_{\text{eff}}$ of PS/SiOx decreased with decreasing $h_0$ over polymer MWs from 2.4 to 2,300 kg/mol \[133, 176\]. Both $D$ and $\eta_{\text{eff}}$ describe transport phenomena in the films and are known to depend on the same sort of local dynamic properties, namely the local
segmental friction coefficients [103, 176]. It is then unclear why $D$ and $\eta_{\text{eff}}$ displayed seemingly inconsistent $h_0$ dependences. In the present study, we simultaneously studied the effects of confinement on the $T_g$, $D$ and $\eta_{\text{eff}}$ of poly(isobutyl methacrylate) films supported by silica (PiBMA/SiOx). Previous experiments showed that the $T_g$ of PiBMA/SiOx was independent of $h_0$ [83, 174], which is different from PS/SiOx. From the perspective of this study, the different behavior of these two systems is viewed as an advantage that will enable the development of better insight about the general phenomenon. Ye et al. reconciled the incompatible depressions in $T_g$ and Inelastic Neutron Scattering (INS) [181] segmental mobility of PS/SiOx by indicating that INS measures the $\sim 5$ ns Debye-Waller factor ($\sim \exp(-q^2 u^2>/3)$ where $q$ is the neutron wavevector), which clearly more strongly weighs the slow components with smaller mean-square-displacements ($<u^2>$). They also noted that there can be contamination of the nanosecond $<u^2>$ by incipient relaxation processes [181]. In this study, we seek reconciliation between dynamics with similar time-scales and quantitative descriptions thereof.

8.2 Experimental Results

In Fig. 8.1(a) and 8.1(b) the $T_g$ and in-plane diffusivity $D$ measured at $T = 106$ °C as a function of film thickness ($h_0 = 15$ to $\sim 300$ nm) are shown. In Fig. 8.1(a), the dashed line denotes the value of $T_{g,\text{bulk}}$ determined by DSC. In Fig. 8.1(b), the dashed line denotes the value of $D_{\text{bulk}}$ obtained by averaging the measured values of $D$ of 120 nm thick films with different photobleached pitch sizes. Figure 8.1(a) clearly shows that the $T_g$ is independent
of $h_0$ and is consistent with $T_{g,\text{bulk}}$. This is in agreement with previous results of PiBMA/SiOx with $M_n = 8.7 \ [174]$ and 300 kg/mol [83] (cf. the current $M_n$ is 10.0 kg/mol). In Ref. [83], a 14 nm thick fluorescently labeled PiBMA layer reported that the local $T_g$ at the free surface was depressed by 6 °C while that at the substrate surface was enhanced by 5 °C. The latter finding was attributed to the hydrogen-bonding interactions between PiBMA and the hydroxyl groups (-OH) on the silica surface. Together, these results reveal that there is a distribution of $T_g$'s in the films, and the effect of the substrate surface exactly balances that of the free surface.

Figure 8.1: (a) Thickness dependence of $T_g$ for PiBMA/SiOx (symbols). The dashed line shows the $T_g$ of bulk PiBMA (= 58 °C) as determined by DSC. (b) Thickness dependence of $D$ for PiBMA/SiOx as measured by FRAPP at 106 °C (= $T_{g,\text{bulk}} + 48$ °C). The dashed line corresponds to $D_{\text{bulk}}$ taken to be the average diffusivity of the 120 nm thick films. The error bars indicate the 95% confidence intervals.

Now we turn to the $D$ data in Fig. 8.1(b). $D$ is also clearly independent of the film thickness $h_0$ and equal to the $D_{\text{bulk}}$ value. These findings are consistent with those
observed by Katzenstein et al. [174] for fluorescently labeled PiBMA/SiOx with $M_n = 8.7$ kg/mol. Similar to the above arguments for $T_g$, the finding of constant $D(h_0)$ may imply cancellation between the effects of the substrate and free surface on the diffusivity. We shall express these concepts mathematically in the Discussion section (Chapter 8.3).

Shown in Fig. 8.2(b) are the $\eta_{eff}$ data plotted versus temperature $T$ for PiBMA/SiOx with thicknesses $h_0$ varied between 10 and 120 nm and $T$ from 74 °C ($= T_{g,\text{bulk}} + 16$ °C) to 106 °C ($= T_{g,\text{bulk}} + 48$ °C). The equivalent $M_{tot}$ versus $T$ data is shown in Fig. 8.2(b). We find that the $\eta_{eff}$ measurement of the 120 nm films is consistent with the viscosity of the bulk PiBMA polymer determined by conventional rheometry. But at the other film thicknesses, the data show that $\eta_{eff}$ decreases with decreasing $h_0$ for the whole range of $T$ studied. Comparing this trend with the $h_0$-invariance of $D$ found above, one can conclude that $D$ and $\eta_{eff}$ of the films depend on the local dynamic properties differently.

**Figure 8.2:** (a) Semi-log plot of effective viscosity $\eta_{eff}$ versus temperature for PiBMA/SiOx with different thicknesses $h_0$ as indicated in the figure legend. (b) Semi-log plot of mobility, $M_{tot} \equiv h_0^3/(3\eta_{eff})$, versus temperature of the same data shown in (a). The solid lines are the best fit to the three-layer model assuming $h_1 = 3.67$ nm as described in the Discussion section (Chapter 8.3.2).
8.3 Discussion

In accordance with current views and results [133, 169, 170, 174], we interpret the confinement effects demonstrated by our data to arise from competition between the antagonistic effects of the free surface and substrate interface on the local dynamics of the polymer. With this, the thickness-invariant $D$ and $T_g$ measurements shown in Fig. 8.1 suggest that the effects of the two surfaces cancel. On the other hand, the $\eta_{\text{eff}}(h_0)$ data of Fig. 8.2 suggest that the effect of the free surface dominates. We first focus on the different dependencies exhibited by $D(h_0)$ and $\eta_{\text{eff}}(h_0)$. We attribute this finding to $D$ and $\eta_{\text{eff}}$ being different functions of the local segmental friction coefficient. Layer models are established to account for the experimental results of $D(h_0)$, $\eta_{\text{eff}}(h_0)$ and also $T_g(h_0)$ in the following sections.

8.3.1 Layer Model Interpretation for the Diffusivity Measurement

For a polymer melt with $N$ segments per chain, the diffusivity $D$ scales with the segmental friction coefficient ($\zeta$) according to [175, 182]:

$$ D = \frac{k_B T}{N \zeta}. \quad (8.1) $$

As before [133, 169], we incorporate dynamic heterogeneity in the films by using a layer model. Specifically, we treat the films to be a stack of $n$ dynamically different layers with thicknesses, $h_i$, and local viscosities $\eta_i$, or equivalently local segmental friction coefficient
\[ \zeta_i, \text{ where } \zeta_i \propto \eta_i \text{ and } i = 1, 2, \ldots, n. \] In FRAPP measurements of \( D \) [175], the pitch width of the photobleached patterns (which is \( \sim \mu \text{m} \)) is much bigger than the film thickness (\( \approx 10 \text{ to } \sim 100 \text{ nm} \) here). Then the majority of the chains in the unbleached region should have diffused many times through all \( n \) layers of the films before reaching the bleached region and being detected. This scenario, together with Eq. (8.1), suggest that

\[
D = \frac{k_B T}{N \langle \zeta_i \rangle},
\]

(8.2a)

where

\[
\langle \zeta_i \rangle \propto \langle \eta_i \rangle = \frac{\sum_{i=1}^{n} \eta_i h_i}{\sum_{i=1}^{n} h_i}.
\]

(8.2b)

### 8.3.2 Layer Model Interpretation for the Effective Viscosity Measurement Using Solution to the Navier-Stokes Equation

As for the effective viscosity \( \eta_{\text{eff}} \), it is derived from the mobility \( M_{\text{tot}} \) from the definition, \( \eta_{\text{eff}} = h_0^{3/2}/(3M_{\text{tot}}) \) (Eq. (4.3)). To find a relation between \( M_{\text{tot}} \) and the current model parameters, namely \( h_i \) and \( \eta_i \), one solves the Navier-Stokes equation for the steady-state velocity profile in the film \( \langle v(z) \rangle \), where \( z \) is the perpendicular distance from an interface of the film, upon application of a pressure gradient \( \nabla P \) parallel to the film, then invoke the definition, \( M_{\text{tot}} = h_0 \langle v(z) \rangle /\langle -\nabla P \rangle \) [133] (where \( \langle ... \rangle \) indicates averaging over \( z \)). We find that the simplest model that can simultaneously account for the \( D \) (Fig. 8.1(b)) and \( \eta_{\text{eff}} \) (Fig. 8.2) data is a three-layer model. By assuming the no-slip boundary condition at
the substrate interface, which has been found applicable to polymer films with low MW (< \sim 100 \text{ kg/mol}) like the films studied here [176], we derive the following expression for $M_{\text{tot}}$:

$$M_{\text{tot}} = \frac{h_1^3}{3\eta_1} + \frac{h_2^3}{3\eta_2} + \frac{h_3^3}{3\eta_3} + \frac{h_1 h_2 (h_1 + h_2)}{\eta_2} + \frac{(h_1 + h_2) h_3 (h_1 + h_2 + h_3)}{\eta_3}, \quad (8.3)$$

where $h_i = h_1 + h_2 + h_3$, $i = 1, 2, 3$ labels the layers from top to bottom in order. We interpret the $i = 1$ top layer to be the surface mobile layer, the $i = 2$ layer to be the bulk-like middle layer, and the $i = 3$ layer the polymer/substrate interfacial layer. Accordingly, one expects $\eta_3 > \eta_2 = \eta_{\text{bulk}} > \eta_1$, which we find from our fit results as discussed below. Fig. 8.3 shows a schematic illustration of the three-layer model described.

**Figure 8.3:** Schematic representation of the three-layer model discussed in the text. In this model, the film is assumed to be made up of (from top) a surface mobile layer ($i = 1$), a bulk-like middle layer ($i = 2$), and a low-mobility polymer layer ($i = 3$) immediate to the substrate surface. The layer thicknesses and viscosities are denoted by $h_i$ and $\eta_i$, respectively.
In a previous study, our former group members [151] measured the effective viscosity of PMMA supported by silica (PMMA/SiOx), and found that a similar three-layer model was able to describe the experimental result. In fitting the data, they had to incorporate a thickness dependence in the mobility of the surface mobile layer ($M_t$). In here, we find the same to be needed. Clearly, $M_t$ depends directly on $h_1$ and $1/\eta_1$. Because the thickness of this layer $h_1$ has been shown to be independent of the film thickness $h_0$ [87, 133], we attribute the thickness dependence of $M_t$ to $1/\eta_1$. Following the form of $M_t(h_0)$ proposed by Li et al. [151], we write

$$\eta_1(h_0) = \eta_1(\infty)\left\{1 + \exp\left[-(h_0 - l_t) / \Delta l_t\right]\right\},$$

(8.4)

where $l_t$ denotes the corresponding film thickness whereat $\eta_1$ changes to 2 times $\eta_1(\infty)$, its value in the thick film limit, and $\Delta l_t$ is the length scale over which the change takes place. Figure 8.4 displays a plot of $\eta_1(h_0)/\eta_1(\infty)$ found to describe the experimental results.
the following, we discuss how we apply the three-layer model to fit the $D$ (Figure 8.1(b)) and $\eta_{\text{eff}}$ (Fig. 8.2) data simultaneously.

As observed above, $D \sim 1/\langle \eta \rangle$, which produces the relation, $D(h_0)/D(\infty) = \langle \eta(\infty) \rangle / \langle \eta(h_0) \rangle$. Experimentally, $D(h_0)$ is thickness-independent, which means $\langle \eta(\infty) \rangle / \langle \eta(h_0) \rangle = 1$ or

$$\eta_{\text{bulk}} = \langle \eta(h_0) \rangle = \frac{\eta_1 h_1 + \eta_2 h_2 + \eta_3 h_3}{h_1 + h_2 + h_3}$$, \hspace{1cm} (8.5a)

$$\Rightarrow \eta_3 = \eta_2 + \frac{h_1}{h_3} (\eta_2 - \eta_1)$$, \hspace{1cm} (8.5b)

where the assumption $\eta_2 = \eta_{\text{bulk}}$ was used. According to Eq. (8.5b), if $\eta_1 < \eta_{\text{bulk}}$, then $\eta_3 > \eta_{\text{bulk}}$. This warrants the above interpretation of the three-layer model.

In fitting the data, we simplify the procedure by making two additional assumptions. First, we assume the third layer thickness, $h_3$ to be equal to the thickness of the irreversibly adsorbed PiBMA layer found on the substrate. The adsorbed layer thickness was attained with a 120 nm thick PiBMA film on SiOx, following a procedure from a previous study [159]. The film was annealed at 106 °C for 18 hrs under argon atmosphere to mimic the environment during the FRAPP measurement. After annealing, the film was subsequently washed with THF, a good solvent for PiBMA. The adsorbed layer thickness was determined as $h_3 = 0.9 \pm 0.3$ nm. The error is the standard deviation.
of five measurements at different locations on the sample. Secondly, we assume that the
temperature dependence of $M_t(T)$ ($\sim 1/\eta_1(T)$) is proportional to $1/\eta_{\text{eff}}(T)$ of the $h_0 = 10$ nm films, which was found to be described by

$$\eta_{\text{eff}}(h_0 = 10 \text{ nm}) = (723 \pm 456 \text{ Pa} \cdot \text{s}) \exp\left(\frac{211 \pm 34 \text{ K}}{T - (329 \pm 2) \text{ K}}\right). \quad (8.6)$$

This assumption stems from the observation that the contribution of $M_t$ to $M_{\text{tot}}$ usually increases as $h_0$ decreases [133, 151]. For $h_1$, we attempt two possible values. In the first attempt, we assume $h_1 = R_{\text{EE}} = 3.67$ nm, where $R_{\text{EE}}$ is the end-to-end distance of the polymer and $\approx \sqrt{6}R_g$. This corresponds to the situation where enhanced surface flow occurs mainly in the top layer of polymer molecules. In the second attempt, we set $h_1$ equal to the Kuhn length of the polymer, which is approximated to be $\approx 1$ nm [60]. This choice of $h_1$ is due to a simulation result of Lam et al. [183] on ten-mer polymer films undergoing driven in-plane flow, which showed that enhanced surface flow existed mainly within a Kuhn length of the free surface.

The fit results based on the above model and assumptions are summarized in
Table 8.1. In comparing the fit values of the model parameters shown in different
columns (corresponding to different values set for $h_1$), one observes that in changing the
value of $h_1$ from 3.67 to 1 nm, only the value of $h_1^3/3\eta_1$ (i.e., the first term on the RHS of
Eq. (8.3)) needs to be adjusted; the other parameters maintain the same values. To
explore the reason, we examined the relative contributions of different terms in Eq. (8.3)
to $M_{\text{tot}}$ at a temperature $T$ of $90$ °C, near the middle of the temperature range studied.
Figure 8.5(a) shows semi-log plots of the different relative contributions as a function of
$h_0$, where $M_i$ denotes $h_i^3/(3\eta_i)$ ($i = 1, 2, 3$) and “Cross terms” denotes the sum of the last two terms in Eq. (8.3). From these plots, one sees that $M_1/M_{\text{tot}}$ exhibits the same $h_0$ dependence for both cases of $h_1 = 1$ and 3.67 nm. In fact, we find that the $M_1/M_{\text{tot}}(h_0)$ dependence of the $h_1 = 1$ nm curve can be described by multiplying that of the $h_1 = 3.67$ nm curve by 0.93. At this time, we do not know the reason for this simple relationship. Empirically, one sees from Fig. 8.5(b) (which displays the same data from Fig. 8.5(a) but on a linear scale) that it is due to partial cancellation of the change in $M_2/M_{\text{tot}}$ and that in $(\text{cross terms})/M_{\text{tot}}$ upon the change in $h_1$ that is incidentally balanced by a constant percentage change in $M_1/M_{\text{tot}}$.

<table>
<thead>
<tr>
<th></th>
<th>$h_1 = R_{\text{EE}} = 3.67$ nm</th>
<th>$h_1 = 1$ nm</th>
</tr>
</thead>
<tbody>
<tr>
<td>$h_1^3/3\eta_1(\infty)$</td>
<td>$(4.3 \pm 0.2) \times \exp\left(-\frac{211}{T - 329}\right)$</td>
<td>$(4.0 \pm 0.2) \times \exp\left(-\frac{211}{T - 329}\right)$</td>
</tr>
<tr>
<td>$l_t$ (nm)</td>
<td>$35 \pm 14$</td>
<td>$35 \pm 14$</td>
</tr>
<tr>
<td>$\Delta l_t$ (nm)</td>
<td>$10 \pm 2$</td>
<td>$10 \pm 2$</td>
</tr>
</tbody>
</table>

**Table 8.1:** Result obtained from the three-layer model fits to the $D$ and $\eta_{\text{eff}}$ data for PiBMA/SiOx assuming two physical values of $h_1$. The values of the other model parameters not given in the table were fixed according to the following: (1) $h_2 = h_0 - (h_1 + h_3)$. (2) $\eta_2 = \eta_{\text{bulk}} = \eta_{\text{eff}}$ of the 120 nm thick PiBMA/SiOx films = $(365 \pm 316$ Pas) $\exp\left[(318 \pm 47\text{ K}) / (T - (323 \pm 3\text{ K}))\right]$. (3) $h_3$ = thickness of the adsorbed layer of PiBMA/SiOx = $(0.9 \pm 0.3$ nm. (4) $\eta_3 = [\eta_2(h_t+h_3)-\eta_1h_1]/h_t$ due to Eq. (8.5).
Figure 8.5: The relative contributions of $M_1$, $M_2$, $M_3$ and the cross terms to $M_{\text{tot}}$ versus $h_0$ in semi-log (a) and linear (b) plots. These data were obtained under $T = 90$ °C and $h_1 = 3.67$ nm (solid lines) and 1 nm (dashed lines), respectively.

It is instructive to compare the fitting results of PiBMA/SiOx with those of PMMA/SiOx [151]. According to Fig. 8.5, the contribution of $M_3$ to $M_{\text{tot}}$ is negligible. This means that in fitting the $\eta_{\text{eff}}$ data for PiBMA/SiOx, we could have set the bottom layer to be dynamically dead ($i.e., M_3 = 0 \Leftrightarrow \eta_3 = \infty$) as was done for PMMA/SiOx [151]. But with the knowledge of $D(h_0)$, we are obliged to set the value of $\eta_3$ according to Eq. 8.5(b). Another important difference between the two results is that the temperature dependence of $M_1(h_0,T)$ was Arrhenius in PMMA/SiOx, but it follows the Vogel-Fulcher-Tammann (VFT) dependence here (Fig. 8.6). This result indicates that cooperativity is present in the transport dynamics of the surface mobile layer of the PiBMA films, but undetectable in the PMMA films. Alongside, one observes that the Kauzmann temperature ($T_K$) of our PiBMA polymer is only $\sim 8$K below the bulk $T_g$ (based on the expression of $\eta_{\text{bulk}}(T)$ of PiBMA given in the caption of Table 8.1) while the $T_g,\text{bulk} - T_K$
values for PMMA are much bigger, \( \approx 72 \) and 64 K for \( M_w = 2.7 \) and 12.4 kg/mol, respectively [151]. Noting that the VFT cooperative dynamics approaches the Arrhenius (uncooperative) one in the limit of \( T - T_K \rightarrow \infty \), then the notably smaller value of \( T_{g,\text{bulk}} - T_K \) suggests that the extent of cooperativity in the transport dynamics of the PiBMA polymer is bigger than that of PMMA for the same \( T - T_g \). A bigger extent of cooperativity is expected to bring about stronger coupling between different layers. This is in agreement with the bigger values of \( l_t \) and \( \Delta l_t \) found of the PiBMA/SiOx films compared to those of PMMA/SiOx (where \( l_t \) and \( \Delta l_t \approx 5 \) and 1 nm, respectively [151]).

We should, however, clarify that the extent of cooperativity mentioned above may differ from the size of cooperativity at the \( T_g (\zeta_c) \) commonly discussed of glassy dynamics [94]. In fact, different temperature dependences had been found between terminal flow and segmental relaxations in polymer melts near the \( T_g \) [184]. Previous experiments on a variety of polymer film systems found that the extent of variation of the thin film \( T_g \) from the bulk value did not correlate with the \( \zeta_c \) value of the polymer [94, 185]. Thus we do not think that that \( \zeta_c \) or extent of cooperativity mentioned above may explain our observations. As demonstrated in Fig. 8.2, our data can be accounted for by assuming that \( 1/D \) and \( \eta_{\text{eff}} \) are different functions of the local segmental friction (\( \zeta_s \)).
Figure 8.6: Comparison of $M_{1,c}$ versus $T - T_g$ found here of the PiBMA/SiOx films ($M_n = 10.0$ kg/mol, solid line) and the PMMA/SiOx films ($M_n = 2.5$ and $11.5$ kg/mol, dashed and dotted line, respectively) reported in Ref. [151].

As discussed in the Introduction (Chapter 8.1), there is a long-standing question concerning the inconsistent $T_g(h_0)$ [93, 94], $D(h_0)$ [102, 103] and $\eta_{\text{eff}}(h_0)$ [133, 176] dependencies found of the PS/SiOx films. In Fig. 8.7(a), we reproduce the data of Frank et al. [102] for the in-plane diffusivity of PS/SiOx with $M_w = 38$ kg/mol at $T = 140$ °C. Figure 8.7(b) displays the $\eta_{\text{eff}}(h_0)$ data, upon normalization by $\eta_{\text{bulk}}$ (taken to be $\lim_{h_0 \to \infty} \eta_{\text{eff}} = 70 \pm 12$ kPa·s), we measured from PS/SiOx with the same $M_w$ at the same temperature. We find that these data can be fit to the above three-layer model (solid lines in Fig. 8.7(a) and 8.7(b)) with the model parameters and details of the fitting procedure are given in Table 8.2. This provides further support to the present proposal that $D$ and $\eta_{\text{eff}}$ are
different functions of the local segmental friction coefficient and so can exhibit divergent $h_0$ dependences.

\begin{figure}[h]
\centering
\includegraphics[width=\textwidth]{figure8.7.png}
\caption{(a) The diffusivity $D$ versus $h_0$ data reported by Frank et al. [102] for PS/SiOx with $M_w = 38$ kg/mol at $T = 140$ °C. (b) Normalized effective viscosity $\eta_{\text{eff}} / \eta_{\text{bulk}}$ versus $h_0$ for PS/SiOx obtained under the same condition. In both panels, the experimental data are shown by the symbols. The best fits to the three-layer model are displayed by the solid lines. (Data of panel (a) was reproduced with permission from the American Chemical Society.)}
\end{figure}

\begin{table}
\centering
\begin{tabular}{|c|c|}
\hline
$h_1 = 3$ nm & \\
\hline
$\eta_1/\eta_2$ & $0.049 \pm 0.006$ \\
\hline
$h_3$ (nm) & $1 \pm 0.5$ \\
\hline
$\eta_3/\eta_2$ & $145 \pm 20$ \\
\hline
$D_\infty$ ($10^{13}$ cm$^2$/s) & $8.6 \pm 0.8$ \\
\hline
\end{tabular}
\end{table}
Table 8.2: Result obtained from the three-layer model fits to the $D$ and $\eta_{\text{eff}}$ data for PS/SiOx assuming $h_1 = 3$ nm. Note that $D$ is not a constant here and determined by Eq. 8.2(a) and 8.2(b), which can be combined to give $D = D_\infty h_0/(h_1 \eta_1/\eta_2 + h_2 + h_3 \eta_3/\eta_2)$. The use of this expression instead of Eq. 8.5 as was done before results in the need for an additional parameter, $D_\infty$. (2) It is assumed that $h_2 = h_0 - (h_1 + h_3)$. This is consistent with the previous observation that $h_1$ is no more than 3 nm for PS/SiOx [133]. Like above, we find that the value of $\eta_1/\eta_2$ co-varies with the value of $h_1$ according to $h_1^2/(3 \eta_1) \approx \text{constant}$. In here, we assume that $h_1 = 3$ nm.

8.3.3 Layer Model Interpretation for the Glass Transition Temperature Measurement

As for the $T_g(h_0)$ dependence, Lipson and Milner [148] pointed out that measurements like ours - that monitor changes in the thermal expansivity of the films at the glass transition - detect the unweighted average of the local $T_g$’s if the films can be considered to be a stack of dynamically heterogeneous layers, each exhibiting the same liquid- and glassy- state thermal expansivities. We find that the $T_g(h_0)$ of our systems conform to this prediction. By using a fluorescently labeled layer that reports the local $T_g$ [170], Ellison and Torkelson found that the $T_g$ of the top layer ($T_{g1}$) of PS/SiOx was significantly depressed (by $\sim 30$ K from $T_{g,\text{bulk}}$) while that of the bottom layer was relatively unaffected (although it is important to note that the bottom layer examined the 12 nm nearest the substrate interface). Then an unweighted average $T_g$ should decrease with decreasing $h_0$, as observed in experiment. For PiBMA/SiOx, Priestley et al. [83] found that the local $T_g$ at the free surface was depressed by 6 K while that at the substrate surface was enhanced.
by 5 K. By using these \( T_{gi} \) values and \( h_1 = 3.67 \) or 1 nm, the unweighted average \( T_g \) again accounts for experimental observations within typical measurement uncertainties.

8.4 Conclusions

In summary, we have examined the correlation between \( T_g \), \( D \) and \( \eta_{eff} \) of nano-confined polymer films supported by a solid substrate. Two systems were considered, namely PiBMA/SiOx and PS/SiOx. For PiBMA/SiOx, the \( T_g \) and \( D \) were invariant with the film thickness, but \( \eta_{eff} \) decreased with decreasing film thickness. For PS/SiOx, the \( T_g \) and \( \eta_{eff} \) decreased with decreasing film thickness while \( D \) exhibited an opposite trend. To account for the observed divergent \( D(h_0) \) and \( \eta_{eff}(h_0) \) dependences, we proposed that they are different functions of the local viscosity \( \eta_i \). Specifically, \( D \sim k_B T / \langle \eta_i \rangle \) and \( \eta_{eff} = h_0^{3/3} M_{tot}(\eta_i) \). By applying these assumptions to a three-layer model, we were able to describe the measurements well. As for \( T_g(h_0) \), we find that Lipson and Milner’s proposal that it is the unweighted average \( T_g \) explains the observations. Considering the variety of confinement effects demonstrated by our systems, the proposed interpretations for \( T_g(h_0) \), \( D(h_0) \) and \( \eta_{eff}(h_0) \) may provide a resolution to the decades-long controversy about how nano-confinement affects different dynamics of polymer films.
CHAPTER 9

Conclusion

Previous research found that, polymer thin films upon nano-confinement often exhibit physical properties different from the bulk. By using techniques of ellipsometry, FRAPP and AFM, we studied how nano-confinement influences several dynamic properties of polymer thin films, including glass transition temperature $T_g$, effective viscosity $\eta_{\text{eff}}$ and diffusivity $D$, and the correlation between these dynamics as well.

Previous experiments showed that the $T_g$ of polymer thin films under nano-confinement could be depressed or increased as the film thickness decreases. While observations of this sort are usually attributed to the effects of the interfaces, some experiments suggested that the molecular weight and tacticity of the polymer might also play a role. To understand the effects of these other factors, the thin film $T_g$ of PαMS and PMMA supported by silica were studied.

Firstly, the effects of MW on the $T_g$ of silica-supported polymer thin films were studied, by employing the polymer PαMS at three different molecular weights, MW, of 1.3, 20 and 420 kg/mol. For the 20 and 420 kg/mol films, the $T_g$ decreased with decreasing film thickness. This variation is generally attributed to the presence of a mobile layer at the free surface, where there is a greater degree of freedom or free-volume for the molecules to move around and so the local $T_g$ is lower. But for the 1.3 kg/mol films, the $T_g$ was independent of the film thickness. With support of literature data, we attribute the different behaviors in $T_g$ to the effect of chain stiffness, which is
expected to dominate at low MWs and causes the $T_g$ to be independent of the free-volume content of the polymer.

In addition to MW, the effects of tacticity on the $T_g$ of polymer films were also studied. As preceding studies of PMMA films have shown that, the $T_g$ could be complicated by the tacticity of PMMA, we studied the $T_g$ of these films as a function of film thickness at two molecular weights (MW = 2.5 and ~50 kg/mol) and two syndiotacticities (s% = 56 and 69 or 79%). We found that the result depends on both the MW and s% in unconventional ways. For the 2.5 kg/mol films, the $T_g$ was depressed for the lower s% films but increased for the higher s% films. For the ~50 kg/mol films, however, the signs of the $T_g$ change were reversed. To understand these observations, we constructed bi-layer films from pairs of the studied PMMAs with roughly the same MW but different s%. Our result suggests that for the higher MW films, both the effects of the free surface and the substrate interface on the $T_g$ are more significant on the higher s% PMMAs than on the lower s% PMMAs. For the lower MW films, however, the significance of the surface and substrate effects are modified, probably due to the effect of chain stiffness on the $T_g$ and different degrees of substrate segregation of the higher s% chains at different MW’s, respectively.

Besides $T_g$, the effects of nano-confinement on some other dynamic properties of polymer films were also studied, in order to resolve a long-standing controversy about the correlations between different dynamics. Specifically, the $T_g$ and $D$ of PS/SiOx had been both found to decrease with decreasing film thickness $h_0$. Assuming the conventional conception that the free surface causes the local dynamics to speed up and the substrate
surface causes the local dynamics to slow down, the \( T_g(h_0) \) found of the PS/SiOx films would suggest that the dynamics of the films are dominated by the free surface, but that of \( D(h_0) \) would imply that the substrate surface dominates. Given that the glass transition involves cooperative, local motions of the chain segments while \( D \) involves large-scale translational motions of the whole chains, it is thus perceivable that the \( T_g \) and \( D \) may exhibit different thickness dependencies. But recent studies found that the effective viscosity \( \eta_{\text{eff}} \) of PS/SiOx decreased with decreasing \( h_0 \) over polymer molecular weights from 2.4 to 2,300 kg/mol. Both \( D \) and \( \eta_{\text{eff}} \) describe transport phenomena in the films and are known to depend on the same sort of local dynamic properties, namely the local segmental friction coefficients. It is then unclear why \( D \) and \( \eta_{\text{eff}} \) displayed seemingly inconsistent \( h_0 \) dependences. In this study, the effects of confinement on the \( T_g \), \( D \) and \( \eta_{\text{eff}} \) of PiBMA/SiOx were simultaneously studied. Both the \( T_g \) and \( D \) were found to be independent of \( h_0 \), but \( \eta_{\text{eff}} \) decreased with decreasing \( h_0 \). We envisage the different \( h_0 \) dependencies to be caused by \( T_g \), \( D \) and \( \eta_{\text{eff}} \) being different functions of the local \( T_g \)'s \((T_g,i)\) or viscosities \((\eta_i)\), which vary with the film depth. By assuming a three-layer model, we were able to account for the experimental data and resolve this inconsistency. By extending these ideas to the analogous data of PS/SiOx, a resolution was found for the long-standing inconsistency regarding the effects of confinement on the dynamics of polymer films.

These studies indicate that there is still much to learn about the dynamics of polymer thin films while at the same time unveil new directions of potential research. Ongoing work in our lab will provide more information about the nano-confinement
effects on the viscosity of polymer films. Additionally, a new method of modifying the film in a controlled way is provided by constructing bi-layer films. The creation of bilayer films, which hereby serves as a way to control the interplay between effects from the surface and the substrate, can be a novel method to tune the interfacial properties of polymer thin films.
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PUBLICATIONS

4. K. Geng, F. Chen and O. K. C. Tsui, Molecular-weight Dependent Tg Depression of Silica-


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