STRUCTURE AND DYNAMICS OF SWOLLEN POLYMER BRUSHES

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STRUCTURE AND DYNAMICS OF SWOLLEN POLYMER BRUSHES

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ABSTRACT

A polymer brush is a monomolecular film in which each polymer chain is attached at one end to a surface or interface. Tremendous attention has been paid to both the basic science and technology of polymer brushes, due to their special properties, which stem from their unique structure arising from the tethering of polymer chains. Especially, research and many applications involve polymer brushes in the swollen state. The main objective of the research presented in this dissertation was to determine the structure and dynamics of polymer brushes under swollen conditions.

The structure of polystyrene brushes swollen in toluene vapor has been determined using neutron reflectivity. For high grafting density brushes, the scaling of the thickness of the brush swollen in solvent vapor with chain length and grafting density agrees quantitatively with the scaling reported for densely grafted brushes swollen in liquid. Deep in the brush, next to the substrate, the shape of the segment concentration profile is the same whether the brush is swollen by liquid or by vapor. Differences in the segment concentration profile are manifested primarily in the swollen brush interface with the surrounding fluid. The interface of the polymer brush swollen in vapor is much more abrupt than that of the same brush swollen in liquid, which agrees well with a simple SCF calculation. This sharper interface should have important implications for fluctuations at the brush surface and the compressibility of the brush surface in the swollen state.
The surface dynamics of polystyrene brushes swollen in toluene vapor have been investigated using X-ray photon correlation spectroscopy. No surface height fluctuations are observable in the currently available experimental time and length scale window for various strongly swollen brushes of grafting densities from 0.04 to 0.61 chains/nm² and swollen thicknesses from 11 to 105 nm. This is remarkable, considering how highly plasticized the layers are from the standpoint of segmental dynamics. The surfaces of the vapor swollen brushes behave like solid surfaces on time scales and length scales pertinent to many practical applications. We attribute slowing of the surface fluctuations to the entropic penalty that has to be paid for fluctuations (which are a collective motion) to occur. Even the surface fluctuations of a 47 nm thick layer of liquid toluene atop a swollen brush are strongly altered by the presence of the adjacent brush chains.

Polymer films containing a layer of untethered chains on top of a brush have been studied by probing the diffusion dynamics of embedded gold nanoparticles with X-ray photon correlation spectroscopy. We found that the local diffusion slows significantly with an increase in the concentration of segments from tethered chains. This change in mobility with depth is more complicated than that envisioned in simple models of a layer of untethered chains with bulk viscosity sitting on top of an immovable brush.
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CHAPTER I
INTRODUCTION

1.1 Polymer Brush

1.1.1 Structure and Scaling Laws of Polymer Brushes

Polymer brushes are monomolecular films in which each macromolecule is attached at one end to a surface or interface [1]. A simple schematic of a polymer brush is shown in Figure 1.1. This special structure significantly alters the film properties, so polymer brushes have attracted attention from both fundamental sciences and practical technologies [2]. Polymer brushes were first used as colloidal stabilizers to avoid flocculation [3]. Recent research on polymer brushes suggests many potential applications including lubrication [4], flow control [5], biotechnology [6], and responsive surfaces [7].

Figure 1.1 Schematic of a polymer brush.
Grafting density, $\sigma$, is an important parameter to describe the structure of a polymer brush, and can be calculated by

$$\sigma = \frac{h \rho N_A}{M_n},$$

(1.1)

where $h$ is the brush thickness, $\rho$ is the bulk density, $N_A$ is the Avogadro’s number and $M_n$ is the number average molecular weight of the grafted polymer chains. The structure of a polymer brush is dependent on not only the grafting density, but also the radius of gyration, $R_g$, of the polymer chains. Taking into account the effect of $R_g$, polymer brushes can be characterized by the reduced tethering density, $\Sigma = \sigma \pi R_g^2$, which represents the number of chains grafted to a surface in the area on that surface that a free chain would occupy under the same conditions. As shown in Figure 1.2, when $\Sigma < 1$, chains are separated from each other and have a normal random coil configuration. This regime of behavior is called the “mushroom” regime; when $\Sigma > 1$, the “brush” regime, chains overlap and stretch; when $\Sigma \approx 1$ a crossover regime [2] is observed.

Figure 1.2 Transition between the “mushroom” regime and “true brush” regime observed in an experiment with a grafting density gradient of polyacrylamide brushes reported by Genzer et al. Reprinted with permission from W. J. Brittain, S. Minko, J. Polym. Sci., Part A: Polym. Chem. 2007, 45, 3505. Copyright 2007 John Wiley and Sons.
When the reduced grafting density is high enough ($\Sigma > 5$), the chains must stretch appreciably normal to the grafting surface to minimize the segment-segment interactions, and therefore their configurations are different from those of the Gaussian coil found in a melt of untethered chains [1]. In some applications or processing steps, polymer brushes are swollen in liquid solvent or solvent vapor, as in solvent annealing [8,9]. When swollen in a good solvent, the brush chains are further stretched from Gaussian coils. The extent to which the brush swells is determined by the competition between the entropic penalty of stretching and the favorable interactions among chains and solvent.

The first theoretical description of a polymer brush swollen in solvent was provided by Alexander and de Gennes [10,11]. The Alexander model [10] considers polymer chains of length $N$ that are adsorbed on an interface with a given grafting density $\sigma$. The free energy $F$ of the chains swollen in good solvent can be written:

$$F = k_1 N (N/\sigma h_s)^{5/4} + k_2 \left( \frac{4\pi}{3} \right)^{1/4} h_s^{7/4} / N^{3/4} \sigma^{1/4},$$  \hspace{1cm} (1.2)

where $h_s$ is the thickness of the swollen brush. The first term on the right side of Equation 1.2 represents the repulsive energy of the polymer layer, and the second term represents the stretching energy of the chains. The thickness of swollen brush $h_s$ is determined by the balance between the repulsive energy and the stretching energy. By minimizing the free energy of chains, one finds:

$$h_s \sim N^{1/3} \sigma^{1/3}.$$  \hspace{1cm} (1.3)

Equation 1.3 indicates that the brush thickness scales as $N\sigma^{1/3}$ when swollen in a good solvent. de Gennes [11] discussed two situations for grafted chains swollen in good solvents: separate coils and overlapping coils, as shown in Figure 1.3. These correspond
to polymer brushes in the “mushroom” regime and in the “brush” regime, respectively. In the “mushroom” regime with a low grafting density, each chain is separated with others, forming roughly a half sphere on the substrate. The sizes of the separated swollen chains scale as $N^{3/5}$, which is the same scaling as for untethered chains in a good solvent. When the grafting density is high enough so that chains are overlapped, the chains are stretched to form a real “brush”. Taking into account the excluded-volume effects, de Gennes obtained the same scaling relationship as Alexander, $h_s \sim N\sigma^{1/3}$. Both Alexander’s and de Gennes’ brush models are based on two assumptions: <1> the polymer chains are uniformly stretched with a step-function segment concentration profile; <2> all chain ends are located at the brush surface. Later, Milner et al. [1] applied self-consistent field (SCF) treatment to swollen brushes, obtaining a “parabolic” segment concentration profile with chain ends distributed throughout the entire brush, which is a more realistic model for polymer brushes swollen in good solvents. Although the SCF brush model is different from the Alexander – de Gennes brush model, it predicts the same scaling relationship:

$$h_s = \left( \frac{12}{\pi^2} \right)^{1/3} N(\omega\sigma)^{1/3},$$

(1.4)

where $\omega$ is the excluded-volume parameter.
The behaviors of a swollen brush are also dependent on the quality of the solvent. In a good solvent, polymer chains tend to swell because the interactions between polymer segments and solvent molecules are more favorable than the interactions among polymer segments. In a $\theta$-solvent, these two kinds of interactions are balanced out. In a bad solvent, the interactions among polymer segments are more favorable than the interactions between polymer segments and solvent molecules; therefore polymer chains collapse uniformly with $h_s$ scaling as $N\sigma$ [1] and the density variations parallel to the grafting surface are smoothed out [13].

The scaling relationships of polymer brushes swollen in solvents have been verified with both simulations [14] and experiments [15-19]. Auroy et al. [15] studied polydimethylsiloxane (PDMS) brushes grafted onto porous silica using small angle neutron scattering (SANS). They confirmed that the thicknesses, $h_s$, of the PDMS brushes
scale as $N \sigma^{1/3}$ when swollen in a good solvent (dichloromethane), and scale as $N \sigma$ when swollen in a bad solvent (acetone), respectively, as shown in Figure 1.4.

![Figure 1.4](image)

Figure 1.4 (a) Plot of $hD^2$ vs. $M$ for grafted layers in poor solvent (acetone). (+) bare silica surface; (●) chemically pretreated silica surface. (b) Plot of $hD^{2/3}$ vs. $M$ for grafted layers in good solvent (dichloromethane). Reprinted with permission from P. Auroy, L. Auvray, L. Leger, *Phys. Rev. Lett.* 1991, 66, 719. Copyright 1991 American Physical Society.

Field et al. [16] used neutron reflectivity (NR) to investigate the polystyrene-poly(ethylene oxide) (PS-PEO) block copolymer chains adsorbed onto quartz by the PEO blocks. When swollen in deuterated toluene, the molecular weight dependence of the thickness of tethered chains agrees well with the scaling laws. The segment concentration profile of the swollen tethered chains can be well described as a parabolic shape. In later NR research on polymer brushes swollen in good solvents [17-19], the segment concentration profiles were progressively improved with increasing resolution, showing a depletion zone next to the substrate for brushes of low
grafting densities and a "tail" at the brush/solvent interface in addition to the parabolic shape, as shown in Figure 1.5.

![Figure 1.5](image.png)

Figure 1.5 Comparison of different segment concentration profiles illustrates that the profile contains a depletion layer and a smooth tail away from the surface. Reprinted with permission from M. S. Kent, L. T. Lee, B. J. Factor, F. Rondelez, G. S. Smith, J. Chem. Phys. 1995, 103, 2320. Copyright 1995 AIP Publishing LLC.

1.1.2 Preparation of Polymer Brushes

Polymer chains can be tethered to a surface by physisorption or covalent binding [2]. One example for end-tethering by physisorption is the PS-PEO block copolymers adsorbed onto quartz by the PEO blocks [16]. Although tethering by physisorption is easy to perform, this physically adsorbed layer is usually unstable due to the weak interactions between the substrate and the chains. Tethered layers created by covalent bonding have enhanced stabilities and therefore they are more promising for potential applications. In
addition, higher grafting densities can be achieved with covalent bonding. The covalently bonded layer can be prepared via either the “grafting-to” or the “grafting from” method, as shown in Figure 1.6. In the “grafting-to” method, polymer chains with functional groups at one end are first prepared and then these functional groups reacted with the substrate surface [20]. This method provides tethered chains with precisely controlled molecular weights and molecular weight distributions. However, the grafting densities are usually limited and accordingly only thin layers can be obtained by the “grafting-to” strategy. Thick tethered layers with high grafting densities can be prepared via the “grafting-from” method [20], in which initiators are first attached onto the substrate to form a self-assembled monolayer (SAM), and then chains are polymerized from the immobilized initiators layer. Polymerization methods that can be used via the “grafting-from” strategy include free radical polymerization [21], anionic polymerization [22,23], and controlled radical polymerization [24-26].

Figure 1.6 “Grafting-to” method (left) and “Grafting-from” method (right).
Rühe et al. [21] first prepared polystyrene (PS) brushes via the “grafting from” method with free radical polymerization. The immobilization of azo initiators onto the silicon oxide surface was followed by the radical chain polymerization of styrene. The brush thicknesses could be controlled using the polymerization conditions of temperature and azo conversion. However, due to the nature of free radical polymerizations, the molecular weight distribution (PDI) of the brush chains was high.

Later, Jordan et al. [22] developed a “grafting-from” method with anionic polymerization. The SAM layer was biphenyllithium initiators on a gold substrate, which initiated the following anionic polymerization of styrene. Quirk et al. [23] also used “grafting-from” anionic polymerization to prepare diblock copolymer brushes on silicon oxide surface. This method provides tethered chains with narrow PDI, but the obtained brush films are thin (18 nm [22] and 24 nm [23]). Besides, the low tolerance for impurities of anionic polymerization further limits the applications of this technique.

Controlled radical polymerizations (CRP) have the advantages over traditional free radical polymerizations of good control of molecular weight and low PDI, as well as higher tolerance for impurities as compared with anionic polymerizations. Therefore, CRP, including nitroxide mediated radical polymerization (NMP) [24] and atom transfer radical polymerization (ATRP) [25,26], have been widely used for preparing polymer brushes via the “grafting-from” strategy. Hawker et al. [24] reported a “grafting-from” method based on NMP to prepare polymer brushes on silicon substrates. Vinyl monomers were polymerized from covalently bonded alkoxyamines or from tethered α-halo esters with (PPh₃)₂NiBr₂. This method allows sequential polymerizations of different monomers to prepare tethered block copolymers on the surface. Fukuda et al. [25] combined the
Langmuir-Blodgett (LB) technique and ATRP to synthesize poly(methyl methacrylate) (PMMA) brushes from silicon wafers. Matyjaszewski et al. [26] also developed a “grafting-from” method based on ATRP to polymerize styrene and acrylates from silicon wafers. Because ATRP is easy to perform and is suited for a variety of monomers, it has become the most popular method for synthesizing polymer brushes. In this work, all the polymer brushes were prepared by the ATRP “grafting from” strategy.

The key of ATRP is the reversible halogen transfer between a dormant species and a transition metal complex. In the particular case of this work, the dormant species is bromine-ended polystyrene (PS-Br), which is activated by the copper complex (CuBr/PMDETA) to generate a propagating radical (PS∙). As a consequence, the copper complex is oxidized to a higher oxidation state (CuBr₂/PMDETA). This process is reversible, establishing an equilibrium strongly shifted to the dormant species (k << k’) with a very low concentration of propagating radicals in the system. The number of initiators determines the number of PS chains and each chain has the same probability to propagate with styrene. Therefore, controllable molecular weight and narrow PDI can be achieved by ATRP. The mechanism of ATRP in this work is shown in Figure 1.7.

![Figure 1.7 Mechanism of ATRP of styrene.](image)
1.1.3 Dynamics of Polymer Brushes

The structure of polymer brushes at equilibrium, including scaling behaviors, segment concentration profiles and chain end distributions, have been extensively studied with theoretical calculations, computer simulations and experiments. However, comparatively fewer research on the dynamics of polymer brushes have been undertaken. The first theoretical description of the deformations of a melt brush surface was provided by Fredrickson and coworkers [27]. For a brush of thickness $h_o$, under the Alexander – de Gennes approximation, the calculated free energy per area of the deformed brush should scale as $q^{-2}$ when $qh_o << 1$, which implies that the surface fluctuations with wavelengths much longer than $h_o$ should be significantly suppressed. They rationalized the suppression of long-wavelength fluctuations using the configurational entropy penalty from the chain stretching required for the surface deformation. The dominating surface fluctuations are expected to have wavelengths comparable to $h_o$. Based on the approximation that the trajectories of the brush chains do not cross, Xi and Milner [28] obtained the same form of the energy of long-wavelength surface waves, with a slightly different coefficient, which confirms Fredrickson’s expectation that long wavelength fluctuations should be suppressed.

Akgun et al. [29] experimentally proved, using X-ray photon correlation spectroscopy (XPCS), that the long wavelength fluctuations are slowed by at least a factor of $10^5$ for melt polymer brushes. In the time (0.1 – 1000 s) and length (620 – 3100 nm) scales available, no surface fluctuations were found for both PS and poly($n$-butyl acrylate) (PBUA) brushes with grafting densities of 0.12 – 0.6 chains/nm$^2$, even at temperatures 170°C above the $T_g$ of the corresponding free chains, while films of
free chains with thicknesses and molecular weights comparable to those of the brushes showed \( q_{\parallel} \)-dependent surface fluctuations, as shown in Figure 1.8.

![Figure 1.8 Intensity-normalized time autocorrelation function vs. delay time at \( q_{\parallel} = 5.3 \times 10^{-3} \text{ nm}^{-1} \) for a 26 nm thick PS brush \((M_n = 28 \text{ kg/mol})\) with \( \sigma = 0.60 \text{ chains/nm}^2 \), 29 nm thick film of untethered PS chains \((M_n = 65 \text{ kg/mol})\) measured at 170°C and 21 nm thick PS brush \((M_n = 115 \text{ kg/mol})\) with \( \sigma = 0.12 \text{ chains/nm}^2 \) measured at 225°C. A schematic of a polymer brush is shown in the inset. Reprinted with permission from B. Akgun, G. Uğur, Z. Jiang, S. Narayanan, S. Song, H. Lee, W. J. Brittain, H. Kim, S. K. Sinha, M. D. Foster, Macromolecules 2009, 42, 737. Copyright 2009 American Chemical Society.

Since many potential applications of polymer brushes involve brushes in swollen states [5,7], the dynamics of brushes swollen in liquids or low molecular weight materials are of both practical and fundamental interest. Uğur et al. [30] studied PS brushes swollen in low molecular weight (2.2k) deuterated polystyrene (d8-PS) with XPCS, showing that despite the plasticization effect, the surface fluctuations were still too slow to be observed at the available times and length scales at temperatures around 50°C higher than \( T_g \) of the short chains.
PS brushes can be highly swollen in a good solvent that has a better plasticization effect, like toluene. The value of $T_g$ near the swollen brush surface (where the solvent concentration is highest) can drop by 150 - 220°C [31]. So the dynamics of brushes swollen in solvent are expected to be quite different from those of brushes swollen by short chains.

Farago et al. [32] first observed the thermal density fluctuations of polymer brushes swollen in solvent using neutron spin-echo spectroscopy (NSE). The polymer brushes were made by dissolving polystyrene-block-polyisoprene (PS-PI) diblock copolymers in $n$-decane, forming spherical micelles with a PS core and a corona of swollen PI tethered chains. The observed multi-decay time relaxation behavior can be explained with a model proposed by de Gennes that treats the corona as a semidilute polymer solution with varying concentration profile [33].

Fytas et al. [34-36] studied the dynamics of PS brushes swollen in solvent using evanescent-wave dynamic light scattering (EWDLS), shown schematically in Figure 1.9. This technique probes the cooperative diffusion of chains throughout the swollen brushes. They first measured the dynamics of the swollen tethered chains prepared by the “grafting-to” method [34]. PS-PEO copolymer chains were attached by PEO blocks on the surface of a glass prism of high-refractive index. While the tethered chains were swollen in toluene, the light was reflected from the back of the prism with the evanescent wave propagating through the swollen layer under total internal reflection conditions. The equilibrium thicknesses, $h_s$, of the swollen tethered layers ranged from 45 nm to 130 nm, but the grafting densities were low (~0.02 chains/nm²) due to the limitation of the “grafting-to” approach. The results revealed that the long-lived fluctuations have a
preferred wavelength of order \( h_s \). Later, they prepared brushes of covalently bonded PS and PBuA brushes (0.05-0.16 chains/nm\(^2\)) using the “grafting-from” method and studied the dynamics of the brushes swollen in good and poor solvent conditions [35,36]. In a good solvent, the dynamics of the swollen brushes that they were able to probe were the cooperative diffusion of chains, which are predicted by theory [37]. When the solvent was changed to one corresponding to the \( \theta \)-condition, a slow relaxation, like the self-diffusion of clusters in a gel, was observed.

Figure 1.9 Schematic diagram of the evanescent wave dynamic light scattering setup with the laser beam undergoing a total reflection. Reprinted with permission from V. N. Michailidou, B. Loppinet, O. Prucker, J. Rühe, G. Fytas, *Macromolecules* 2005, 38, 8960. Copyright 2005 American Chemical Society.

Semenov et al. [38] theoretically calculated the excess free energy of a small sinusoidal deformation of a polymer brush swollen in a good solvent, which includes two contributions: <1> the energy due to the chain stretching, and <2> the energy arising from inhomogeneous segment distribution. The deformation energy is related to the scattering function, \( S(q) \). The theoretical calculations of \( S(q) \) were then compared with
the EWDLS experiment on the PS-PEO brushes [34], showing qualitative agreement for all brushes except the thickest one. Later, they identified three relaxation modes for the experimental results: <1> a fast cooperative hydrodynamic mode, which is the single-fluid cooperative motion of polymer segments together with the solvent; <2> a slow drag mode, which is the drag motion of the segments with respect to the solvent; and <3> a slowest anchor-sliding mode, which is the motion of the anchoring blocks (PEO) on the adsorbing surface [39].

1.2 X-ray and Neutron Reflectivity

1.2.1 Introduction

X-ray reflectivity (XR) and neutron reflectivity (NR) are useful tools for studying thin films. They can provide information on the film thickness, the roughness or width of the interface, and the variation of structure with depth in the film. NR and XR have been widely used for research on the surfaces and interfaces of thin films. The fundamental concepts of NR and XR will be introduced in detail in this section, and the experimental measurements and data analyses will be discussed in following chapters.

1.2.2 Fundamental Principles

When a beam (light, X-ray, or neutron) is incident on an interface between two phases, some energy will be reflected from the interface with the reflected beam, and the other part of the energy will pass through the interface with the refracted beam. The reflected beam intensity relative to the refracted beam intensity is determined by the
refractive indices of the two phases. For neutron and X-ray beams, the refractive index, \( n \), of condensed phase is usually less than unity. \( n \) can be written as

\[
n = 1 - \delta + i\beta, \tag{1.5}
\]

where \( \delta \) is the real part and \( \beta \) is the imaginary part. \( \delta \) can be written as

\[
\delta = \frac{\lambda^2}{2\pi} \left( \frac{b}{V} \right), \tag{1.6}
\]

where \( \lambda \) is the wavelength of the incident beam and \( b/V \) is the scattering length density (SLD) of the phase. The SLD is a function of electron density for X-rays and is a function of neutron scattering length for neutron beams. For X-rays \( \beta \) describes the absorption of the phase, and can be written as

\[
\beta = \frac{\mu\lambda}{4\pi}, \tag{1.7}
\]

where \( \mu \) is the linear absorption coefficient determined by experiment.

For NR, the value of \( \beta \) is usually much smaller than that of \( \delta \) for most polymer materials and often can be neglected. However, the \( \beta \) value for XR will become larger when the sample contains high atomic number elements like Au, and therefore must be taken into account.

The contrast for XR comes from differences in electron density, \( \rho_e \), which is determined by the atomic numbers of elements \( i \), \( Z_i \), in the material and its mass density, \( \rho \),

\[
\rho_e = \frac{N_A \rho \sum Z_i}{M_n}, \tag{1.8}
\]

where \( N_A \) is Avogadro’s number and \( M_n \) is the molecular weight of the characteristic repeating structure. For XR, SLD is proportional to \( \rho_e \).
\[
\left( \frac{b}{V}_x \right) = r_e \rho_e, \tag{1.9}
\]

where \( r_e \) is the electron radius (2.82 \( \times \) 10\(^{-6}\) nm).

The contrast for NR is due to differences in the neutron SLD, which can be written as

\[
\left( \frac{b}{V} \right)_n = \frac{N_A \rho \sum b_i}{M_n}, \tag{1.10}
\]

where \( b_i \) is the neutron scattering length of element \( i \). The value of \( b_i \) is not proportional to \( Z_i \). Due to the huge difference in neutron scattering lengths between hydrogen (\( b_H = -3.74 \times 10^{-6}\) nm) and deuterium (\( b_D = 6.67 \times 10^{-6}\) nm), selective deuteration is a useful method to provide contrast for NR measurements.

1.2.3 Specular Reflectivity

NR and XR are performed in the specular reflection geometry, as shown in Figure 1.10. The X-ray or neutron beam is incident with angle \( \theta_0 \) at a sharp interface between two homogeneous media with refractive indices of \( n_0 \) and \( n_1 \), respectively. The angle at which the beam is refracted, \( \theta_1 \), can be calculated according to Snell’s law,

\[
n_0 \cos \theta_0 = n_1 \cos \theta_1. \tag{1.11}
\]

When \( n_0 \) is greater than \( n_1 \), \( \theta_0 \) should be greater than \( \theta_1 \), implying that \( \theta_1 \) could become 0 when \( \theta_0 \) is decreased to a certain value, the critical angle (\( \theta_c \)), which can be calculated as

\[
\theta_c \equiv \sqrt{2\delta}.
\]

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The reflectivity, $R$, is the ratio of the reflected beam intensity to the incident beam intensity. When $\theta_0 \leq \theta_c$, $R = 1$ if the absorption is negligible. This means the incident beam is totally reflected by the interface. When $\theta_0 > \theta_c$, $R$ will decrease rapidly with $\theta_0$ because more and more energy of the incident beam is refracted. The wave vector normal to the interface (the $z$ component) of the incident beam is

$$k_{z,0} = \frac{2\pi \sin \theta_0}{\lambda_0}. \hspace{1cm} (1.13)$$

From Equation 1.11 we can obtain

$$n_0^2(1 - \sin^2 \theta_0) = n_1^2(1 - \sin^2 \theta_1). \hspace{1cm} (1.14)$$

According to the definition of $\theta_c$,

$$n_0 \cos \theta_c = n_1. \hspace{1cm} (1.15)$$

Therefore,

$$n_0^2(1 - \sin^2 \theta_c) = n_1^2. \hspace{1cm} (1.16)$$

Combining Equations 1.14 and 1.16, we obtain

$$n_1^2 \sin^2 \theta_1 = n_0^2 \sin^2 \theta_0 - n_0^2 \sin^2 \theta_c. \hspace{1cm} (1.17)$$

According to Snell’s Law,

$$n_1 v_1 = n_0 v_0, \hspace{1cm} (1.18)$$
where \( v_1 \) and \( v_0 \) are the velocities of the beam in the two media, respectively.

Assuming that the frequency \( f \) remains constant, we obtain

\[
\frac{v_1}{\lambda_1} = \frac{v_0}{\lambda_0} = f. \tag{1.19}
\]

Combining Equations 1.17, 1.18 and 1.19, we obtain

\[
\frac{\sin^2 \theta_1}{\lambda_1^2} = \frac{\sin^2 \theta_0}{\lambda_0^2} - \frac{\sin^2 \theta_c}{\lambda_0^2}. \tag{1.20}
\]

Based on Equation 1.13, we obtain

\[
k_{z,1}^2 = k_{z,0}^2 - k_{z,c}^2, \tag{1.21}
\]

where \( k_{z,0} \) and \( k_{z,1} \) are the wave vectors normal to interface of the incident beam and the refracted beam, respectively, and \( k_{z,c} \) is the value of \( k_{z,0} \) when \( \theta_0 = \theta_c \).

The reflection coefficient, which is the ratio of the amplitudes of the reflected beam and the incident beam, at a sharp interface between two media 0 and 1 can be given by

\[
r = \frac{k_{z,0} - k_{z,1}}{k_{z,0} + k_{z,1}}. \tag{1.22}
\]

Fresnel provided the \( R \) expression based on \( r \),

\[
R = rr^* = \left| \frac{k_{z,0} - k_{z,1}}{k_{z,0} + k_{z,1}} \right|^2 = \left| \frac{q_{z,0} - q_{z,1}}{q_{z,0} + q_{z,1}} \right|^2 = R_F(q_{z,0}), \tag{1.23}
\]

where \( r^* \) is the complex conjugate of \( r \) and \( q_{z,0} \) is the magnitude of the scattering vector, which for the special case of specular reflectivity has a value of \( 2k_{z,0} \).

Combining Equations 1.21 and 1.23, we obtain

\[
R_F(q_{z,0}) = \left| \frac{k_{z,0} - \sqrt{k_{z,0}^2 - k_{z,c}^2}}{k_{z,0} + \sqrt{k_{z,0}^2 - k_{z,c}^2}} \right|^2. \tag{1.24}
\]

When \( k_{z,0} \gg k_{z,c} \), Equation 1.24 can be written as
\[ R_F(qz,0) = \frac{1 - \left[ 1 - \left( \frac{k_{z,c}}{k_{z,0}} \right)^2 \right]^2}{1 + \left[ 1 - \left( \frac{k_{z,c}}{k_{z,0}} \right)^2 \right]^2} \]

\[ \approx \frac{1}{16} \left( \frac{k_{z,c}}{k_{z,0}} \right)^4 = \frac{1}{16} \left( \frac{q_{z,c}}{q_{z,0}} \right)^4, \quad (1.25) \]

which makes clear that reflectivity decays as \( q^4 \) at large \( q \) for an ideal sharp interface.

When a uniform thin film with a thickness of \( h \) is deposited on a substrate, there are three media and two interfaces (air/film and film/substrate). The reflected beam involves radiation reflected from both interfaces, as shown in Figure 1.11. The overall reflection coefficient can be written as

\[ r = \frac{r_{0,1} + r_{1,2} e^{2i k_{z,1} h}}{1 + r_{0,1} r_{1,2} e^{2i k_{z,1} h}}, \quad (1.26) \]

where \( r_{0,1} \) and \( r_{1,2} \) are reflection coefficients at air/film interface and film/substrate interface, respectively. Based on Equation 1.23, \( R \) can be written as

\[ R = \frac{r_{0,1}^2 + r_{1,2}^2 + 2r_{0,1} r_{1,2} \cos(2k_{z,1} h)}{1 + r_{0,1}^2 r_{1,2}^2 + 2r_{0,1} r_{1,2} \cos(2k_{z,1} h)}. \quad (1.27) \]

**Figure 1.11** Schematic of reflections and refractions at two sharp interfaces of a thin film deposited on a substrate.

The beams reflected from different interfaces interfere with one another, leading to a series of maxima and minima in plots of the reflectivity. These are called “Kiessig fringes” [40]. The thickness of the film, \( h \), can be easily estimated using the distance between two consecutive minima, \( \Delta q_{z,1} \), by
\[ h = \frac{2\pi}{\Delta q_{z,1}} \cong \frac{2\pi}{\Delta q_{z,0}} \text{ for } (q_{z,0} \gg q_{z,c}), \tag{1.28} \]

where \( q_{z,c} \) is the scattering vector magnitude at the critical angle.

An example of X-ray reflectivity for a tethered PS layer on a Si wafer is shown in Figure 1.12. The XR data demonstrate several typical features, such as the Kiessig fringes, a sudden drop in reflectivity at the value of the scattering vector corresponding to the critical angle, \( q_{z,c} \), and the power law decrease in the envelope of the total reflection when \( q_{z,0} > q_{z,c} \). The reflectivity raw data can provide some simple information about the film, like the thickness and other characteristic lengths of periodic structure, without detailed analysis. However, more detailed information, such as the interface roughness and the SLD profile, cannot be directly extracted from the reflectivity data because of the loss of phase information \([41,42]\). Therefore, a more complicated analysis of the reflectivity data, “fitting”, has to be performed to obtain the detailed information. In a fitting process, simulations of the scattering from a candidate structural model for the film are compared with the experimental reflectivity data, adjusting parameters of the model by a nonlinear regression to find the “best fit”. Please be noted that there might be candidate structural models showing mathematically good fit but indeed not physically realistic. Therefore, understanding the process of making the sample and the structural information obtained from auxiliary techniques is important to rule out those unrealistic structural models.
1.2.4 Roughness and Diffuseness

An interface in the real world is not ideally sharp, rather it shows a gradient in properties from one medium to another. There are two kinds of deviations from the ideally sharp interface: <1> roughness and <2> diffuseness. Interface roughness means the height of the interface is varying above and below the average height with change in lateral position. Interface diffuseness means the SLD continuously and gradually varies across the interface. Schematics of interface roughness and interface diffuseness are shown in Figure 1.13.
Although these two structures are different, they can be represented by the same laterally averaged, one dimensional SLD profile that continuously changes in the direction normal to the interface, as shown in Figure 1.14. Therefore, the specular reflectivity technique alone cannot distinguish interface roughness from interface diffuseness. In other words, the interface roughness and the interface diffuseness “look” the same to specular reflectivity (NR/XR).

Figure 1.14 Depth profile of SLD for interface roughness or interface diffuseness.

Considering a single interface with a root mean square roughness, $\sigma$, the reflectivity can be approximated as

$$R(q_{z,0}) \approx \frac{16\pi^2 r_0^2 (\Delta \rho_e^2)}{q_{z,0}^4} e^{-q_{z,0}^2 \sigma^2} \text{ for } (q_{z,0} \gg q_{z,c}). \quad (1.29)$$

At large $q_{z,0}$, Equation 1.29 is equivalent to

$$R(q_{z,0}) = R_F(q_{z,0}) e^{-q_{z,0}^2 \sigma^2}. \quad (1.30)$$

Equation 1.30 implies that reflectivity is very sensitive to the roughness of the interface, especially at high $q_{z,0}$.  

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1.3 X-ray Photon Correlation Spectroscopy

1.3.1 Introduction

X-ray photon correlation spectroscopy (XPCS) is a powerful tool for research on the dynamics of surfaces, interfaces and thin films [43]. The basic principle of XPCS is the same as that of photon correlation spectroscopy (PCS), which uses the visible light and is also called dynamic light scattering (DLS) [44]. When a coherent light / X-ray beam is scattered from a disordered system, the scattered beam will form a “speckle pattern” [45] on a 2D detector due to the interference among the scattered waves. If there are dynamics in the system, the speckle pattern will change with time because of the changing phase differences of the scattered waves. By analyzing the changing speckle pattern, we can obtain dynamical information about the system. Compared with visible light, X-rays have shorter wavelengths and accordingly can probe higher values of $q$. Therefore, XPCS can be used to study dynamics at a much shorter length scale than DLS can be. However, it is more difficult to observe the speckle pattern from X-rays than that from laser beam. First, the X-ray beam is required to be at least partially coherent, while X-rays created from sources providing incoherent beams. Second, the X-ray beam should be of high brilliance. These two key requirements are fulfilled with the advent of third generation synchrotron radiation sources, which can generate (partially) coherent X-ray photons with sufficiently high flux for XPCS. The beamlines at synchrotron laboratories that can perform XPCS include: 8-ID-I of the Advanced Photon Source (APS), Argonne National Laboratory, USA; ID10A at the European Synchrotron Radiation Facility (ESRF), France; and P10 at PETRA III, Deutsches Elektronen-Synchrotron (DESY), Germany.
Unlike specular reflectivity techniques, which can only probe the laterally averaged profile in the direction normal to the surface, XPCS can obtain information on the surface in the lateral direction based on the radiation scattered in off-specular directions. As shown in Figure 1.15, in the off-specular geometry the angle of scattering is different from the angle of incidence and may not even lie in the place of incidence. This results in scattering vectors, \( q \), that are away from the direction normal to the surface. Therefore, \( q \) consists of two components: <1> the component perpendicular to the surface, \( q_z \), and <2> the component parallel to the surface, \( q_x/q_y \). If the surface is assumed to be isotropic in x and y directions, then \( q_x/q_y \) can be represented as \( q_\parallel \), the in-plane scattering vector.

![Schematic of the experimental setup for XPCS](image)


XPCS can measure the normalized intensity-intensity time autocorrelation function, also called \( g_2(q, t) \), which is defined as

\[
g_2(q, t) = \frac{\langle I(q, t')I(q, t' + t) \rangle}{\langle I(q, t') \rangle^2} \quad (t > 0),
\]

(1.29)

where \( I(q,t') \) is the scattering intensity at scattering vector \( q \) at time \( t' \), \( t \) denotes the delay
time, and the angular brackets represent averages over time $t'$. When XPCS probes the sample surface using a grazing reflection geometry, as in Figure 1.15, $q$ is specifically the in-plane scattering vector, $q_{||}$. In this case, Equation 1.29 can be written as

$$g_2(q_{||}, t) = \frac{\langle I(q_{||}, t')I(q_{||}, t' + t) \rangle}{\langle I(q_{||}, t') \rangle^2} \quad (t > 0). \quad (1.30)$$

If the dynamics of the sample surface at a given $q_{||}$ follow a single exponential decay function, the $g_2$ function can be expressed as

$$g_2(q_{||}, t) = 1 + \beta e^{-\frac{2t}{\tau}}, \quad (1.31)$$

where $\tau$ is the relaxation time of the sample surface at a given value of $q_{||}$ and $\beta$ is the speckle contrast.

1.3.2 Research on Surface Dynamics of Liquids using XPCS

Liquid surfaces are decorated with thermally activated capillary waves, i.e. surface fluctuations. The surface fluctuations on small molecule liquids have been widely studies [46-50] and those on polymeric liquids somewhat less so [51-55].

1.3.2.1 Surface Dynamics of Small Molecule Liquids

Seydel et al. [46] first successfully applied XPCS to detect the overdamped capillary waves on liquid glycerol surfaces, as shown in Figure 1.16. The experiments were performed under grazing incidence conditions with incident angles below the critical angle of total reflection so that the penetration depth of radiation at the air interface of the sample was around 8 nm. They found the dynamics of the thermally activated capillary waves on glycerol surfaces were exponentially slowed down when the temperature was
cooled below 273K, implying the freezing of the surface fluctuations due to the increased viscosity at low temperatures.

![Figure 1.16](image.png)

**Figure 1.16** Intensity-intensity correlation function $g_2(\tau)$ from a glycerol surface at $T = 253$ K (open circles). The length scale that was probed is $x_0 = 56$ μm. The correlation function of the monitor signal is given by the open triangles. The solid line is a fit according to $g_2(t) = 1 + \beta \exp(-t/\tau)$ from which the two parameters $\beta$ (contrast) and $\tau$ (time constant of overdamped capillary waves) are obtained. Reprinted with permission from T. Seydel, A. Madsen, M. Tolan, G. Grübel, W. Press, *Phys. Rev. B* 2001, 63, 073409. Copyright 2001 American Physical Society.

Gutt et al. [47] studied liquid water surfaces using XPCS under grazing incidence. The autocorrelation function is shown in Figure 1.17, indicating there are propagating capillary waves on the liquid water surface. They found that the measured intensity-intensity autocorrelation functions were heterodyne signals – the combination of the $1^{\text{st}}$ and $2^{\text{nd}}$ correlation functions, $g_1(q, t)$ and $g_2(q, t)$. This heterodyne mixing can be rationalized by an interference effect between the specular reflection and the diffuse scattering.

Madsen et al. [48] observed the transition from propagating to overdamped dynamic behavior of capillary waves on a liquid surface using XPCS, as shown in Figure 1.18. The experiments were performed in a sample cell described in Ref. [49]. The liquid sample was a mixture of water and glycerol (65% weight concentration of glycerol), which clearly showed propagating capillary waves at $30\degree C$, overdamped waves at $5\degree C$, and a transition state at $12\degree C$. Later, Sloutskin et al. [50] reported a similar transition from propagating to overdamped capillary waves on an ionic liquid surface.
1.3.2.2 Surface Dynamics of Polymer Films

The surface fluctuations on polymer melts are expected to be overdamped capillary waves due to the high viscosity. Kim et al. [51] first used XPCS to study the surface dynamics of entangled polymer films above $T_g$. These proved to be well described as overdamped capillary waves on viscous liquid films in terms of the hydrodynamic continuum theory (HCT) when film thicknesses were greater than $4R_g$, where $R_g$ is the unperturbed chain radius of gyration. Based on the theories of surface fluctuations on viscoelastic films [56,57], Kim et al. argued that the relaxation time $\tau(q_{||})$ for overdamped capillary waves on a polymer film of thickness $h$ could be described in the conditions they studied with the relation

$$\tau(q_{||}) \cong \frac{2\eta\left[\cos^2(q_{||}h) + (q_{||}h)^2\right]}{\gamma q_{||} \left[\sin(q_{||}h)\cos(q_{||}h) - q_{||}h\right]},$$

(1.32)

Figure 1.18 Normalized intensity-intensity autocorrelation functions of the scattered intensity at $q = 5.6 \times 10^{-6}$ Å$^{-1}$ taken at different temperatures. The data have been shifted along the ordinate for clarity. Reprinted with permission from A. Madsen, T. Seydel, M. Sprung, C. Gutt, M. Tolan, G. Grübel, Phys. Rev. Lett. 2004, 92, 096104. Copyright 2004 American Physical Society.
where $\eta$ is the viscosity, $\gamma$ is the surface tension. Equation 1.32 neglects the elastic modulus present in the more general theory and implies that $\tau(q_{||})/h$ is only a function of $q_{||}/h$ and is proportional to $\eta/\gamma$. This behavior has been well verified by XPCS experiments on PS ($M_n = 123$ kg/mol) melt films with various thicknesses (84 – 333 nm) at different temperatures (150 – 170°C) substantially above $T_g$, as shown in Figure 1.19.

![Figure 1.19 $\tau/h$ vs. $q_{||}/h$ for film thicknesses 84 nm (circles), 170, 177 nm (triangles), and 312.5, 318, 333 nm (diamonds). The drawn curves are calculated using the hydrodynamic continuum theory expression of Equation 1.32. Reprinted with permission from H. Kim, A. Ruhm, L. B. Lurio, J. K. Basu, J. Lal, D. Lumma, S.G. J. Mochrie, S. K. Sinha, Phys. Rev. Lett. 2003, 90, 068302. Copyright 2003 American Physical Society.](image)

Later, Jiang et al. [52] studied the surface dynamics of much thinner films ($h = 1 - 4R_g$) of the same 123k PS. When the film thickness was less than $4R_g$, the surface dynamics were slowed, and the dependence of $\tau(q_{||})$ vs. $q_{||}$ changed shape. The authors contended that this was due to a Guiseelin brush [58] formed by chains becoming pinned onto the substrate, and the effects of a shear modulus ($\mu$) had to be taken into account.
Accordingly, the more general expression from Jäckle’s theory [57] that includes the modulus must be used

\[
\tau'(q_\parallel) \approx \frac{\tau(q_\parallel)}{1 + \tau(q_\parallel)(\mu/\eta)},
\]

(1.33)

where \(\tau(q_\parallel)\) is defined in Equation 1.32. When the film thickness was further decreased to \(1R_g\), the surface dynamics were no longer observable in the experimental window, implying a static surface or a surface with very slow dynamics.

Jiang et al. [53] further studied the surface dynamics of PS films of a wide range of \(M_n\) and at various temperatures. For entangled PS \((M_n > 30 \text{ kg/mol})\) melt films, the \(g_2\) functions showed single exponential decays at temperatures well above \(T_g\). With the decrease of temperature, the \(g_2\) functions evolved to stretched exponential decays. Interestingly, when the temperature was further decreased to near \(T_g\), a single exponential relaxation showed up again. The single exponential surface relaxations at temperatures much higher than \(T_g\) manifested the viscous flow behavior. However, the single exponential surface relaxations near \(T_g\) corresponded to local segmental motions of Rouse dynamics. Accordingly, the stretched exponential relaxations at intermediate temperatures could be explained as resulting from the combinations of two modes of dynamics. For unentangled PS \((M_n < 30 \text{ kg/mol})\) melt films, only pure single exponential relaxations were observed at all temperatures above \(T_g\).

The architectures of polymer chains also have important effects on the dynamics of surface capillary waves. Wang et al. [54] studied the surface fluctuations of unentangled cyclic PS films. Similar to linear PS films [51], the surface dynamics of cyclic PS films with sufficiently large thicknesses could be well described by HCT of overdamped
capillary waves. For these cyclic PS films, the viscosities derived from the XPCS data ($\eta_{xpcs}$) agreed well with the bulk viscosities ($\eta_{bulk}$). However, cyclic PS films showed a confinement effect even when the film thickness was around $10R_g$, while for films of entangled linear PS confinement effects occurred only when the film thickness was less than $4R_g$ [52].

Wang et al. [55] also studied the surface fluctuations of sufficiently thick (~ 100 nm) films of branched PS, including 6-star, 6-pom, and 6-end architectures, which are shown in Figure 1.20. Unlike linear PS films [51] or cyclic PS films [54], which showed good agreement between $\eta_{bulk}$ determined by conventional rheological measurements and $\eta_{xpcs}$ inferred from the surface fluctuation behavior, the values of $\eta_{xpcs}$ were always higher than those of $\eta_{bulk}$ for these branched PS films. This discrepancy in viscosity varied significantly with the chain architecture, greatest for 6-end, less dramatic for 6-star, and least strong for 6-pom, as shown in Figure 1.21. This finding revealed a profound effect of branching on the confinement of polymer films.

![Figure 1.20 Schematics of the architectures of branched chains studied by Wang et al. [55]](image-url)
Figure 1.21 Comparison of viscosities obtained from XPCS data (open symbols) with viscosities from bulk rheology (filled symbols) as a function of $T - T_{g,\text{bulk}}$ for branched architectures as marked. Reprinted with permission from S. F. Wang, S. Yang, J. Lee, B. Akgun, D. T. Wu, M. D. Foster, *Phys. Rev. Lett.* 2013, 111, 068303. Copyright 2013 American Physical Society.

1.3.3 Research on Dynamics inside Films using XPCS

Besides the surface dynamics, XPCS can also probe the dynamics inside films by adjusting the incident angle. For the research on the surface dynamics of liquids mentioned above, the incident angle of the X-ray beam must be below the critical angle of the total external reflection of the film, so that the electric field intensity (EFI) decays exponentially into the film with a maximum at the film surface. In this case, the scattering signals probe the dynamics of the film structure over a depth of ~ 9 nm near the surface. Since the contrast between the film and vacuum is much larger than the contrast due to small density fluctuations in the material beneath the surface, only the
surface fluctuations are probed. Thus this is called “surface-mode”. When the incident angle is just above the critical angle, the EFI is enhanced by resonance with a maximum at around the center of the film (the first-resonance enhancement) [59] and therefore the scattering signals probe predominantly (though not exclusively) the dynamics at the center of the film if there is sufficient contrast there, corresponding to what is called “center-mode”. The schematics of the surface-mode and the center-mode measurements are shown in Figure 1.22.

![Surface Mode and Center Mode Schematics](image)

Figure 1.22 Schematics of the surface-mode and the center-mode varieties of XPCS.

Sufficient scattering contrast is required for XPCS to probe the dynamics. For the dynamics of surface fluctuations, the contrast stems from the different electron densities of the film and the vacuum/vapor. However, inside a homopolymer film the contrast created by variations in local density is so weak as compared to the contrast at the surface that in order to study the dynamics inside the film, metal nanoparticles with high electron densities, like gold nanoparticles (AuNPs) [60,61], are usually added as “markers” to provide the necessary contrast for XPCS. The dynamics studied then are not surface fluctuation dynamics, but rather the dynamics of the particles themselves.
Koga et al. [62,63] inferred the dynamics of PS films (128 nm) from the dynamics of AuNPs used as makers. The AuNPs were functionalized with octadecanethiol (C\textsubscript{18}H\textsubscript{37}SH) layers in order to keep them dispersed in the PS. The average radius of the Au core was around 1.5 nm and the thickness of the C\textsubscript{18}H\textsubscript{37}SH layer was around 1.3 nm. The surface-mode and the center-mode XPCS measurements were performed to track the dynamics of the AuNPs at the surface and near the center of PS films, respectively. All the XPCS data exhibited single exponential decay functions in both the surface-mode and the center-mode measurements at temperatures far above T\textsubscript{g} (156 – 186 \degree C). Power-law behaviors with $\tau \sim q^2$ were observed in both modes, corresponding to the Brownian diffusive motions of the AuNPs at the surface and at the center of the film, as shown in Figure 1.23. For entangled PS ($M_n = 123, 200, 290$ and $400$ kg/mol) films, the dynamics of AuNPs at the surface were about 50% faster than those near the center of the film, showing that the viscosity at the film surface, $\eta_{\text{sur}}$, was about 30% lower than that of the rest of the film, $\eta_{\text{res}}$. By fitting the data with the Williams-Landel-Ferry (WLF) equation, the $T_g$ at the surface and near the center of the film were inferred to have similar values ($\sim 100$ \degree C), implying that the decreased viscosity at the film surface had nothing to do with a reduction in $T_g$. For the unentangled PS ($M_n = 30$ kg/mol) film, the value of $\eta_{\text{sur}}$ was almost the same as the value of $\eta_{\text{res}}$, implying that the decreased viscosity at the film surface was related to the chain entanglements. In addition, $\eta_{\text{sur}}$ scaled with $M_n^{3.4}$ except for the unentangled PS ($M_n = 30$ kg/mol), indicating that on the film surface the polymer chains were still entangled and their motions followed the reptation mechanism. Considering the fact that the probing depth at the surface ($\sim 9$ nm) was comparable to the
tube diameter of the entangled PS chains, the authors argued that the decreased surface viscosity could be attributed to reduced entanglements at the film surface.


Koga et al. [64,65] further investigated the entangled PS (M_n = 123 kg/mol) films with different thicknesses (32, 57, 128 and 235 nm) using the “marker” XPCS method. The dynamics of AuNPs in the thinner films (32 and 57 nm) showed stretched exponential decay functions, implying a wider spectrum of dynamics due to the heterogeneity of the thinner films. In addition, the dynamics of AuNPs in the two thinner films were much slower than those in the thicker films both at the surface and near the center of the films. The suppressed dynamics could be rationalized as arising from an effect of a very thin (~ 7 nm) layer irreversibly adsorbed to the substrate being propagated into the film interior and overcoming the effect of a surface mobile layer, leading to long-range perturbations to the local viscosity even far away (up to ~ 60 nm)
from the substrate. This is one of the most important observations from the literature relevant to the research project described in Chapter V.

For a buried interface in a bilayer film with enough electron density contrast, the dynamics can be directly measured without the markers. Hu et al. [66] investigated a bilayer film consisting of a PS layer on top of a poly(4-bromo styrene) (PBrS) layer. The experiments were performed with different incident angles, probing the thermally driven dynamics at both the PS film surface and the PS/PBrS interface. The PS film surface showed double relaxations: a fast mode and a slow mode. The buried PS/PBrS interface only showed a slow mode single relaxation, which was similar to the slow mode relaxation on the PS film surface in terms of magnitude and $q_{||}$ dependence. The dynamics of the bilayer films were explained as arising from the existence of a thin low-viscosity mixed layer between the PS and PBrS layers.
CHAPTER II
EXPERIMENTAL

2.1 Materials

Styrene (Aldrich, 99%), \(N,N',N'',N''\)-Pentamethyldiethylenetriamine (PMDETA, Aldrich, 99%), ethyl \(\alpha\)-bromoisobutyrate (E2Br-iB, Aldrich, 98%) were purified by passing through activated basic alumina in a column. Dodecyltrichlorosilane (DTS, Alfa Aesar, 96%) was purified by vacuum distillation before use. CuBr (Aldrich, 99.999%), anhydrous toluene (Aldrich, 99.8%), deuterated toluene (d_8-toluene, Aldrich, 99.6%), anhydrous anisole (Aldrich, 99.7%) and chloroform (Fisher Scientific, 99.9%) were used as received. Silicon Wafers (100) with thickness of 625 ± 20 um were purchased from EI-Cat Inc. (11-(2-Bromo-2-methyl)propionyloxy)undecyltrichlorosilane was purchased from ATRP Solutions Inc. AuNPs (octadecanethiol modified, \(d = 5 \pm 1 \) nm) were purchased from Nanopartz Inc. Deuterated polystyrene (d_8-PS, \(M_n = 2200, \text{PDI} = 1.07\)) was purchased from Polymer Source Inc.

2.2 Preparation of PS Brushes via Surface ATRP

2.2.1 Deposition of Surface ATRP Initiator on Silicon Wafer

Silicon wafers were cleaned in a newly made “piranha” solution [67] (concentrated H\(_2\)SO\(_4\)/30% H\(_2\)O\(_2\), 70/30 by volume) at 90-100 °C for 1 h, and then rinsed with distilled water and dried with technical grade N\(_2\) gas.
A crystallizing dish was placed in a dry box. 30 mL anhydrous toluene and 0.15 mL (11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane (surface ATRP initiator) were added to the dish. A freshly cleaned silicon wafer (60mm × 40mm) was then put into the dish. The dish was sealed by a cap with rubber gasket and heated at 60 °C for 4 h. Then the initiator-modified silicon wafer was taken out, washed with toluene and ethanol, and then dried with technical grade N₂ gas.

In order to adjust the grafting densities, 0.15 mL DTS was first deposited at 60 °C on the silicon wafer as spacer molecules. Then the surface ATRP initiator was deposited to backfill the empty spaces on the wafer. This procedure reduced the initiator density on the wafer surface to prepare polymer brushes with lower grafting densities. DTS deposition was performed in the dry box because DTS is highly sensitive to air and humidity. The schematics of the preparation of polymer brushes with high and low grafting densities are shown in Figure 2.1. The deposition times were varied to yield different grafting densities, as shown in Figure 2.2.
Figure 2.1 Schematics of the preparation of polymer brushes with high (left) and low (right) grafting densities.

Figure 2.2 Dependence of grafting density on the DTS deposition time.
2.2.2 Surface ATRP from Silicon Wafer

PS brushes with different grafting densities ($\sigma = 0.05-0.67$ chains/nm$^2$) were prepared via surface ATRP from the initiator-modified silicon wafers. CuBr was added to a 100 mL flask with a magnetic stir bar. The flask was sealed with a rubber septum. Anisole and styrene were injected into the flask with a syringe and then the flask purged with technical grade N$_2$ for 2 h. After three vacuum/purge cycles, a N$_2$ atmosphere was achieved inside the flask. Then, PMDETA was injected into the flask using a syringe. The mixture in the flask was stirred at 90°C until it became a homogeneous solution. Then the flask was transferred to the dry box. In the dry box, the initiator-modified silicon wafer was put in a crystallizing dish, to which the solution in the flask and then the free initiator E2Br-iB were added. The following are the typical concentrations of the reactants and solvent: $[\text{Styrene}]_0 = 3.9$ M, $[\text{anisole}]_0 = 5$ M, $[\text{PMDETA}]_0 = 25$ mM, $[\text{CuBr}]_0 = 12$ mM and $[\text{E2Br-iB}]_0 = 5$ mM. The dish was sealed by a cap with rubber gasket to prevent evaporation. The reaction temperature was 90-100°C, and the reaction time was varied depending on the brush thickness needed. After the polymerization was finished, the PS brush was extracted with toluene in a Soxhlet extractor for 24 h, and then sonicated in toluene for 2 h, to remove the free polymer chains. Then the PS brush was annealed at high vacuum at 120°C for 18 h to remove the residual solvent.

The molecular weight of the tethered chains in the brush was estimated by measuring with GPC free PS chains polymerized in solution at the same time the PS brush was synthesized. According to earlier studies in the literature, the molecular weight of polymer chains grown in solution, $M_{n,\text{soln}}$, and that of polymer chains grown from the surface, $M_{n,\text{surf}}$, are within 10% for NMP [24,68], reversible addition-fragmentation chain
transfer (RAFT) [69], and ATRP [70]. In all these studies, the polymer chains have been grown on nanoparticles in order to have enough chains when they are cleaved from the surface for analysis with GPC. In later research, Charleux’s work [71] on various substrates showed that $M_{n,\text{soln}}$ and $M_{n,\text{surf}}$ could be quite different, depending on the shape of the particles, with this difference disappearing as the particles become spherical and monodisperse. Work by Spencer et al. [72] found a good correlation between the grafting density and the ratio $M_{n,\text{soln}}/M_{n,\text{surf}}$ for the acrylate and methacrylate based monomers. However, there was no difference between $M_{n,\text{soln}}$ and $M_{n,\text{surf}}$ for PS at the grafting density of 0.33 chains/nm$^2$. They have explained that good agreement between $M_{n,\text{soln}}$ and $M_{n,\text{surf}}$ for PS chains with the lower reaction rates for PS, for which the influence of crowding at the reaction site will be minimized. In fact, their reaction rates for PS (see their Supporting Information) were almost a factor of 10 higher than our reaction rate. They performed bulk polymerizations, and in 6 h the molecular weights of their PS chains were around 60k, while with our polymerization conditions we would have grown PS chains with $M_{n,\text{soln}}$ of 6k in that time. Therefore, one would expect that the $M_{n,\text{soln}}/M_{n,\text{surf}}$ ratio would be closer to unity in our case. Based on all the earlier literature, our approximation that $M_{n,\text{soln}} \approx M_{n,\text{surf}}$ should be valid. Nonetheless, we estimate that there are 10% uncertainties in the values of grafting density and $M_n$ of the grafted chains based on earlier reports that used synthetic protocols similar to ours.
2.3  NR Measurements of PS Brushes Swollen in Toluene Vapor

NR is a non-destructive technique, which can probe “buried” structure inside a film in the direction normal to the surface. Information on the film thickness, interfacial roughness and SLD profile can be obtained by fitting the NR data. The brushes were swollen by exposure to d₈-toluene vapor in a closed chamber that contains a trough for liquid solvent, as shown in Figure 2.3. Enough liquid d₈-toluene was placed in the trough to ensure that once the atmosphere within the chamber was saturated it remained so. Because of the volatility of the toluene, the atmosphere saturated quickly. The characteristics of the PS brushes studied in this work are summarized in Table 2.1. PS brushes with high grafting densities (PS1 – PS6) were studied using NR at the Liquids Reflectometer (BL-4B) at the Spallation Neutron Source (SNS) at Oak Ridge National Laboratory. NR measurements of PS brushes with low grafting densities (PS7 – PS9) were performed at the NG7 reflectometer at the National Institute of Standards and Technology (NIST).

![Schematic of the chamber for NR measurement of a vapor swollen polymer brush.](image)

Figure 2.3 Schematic of the chamber for NR measurement of a vapor swollen polymer brush.
### Table 2.1 Information of PS Brushes.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$\sigma^a$ (nm$^2$)</th>
<th>$M_n^b$ (g/mol)</th>
<th>$h_o^c$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS1</td>
<td>0.63</td>
<td>20000</td>
<td>20.0</td>
</tr>
<tr>
<td>PS2</td>
<td>0.60</td>
<td>43100</td>
<td>40.6</td>
</tr>
<tr>
<td>PS3</td>
<td>0.61</td>
<td>52900</td>
<td>51.3</td>
</tr>
<tr>
<td>PS4</td>
<td>0.67</td>
<td>53700</td>
<td>57.3</td>
</tr>
<tr>
<td>PS5</td>
<td>0.64</td>
<td>74500</td>
<td>75.5</td>
</tr>
<tr>
<td>PS6</td>
<td>0.67</td>
<td>95300</td>
<td>101.7</td>
</tr>
<tr>
<td>PS7</td>
<td>0.28</td>
<td>52100</td>
<td>23.1</td>
</tr>
<tr>
<td>PS8</td>
<td>0.16</td>
<td>73800</td>
<td>19.0</td>
</tr>
<tr>
<td>PS9</td>
<td>0.05</td>
<td>76500</td>
<td>5.6</td>
</tr>
</tbody>
</table>

$^a$ Calculated using $\sigma = \rho N_A h_o / M_n$, where $N_A$ is Avogadro's number and $\rho = 1.05$ g/cm$^3$.

$^b$ Measured with GPC using THF at 35 °C with refractive index and laser light scattering (Wyatt Technology, DAWN EOS, $\lambda = 690$ nm) detectors.

$^c$ Dry brush thickness in air measured with NR ($\pm 0.1$ nm).

#### 2.4 XPCS Measurements of PS Brushes Swollen in Toluene Vapor

The swollen brush surface fluctuations were studied with XPCS at Sector 8-ID-I of the Advanced Photon Source (APS) at Argonne National Laboratory. A closed chamber containing solvent wells, shown schematically in Figure 2.4, was used to provide saturated vapor conditions. The brush temperature, $T_b$, and solvent temperature, $T_s$, were independently controlled to ±0.01 °C. The X-ray beam (7.35 keV) had dimensions of 20 × 20 μm$^2$ with a typical intensity of $\sim 1 \times 10^{10}$ photons/s. The incidence angle of the X-ray beam was 0.14°, which was below the critical angle of PS, 0.16°, so that the EFI decayed exponentially into the brush over a depth of around 9 nm. In this case, the scattering from the brush surface dominated, while that from the brush/substrate interface was negligible.

The fluctuations of the surface were characterized using the intensity–intensity time autocorrelation function, $g_2(q_\|, t)$, given by

$$g_2(q_\|, t) = \frac{\langle I(q_\|, t') I(q_\|, t' + t) \rangle}{\langle I(q_\|, t') \rangle^2} \quad (t > 0) \tag{2.1}$$
where \( I(q_{||},t') \) is the scattering intensity for in-plane wave vector \( q_{||} \), at time \( t' \), the angular brackets correspond to ensemble averages over time \( t' \), and \( t \) is the delay time. This function is characteristic of the fluctuations on the film surface only.

![Schematic diagram of the chamber for XPCS measurement of a vapor swollen polymer brush.]

Figure 2.4 Schematic of the chamber for XPCS measurement of a vapor swollen polymer brush.

2.5 XPCS Measurements of PS Brushes with AuNPs as “Markers”

2.5.1 Preparation of Tethered-Untethered Bilayer Films with AuNPs

The d\(_8\)-PS was added to an AuNPs/chloroform solution, followed by sonication for 30 minutes. A tethered-untethered bilayer film with AuNPs was prepared by spin-coating the AuNPs/d\(_8\)-PS/chloroform solution onto a PS brush. The weight percentage of AuNPs in the d\(_8\)-PS/AuNPs mixture was 2\% (0.1 vol \%). Then this bilayer film was annealed at 100°C for 16 hours in a high vacuum (ca. 1×10\(^{-7}\) Pa) oven.

2.5.2 Preparation of Tethered Single Layer with AuNPs

A PS brush was immersed in 1 mL AuNPs/chloroform solution in a vial for 6 hours. 20 mL ethanol was then quickly poured into the vial. Then, the PS brush was washed with ethanol, dried with \( \text{N}_2 \), and annealed at 110°C for 16 hours in the high vacuum oven.
2.5.3 Surface-Mode and Center-Mode XPCS Measurements

The XPCS measurements were performed at Sector 8-ID-I of the APS at Argonne National Laboratory. The X-ray beam (7.35 keV) had dimensions of $20 \times 20 \, \mu \text{m}^2$ with a typical intensity of $\sim 1 \times 10^{10}$ photons/s. The primary experimentally determined quantity is the intensity-intensity time autocorrelation function, as shown in Equation 2.1. In what we denote as "surface-mode" measurements, the X-ray beam struck the surface at an angle of $0.15^\circ$ with respect to the surface, which was below the critical angle for PS, $0.16^\circ$, so that the EFI decayed exponentially into the film. The scattering analyzed in this measurement came primarily from the surface and material down to a depth of ca. 9 nm. In what we call here the "center-mode" measurement, the incidence angle of X-ray beam was just above the critical angle at the angle for the first resonance enhancement of the EFI. In this case the EFI had a maximum at the center of the film and the motion of AuNPs near the film center dominated the scattering behavior.
CHAPTER III

STRUCTURE OF POLYMER BRUSHES SWOLLEN IN GOOD SOLVENT VAPOR


3.1 Introduction

There have been fewer studies [73-77] of brushes swollen in vapor than there have been of brushes swollen in liquid. Biesalski and Rühe [73] demonstrated the swelling of polyelectrolyte brushes at various relative humidities and studied the kinetics of swelling. Armes et al. [74] demonstrated that a polyelectrolyte brush could swell in response to the presence of acidic vapor. Rabin et al. [75] analyzed a mean-field lattice model of brush swelling in water vapor to explain how a DNA brush could contract for low degrees of water uptake. Genzer et al. [76] studied how the swelling of polyelectrolyte and polyzwitterion brushes in water vapor varies with relative humidity levels using NR, XR, and spectroscopic ellipsometry. Beers et al. [77] reported measurements of the swelling of two poly(methyl methacrylate) brushes in a variety of organic solvent vapors using XR, providing values of the swelling ratio and how it varies with solvent quality. They also reported X-ray scattering length density (XSLD) profiles for samples and on the basis of those XSLD profiles argued that the swelling with vapor yielded a steplike polymer segment density profile, not a parabolic profile as that observed in liquid-swollen brushes.
in the strong stretching regime. However, XR is not very sensitive to the polymer segment density depth profile as compared to NR because greater contrast can be achieved with NR using deuterium labeling of the solvent. Those authors went on to note that they expected brush swelling with saturated vapor and liquid to be identical, insofar as the solvent chemical potential in the two systems is the same. They remarked, however, that in the membrane community [78] it is known that the swelling of membranes in liquid is, in general, not the same as swelling in saturated vapor, and they argued that differences between brush swelling by vapor and liquid require further study. Here we show, using NR measurements, that while the same scaling of swollen brush thickness with \( N\sigma^{1/3} \) is found for organic-vapor-swollen brushes as for organic-liquid-swollen brushes and the shape of the concentration profile inside the brush is quite similar for the two cases, the interface between the brush and surroundings is, indeed, more abrupt for the vapor case.

3.2 Results and Discussion

3.2.1 Scaling Behavior of High Grafting Density Brushes

The NR fitting results and corresponding SLD profiles for high grafting density PS brushes (PS1 – PS6) dry and swollen are shown in Figure 3.1. NR data for the dry brushes were collected and fitted for values of \( q \) up to 0.09 Å\(^{-1}\), as shown in Figure 3.2. The NR data were fitted using MOTOFIT, a fitting analysis package running in IGOR PRO. The data from each dry brush can be fitted well with a structure model that envisions three primary layers: the silicon oxide, the initiator layer, and the brush itself. Additionally, a finite interface width is associated with each interface. The data for the
dry brush were fitted well using the SLD of bulk PS, $1.42 \times 10^{-6}$ Å$^{-2}$. The kinetics of vapor penetration into the brush were observed by consecutive NR measurements after exposure to vapor, as shown in Figure 3.1. Typically, measurements over a $q$ range of $0.011 – 0.047$ Å$^{-1}$ were run about every 10 min. This small range of $q$ was required to allow quick measurements. In the following text, the nominal measurement time in the kinetic measurements is taken as the mean of measurement start and finish times. We keep in mind the fact that the sample structure was changing over the time for one measurement. The largest error due to this time resolution was present in the earliest measurements. The change in brush thickness with swelling was apparent from movement to the left of the Kiessig minima in the reflectivity curves. The rate of increase in thickness due to swelling was highest in the beginning and decreased with time. The first two curves in the collections for various times, measured over a smaller range of $q$, clearly demonstrated increases in sample thickness at those times, but the change in sample structure was so rapid and the $q$ range so limited that it was of limited utility to suggest a full SLD profile from a fit. For later times, the SLD profile had to reflect variation in the concentration of PS segments with depth because of the penetration into the brush of d$_{8}$-toluene, which has an SLD of $5.66 \times 10^{-6}$ Å$^{-2}$. 
Figure 3.1 NR curves (left) and SLD profiles (right) of high grafting density PS brushes dry and swollen in d$_8$-toluene vapor.
Figure 3.1 NR curves (left) and SLD profiles (right) of high grafting density PS brushes dry and swollen in d₈-toluene vapor. (continued)

Figure 3.2 NR curves and best fits for dry brushes measured with larger range of $q$. 

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The values of $\chi^2$ for the fits are shown in Table 3.1. The NR curves plotted as $Rq^4$ vs. $q$ are shown in Figure 3.3 to make more evident the quality of the fits.

<table>
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<th>PS4</th>
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Figure 3.3 NR curves plotted as $Rq^4$ vs. $q$ for swollen brushes (a) PS2 (b) PS4 (c) PS5 (d) PS6 at the greatest extent of swelling.
The SLD profiles for fitting the reflectivity curves from the swollen brushes were created using the simplest possible model. By subdividing the SLD profile for the polymer-containing part of the sample into additional layers and using convolution of the interfaces between pairs of those fictitious layers with error functions, smooth curves of SLD variation through the brush and into the vapor were created. The parameters of the error functions used for this smoothing to remove boxlike steps in the SLD profile within the swollen brush have no physical meaning. They are simply part of a protocol to generate a SLD profile that is able to provide a fit to the data. The number of layers was kept as small as possible to provide a good fit with a simple modeling approach. In some cases, subdividing the swollen brush portion of the SLD profile into three layers was sufficient, while in other cases that portion had to be subdivided into four or five layers. Generally, more layers were required to properly capture the shape of the SLD profile for the thicker brushes. The one interface for which the standard deviation, $s$, of the convoluting function had the most significance was that between the last layer of the swollen brush region and the vapor region. The width of that convoluting function is related to the microroughness of the swollen brush/vapor interface as well as the interface diffuseness characterized by the gradual variation of the ratio of air/toluene molecules/polymer that occurs across that interface. For the dry brush, $s$ is a clear measure of interface microroughness. For the swollen brushes, $s$ is a quantity that captures the effective interface width averaged over the beam footprint and contains contributions from both microroughness and diffuseness in a way that cannot be further detailed using specular reflection measurements alone. Nonetheless, the consideration of this parameter is sufficient to extract the central result that the interface between the
brush and surroundings is sharper for the case of vapor swelling than for the case of liquid swelling.

Within 25 min, toluene penetrated the brush all the way to the base of the chains. With the mobility increased by the presence of toluene, the chains then rearranged to accommodate the toluene molecules primarily in the outermost region of the brush, while the volume fraction of solvent in the lower region of the brush stayed close to 0.1. After 90 min, the SLD profile changed little with time, meaning that the swelling had nearly attained its equilibrium character. At the brush interface with the saturated vapor, the SLD value drops over a short depth to nearly zero. This drop in SLD is much more abrupt than that associated with the interface between the swollen brush and liquid solvent. The reflectivity measurement is very sensitive to the effective width of this drop, which manifests the projection of the 3D variation of the segment concentration depth profile onto the surface normal [42]. As noted above, the width of the SLD drop is quantified as the standard deviation, $s$, of the error function used to create that part of the SLD profile [79], with the full width of the convoluting function at half-maximum being $2.35s$.

These widths of the interface for the swollen brushes as characterized approximately with $s$ increase with the thickness of the corresponding dry brush. However, the systematic increase in the width of the swollen interface with brush thickness does not correlate to variations among the microroughness values of the dry brush surfaces because those are scattered about an average value of $1.8 \pm 0.4$ nm, as shown in Table 3.2. The key point is that these swollen interface widths are all much smaller than the distance over which the tail of the segment concentration profile for a brush swollen in liquid can extend, which is greater than 10 nm for brush chains of 20000 g/mol molecular
weight [19]. For the equilibrium swollen brush measured with higher resolution (to higher $q$), fitting the data required an even smaller interface width than used to fit the data from the more limited $q$ range (Figure 3.4), so there is no question that the interface width is smaller for brushes swollen with vapor than for brushes swollen with liquid.

![Figure 3.4 NR curve and fit ($\chi^2 = 5.2$) for brush PS4 swollen in d$_8$-toluene vapor, measured over a larger range of $q$, with the SLD profile shown in the inset.](image)

For comparison with theoretical treatments of the scaling relationship between brush thickness and molecular parameters, it is necessary to define operationally the equilibrium thickness, $h_s$, for the vapor swollen brush. Because the interface with vapor is reasonably abrupt, $h_s$ may simply be taken as the height from the initiator layer to the middle of the interface with vapor, as shown in Figure 3.5.
The scaling of thickness for the dry brush and that for the brush swollen in toluene vapor are shown in Figure 3.6, where our data are compared with those of Chapel et al. [18] and Kuhl et al. [19] for dry PS brushes and brushes swollen in liquid toluene. The detailed information on these data is shown in Table 3.2. For the dry brush plot, we report one result from Chapel et al. for which numerical data for both $N$ and $\sigma$ are reported and for which the grafting density ($0.55$ chains/nm$^2$) is most similar to ours. (They present additional data in a plot of $h_o$ vs. $N\sigma$). From Kuhl et al., we include four data points for which both $N$ and $\sigma$ are reported, with $\sigma$ varying between 0.40 and 0.49 chains/nm$^2$. The scaling for our dry brushes is consistent with that for these published examples and also with theoretical expectations for brushes in the dense grafting regime. For the swollen brushes, we compare to the one result from Chapel et al. (for a grafting density of
0.55 chains/nm$^2$) and to several data points from Kuhl et al. for which $\sigma$ varies between 0.40 and 0.49 chains/nm$^2$ and the relationship between $h_s$ and $N\sigma^{1/3}$ is reported in a plot. Despite the fact that the detailed interface shapes for the brushes swollen in vapor are different from those for brushes swollen in liquid, the scaling behavior of the thicknesses is the same. Not only the exponents but also the prefactors are the same. We note, however, that Kuhl et al. define the brush thickness as the intercept with the abscissa of a power law fit to their experimental volume fraction profile.

Figure 3.6 a) Thickness of dry PS brushes scales with $N\sigma$; b) Thickness of PS brushes swollen in toluene vapor scales with $N\sigma^{1/3}$. Data from the work of Chapel et al. [18] (open triangles) and Kuhl et al. [19] (open circles) for brushes swollen in toluene liquid are shown for comparison. Data from this work are shown with filled squares.
Table 3.2 Comparison of PS Brushes Swollen in Vapor and in Liquid.

<table>
<thead>
<tr>
<th>Group</th>
<th>Swollen in</th>
<th>Sample</th>
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<th>$N^b$</th>
<th>$\sigma^c$ (nm$^2$)</th>
<th>$h_o$ (nm)</th>
<th>$s_o^e$ (nm)</th>
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$^a$ Measured with GPC using THF at 35 °C with refractive index and laser light scattering (Wyatt Technology, DAWN EOS, $\lambda = 690$ nm) detectors.

$^b$ Average number of repeat units per brush chain ($N = M_n/104$).

$^c$ Calculated using $\sigma = \rho N_A (h_o/M_n)$, where $N_A$ is Avogadro's number and $\rho = 1.05$ g/cm$^3$.

$^d$ Dry brush thickness in air measured with NR (± 0.1 nm).

$^e$ Roughness of the dry brush in air as measured with NR and expressed as the parameter of the error function used to smear the SLD profile.

$^f$ Swollen brush thickness in toluene vapor measured with NR (± 0.1 nm).

$^g$ Interface width of swollen brush in toluene vapor measured with NR, expressed as the parameter of the error function used to smear the SLD profile.
3.2.2 Segment Concentration Profiles of Swollen Brushes

The SLD profile of the swollen brush can be converted to the PS segment concentration profile starting from the initiator layer to the brush/vapor interface using the equation

$$ SLD_{\text{fitted}} = \phi_{PS}(SLD_{PS}) + (1 - \phi_{PS})(SLD_{d_8-\text{toluene}}), \quad (3.1) $$

where $\phi_{ps}$ is the volume concentration of PS segment. For the brush swollen in liquid, only two components, PS and $d_8$-toluene, need be considered as contributing to the SLD over the whole depth of interest. In the case of swelling with vapor, at the brush/vapor interface three components are present: PS, $d_8$-toluene, and air. Thus, the value of $\phi_{ps}$ in the interface region cannot simply be calculated using Equation 3.1. In order to reduce the SLD profile to a profile of PS segment concentration we have identified a depth at which the interface region begins and then assumed that in the brush/vapor interface region the polymer segment concentration falls to zero over the same length that the SLD falls to zero and with the same shape that the SLD profile falls to zero, as shown in Figure 3.7.

![Figure 3.7 Convert the SLD profile to the PS segment concentration profile.](image-url)
The area under the segment concentration profile is proportional to the mass of PS in the brush. If the model for fitting the NR curve is physically correct, good agreement between the area under the profile for the dry brush and that for the corresponding swollen brush should be obtained. Kuhl et al. [19] report that the mass of brush polymer determined from their segment concentration profiles for the dry and liquid swollen conditions agreed to within ±5%. In Figure 3.8, we compare the segment concentration profiles of PS brushes in dry and vapor swollen conditions. For PS1, we found a discrepancy of 6% between the integrals under segment concentration profiles for the dry and swollen conditions. Part of the error in matching the mass of polymer for dry samples and swollen samples may be attributed to our simplifying assumption for converting the SLD profile to the segment concentration profile with three components present (air, polymer, and d₈-toluene) rather than just two. It becomes more difficult to match the mass of polymer for the fit to the NR curve as the brush thickness increases, which may be due to the smaller q range (0.011 – 0.047 Å⁻¹) of the NR measurements compared with that for PS1 (0.008 – 0.092 Å⁻¹). In addition, the apparent mass of the vapor swollen brush is always higher than that of the corresponding dry brush, which indicates a systematic error.
In Figure 3.9, we compare the segment concentration profile measured for our brush PS1 swollen in vapor and that for a brush K3 swollen in liquid from the work of Kuhl et al. [19] When comparing the segment concentration profiles, we must consider the difference in the overall mass of polymer in the brush as well as the difference in grafting density and means of swelling. The chain molecular weight of K3 is 20000 g/mol, which is same as that of PS1. However, K3 has a grafting density 24% lower than that of PS1 (0.48 vs. 0.63 chains/nm$^2$). The dry thickness reported for K3 (15.2 nm) is also 24% lower than that for PS1 (20 nm), which agrees well with the difference in grafting density according to the scaling relationship, $h_o \sim N\sigma$. In addition, the area under the profile for
the liquid swollen brush K3 is 25% below that under the profile for the vapor swollen brush PS1, which is consistent with the 24% lower initial mass in the brush K3.

Figure 3.9 Segment concentration profile for brush PS1 ($M_n = 20000$ g/mol, $h_o = 20$ nm, $\sigma = 0.63$ chains/nm$^2$) swollen in vapor (red line) is compared with that for brush K3 ($M_n = 20000$ g/mol, $h_o = 15.2$ nm, $\sigma = 0.48$ chains/nm$^2$) from Kuhl et al. [19] (blue line).

An important observation of this work is that the two profiles have quite similar shapes for roughly the bottom half of the brush that is closer to the substrate. In that part of the brush, for which crowding due to tethering at the surface is the predominant feature, the brushes behave similarly upon swelling. We note that the segment concentration at the substrate surface is 5% lower for the brush swollen in liquid, but this is due to its having a lower grafting density. This difference is consistent with previous experimental [17] and numerical SCF results [80] for brushes swollen in liquid showing that the segment concentration at the substrate surface decreases as the grafting density decreases. Our value of segment volume fraction at the substrate, or maximum segment volume fraction, $\phi_m$, for PS1 ($\sigma = 0.63$ chains/nm$^2$) is 0.83, which falls between the value
of 0.79 for K3 ($\sigma = 0.48$ chains/nm$^2$) from Kuhl's work and the value of 0.85 from Chapel's work, which claims a value of $\sigma$ of order 1 chains/nm$^2$.

The key differences in the segment concentration profiles are found in that part adjacent to the surroundings. The segment concentration drops off more slowly for the brush next to good solvent liquid, which provides a hospitable environment for the chains. The portions of the chains of the wet brush present a sharper interface when next to good solvent vapor, as shown in Figure 3.10. This sharper interface reflects the preference for the density of the solvent to be either that of liquid or that of vapor in two-phase coexistence. Because the solvent quality is good for the polymer, we likewise expect the preference for the density of the polymer solution to be either that of a liquid or vapor, leading to confinement of the chains by a sharper interface of the wet brush with vapor.

![Figure 3.10 PS segment concentration profiles for a brush (K3) swollen in liquid and the brushes (PS1-PS6) swollen in vapor in order of increasing thickness.](image)
We illustrate this effect by comparison with the result from a simple SCF calculation shown in Figure 3.11. For the case of the brush in solvent, we use a standard harmonic free energy \( F(\rho)/kT = (1/2)v(\rho_0-\rho)^2 \) in the segment density normalized to its bulk value, \( \rho \), to capture the free-energy penalty for density fluctuations to quadratic order. \( kT \) is the Boltzmann constant multiplied by the temperature, and the parameter \( v \) can be considered to be an excluded volume parameter. For the case shown here, the values of the statistical segment length \( b = 0.76 \text{ nm} \) and \( v = 0.033 \text{ nm}^3 \) for the brush in liquid are those used by Kuhl et al. [19] For the case of contact with solvent vapor, we extend this quadratic free energy to the next-order cubic term, \( F(\rho)/kT = (1/2)v(\rho_0-\rho)^2 - c(\rho_0-\rho)^3 \), which allows modeling of two minima corresponding to liquid and vapor densities. This functional preserves the form of the quadratic penalty for density deviations when densities are near that of the bulk liquid. The parameter \( c \) controls the magnitude of the free-energy barrier between vapor and liquid densities as well as the depth of the vapor-phase free energy. The values of \( c = 0.003 \text{ nm}^6 \) and \( v = 0.09 \text{ nm}^3 \) are selected to give the same brush height as in the experiment. Even with the simple functional used here, the fact that the interface at the surface of the swollen brush is much sharper for the vapor case is readily apparent, in good qualitative agreement with the experimental finding.
Figure 3.11 PS segment concentration profiles calculated from SCF theory for the brushes shown in Figure 3.10.

A more complete analysis would involve incorporating modeling of the solvent/polymer interaction and its influence on the effective free-energy functional of the solvent and polymer concentrations. One might make the assumption that there is a relatively sharp interface between a region consisting of the brush and solvent and a region of solvent vapor. The interfacial width between these two regions would be comparable to the width of the pure solvent/vapor interface. For polymers that are not too short, it would also be much narrower than the scale over which the polymer concentration profile varies, i.e., the brush height. In this scenario, one might imagine this liquid/vapor interface to play the role of a confining wall that is semipermeable to solvent. As solvent is removed from the brush in a bulk liquid, this interface moves toward the grafting wall. At vapor-liquid coexistence, there is no free-energy penalty for this motion as a result of the equal chemical potentials of the solvent in the two phases.
However, as the interface contacts the brush, additional removal of solvent invokes the free-energy cost of desolvating the polymer (assumed to be positive for a good solvent) as well as the cost of compressing the brush, also positive. Thus, in the absence of other forces, the equilibrium profile of a brush in contact with solvent vapor would be essentially the same parabolic profile as when the brush is in contact with solvent liquid. That the observed profile corresponds to a compressed brush could be explained by two hypotheses. First, the system may not be at thermodynamic equilibrium. This might be the case if, for instance, the temperature of the brush were a little higher than that of the solvent vapor, driving the system toward drying. Moreover, the free-energy cost of compressing the outermost portion of the brush is relatively low; compressing the exponential tail of the parabolic profile corresponds to an energy scale of only $kT$ for the outermost "blob" and could easily occur under even mildly drying conditions. Second, there may be effective attractive interactions with the grafting surface, for example, by van der Waals attractions for sufficiently thin films. Despite the origin of the sharper interface of the vapor swollen brush, this smaller interface width should have important implications for fluctuations at the surface of the brush and the compressibility of the brush surface in the swollen state. Specifically, the behavior of the brush surface during solvent annealing [8,9] and the microroughness and interface width after solvent removal would be impacted by any fluctuations and the form of the interface next to vapor.
3.2.3 Low Grafting Density Brushes Swollen in Vapor

The PS brushes with low grafting densities swollen in d$_8$-toluene vapor were studied at the NG7 reflectometer of NIST. The NR data for films under dry and swollen conditions and their corresponding SLD profiles are shown in Figure 3.12.

Figure 3.12 NR curves and SLD profiles of low grafting density PS brushes (PS7 and PS8) at dry condition and swollen in d$_8$-toluene vapor.
The \( q \) range measured at NIST (0.008 – 0.22 Å\(^{-1}\)) was much larger than that measured at Oak Ridge National Laboratory (0.011 – 0.047 Å\(^{-1}\)). In addition, these samples had been swollen in \( d_8 \)-toluene vapor for longer times (> 12 h) before the NR measurements. There are two noticeable features for the SLD profiles of swollen brushes with low grafting densities (PS7 and PS8). First, the SLD values close to the substrates are higher than those of swollen brushes with high grafting densities (PS1 – PS6). Second, their brush/vapor interfaces are sharper than those of PS1 – PS6.

By the method described in Figure 3.7, the SLD profiles of PS7 and PS8 under swollen condition can also be converted to the PS segment concentration profiles, which are compared with that of PS1 in Figure 3.13.

![Figure 3.13 PS segment concentration profiles of brushes with different grafting densities swollen in \( d_8 \)-toluene vapor.](image)

The PS segment volume fractions at the substrate (\( \phi_m \)) for PS7 and PS8 are 0.46 and 0.30, respectively, both of which are obviously lower than that of PS1 (0.83). When chains are grafted with higher density less \( d_8 \)-toluene is allowed to penetrate into the
brush layers and reach the substrate. Another observation is that the brush/vapor interfaces for the low grafting density brushes swollen in vapor are narrower than those for the higher grafting density brushes. As shown in Table 3.2, those for PS7 and PS8 are only 0.4 nm and 0.2 nm, respectively, compared with values for $s$ of 1.1-3.6 nm for PS1-PS6. The interface widths for the lower grafting density brushes are comparable to those of pure liquid/vapor interfaces on normal liquids, such as alkanes [81], ethanol [82] and water [83]. The sharper interfaces for the swollen brushes with lower grafting densities are due to the lower PS segment concentrations at the interfaces. The behavior is more like that of a pure liquid/vapor interface.

The NR data and the corresponding SLD profile for PS9, which has a very low grafting density of 0.05 chains/nm$^2$, are shown in Figure 3.14. The SLD profile for the swollen brush PS9 is quite different from those for PS1-PS8. The PS segment concentration profile for PS9, shown in Figure 3.15, was obtained by the method described in Figure 3.7. The value of $\phi_m$ for PS9 is only 0.04, indicating that $d_8$-toluene predominated in the region close to the substrate. In addition, the $\phi_{ps}$ of PS9 inside the swollen brush increases with the distance from the substrate, which is different than PS1-PS8. Another interesting finding is the broad brush/vapor interface (3.5 nm). All these peculiar features of this sample may be due to the very low grafting density.
Figure 3.14 NR curves and SLD profiles of PS9 dry and swollen in d₈-toluene vapor.

Figure 3.15 PS segment concentration profile of PS9 swollen in d₈-toluene vapor.
CHAPTER IV
SURFACE DYNAMICS OF POLYMER BRUSHES SWOLLEN IN GOOD SOLVENT VAPOR


4.1 Introduction

Thermally induced surface height fluctuations of polymer films determine a variety of properties of polymer surfaces and interfaces, including the width of the interface between immiscible polymers [84] and between domains of ordered block copolymers [85], adhesion [86], and dewetting [87]. Therefore, these surface fluctuations are important to a fundamental understanding of thin films and to their applications. Kim’s pioneering work [51] probed surface fluctuations on films of entangled PS using XPCS. They showed that these fluctuations could be well described by HCT [57] of overdamped capillary waves when the film thicknesses are greater than $4R_g$. When the film thickness is less than $4R_g$ [52], an elastic modulus is required to account for the dependence of relaxation time on scattering vector, and Jiang et al. surmised this is due to the formation of a Guiselin brush [58] resulting from the pinning of chains next to the substrate by physisorption. When the film thickness is further decreased to $1R_g$, the surface fluctuations are no longer observable in the experimental window.
An extreme and well-defined case of tethering of chains to a substrate is that of the densely grafted “polymer brush” [1]. Fredrickson et al. [27] and Milner et al. [28] theoretically proved that surface fluctuations of long wavelength on a melt brush will be significantly suppressed. Akgun et al. [29] demonstrated experimentally with XPCS that the long wavelength fluctuations are slowed by at least a factor of $10^5$ for homopolymer melt brushes. Many proposed applications involve brushes in the swollen state [5,7,74-76], and any processing of brushes with solvent, such as solvent annealing, likewise involves swollen, rather than melt, brushes. Thus, the mobility of the surfaces of brushes plasticized by swelling with a low molecular weight material is of practical as well as fundamental interest. Here we consider those fluctuations for brushes swollen in vapor. NR measurements [88] presented in the previous chapter have shown that the interface between a swollen PS brush and the surrounding vapor is sufficiently sharply defined so that the fluctuations of that interface should be measurable with XPCS. However, we show that even with the very substantial plasticization that results from swelling by a good solvent vapor, the brush surface appears solidlike on time and length scales pertinent to many experimental investigations and industrial processes.

4.2 Results and Discussion

4.2.1 Structure of Vapor Swollen Brushes

The first step to elucidating the dynamics of the swollen brush surface was to determine the structure of the swollen brush and identify conditions under which the brush was swollen, but did not have a layer of condensed toluene on top, as shown schematically in Figure 4.1(a). Reflectivity measurements with X-rays or neutrons were
used to do this. Figure 4.2 presents the XR curves measured at the XPCS beamline for PS11 and PS12 in their dry state and after swelling with vapor. Fitting the curves with a parametrized model of the electron density (ED) profile of the brush using nonlinear least-squares regression yielded the ED profiles shown. The increase in thickness with swelling is apparent from narrowing of the fringes even without detailed analysis. We noted that the swollen brush thicknesses, $h_s$, were quite sensitive to the temperature differences between $T_b$ and $T_s$ ($\Delta T = T_b - T_s$). At a given value of $T_b$, we could manipulate the thickness of the swollen brush, $h_s$, by simply varying $\Delta T$.

Figure 4.1 Schematic of (a) the swollen brush next to vapor and (b) the swollen brush with a layer of condensed toluene on top.
Figure 4.2 XR curves and ED profiles of (a) PS11 before and after swelling with toluene vapor \( T_b = 30 \, ^\circ C / \Delta T = 0.6 \, ^\circ C \) and (b) PS12 before and after swelling with toluene vapor \( T_b = 30 \, ^\circ C / \Delta T = 0.9 \, ^\circ C \). For clarity, the XR curves of the swollen brushes have been offset vertically by a factor of 10.

To verify that the brush is swollen, but has no condensed liquid layer atop it, we compare with the results of NR measurements [88] of PS brushes at equilibrium states of swelling. NR readily detects the difference between perdeuterated solvent and the brush.
chains. (The effect of deuteration of the solvent on brush swelling is small and may be neglected here.) Those NR measurements showed that the maximum thicknesses, $h^*$, of brushes swollen with saturated toluene vapor at room temperature, plotted in Figure 4.3, follow the same scaling relationship with chain length and grafting density ($h^* \sim N \sigma^{1/3}$) as found for high grafting density PS brushes swollen in toluene liquid [19]. Values of $h_s$ measured with XR at 8-ID-I that were less than the $h^*$ measured with NR were taken to correspond to brushes without liquid solvent on top. For the two lower grafting density brushes, PS13 and PS14, the same samples as measured with XR were also measured with NR to determine the swollen thickness with or without a toluene layer on top.

Figure 4.3 Maximum swollen thicknesses, $h^*$, of PS brushes swollen in saturated deuterated toluene vapor as a function of $N \sigma^{1/3}$ (open squares) together with a linear fit to the data (line) and thicknesses, $h_s$, of PS10 ($T_b = 28$ °C / $\Delta T = 3$ °C), PS11 ($T_b = 30$ °C / $\Delta T = 0.6$ °C), and PS12 ($T_b = 30$ °C / $\Delta T = 0.9$ °C) swollen in toluene vapor for XPCS measurements (solid squares).
The five PS brushes were studied in swollen states with XPCS. Their dry thicknesses, $h_o$, and grafting densities are summarized in Table 4.1 along with $h^*$ determined as noted and $h_s$ for various temperature conditions obtained from XR measurements just before XPCS measurements.

Table 4.1 Characterization of PS Brushes.

<table>
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<tr>
<th>Sample</th>
<th>$h_o$ $^a$ (nm)</th>
<th>$M_n$ $^b$ (g/mol)</th>
<th>$\sigma$ $^c$ (chains/nm$^2$)</th>
<th>$h^*$ (nm)</th>
<th>$h_s$ $^{f,g}$ (nm)</th>
<th>$T_b$ (°C)</th>
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<tr>
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<td>99100</td>
<td>0.51</td>
<td>162.8$^d$</td>
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<td></td>
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</table>

$^a$ Dry brush thickness in air measured with XR (± 0.1 nm).
$^b$ Measured with GPC using THF at 35 °C with refractive index and laser light scattering (Wyatt Technology, DAWN EOS, $\lambda = 690$ nm) detectors.
$^c$ Calculated using $\sigma = \rho N_A h_o / M_n$, where $N_A$ is Avogadro’s number and $\rho = 1.05$ g/cm$^3$.
$^d$ Maximum swollen thickness interpolated from data in Figure 4.3.
$^e$ Maximum swollen thickness measured with NR (± 0.1 nm).
$^f$ Swollen brush thickness measured with XR (± 0.1 nm) just before XPCS measurements.
$^g$ Shaded entries correspond to states with a condensed toluene layer atop the brush.

When $\Delta T$ was greater than 0.5 °C, the value of $h_s$ was lower than that of $h^*$, indicating there was no condensed toluene layer on top of the swollen brush. Varying $\Delta T$ made it possible to move the swollen brush thickness closer to or farther away from the maximum value. For these conditions XPCS measured the surface fluctuations of the swollen brush, rather than fluctuations of a condensed toluene layer atop the brush. When
\( \Delta T \) was less than 0.5 \( ^\circ C \), the value of \( h_s \) was higher than that of \( h^* \), implying there was a condensed toluene layer on top of the swollen brush, as shown in Figure 4.1 (b). In this case, XPCS measured the surface fluctuations of the condensed toluene layer on top of the swollen brush.

4.2.2 Surface Dynamics of Swollen Brushes Without Condensed Liquid Layer

The XPCS data provide information about surface fluctuations with a range of characteristic wavelengths, \( \lambda \), dictated by the range of \( q|| \) probed, \( \lambda \sim 2\pi/q|| \), and range of relaxation times set by the detector capabilities and length of experiment. The XPCS measurements for the high grafting density PS brushes (PS10, PS11, and PS12) probed a \( q|| \) range of 0.003-0.01 nm\(^{-1} \), corresponding to length scales from 630 to 2100 nm. For the low grafting density brushes (PS13 and PS14), the \( q|| \) range was 0.001-0.008 nm\(^{-1} \), corresponding to 790-6300 nm. The PS brushes were investigated for a \( T_b \) range of 28-50 \( ^\circ C \), and the \( h_s \) were controlled by adjusting \( \Delta T \). As shown in Figure 4.4, the intensity–intensity autocorrelation functions for the surfaces of the PS brushes swollen with toluene vapor showed no evidence of relaxation of the surfaces. The surfaces did not relax in the time window and on the length scales investigated, even though the chains were highly plasticized with good solvent. When \( T_b \) was changed, \( \Delta T \) was adjusted to keep a similar value of \( h_s \). For example, when brush PS10 was at \( T_b = 40^\circ C / \Delta T = 5^\circ C \), its \( h_s \) was 28.5 nm, similar to that at \( T_b = 28^\circ C / \Delta T = 3^\circ C \), as shown in Table 4.1. Even when the temperature was higher, allowing for higher solvent mobility, no relaxation was observed, as shown in Figure 4.4(e). The same was true for PS11 at \( T_b = 45^\circ C / \Delta T = 5^\circ C \) and PS12 at \( T_b = 50^\circ C / \Delta T = 20^\circ C \).
Figure 4.4 Intensity-intensity autocorrelation functions at values of $q\parallel$ indicated in the legends for vapor swollen brushes (a) PS11 at $T_b = 30^\circ C / \Delta T = 0.6^\circ C$, (b) PS12 at $T_b = 30^\circ C / \Delta T = 0.9^\circ C$, (c) PS13 at $T_b = 30^\circ C / \Delta T = 0.5^\circ C$, (d) PS14 at $T_b = 30^\circ C / \Delta T = 2^\circ C$ and (e) PS10 at $T_b = 40^\circ C / \Delta T = 5^\circ C$. 
Figure 4.4 Intensity-intensity autocorrelation functions at values of $q_\parallel$ indicated in the legends for vapor swollen brushes (a) PS11 at $T_b = 30^\circ C / \Delta T = 0.6^\circ C$, (b) PS12 at $T_b = 30^\circ C / \Delta T = 0.9^\circ C$, (c) PS13 at $T_b = 30^\circ C / \Delta T = 0.5^\circ C$, (d) PS14 at $T_b = 30^\circ C / \Delta T = 2^\circ C$ and (e) PS10 at $T_b = 40^\circ C / \Delta T = 5^\circ C$. (continued)

When the grafting density is reduced, the brush chains have more freedom for movement when swollen. When more solvent can be imbibed in the brush, the plasticization effect will be even stronger. However, even the brush PS13, for which the grafting density was 0.29 chains/nm$^2$, showed no surface relaxation in the time and length scale window investigated when swollen with toluene vapor. This is shown in Figure 4.5 in two other representations of the data. Figure 4.5(a) presents the entire speckle pattern
collected by summing all 256 frames of the XPCS data set. The speckle character is evident. If the surface were moving, the speckles would have been smeared out by the averaging over ca. 278 s. In Figure 4.5(b), the coherent scattering intensity averaged over the first 128 frames along a line of pixels in the speckle pattern corresponding to $q_\parallel = 0.0013$ nm$^{-1}$ is compared with the coherent scattering intensity along the same line obtained by summing over the last 128 frames. They are identical within the statistical uncertainties, indicating that the surface did not move in the 278 s over which these data were collected. Even if the grafting density is further reduced to 0.04 chains/nm$^2$ (PS14), the surface fluctuations are slowed so much that they cannot be seen in the experimental window, as shown in Figure 4.4(d).

![Figure 4.5](image)

Figure 4.5 (a) Speckle pattern for vapor swollen brush PS13 at $T_b = 30$ °C / $\Delta T = 0.5$ °C obtained by summing over all 256 frames. The speckle character is evident despite the averaging. (b) Comparison of coherent scattering intensity averaged over the first 128 frames along a line of pixels in the speckle pattern corresponding to $q_\parallel = 0.0013$ nm$^{-1}$ with the coherent scattering intensity along the same line obtained by summing over the last 128 frames. They are the same within statistical uncertainty.

Tethered chains in the densely grafted brushes are highly stretched because the distance between grafting points is smaller than the unperturbed chain radius of gyration,
$R_g$. The entropic cost for stretching of the chains leads to a suppression or slowing down of the surface fluctuations [27]. When the densely grafted polymer brushes are swollen in good solvent, the plasticization by solvent molecules increases chain segment mobility, which should make the surface fluctuations faster. Assuming that one can define a local $T_g$ that varies with solvent concentration, this $T_g$ will not be uniform with depth in the brush. The variation in local $T_g$ with depth was calculated from a published data on the variation of $T_g$ with toluene concentration in a PS/toluene mixture [31] using the PS segment concentration profiles shown in Figure 3.13. Details of the procedure are given in Appendix. $T_g$ variations calculated this way for two PS brushes (PS1 and PS7) swollen in toluene vapor at equilibrium are shown in Figure 4.6. These two samples correspond very closely to two brushes (PS10 and PS13) measured with XPCS. For PS brushes highly swollen in toluene vapor, the $T_g$ near the brush surface can be 150-230°C lower than in pure PS. In the case of PS1 the brush immediately adjacent to the substrate is probably still glassy at temperatures characteristic of the XPCS measurements. However, in the case of PS7 the entire brush is clearly in a fluid state throughout its depth at temperatures used in XPCS measurements. Nonetheless, no long-wavelength fluctuations ($\lambda \gg h_s$) were seen here on the surface of any polymer brush swollen with good solvent vapor, even though the segmental dynamics of the brush chains should be very fast due to the substantial plasticization by the solvent. On the long in-plane length scale probed here, the swollen brush still behaves essentially like a solid and there are no thermally populated surface fluctuations on the length scales that can be probed here. This is due to the entropic penalty that must be paid to further stretch chains to form long wavelength surface waves [27,28].
Figure 4.6 $T_g$ variation inside PS brushes swollen in toluene vapor at equilibrium.

To the degree that the surface fluctuation behavior of the brushes can be understood approximately by comparison with the HCT of surface fluctuations [57], we may rationalize the observed behavior in the following way. The surface fluctuations are dictated not only by the mobility at the surface, but also by the viscosity [51] and elasticity [52] of the material at all depths in the film, down to the substrate. We conjecture in the present case that we have a strong gradient in both viscosity and elasticity with depth, in general, due to the variation in solvent concentration with depth. In other work we are investigating how large this gradient in viscosity with depth is for PS brushes swollen with 2.2K $d_8$-PS. We imagine that the viscosity of the topmost layer of the swollen brush is much lower than that of the portion of the brush closest to the substrate, so that even if a thin (perhaps a few nanometers) layer of highly mobile material is present next to the surface, that is not sufficient for the surface fluctuations to move into the time window available with current XPCS experiments. The lack of
mobility of the vapor swollen brush surface, in contrast to the “surface” of a brush swollen in liquid, could also be connected with the fact that the interface between the swollen brush and the surrounding vapor [88] is much sharper than that between a swollen brush and surrounding liquid. This leads to a lower compressibility of the brush here. We see that this difference of the interface between the brush and its surroundings has important implications for its behavior. On the time and length scales pertinent to many practical applications the surface of the vapor swollen brush behaves as though it is solidlike at temperatures at least 150°C above the effective glass transition temperature.

4.2.3 Surface Dynamics of Condensed Liquid Layers on Swollen Brushes

In a separate type of experiment the temperatures of brush and solvent were adjusted for the two brushes of lower grafting density so that the thickness of the sample exceeded the value of $h^*$. In this case the beam was being scattered by a layer of condensed toluene on the surface of the brush rather than from the surface of the swollen brush, as shown schematically in Figure 4.1(b). The thickness, $h_c$, of the condensed liquid layer on top of the vapor swollen brush, given by $h_i - h^*$, for PS13 at $T_b = 28.5°C / ΔT = -0.5°C$, PS14 at $T_b = 30°C / ΔT = 0.4°C$, and PS14 at $T_b = 30°C / ΔT = 0.1°C$ is about 29, 15, and 47 nm, respectively. The $g_2$ functions from these condensed toluene liquid layers atop the swollen PS brushes are also horizontal at values above unity in the experimentally accessible window of time, as shown in Figure 4.7. No surface fluctuations were seen on the length scales investigated (790–6300 nm).
Figure 4.7 Intensity–intensity autocorrelation functions at values of $q_{||}$ indicated in the legends for condensed toluene liquid layers atop the swollen brushes (a) PS13 at $T_b = 28.5^\circ C / \Delta T = -0.5^\circ C$, (b) PS14 at $T_b = 30^\circ C / \Delta T = 0.4^\circ C$ and (c) PS14 at $T_b = 30^\circ C / \Delta T = 0.1^\circ C$. 
We suppose that in the sample PS13 ($\sigma = 0.29$ chains/nm$^2$) with condensed liquid toluene on top the interface between the brush and liquid is similar to that seen by Kuhl et al. [19] for samples with somewhat larger $\sigma$ (0.4–0.42 chains/nm$^2$). That is the interface is much broader than for swollen brush next to vapor, so identification of what is “swollen brush” and what is the “condensed liquid layer” on top is approximate. It is likely that within the layer designated as the condensed liquid layer there are a few polymer chains, perhaps chains corresponding to the highest molecular weight portion of the molecular weight distribution. For sample PS14, for which the grafting density is much lower (0.04 chains/nm$^2$), the interface between swollen brush and neighboring fluid is even broader (segment concentration profile from NR shown in Figure 3.15). In any case it is remarkable that the liquid sitting next to the brush behaves as though it has been tethered so as to dramatically increase its effective viscosity, pushing the time scale of the fluctuations on the liquid at $q_\parallel$ of ca. 0.004 nm$^{-1}$ up by at least 8 orders of magnitude (from $10^{-5}$ to $>10^3$ s) and out of the experimental window for our XPCS apparatus.
CHAPTER V
DYNAMICS OF GOLD NANOPARTICLES IN TETHERED-UNTETHERED
BILAYER FILMS

5.1 Introduction

Ultrathin polymer films have been widely studied for decades because of the important differences between bulk behavior and behavior in thin films, for example with respect to dewetting [89-93], polymer diffusion [94-96], segmental dynamics [97-98], physical aging [99], chain entanglement [100], crystallization [101-103], and glass transition temperature \( T_g \) [104-113]. These behaviors of ultrathin polymer films are usually different from those of the bulk due to “nanoconfinement effects”. Many recent investigations [114-121] imply that the nanoconfinement effect is closely related to an irreversibly adsorbed layer next to the substrate, which can be readily formed by physisorption in thermal annealing procedures for supported polymer thin films. This irreversibly adsorbed layer is essentially a layer of polymer chains tethered onto the substrate, also known as a “Guiselin brush” [58]. While the impact of such physisorbed layers is very broad, much remains to be learned about both them and a still broader class of phenomena involving film behavior influenced by the tethering of chains in the film.

Koga and coworkers [64], Napolitano and coworkers [116] and other research groups have been elucidating the role that a Guiselin brush can play in altering the mobility of film. A challenge of that work is the difficulty in precisely characterizing the
nature of the tethering at the substrate. Koga's measurements [64] of viscosity change with depth in melt films with a Guiselin brush at the substrate found no viscosity increase at a distance of 64 nm ($6.7R_g$) from the substrate for 123k PS chains. However, at 28.5nm ($3R_g$) from the substrate the viscosity was about ten times that of the bulk. This correlates with the observation of Jiang et al. [52] that surface motion is noticeably slowed and elasticity begins to play a role for films of entangled 123k chains at $2R_g$ thickness. This long-range effect from the substrate can be explained by propagating the substrate effect by entanglement of chains with the Guiselin brush layers. However, Russell and coworkers [94] noted in their early work that the depth from a substrate above which no diminution of diffusional mobility could be seen corresponded to the length of a chain (ca. 31k) attached at the substrate and fully extended toward the surface, or about $25R_g$. For such a long distance, only an entanglement effect is not sufficient to explain the slowed dynamics and is not sufficient to explain behavior in unentangled systems.

A more well-defined tethering is that in films having chains intentionally covalently bound to the substrate by one terminus in a controlled way. When the tethering or "grafting" is sufficiently dense those chains form a structure at one extreme of the tethering spectrum known as the densely grafted brush. Pure densely grafted brushes have a variety of extraordinary properties due to the strong stretching of the grafted chains including surface fluctuation dynamics slower by many orders of magnitude than those of analog layers of untethered chains [29]. When untethered chains are placed atop this well-defined, highly tethered layer, if they interpenetrate with the underlying brush the dynamics of the top layer chains are also strongly influenced by the tethering [30].
Indeed, even a layer of solvent molecules atop a brush can have its surface dynamics dramatically slowed by the interactions with the brush [122]. Also the surface fluctuations of films of polymer chains containing a small fraction of end grafted chains can be slowed very substantially [123]. The precise mechanism by which the chain tethering changes the surface dynamics of a layer in which these grafted chains are present has not yet been described in detail. Phenomenologically the surface fluctuation dynamics can be modeled as resulting from a thin layer of untethered chains with bulk viscosity sitting on top of an immovable brush of infinite viscosity [30], but the variation of viscosity with depth must be more gradual. Koga et al. [62-65] determined how viscosity varies with depth in annealed PS films with Guiselin brushes using XPCS with AuNPs as probes of local diffusive dynamics. In this work, similar XPCS measurements provide detailed information on how the diffusive dynamics of the AuNPs vary gradually, though dramatically, with depth down through the interface between a top layer of untethered chains and an underlying, well-defined, densely grafted brush.

5.2 Results and Discussion

5.2.1 Dynamics inside Tethered-Untethered Bilayer Films with AuNPs

These bilayer films were designed to have similar untethered layer thicknesses (~48 nm), but different tethered layer thicknesses (19, 36 and 77 nm), so that the structure halfway through the depth of the sample corresponds to three different important situations with respect to concentration of segments of tethered chains, $\phi_t$. As shown in Figure 5.1, (a) the region halfway through the Brush19_AuPS48 sample is nearly exclusively composed of untethered chains mixed with AuNPs; (b) the region
halfway through the Brush36_AuPS48 sample is inside the interfacial region between the layer of pure untethered chains and the layer of pure tethered chains; (c) the region halfway through the Brush77_AuPS47 sample is deep inside the swollen brush where \( \phi_t \) approaches unity; and (d) a sample containing only a spin-coated layer of untethered chains with AuNPs on a Si wafer (Si_AuPS102, no brush) was made as a reference sample. The brush in the bilayer film, having no loops or trains, is structurally better defined than a Guiselin brush. The characteristics of the bilayer films are summarized in Table 5.1.
Figure 5.1 Schematics of the structures of the tethered-untethered bilayer films with AuNPs (a) Brush19_AuPS48, (b) Brush36_AuPS48, (c) Brush77_AuPS47 and (d) reference sample Si_AuPS102. The region primarily probed by the center-mode XPCS experiment, corresponding to an antinode in the evanescent field created in the film, is highlighted.
Table 5.1 Tethered-Untethered Bilayer Films with AuNPs and Reference Sample.

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<th>Sample</th>
<th>$h_a$ ($a$)</th>
<th>$M_n$ ($b$) (g/mol)</th>
<th>$\sigma$ ($c$) (nm)$^2$</th>
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</table>

$^a$ PS brush thickness measured using ellipsometry.

$^b$ Measured with GPC using THF at 35 °C with refractive index and laser light scattering (Wyatt Technology, DAWN EOS, $\lambda = 690$ nm) detectors.

$^c$ Calculated using $\sigma = \rho N_A h_o/M_n$, where $N_A$ is Avogadro's number and $\rho = 1.05$ g/cm$^3$.

$^d$ Change in thickness of the sample upon spin-coating the untethered chains as determined using ellipsometry.

The tethered-untethered bilayer films with AuNPs as “markers” were studied using the center-mode XPCS for understanding the effect of the tethered chains on the dynamics inside the films. The $g_2$ function curves obtained from the center-mode XPCS for Brush19_AuPS48 and Brush36_AuPS48 are shown in Figure 5.2. These can be well fitted using a single exponential function, $g_2 = 1 + \beta \exp\left(\frac{-2t}{\tau}\right)$, where $\beta$ is the speckle contrast and $\tau$ is the relaxation time.
Figure 5.2 The $g_2$ function curves from center-mode XPCS measurements of Brush19\_AuPS48 at (a) 110°C and (b) 120°C, and Brush36\_AuPS48 at (c) 110°C and (d) 120°C.

The log-log plots of $\tau$ vs. $q_\parallel$ for these bilayer films are compared in Figure 5.3. The data for Brush19\_AuPS48 and Brush36\_AuPS48 manifest a power-law relationship, $\tau \sim q_\parallel^{-2}$, and the solid lines correspond to the best fits of the power law relationship to the data. The -2 exponent indicates that the dynamics observed with center-mode XPCS are those associated with diffusive motion of the AuNPs in the films. For Brush77\_AuPS47, however, the diffusive motion of the AuNPs was too slow to be observed in the experimental window. The dashed lines shown in Figure 5.3 are to indicate that the relaxation times must be at least this large assuming that the -2 exponent holds for those data as well. The diffusion coefficients, $D$, of the AuNPs, which are calculated using
\[ \tau = \frac{1}{2Dq^2} \] [62-65], reveal that the dynamics of the AuNPs were highly influenced by the structure of the tethered-untethered bilayer film. The values of the diffusion coefficients of the AuNPs near the centers of the bilayer films and the reference film are shown in Table 5.2. Among the three bilayer samples, Brush19_AuPS48 showed the fastest AuNP diffusion; the diffusion of the AuNPs in Brush36_AuPS48 was approximately 20% slower than that in Brush19_AuPS48 at both 110°C and 120°C; the AuNP diffusion in Brush77_AuPS47 was so slow that it could not be seen even at 120°C. This means that the diffusion rate decreased by more than three orders of magnitude upon moving from the region of the sample just above the top of the swollen brush down to well inside the swollen brush.

Figure 5.3 Log-log plots of \( \tau \) vs. \( q \) for bilayer films measured with center-mode XPCS at (a) 110°C and (b) 120°C. The dashed lines for the thickest sample indicate that the relaxation times were so large that they were out of the experimental window. If they also display a \( q^2 \) dependence, then they would be at least as large as indicated by the dashed line.
Table 5.2 Measured Diffusion Coefficients of the AuNPs near the Centers of the Films.

<table>
<thead>
<tr>
<th>Sample</th>
<th>T (°C)</th>
<th>D (nm²/s)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Si_AuPS102</td>
<td>100</td>
<td>13 ± 4</td>
</tr>
<tr>
<td>Brush19_AuPS48</td>
<td>100</td>
<td>1.2 ± 0.05</td>
</tr>
<tr>
<td></td>
<td>110</td>
<td>9.6 ± 0.6</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>81 ± 10</td>
</tr>
<tr>
<td>Brush36_AuPS48</td>
<td>110</td>
<td>8.0 ± 0.4</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>62 ± 7</td>
</tr>
<tr>
<td>Brush77_AuPS47</td>
<td>110</td>
<td>&lt; 0.05</td>
</tr>
<tr>
<td></td>
<td>120</td>
<td>&lt; 0.05</td>
</tr>
</tbody>
</table>

Compared with the reference sample, the diffusion coefficient is markedly smaller at the center of the Brush19_AuPS48 sample, for which the depth probed corresponds to an environment about 6 nm above the top edge of the interfacial region in the bilayer sample, as shown schematically in Figure 5.1(a) and by comparison with a depth profile in Figure 5.4. At the depth from which the strongest scattering signal comes the material is nearly exclusively untethered chains. Nonetheless, at 100 °C the value of $D$ is 10 times lower than that for the reference sample. Already just above the interfacial region with the brush the diffusion of AuNPs is strongly influenced by the tethering of the brush chains.
Figure 5.4 SLD profiles of bilayer films deduced from the work of Uğur et al. [30] The vertical lines represent the centers of these samples.

We are surprised then to find that when the depth probed is actually within the brush/untethered chains interface, about 4 nm above the center of the interfacial region, as pictured in Figure 5.1(b) and Figure 5.4, the value of $D$ for Brush36_AuPS48 is only about 20% lower than that for Brush19_AuPS48. Why isn't the decrease larger? We conjecture this is due at least in part to some difference in the character of the brushes in the two samples. The molecular weight distribution for the 36 nm brush is cleaner than that of the 19 nm brush, which contains a small shoulder indicating the presence of chains about six times larger than the mean of the primary distribution, as shown in Figure 5.5. These large chains comprise only about 1% of the tethered chains, but they may play an important role. Since they are few in number, out beyond the bulk of the brush they are probably not strongly stretched, but they are able to penetrate substantially into the region we otherwise regard as "untethered". If the molecular weight distributions
for the brush chains in Brush19_AuPS48 and Brush36_AuPS48 were more similar we expect that the difference between the values of $D$ for these two samples would be larger.

![Graph](image)

Figure 5.5 GPC for free chains formed at the same time the brushes were synthesized for samples (a) Brush19_AuPS48 and (b) Brush36_AuPS48.

The next decrease in $D$ that occurs with increasing depth into the tethered region of the bilayer sample is very dramatic. When the AuNP motion at the bottom of the brush/untethered chains interface in Brush77_AuPS47 is probed (Figures 5.1(c) and 5.4)
the relaxation time is so large that it is outside the experimental window (Figure 5.3). The value of $D$ has decreased by at least another three orders of magnitude lower so that it is at least four orders of magnitude smaller than that in the reference sample at 120°C. The strongly slowed diffusion in this case is consistent with surface relaxations being too slow to be observed for neat PS brushes of this sort [29], for such brushes swollen with 2.2k chains [30], and even for such brushes swollen with toluene [122].

While the changes in $D$ with depth may be explained in part by the mixing of higher $T_g$ tethered chains ($T_g = 100°C$) with lower $T_g$ untethered 2.2k chains (68°C), this mixing effect on $T_g$ is insufficient to fully explain the results. We consider how $\phi_t$ varies among the film regions probed. For the reference sample, $\phi_t$ is zero for all depths and its value of $D$ is highest. For the bilayer samples, we estimate the value of $\phi_t$ at the center of the film by comparison with the SLD depth profiles of similar bilayer samples measured by Uğur et al. [30] and calculating from the SLD at the center of the film a value of $\phi_t$. For Brush19_AuPS48 the value of $\phi_t$ at the sample center appears to be zero within the uncertainties of the analysis of the NR data. However, due to the presence of a few quite large chains in the molecular weight distribution (Figure 5.5), we expect the value of $\phi_t$ is, in fact, nonzero. This explains how the value of $D$ can be a factor of 10 smaller than that for the reference sample. However, this is clearly not simply an effect of changing $T_g$ by mixing chain lengths since the value of $\phi_t$ is imperceptible. For Brush36_AuPS48 the center of the sample has a measurable concentration of brush chains, $\phi_t \sim 0.3$. The increase in local $T_g$ that could be expected due to mixing is 7°C. The value of $D$ is about a factor of 12 smaller than that of the reference sample, a larger decrease than can be explained solely by the shift in $T_g$ with mixing. The most dramatic decrease in $D$ is seen
in Brush77_AuPS47 when the region probed is centered about the bottom of the brush/untethered chains interface where $\phi_t > 0.95$. The value of $D$ in that region is at least a factor $10^4$ smaller than the reference value, while a calculated increase in local $T_g$ due to mixing would be 30°C. This is a large $T_g$ shift, but still below that required to explain a 10000 fold decrease in $D$.

These results establish that even in the absence of entanglements between tethered chains and untethered chains the nonzero $\phi_t$ in the interfacial region leads to a strong reduction in mobility. The tethering influence of the substrate is not propagated into the film by long chains threading through loops of chains strongly adsorbed to the surface. The reduction in mobility is partially due to the mixing of higher $T_g$ tethered chains with lower $T_g$ untethered chains. However, more importantly the additional change over and above what can be ascribed to mixing of chain sizes is due to hydrodynamic interactions between the tethered and untethered chains, similar to those seen between tethered chains and low molecular weight solvents by Dhinojwala, Cho, and Granick [124,125]. Further work will be needed to clarify even in such systems of well-defined tethering how the tethered chains influence their surroundings. That understanding will have implications for a variety of technologies, but most obviously for nanocomposites reinforced with nanoparticles covered with grafted chains.

For the case of a viscous liquid environment, the diffusion rate observed for the AuNPs can be further related to the viscosity, $\eta$, of the material at the center of the sample where the EFI is highest. Koga et al. [62] did this for polymer films in which some chains were physisorbed at the substrate, and calculated the value of $\eta$ from $D$ using the Stokes-Einstein equation, $D = k_B T / 6 \pi \eta R$, where $k_B$ is the Boltzmann constant, $T$
is the absolute temperature, and $R$ is the effective radius of the AuNPs. They have made two assumptions in this. First, they have assumed that for all cases they considered the model of the film as a viscous liquid is appropriate. Second, they have assumed the validity of the Stokes-Einstein equation. They argue that to apply the Stokes-Einstein equation for a nanoparticle in a polymer film, $R$ should meet the condition $R_g > R >> a$, where $R_g$ is the unperturbed chain radius of gyration and $a$ is the correlation length of the polymer, which can be the size of a monomer unit. In our system the $R_g$ of the untethered chains (ca. 1.2 nm) is definitely smaller than $R$ (2.5 nm), therefore application of the Stokes-Einstein equation is problematic for our reference sample. For the tethered-untethered bilayer films, the structures are complicated, combining stretched tethered chains with low molecular weight untethered chains. For the Brush77_AuPS47, $R$ is smaller than the tethered chain $R_g$, but we come up against the question of whether the environment can be appropriately described by a viscosity. The concentration of tethered chains is high, and the tethered chains can be entangled. In this case describing the resistance to mobility of an AuNP with a friction factor calculated from the Einstein relation, $D = k_B T/f$, is still valid, but discussion of a viscosity is problematic. Therefore we have cast our discussion of changes in the mobility of the sample with depth in terms of diffusion, even though for regions with low tethered chains concentration a viscosity could still be defined.
5.2.2 Surface Dynamics of Tethered-Untethered Bilayer Films with AuNPs

The surface-mode XPCS measurements were also performed to study the surface dynamics of the bilayer films with AuNPs. The log-log plots of $\tau$ vs. $q_\parallel$ for Brush36_AuPS48 and Brush77_AuPS47 at different temperatures are shown in Figure 5.6.

![Log-log plots of $\tau$ vs. $q_\parallel$ measured with surface-mode XPCS for (a) Brush36_AuPS48 and (b) Brush77_AuPS47 at different temperatures.](image)

For both samples, the surface dynamics were accelerated with the increase in temperature. At the same temperature, the surface dynamics of Brush77_AuPS47 were obviously slower than those of Brush36_AuPS48, which means that the tethered layer thickness also affects the surface dynamics of the bilayer films, even though there is no tethered chain in the surface. Unlike the $\tau \sim q_\parallel^{-2}$ relationship for the dynamics inside the bilayer film shown in Figure 5.3, the surface dynamics manifest a different power-law relationship, $\tau \sim q_\parallel^{-4}$, which means that the observed dynamics from the surface-mode XPCS were not the diffusive motions of AuNPs near the film surface. In Figure 5.7, the log-log plot of $\tau$ vs. $q_\parallel$ for Brush77_AuPS47 at 100 °C is compared with that for a
tethered-untethered bilayer film of similar structure but without AuNPs, Brush76_PS45, for which the observed surface dynamics were the thermally induced surface height fluctuations on the bilayer film [30]. The fact that the two samples have the same power-law relationship \( \tau \sim q_{||}^{-4} \) implies that the observed surface dynamics for Brush77_AuPS47 were, in fact, also the surface height fluctuations on the film. In addition, in the present work the surface fluctuations on the bilayer samples are seen to slow as the brush thickness is increased, which is also consistent with results reported by Uğur et al. [30]

![Figure 5.7 Log-log plot of \( \tau \) vs. \( q_{||} \) for Brush77_AuPS47 and Brush76_PS45 at 100 °C (Brush76_PS45 is a bilayer with a 45 nm thick film of untethered d8-PS spin-coated on a 76 nm thick PS brush).](image)

In this work, the surface-mode XPCS results reflect not the motion of particles near the surface, but rather the fluctuations of the surface itself. Only the surface fluctuations observed in the surface-mode XPCS implies that the scattering intensities from the film surface are more significant than those from the AuNPs. This contrasts with the work of
Koga et al. [62-65] which reported measurements of AuNP diffusion near the surface of samples with a higher (2x) concentration of AuNPs using surface-mode XPCS. However, our observation of surface fluctuations despite the presence of the AuNPs probes is consistent with work of Green et al. [126], who measured surface fluctuations in AuNPs containing blend films using the surface-mode geometry.

5.2.3 Structure and Dynamics of Tethered Single Layer Films with AuNPs

In order to further understand the properties of the tethered layer, the tethered single layer films with AuNPs have also been studied. The characteristics of these single layer samples in this work are summarized in Table 5.3.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$h_b$ (nm)</th>
<th>$M_n$ (g/mol)</th>
<th>$\sigma$ (chains/nm$^2$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Brush46_Au</td>
<td>46</td>
<td>52900</td>
<td>0.55</td>
</tr>
<tr>
<td>Brush32_Au</td>
<td>32</td>
<td>30600</td>
<td>0.66</td>
</tr>
<tr>
<td>Brush10_Au</td>
<td>10</td>
<td>9800</td>
<td>0.65</td>
</tr>
</tbody>
</table>

Table 5.3 Tethered Single Layer Films with AuNPs.

$^a$ PS brush thickness measured using ellipsometry.
$^b$ Measured with GPC using THF at 35 °C with refractive index and laser light scattering (Wyatt Technology, DAWN EOS, $\lambda = 690$ nm) detectors.
$^c$ Calculated using $\sigma = \rho N_A h_o / M_n$, where $N_A$ is Avogadro's number and $\rho = 1.05$ g/cm$^3$.

The procedure and mechanism of preparing a tethered single layer film with AuNPs are shown in Figure 5.8. PS brush chains are collapsed in “dry” condition since air can be viewed as a bad solvent for PS. When the brush is immersed in the AuNPs/chloroform solution in a vial, the chains will be swollen and be stretched due to the good solvent environment, so that the AuNPs can penetrate into the brush [9]. Then enough ethanol is quickly poured into the vial, converting the environment to a bad solvent for PS.
Therefore, the PS brush chains will be collapsed again, trapping the AuNPs inside the brush to form the tethered single layer film with AuNPs. After washed and dried, the tethered single layer films with AuNPs are supposed to have the structure as shown in Figure 5.9.

Figure 5.8 Procedure and mechanism of preparing a tethered single layer film with AuNPs.

Figure 5.9 Schematic of a tethered single layer film with AuNPs.

The Atomic Force Microscopy (AFM) topography images of the tethered single layer films with AuNPs are shown in Figure 5.10. These images are the representative ones from multiple measurements of similar results and the surface rms roughnesses, $R_{\text{rms}}$, are the averaged values of multiple measurements of 2 um $\times$ 2 um AFM images.
Figure 5.10(a1) is the AFM image of Brush46_Au as prepared before any thermal annealing, which shows two types of features on the sample surface: the small dots and large clumps. The small dots are the AuNPs confined in the surface region of the tethered layer, since they demonstrate the sizes comparable to those of the AuNPs. The large clumps are the aggregated AuNPs on the sample surface, formed when the AuNPs were exposed to the bad solvent, ethanol. These Au clumps are actually the defects on the sample surface, however, they cannot be removed by washing or even sonication, probably due to the strong interaction with the polymer matrix. After the XPCS measurements with a heating cycle of 110 °C-150 °C-200 °C-220 °C, the surface of Brush46_Au became smoother, as shown in Figure 5.10(a2). Its surface $R_{\text{rms}}$ is decreased to $1.6 \pm 0.4$ nm from that of the as-prepared sample, $2.7 \pm 0.5$ nm. The AFM image of the as-prepared Brush32_Au, shown in Figure 5.10(b1), is similar to that of Brush46_Au, demonstrating the AuNPs small dots and the aggregated Au clumps. As shown in Figure 5.10(b2), after the XPCS measurements with a heating cycle of 200 °C-220°C, its surface also became smoother with the $R_{\text{rms}}$ decreased to $2.5 \pm 0.2$ nm from that of the as-prepared sample, $4.2 \pm 0.6$ nm. In addition, the smoother surface after XPCS measurements with a heating cycle is also found for the sample Brush10_Au, as shown in Figure 5.10(c1) and Figure 5.10(c2). This phenomenon implies that the AuNPs in the surface region along with the aggregated Au clumps went deeper inside the polymer matrix after the heating cycle during the XPCS measurements.
Figure 5.10 AFM images of Brush46_Au (a1) as prepared before annealing ($R_{\text{rms}} = 2.7 \pm 0.5$ nm) and (a2) after XPCS measurements with a heating cycle of 110°C-150°C-200°C-220°C ($R_{\text{rms}} = 1.6 \pm 0.4$ nm). AFM images of Brush32_Au (b1) as prepared before annealing ($R_{\text{rms}} = 4.2 \pm 0.6$ nm) and (b2) after XPCS measurements with a heating cycle of 200°C-220°C ($R_{\text{rms}} = 2.5 \pm 0.2$ nm). AFM images of Brush10_Au (c1) as prepared before annealing ($R_{\text{rms}} = 3.7 \pm 0.4$ nm) and (c2) after XPCS measurements with a heating cycle of 110°C-150°C-220°C-150°C ($R_{\text{rms}} = 3.1 \pm 0.5$ nm).
XR measurements were also performed during the XPCS measurements to probe the structure of the tethered single layer films with AuNPs. Figure 5.11 shows the XR curves and their ED profiles of these samples, indicating that there are AuNPs buried inside the tethered layer to a certain depth from the surface. For Brush46_Au, the AuNPs can reach a depth of ~ 20 nm from the surface. However, for Brush32_Au and Brush10_Au, the depths containing AuNPs are only ~ 10 nm and ~ 5 nm, respectively. This indicates that the ability of holding AuNPs is increased with the thickness of tethered layer.

![Figure 5.11 XR curves and ED profiles of (a) Brush46_Au at 200 °C, (b) Brush32_Au at 200 °C, and (c) Brush10_Au at 150 °C.](image-url)
Figure 5.11 XR curves and ED profiles of (a) Brush46_Au at 200°C, (b) Brush32_Au at 200°C, and (c) Brush10_Au at 150°C. (continued)
XPCS was used to study the dynamics of the AuNPs in the tethered layers. For Brush46_Au, both the surface-mode and center-mode XPCS measurements were performed at 110 °C, 150 °C, 200 °C and 220 °C; for Brush32_Au, the surface-mode XPCS measurements were performed at 200 °C and 220 °C; for Brush10_Au, the surface-mode XPCS measurements were performed at 110 °C, 150 °C and 220 °C. For all these measurements, unlike those for the AuNPs in films of untethered polymer chains, no $q_{||}$-dependent dynamics were observed in the experimental window. This implies that the tethered chains significantly suppress the dynamics of AuNPs, which logically agrees well with the slowed dynamics of AuNPs in the tethered-untethered bilayer films.
CHAPTER VI

SUMMARY

The research presented here illuminates three aspects of the structure and dynamics of polymer films involving densely grafted brush layers. The first portion provides insights pertinent to the solvent annealing processing of brush layers. The scaling of the height of densely grafted brushes in solvent vapor with grafting density and chain length is found to be consistent with that for the same brushes swollen in liquid. The key difference between the structure of brushes swollen in liquid and the structure of those swollen in vapor is in the width of the interface. The brush/vapor interface is much sharper than the brush/liquid interface, a finding in agreement with a simple SCF calculation. This smaller interface width should have important implications for fluctuations at the brush surface and the compressibility of the brush surface in the swollen state. Specifically, the behavior of the brush surface during solvent annealing and the microroughness and interface width after solvent removal will be impacted by any fluctuations and the form of the interface next to vapor. An interesting question for future research is what the structure of an irreversibly adsorbed layer is when swollen in good solvent vapor. This structure may be studied using NR and may provide clues to the nature of the irreversibly adsorbed layer.

The second portion of the work addressed how thermally stimulated fluctuations on a brush surface are modified by plasticization of the brush by swelling with good solvent
vapor. No surface height fluctuations are observable in the current experimental time and length scale window for XPCS for various strongly swollen PS brushes of grafting densities from 0.04 to 0.61 chains/nm$^2$ and swollen thicknesses from 11 to 105 nm. Although the brushes are highly plasticized by solvent and should have faster segmental dynamics, the surfaces of the vapor swollen brushes behave like solid surfaces on time scales and length scales pertinent to many practical applications. The slowing of the surface fluctuations is due to the entropic penalty for fluctuations to form. Presumably if one were able to measure out to sufficiently high values of $q_{\parallel}$ one would be able to see differences due to the plasticization for fluctuation wavelengths on the order of the brush thickness [27], but these differences are not apparent in the time and length scale window currently available. Even in the case that a 47 nm thick layer of liquid toluene is placed on a swollen brush and the surface fluctuations should move into a range of time and length scale closer to the experimental window, no movement can be seen. An interesting question for future research is how the surface fluctuations for a layer of untethered chains change when that layer is swollen in good solvent vapor.

The final portion addressed the variation in mobility with depth for a system in which short untethered chains are on top of a brush. In such a sample the local AuNP diffusion rate decreases significantly down through the sample with the increase in the concentration of segments of tethered chains. This variation in mobility with depth in such bilayer films is more complicated than that described with the model of a layer of untethered chains with bulk viscosity sitting on top of an immovable brush. The actual variation in mobility with depth needs to be characterized with even better resolution. One application in which this variation plays an important role is the use of polymer
modified nanoparticles in matrixes of free polymer chains to create nanocomposites with various properties.
REFERENCES


[67] Piranha solution is dangerous due to the hydrogen peroxide and sulfuric acid. Appropriate protections, such as acid-resistant gloves, goggles and lab coats, must be used when handling the piranha solution.


APPENDIX

CALCULATION OF $T_g$ VARIATION IN VAPOR SWOLLEN BRUSH

For a PS/Toluene solution, the relationship between the weight fraction of toluene, $W_{Toluene}$ and the decrease in $T_g$ relative to bulk PS was obtained from Ref. [31] and is shown in Figure A.1(a). This relationship can be converted to the relationship between the volume fraction of PS, $\phi_{PS}$, and the decrease in $T_g$ as shown in Figure A.1(b). The variation in the local $T_g$ with depth for a vapor swollen brush, shown, for example, in Figure 4.16, was then calculated from the PS segment concentration profile shown in Figure 3.13 using the relationship in Figure A.1(b).

![Figure A.1](image)

Figure A.1 Relationship between the concentration of a PS/Toluene solution and the decrease in $T_g$ expressed as (a) weight fraction, and (b) volume fraction. Data in (a) from Ref. [31].