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INTERFACE STRUCTURE OF DIBLOCK COPOLYMER BRUSHES AND
SURFACE DYNAMICS OF HOMOPOLYMER BRUSHES AND BILAYERS OF
UNTETHERED CHAINS ON BRUSHES

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ABSTRACT

The main objective of the work presented in this dissertation is to understand the internal structure and surface dynamics of diblock copolymer brushes (DCBs). DCBs have garnered enormous interest in recent years due to their stimuli-responsive behavior. The characteristics of a surface of a DCB can be changed reversibly from those of one type to those of another by using a selective solvent for one block. There has not been any experimental study to prove either the dry state structure or the surface rearranged structure or the mechanism of that rearrangement. Understanding the dynamics of the brush/air interface and internal interfaces is also important to understanding the switching mechanism, and the dynamics at the air surface have further implications for wetting, friction and adhesion.

Using neutron reflectivity (NR), we have resolved the internal structure of DCBs of polystyrene-*b*-poly(methyl acrylate) (PS-*b*-PMA) and PMA-*b*-PS. The internal brush structure depends strongly on the block sequence and the value of χN (χ : Flory-Huggins interaction parameter, N : length of the chains). For dPS-*b*-PMA films, when $\chi N \leq 23$, a model of two layers with an interfacial region of finite width provides a good description of the data. When χN is higher, a third layer must be included in the model. A third layer is consistent with the presence of a lateral ordering in the center of the brush, as evidenced by correlation peaks in grazing incidence small angle scattering (GISAXS) data from these samples. For PMA-*b*-dPS samples,

when $\chi N > 23$, the change in reflectivity due to a 3-D structure in the middle of the film may be modeled with a dramatic increase of interface width.

In-situ NR measurements of DCBs in selective solvents show that the structure changes in a way to minimize the unfavorable interaction between solvent and the solvophobic block. How the chains in a DCB minimize this unfavorable interaction depends also on the solvent quality, the ratio of chain lengths of the polymer blocks, block sequence and details of the brush composition determined by nonidealities in the synthesis DCBs. A switching of the surface character is not easily obtained unless optimum conditions are provided. More work with DCBs of various block lengths should be pursued. When DCBs are swollen with a solvent good for both blocks, they behave in a manner similar to that for homopolymer brushes, with scattering length density (SLD) profile having, overall, a parabolic shape.

The dynamics of surface height fluctuations of molten homopolymer brushes have been investigated using X-ray photon correlation spectroscopy (XPCS). Within the range of time (0.2 -1100 s) and length scale (0.6-3 μm) studied, no relaxation of fluctuations of the brush surfaces are detectable. This is true for PS brushes of thicknesses of 9 - 101 nm and high grafting density (>0.5 chains/ nm^2) at temperatures up to 130°C above bulk T_g . Even reduction of the grafting density from 0.6 to 0.1 chains/ nm^2 does not bring the relaxation into the measurement window.

Tethering not only changes the surface dynamics of grafted chains but also the surface dynamics of 2.2k dPS chains spun cast on top of a PS brush. The relaxation of surface height fluctuations on a melt of a certain quantity of PS chains spun cast on top of a PS brush becomes slower than the relaxation of surface height fluctuations on a melt of the same quantity of PS chains placed on top of a bare silicon surface. As the thickness of the brush layer increases (h_b), the relaxation time (τ) of fluctuations on top of the “bilayer” becomes larger. A model of single layer of viscous fluid on

a rigid substrate with a non-slip boundary condition does a good job of capturing the data. Calculated thicknesses from the model that are “effective” for the observed surface dynamics are decreases with increasing h_b .

NR measurements reveal the actual structure of the bilayer films. The structure model consists of a bottom layer of one SLD, a top layer of a second SLD, and an interface between the two layers is found to be reasonable. The “top” layer thicknesses observed with NR are the same as the “effective” thicknesses from the single viscous layer analysis of the XPCS data within the uncertainties.

As the grafting density of the brush is reduced, the surface dynamics of the layer of spun cast chains on top of the brush become slower. This is due to increasing of free chains into the brush and a decrease in the “effective” thickness of the layer of free chains on top.

Increasing the molecular weight of the free chains, M_n , decreases the interface width. Interface width is a decreasing function of M_n and decays exponentially with increase of M_n .

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Hayati guzel, yasanilir ve katlanilir kilan iki ozel insan,
annem Sevda ve babam Abdurrahman Uğur'a...

CHAPTER I

INTRODUCTION

1.1 Introduction to and Review of the Properties of the Polymer Brushes

A polymer brush is an assembly of long chain molecules attached by one end to a surface or interface with a density of attachment points high enough that the chains are forced to stretch away from the interface much further than would a typical untethered chain [9] that happens to have one end at or near interface. This stretching of the chains away from the typical behavior of Gaussian coil configurations of flexible chains in melt gives polymer brushes their peculiar and useful properties.

Polymer brushes first attracted attention when it was found that grafting polymer molecules to colloidal particles was a very effective way to prevent flocculation [10]. Thus, they were first used as stabilizers. There are other potential applications in a wide array of areas of interest such as adhesion [11–17], lubrication [18, 19], tribology [20], chromatography [21, 22], rheology [23], wetting [24–36], microfluidics [37–41] and protein and cell-resistant biosurfaces [42–44].

A polymer brush can be built by attaching chains to the substrate either chemically or physically. Physical attachment, physisorption, depicted in Figure 1.1a, is achieved by self-assembly of diblock copolymers on a substrate. [45, 46]. To effect the physisorption of a diblock-copolymer, surface and solvent are chosen in such a way that one block is strongly attracted to the substrate while the other block interacts more favorably with the solvent. One simple example is polystyrene-*b*-poly(ethylene oxide) (PS-*b*-PEO) on mica in toluene. The PEO segment is attracted

to the hydrophilic surface while the PS block is preferentially swollen by the organic solvent. The thickness (h) and the grafting density (σ) of physically attached brushes are not controllable. Physisorbed brushes are also not stable, since desorption of the molecules from the substrate can easily occur in a solvent or at high temperature and the polymer can be displaced by other adsorbents. Fixing chains to the substrate with covalent attachment can overcome these problems.

Covalent attachment can be done in two approaches. In the first approach called “grafting to” [47], shown in Figure 1.1.b, end-functionalized polymers are reacted with anchor groups on the substrate surface [48–50]. The advantage of this approach is that polymers with a precisely controlled molecular weight distribution can be used. The disadvantage of this approach is that the thickness is limited, the grafting density is low (≤ 0.1 chains/nm²), and grafting density decreases with increasing molecular weight of the chains. Denser brushes cannot be obtained because the attachment of chains may be hindered by chains already attached to a surface. Thicker brushes with high grafting density can be obtained with the second approach called “grafting from” [47], shown in Figure 1.1, in which initiators are immobilized onto the substrate [51,52] and polymer chains are grown *in-situ* from the immobilized initiator layers. Such polymerizations have so far been realized using free radical polymerization [51–54] or controlled radical polymerization [55–64]. The thickness of the brush can be controlled by polymerization time, amount or type of monomer charged and a wide range of functional monomers can be used. The primary limitations for this approach are the variation in initiator efficiency with initiator type, and the rate of diffusion of monomer to active polymerization sites.

Brush structure can be characterized by the grafting density σ (chains/nm²) or, equivalently, distance between grafting points (d) as suggested in Figure 1.2.

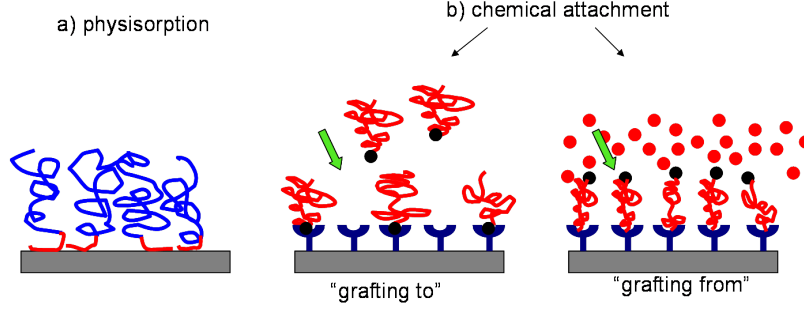


Figure 1.1: Schematic illustrations of a) a physically attached diblock copolymer brush, and b) chemically attached brushes by “grafting to” and “grafting from” approaches.

Grafting density can be calculated by

$$\sigma = h\rho N_A/M_n \quad (1.1)$$

where h is brush thickness, ρ is bulk density, N_A is Avogadro’s number, M_n is number average molecular weight of the chains [65]. If one imagines the grafting points as falling on a simple square lattice, then it follows that $\sigma = d^{-2}$. As the distance between grafting points is reduced past the projection on the surface of the radius of gyration (R_g) of an unperturbed chain, the chains start to overlap. This transition between what is known as the “mushroom” regime for tethered layers to the “brush” regime is a very important one which is explained more in the following text. Since it is the ratio of distance between grafting points to R_g that dictates the degree of overlap among chains, and therefore the degree of chain stretching, an important parameter of the brush structure is the reduced tethered density (Σ); $\Sigma = \sigma\pi R_g^2$, where R_g is the unperturbed radius of gyration of a tethered chain at specific experimental conditions of solvent and temperature. Σ can be interpreted as the number of chains that occupy the volume a free chain would normally occupy under the same conditions.

For brushes, several regimes with different static and dynamic characteristics can be associated with specific ranges of grafting density and solvent quality. In respect to the grafting density, one distinguishes three regimes in Figure 1.2. (i) In the “**mushroom**” regime, where $d > R_g$ or $\Sigma < 1$, chains do not overlap, stretching does not occur and chains take on a typical random coil configuration. (ii) In the “**pancake-like**” [66] regime where chains start to overlap, $\Sigma = 1$ and there is a strong attractive force between the polymer chains and substrate, chains are flattened out like a pancake. (iii) In the “**brush**” regime, where $d < R_g$ or $\Sigma > 1$, chains overlap. Once d is much smaller than R_g the chains can no longer fill volume acceptably simply by interpenetrating one another, but rather they also stretch away from the substrate. In order to approach the “true brush” regime, in which the properties peculiar to brushes clearly manifest themselves, it is necessary to reach sufficiently high stretching of the polymer chains, typically characterized by $\Sigma > 5$, where the value of five represents an average of results from several studies [67]. One key experimental study is done by Genzer and coworkers [68] studied the dependence of film thickness versus initiator density for a polyacrylamide brush and observed a crossover where the relationship of brush thickness to σ changed from zero order to 1/3 order. For this system, they observed that mushroom-to-brush regime transition occurs around $\sigma \approx 0.065$ chains/nm² ($\Sigma \approx 6$) for M_w of 17000 g/mol and PDI of 1.7.

With respect to solvent quality there are three regimes: (i) in poor solvent, polymer-polymer segment interaction is bigger than polymer-solvent interaction. (ii) in theta (θ) solvent, polymer-polymer and solvent-solvent interactions are balanced, polymer segments has no preference to segments or solvents which results in zero excluded volume. (iii) in good solvent, polymer-solvent interaction is bigger than polymer-polymer interaction which results in swelling of polymer chains.

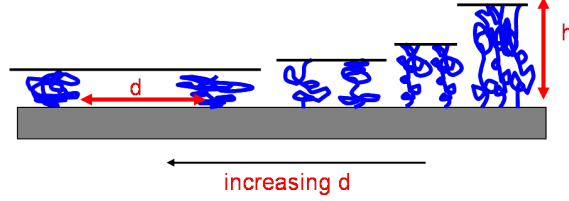


Figure 1.2: Schematic illustration of the variation in chain stretching with grafting density where d is the distance between neighboring chains and h is the brush thickness.

1.2 Scaling Laws and Theoretical Models for Describing a Polymer Brush

The simplest model to describe the properties of polymer brushes has been introduced by Alexander [69] and de Gennes [66]. The Alexander model considers a flat brush surface of monodisperse flexible chains of N monomers with a monomer size of a . In a good solvent $R_g \sim N^{3/5}$, while in θ -solvent $R_g \sim N^{1/2}$. The Alexander model is based on two assumptions. The concentration profile is assumed to be step-like, as shown in Figure 1.3 c. According to this assumption, the average segment density in a brush of thickness h is $\phi = N\sigma/h = \text{constant}$. Second, the chains are uniformly stretched so that the free end of each chain in the brush located at the brush surface.

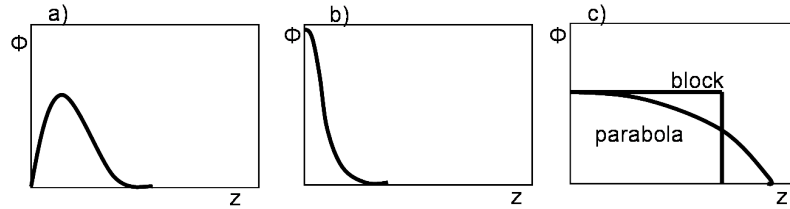


Figure 1.3: Polymer segment volume fraction profiles for different regimes a) “mushroom” b) “pancake-like” c) “brush”.

The Alexander model considers the interplay of two terms: F_{int} , the free energy of the monomer-monomer or monomer-solvent interactions and F_{el} , the free energy contribution due to the elastic restoring force. This interplay determines the thickness of the layer [65]. Stretching of the chains normal to the grafting plane

increases the brush thickness, lowering the polymer concentration in the layer and decreasing the value of F_{int} , with the price of increasing F_{el} . The free energy per chain is given by

$$F = F_{int} + F_{el} \quad (1.2)$$

where

$$F_{int} \approx \phi N \nu = (N \sigma / h) N \nu \quad (1.3)$$

with ν being the excluded volume parameter. The elastic contribution,

$$F_{el} \approx h^2 / R_g^2 \quad (1.4)$$

regards each polymer chains as an entropic “spring” with a spring constant kT/R_g^2 . This leads to a free energy per chain of:

$$F = F_{int} + F_{el} \approx kT \left(\frac{h^2}{Na^2} + \nu N \left(\frac{N\sigma}{h} \right) \right). \quad (1.5)$$

Minimization of free energy with respect to brush height h , leads to the scaling relationship

$$h \sim N(\nu \sigma a^2)^{1/3} \quad (1.6)$$

This result suggests that brush height increases linearly with the number of monomer chains, N , while in the case of free chains in a good solvent the size of the coil increases as $N^{3/5}$. The above expression overestimates the free energy of the brush, but it gives the right scaling for the dependence of brush thickness on N .

In the model of deGennes [66], scaling arguments are used to take into account the effects of the excluded volume correlations and self-avoidance. The polymer layer

is pictured as a close-packed array of uniform blobs with a size $\xi \approx \sigma^{-1/2}$ normal to the grafting surface as shown in Figure 1.4.

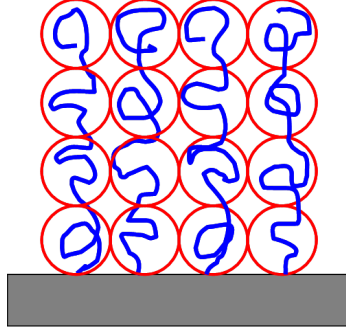


Figure 1.4: Schematic of a flat, tethered layer with the de Gennes model of a chain with a blob representation.

Each blob is assigned a free energy of kT . Each blob contains $g \approx \xi^{5/3}$ monomers and the number of blobs per chain equals F_{ini}/kT . The elastic free energy is modified by taking chain to behave as a Gaussian chain at large scales, but with the subunits being the excluded volume blobs. This model leads to the following scaling: $h \approx N\sigma^{1/3}$.

Both Alexander and de Gennes models and scaling arguments assume that each chain behaves identically with all others, resulting in a step-function density profile. Later work [9, 70–74] shows that these models miss some features of actual brushes. First, the conformations of different chains in the brush do not have to be similar and the chain end density is proportional to the distance from the surface near the surface, passes through a maximum and returns to zero at the outer edge of the brush. This picture differs strongly from that of Alexander’s. Milner et al. [72] shows that for polydisperse brushes free ends of longer chains are further from the grafting surface than are those of shorter ones. In these recent works researchers also contend that the density profile is parabolic (Figure 1.3.c) in good solvents and becomes like a step function in poor solvents [75–79]. The brush thickness decreases

smoothly with decrease in solvent quality, while with free chains the collapse of chain size upon decreasing solvent quality is more abrupt.

Theoretical studies with self-consistent field (SCF) theory can provide more realistic descriptions of the density profile than can the scaling methodologies. In SCF theory it is assumed that polymer chain interacts with its neighbor more than it does with itself. SCF models connecting molecular weight and grafting density with the brush height offer simple scaling laws:

$$h = \frac{12^{1/3}}{\pi^2} (\sigma\nu)^{1/3} N \text{ or } h \approx N(\sigma\nu)^{1/3}. \quad (1.7)$$

This leads to a segment density profile of:

$$\phi(z) = (B/\nu)(h^2 - z^2) \quad (1.8)$$

where $B = \pi^2/8N^2$.

So in SCF theory, brush height has the same functional dependence as that predicted by the simple energy balance argument that led to Eq. 1.6. Early experimental work found that experimental scattering data could be reasonably described using a parabolic segment density profile for polymer brushes in good solvents [80–82]. Auroy and co-workers [81] used small-angle neutron scattering for PS grafted on porous silica and found that the data were fitted reasonably a parabolic profile and neutron reflectivity (NR) curves were similarly reconciled with parabolic profiles [71, 83], but later experimental work provided a more sophisticated picture.

One difference between the parabolic profile used in early experimental studies and the SCF theory calculations based on Eq. 1.8 is at the tip of the profile, as shown in Figure 1.5. In the parabolic profile the segment density goes abruptly to

zero. However, experimental data for some systems can be better fit using a profile having a more gradual and exponential decay of concentration to zero because the end of each chain is not strongly stretched and there are fluctuations of locations of chain ends. Wijmans et al. [1] take into account these limitations using numerical SCF calculations and show that this deviation between the parabolic profile and the profile that best fits experimental data becomes less important as molecular weight increases, as shown in Figure 1.5. Deviations from the parabolic profile are also found close to the wall. Experimentally there occurs a depletion region close to the wall due to unfavorable interactions between the wall and polymer segments. For favorable interactions there could be enhancement in polymer segment density next to the wall, whereas for neutral wall-polymer interactions the deviation at the wall between the actual concentration and the parabolic profile reaches zero.

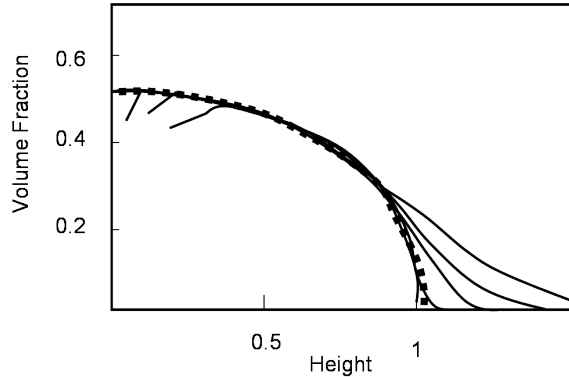


Figure 1.5: A comparison of numerical solutions of the SCF equations with the parabolic classical approximation (dashed curve) in theta solvent. The solid curves are for grafted chains with degrees of polymerization of 600, 100, 50 and 25, in order of increasing deviation from the parabolic profile [1].

The effect of solvent quality on the brush height expressed by Equation 1.7 is for the conditions with good solvent. If the solvent quality is reduced while keeping the grafting density constant, brush extends less. At the θ -temperature, the excluded volume parameter becomes zero. In that case, modification of the stretching energy

term to include the energy cost of compressing the brush leads to the scaling relation [75]:

$$h = N\sigma^{1/2}f(t/\sigma^{1/2}) \quad (1.9)$$

where t is $((T - T_\theta)/T)$ for solvent conditions above, at and below the θ -point and the function $f(x)$ has the properties

$$f(x) = \begin{cases} x^{1/3} & \text{for } x \gg 1 \\ |x|^{-1} & \text{for } x \ll 1 . \end{cases} \quad (1.10)$$

Lai [75] observed by Monte Carlo (MC) simulations that in the bad solvent regime, monomers belonging to different chains are attracted to each other causing the partial phase separation and “pinned micelle” structure. The stability of this laterally inhomogenous structure depends on the chain length, surface quality and surface coverage. Shortly after this work, Ross and Pincus [76] used random phase approximation and Alexander step density profile to calculate the structure factor and concluded that there is no instability in the poor solvent regime. They found that polymer brush collapsed uniformly, density variations in the direction parallel to the grafting plane being smoothed out by positive osmotic pressure in the layer.

In a more recent study, Romiszowski and Sikorski [77] using MC simulations studied the structure of ideal brushes consisting of two kinds of block segments: athermal, attached to surface and the interacting upper part. It was shown that for good solvent conditions, height of the chains increases with change of grafting density up to 25%. For bad solvent conditions, up to moderate grafting density (0.125%), brush height increases followed by a decrease with increase of grafting density. This could be the result of competition of two factors; one of which is the increase of the system density leading to elongation of the chains along z-axis, and second is the

tendency of chains to increase the number of segment-segment contacts. Hansen *et al.* [78] investigated the stretching of brushes in good solvent in the limit of very high grafting densities using MC simulations. They showed that the brush profile and height went to a rapid transition from the SCF regime to the fully stretched regime around $\sigma \simeq 10$. Beyond transition value, profile showed universal, quasiparabolic profile and above transition profile changes into a quasirectangular shape, while the fluctuations of the end-monomer altitude drops sharply, giving a rather flat brush-solvent interface.

Most theoretical studies of polymer brushes have focused on average properties at equilibrium, such as layer height, distribution of chain ends, and monomer concentration. Fredrickson *et al.* [84] was concerned with the deformation behavior and fluctuations on the surfaces of brushes. They considered the response of a molten polymer brush (unit volume fraction of polymer within the layer) to a nonuniform, volume-conserving deformation. The particular deformation of interest is a small-amplitude sinusoidal displacement of the brush free surface (opposite the grafting surface). They considered the Alexander-de Gennes model of a strongly stretched brush in which the free ends are assumed to be located at the free surface. Since chains are attached to the substrate with a distance smaller than the R_g , lateral displacements cause a configurational entropy penalty. Thus, surface modes with wavelengths greater than the film thickness are strongly suppressed on the surface of a brush. Short wavelength fluctuations should also be suppressed due to surface tension. Competition between elastic restoring force at long wavelengths and surface tension penalty at shorter wavelengths should lead to an energetically preferred wavelength on the surface of a brush that is typically on the order of the equilibrium brush height, h . This pioneer work is very useful in the sense to understand surface fluctuations to describe the structure of homopolymer brushes as

well as to understand the fluctuations of block copolymer brushes on both internal substrate interface and the interface with block's surroundings. However, this work shows the suppression of fluctuations based on thermodynamic theory. It remains to demonstrate this suppression directly with a measurement of surface dynamics.

As a conclusion, we have seen that there is an extensive theoretical work carried out on the surface and internal structure of polymer brushes. On the other hand, experimental studies appear scarce due to chemical difficulties. Following section will give a review on experimental studies on brushes covering synthesis and structure of brushes.

1.3 Literature Review of Experimental Studies of Polymer Brushes

Experimental work with polymer brushes can be roughly broken down into studies dealing with i.) synthesis of brushes, ii.) their structure. Throughout this dissertation, for the synthesis of brushes the emphasis will be put on the polymer brushes formed by covalent attachment. In order to synthesize polymer brushes by establishing a chemical bond between the polymer molecules and the surfaces, chains can be attached to the appropriate surfaces such as surfaces of carbon black, gold or silicon wafers. Extensive study have been made on synthesis of brushes by “grafting to” approach. End-functionalized polymers with a narrow molecular weight distribution can be synthesized by living anionic [85–88], cationic, radical [89], group transfer and ring opening metathesis polymerizations to be attached on previously functionalized substrates. In general, by “grafting to” approach only a small amount of polymer can be immobilized onto the surface which gives polymer brushes with a low grafting density and low film thickness. Since we are interested in thick polymer brushes with high grafting densities, we will explore the “grafting from” approach more detailly.

In “grafting from” approach, initiators are immobilized at the substrate by treating the substrate with plasma or glow discharge in the presence of a gas or forming initiator-containing self assembled monolayers (SAMs) on the substrates. Several groups used the plasma and glow-discharge treatment to introduce initiators onto substrate surfaces [37–40, 90–93]. However, with this method it is difficult to control the type and amount of the initiator and polymerization is not well-defined. Thus, the SAM technique to immobilize initiators on the substrate surfaces gives more well-defined polymerization compared to plasma or glow discharge treatment.

In earlier work, immobilization of radical initiators usually involved a series of steps [94–98]. First, anchor molecules were immobilized on the solid substrate surface and then the initiating species were linked to the anchor molecules in one or more additional steps. Minko *et al.* [99–105] did theoretical and experimental study in radical polymerization initiated from a solid substrate. In experimental study, they immobilized radical initiators on silicon wafers, glass or ultrafine powders by either physisorption of azo or peroxide macroinitiators or chemical immobilization of azo initiators. Sidorenko [106] used the same approach to synthesize mixed or heterogenous PS and PVP polymer brushes by grafting on silicon wafers. Velten *et al.* [107, 108] to graft PS chains on mica surfaces attached peroxide radical initiators with cationic group to mica by ion-exchange reaction. These methods to immobilize initiator on the surfaces requires several steps which may cause low grafting density of initiators and consequently brushes. Side reactions taking place in initiator immobilization could cause undesired structures on the surface.

To avoid these problems, Ruhe and co-workers [51, 52, 109–113] did a initiator immobilization by one step by SAM technique. A initiator molecule containing anchoring group linking the initiator to the surface, the initiator and a cleavable group. A series of azo initiators were previously synthesized and immobilized onto

the surface with a single step and followed by *in situ* radical polymerization of styrene or other monomers. Another unique feature of their strategy was that the initiator molecules contained a cleavable group. Therefore the grafted chains could be cleaved off and analyzed. From the molecular weight analysis of those degrafted chains, the mass of the grafted polymer and the specific surface area, the number of polymer chains per unit area was calculated. They were first to synthesize PS brushes from azo-initiators using the “grafting from” approach in combination with conventional radical polymerization and achieved 2-3 μm thick PS brushes.

Following Ruhes work, Jordan *et al.* [55,56] did polymerization of 2-ethyl-2-oxazoline by cationic ring-opening polymerization followed by styrene polymerization on gold surface by anionic polymerization by Jordan *et al.* [57] and Mathers *et al.* [114]. Although surface initiated anionic and cationic polymerizations yield mono disperse chains, they have rarely been studied for the following reasons. These polymerizations require highly pure reactants, they are not tolerant of impurities and the variety of monomers to polymerize using these techniques is limited. Edmonson and co-workers [115] reached a PS brush thickness of 18 nm with anionic polymerization in 3 days and 30 nm thickness with cationic polymerization in one hour. Fukuda *et al.* [58] synthesized poly(methyl methacrylate) (PMMA) brushes on silicon substrates by the combined use of Langmuir-Blodgett technique to immobilize a well-organized set of initiators on the substrate with the “grafting from” approach but using a controlled radical polymerization (CRP) technique, atom transfer radical polymerization (ATRP). Shortly thereafter, Hawker *et al.* [116] synthesized PS brushes on silicon substrates using another CRP technique, nitroxide mediated radical polymerization (NMRP). CRP techniques are comparatively simple to perform, they provide excellent control of chain molecular weight with polydispersities of 1.1-1.5, they are tolerant of impurities, and they can provide brush thicknesses larger than that those

provided by carbocationic and anionic polymerization. Thus, it is preferable to use CRP techniques to synthesize polymer brushes for studies in which variation of brush thickness is important. Among CRP techniques, ATRP is the most widely used to synthesize polymer brushes since it has been studied for variety of monomers under various conditions in solution. CRP techniques also provide synthesis of brushes with functional groups or synthesis of block copolymer brushes.

Gaining knowledge on synthesis of brushes provided researchers to investigate the structure of brushes and comparison of these studies with scaling arguments and theoretical studies. Early experimental work [1, 80–82] already showed that the segment density profile of a PS brush in a good solvent has a parabolic shape with a tail. Later, Karim *et al.* [117] using neutron reflectivity studied the segment density profile of PS brushes grafted on silicon surface. They found that brush density profile had the form

$$\phi(z) = \begin{cases} \phi_s [1 - (z/h)^2]^\alpha & , z < h , \\ 0 & , z > h , \end{cases} \quad (1.11)$$

where ϕ_s is the polymer volume fraction at the silicon surface, h is the height of the brush, and α is the profile exponent which is taken to be a measure of the density profile shape. They found the value of α is 1.0 for a brush in good solvent and 0.5 for a brush in a theta solvent, in good agreement with values from SCF predictions. Other studies have reported the parabolic density of polymer brushes with high grafting density in good solvent [118–120]. Spiliopoulos *et al.* [79] performed the first direct measurement of the free-end distribution of polymer brushes in good solvent. Using neutron reflectivity and labeling the last 16% of the monomers of PS chains, they determined the end-segment profile of brushes. They showed that the free ends are distributed throughout the brush layer and that the distribution peak is located within the brush and not at the height of the layer.

Akgun *et al.* [121] performed off-specular scattering on quenched homopolymer PS brushes and melt poly(n-butylacrylate) brushes synthesized by free radical polymerization and they found that the surfaces are self-affine. The observed scattering cannot be explained as resulting from capillary wave action in the range of length scale investigated, nor can it be rationalized as resulting from an island-like surface morphology. This supports the possibility that the dynamics of the brush surface are altered dramatically from those observed for comparably thick films of untethered chains. A variety of solid surfaces of various materials are known to produce scattering consistent with the self-affine surface model, but this was the first time such a surface has been observed for a material far above the bulk glass transition temperature. However, it still remains to demonstrate this behavior of surface structure and dynamics of brushes with a direct measurement. This understanding of polymer brush surface and interface fluctuations will help properly describe the structure of diblock copolymer brushes (DCBs), particularly interesting class of brushes in which each chain is a diblock copolymer. The details of the fluctuations occurring at the interfaces between A-rich and B-rich domains of DCBs will determine the manner in which a rearrangement occurs, because if the hypothetical lamellar “as-deposited” state rearranges with the treatment of selective solvent for bottom block, the lamellar structure must become unstable as a result of growing fluctuations of the domain/domain interface and the interface with solvent. However, no experimental results have been published for the fluctuation behavior of interface of a DCB either in the melt or in the solvent-swollen state.

The phase behavior of bulk melts of block copolymer chains has been extensively studied and it is well-known that they show microphase separation if the interactions between like segments are sufficiently more favorable than the interactions between segments of the two blocks [122, 123]. In the case of microphase sep-

aration the junction between a pair of blocks in a chain may be thought of as being tethered at the interface between microphases and the ordered chains form a sort of brush on both sides of the interface. In the strong segregation limit, in which the two blocks are quite different or chain molecular weight is sufficiently high, it has been shown that melts exhibit ordered morphologies that can vary in a wide range among spherical, hexagonal, lamellae and gyroid symmetries, depending on the volume composition of each chain. When the diblock copolymer is near a surface or confined between two solid surfaces, it self-assembles into an ordered structure with a specific microdomain orientation, either parallel or normal to the surface, depending on the interaction between the blocks in the copolymers and interfaces [124–130]. When diblock copolymers are attached to a substrate, even more complex phase separation behavior is induced. Depending on grafting density, surface energy of both blocks that are in contact with air, solvent or solid, or molecular parameters such as Flory-Huggings interaction parameter and the molecular weight of the polymer chains, a variety of morphologies can be obtained. While there has been extensive theoretical study on the morphology of DCBs, no experimental results have been reported.

Experimentally the investigation of DCBs started with the introduction of controlled polymerization techniques, especially ATRP, which allows simple adjustment of structure and composition of the brush, and which provide the ability to prepare diblock copolymers by sequential activation of the dormant chain end in the presence of different monomers. Husseman et al. [116], using surface initiated NMRP and ATRP, synthesized block copolymer brushes on silicate substrates in which the first block was PS and the second block was a 1:1 random copolymer of PS and PMMA. This is a very interesting variant on block copolymer brush structure which will not be considered further here. In the following we will assume that both “blocks” in a DCB indeed contain segments of only one type.

Zhao and Brittain were the first to consider explicitly the “switching” opportunities presented by DCBs. Zhao, Brittain and coworkers [2–4, 131] synthesized DCBs of PS-*b*-poly(acrylate) in which the first block was a homopolymer brush of PS polymerized from a self assembled monolayer using a carbocationic polymerization and the second block was polyacrylate polymerized by the ATRP of MMA from the chloro-terminated PS chains. They investigated the DCBs using several techniques, including ellipsometry, attenuated total reflectance FTIR (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), water contact angle measurements and atomic force microscopy (AFM). All of these are useful with thin films, with contact angle and AFM being particularly sensitive to the character of the surface. They found that the DCBs of PS-*b*-PMMA are stimuli responsive. That is, it appeared the surfaces of these brushes changed with treatment of the brushes with solvents. The advancing water contact angle of a dry DCB of PS-*b*-PMMA, with 23 nm PS block and 14 nm PMMA block, was 75°, which is characteristic of PMMA and changed to 99°, which is characteristic of PS after the brush was treated with cyclohexane. Cyclohexane is a good solvent for PS with M_n of $\sim 30k$ at 35°C and a poor solvent for PMMA. Subsequent treatment of the brush with dichloromethane, a good solvent for both polymers, returned the contact angle back to the original value of 75°. The surface rearrangement process was found to be reversible even after many rearrangement cycles. The contact angle change was attributed to “switching” of the DCBs in which there was postulated to be reversible changes in the chemical composition at the polymer/air interface. XPS analysis confirmed the compositional changes after treatment with the selective and good solvents. AFM measurements [2] showed that the surface of a dry PS-*b*-PMMA brush was relatively smooth, with root-mean-square roughness of 0.8 nm (over a $1\mu\text{m} \times 1\mu\text{m}$ sampling area) after dichloromethane treatment. After treatment of this DCB with cyclohexane at 35 °C for an hour, the rms roughness

increased to 1.8 nm and an irregular worm-like structure formed at the surface. A nanopattern was formed if mixed solvents of dichloromethane and cyclohexane are used and the composition of solvent was gradually changed from dichloromethane to cyclohexane.

These studies showed that the DCBs are stimuli responsive materials and that properties of their surfaces can be changed from those characteristic of one polymer block to those characteristic of the other polymer block by just treating the material with an appropriate solvent.

The picture of the “switching” surface rearrangement suggested by the authors is shown in Figure 1.6. After synthesis of a DCB, it is taken out of the polymerization solution, washed with solvents to remove any untethered polymer chains and then dried by blowing technical grade nitrogen over the brush. This state of the brush has been denoted as the “as-deposited” state. Zhao et al. [2–4] conjectured that an “as-deposited” brush has a lamellar structure with a bottom layer formed predominantly by the first block synthesized first and a second layer on top containing predominantly the block synthesized second, as shown in the cartoon on the left side of Figure 1.6. It was assumed that there is a very sharp interface between the domains rich in the two polymer blocks. They explained the chemical composition changes at the surface after selective solvent treatment determined by contact angle measurement, and XPS by hypothesizing that the PS blocks stretch and cover the aggregated PMMA blocks, allowing the PMMA blocks to form a core under a layer of PS blocks to minimize unfavorable interactions with cyclohexane. This switching results in an array of micelles with ellipsoid shapes. This state of the brush at this point is denoted as the “switched” state, and a cartoon of the structure conjectured by the authors is shown in the right side of the Figure 1.6. These predictions of simple structural models or cartoons were produced using the insight provided by

consideration of several characterization techniques. However, these cartoons must be considered as highly-idealized visualizations.

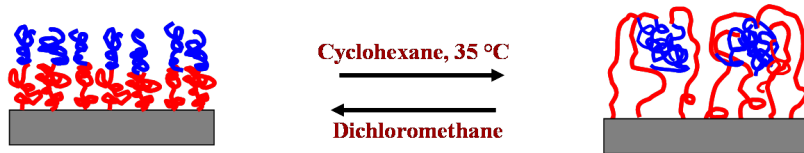


Figure 1.6: Cartoon representations of the “as-deposited” structure and layer structure rearrangement associated with “switching” of PS-*b*-PMMA brushes suggested by Zhao *et al.* [2–4].

After this seminal paper, DCBs garnered enormous interest. Published theoretical and experimental work on DCBs has mostly focused on their switching properties. Despite the fact that the switching abilities of various diblock brushes in different solvents have been shown in previous studies [2–4, 131–142] the mechanism of the surface rearrangement is still not known. Neither the internal structures of the “as-deposited” state nor that of the “switched” states has been investigated and clearly defined. In addition, none of the characterization techniques used in these earlier studies can probe both the surface and internal structure of DCBs in a complementary way. While AFM and contact angle measurements only probe the outer surface of the DCBs, XPS probes the top 7-10 nm of the sample. To understand how the surface rearrangement proceeds, one must probe the internal structures of the “as deposited” and “switched” states or, more generally the swollen state structures.

1.4 Objective of Research

The main objective is to understand the internal structure of “as-deposited” and “switched” states of DCBs and understand the mechanism of switching. A first specific goal is to understand the DCBs response to and interaction with different solvents. A second specific goal is to understand the effect of tethering on surface

dynamics of brushes, starting with homopolymer brushes. A third specific goal will be to extend this understanding of interfacial dynamics to the case in which the material next to the homopolymer brush, and perhaps swelling the brush, with molten, untethered polymer chains. This will require exploration of the penetration of the free chains into the brush in order to understand the surface dynamics. We will determine how interface width between these two layers varies with the characteristics of the free chains and brush layer. X-ray Photon Correlation Spectroscopy (XPCS) will be used to study the interfacial dynamics, while the interface width will be probed with neutron reflectivity.

1.5 Overview of Dissertation

The text of the dissertation is organized as follows. In Chapter 2, the basic principles of specular and off-specular X-ray and neutron scattering and X-ray photon correlation spectroscopy (XPCS) are explained. Theoretical models to explain scattering phenomena are presented as well. Chapter 3, Experimental, gives procedures for the synthesis of homopolymer and diblock copolymer brushes (DCBs) and explains working principles of scattering methods used to characterize those brushes. In Chapter 4 results on the internal structure of “as-deposited” DCBs as resolved in the direction normal to the surface are presented. Insights in the structures formed upon swelling in different solvents or “switching” of DCBs provided by *in-situ* NR measurements are presented as well. In Chapter 5, the relaxation of surface height-fluctuations on PS and P*n*BA (poly(*n*-butylacrylate)) homopolymer brushes are investigated using XPCS and comparison made with the dynamical behavior of untethered free chains. Then the change in surface dynamics made by placing a PS brush between the substrate and a layer of untethered PS chains ($M_n = 2.2\text{k g/mol}$) is investigated. The

effects of thickness of untethered chains (h_u), brush thickness (h_b) and brush grafting density (σ), and molecular weight of the untethered chains on surface dynamics are all explored.

CHAPTER II

PRINCIPLES OF X-RAY AND NEUTRON SCATTERING

2.1 Introduction

X-ray and neutron scattering techniques have emerged as powerful tools for the investigation of the surface and interface behavior of polymers. They are useful in characterizing both the air interface of a sample and interfaces at some distance from the polymer surface and they can probe structure both parallel and normal to the interfaces. They can provide information on electron density differences between interfaces, roughness at sharp interfaces, interface width and in-plan correlations. The surfaces and interfaces of liquids, polymers, organic multilayers, etc., can be investigated on an atomic length scale. These techniques can be non-destructive when using low doses, the spatial resolution perpendicular to the interface is of order 1 nm, and the penetration depth can be varied from a few nanometers to over millimeters, depending on the incident angle and the energy of the incoming beam. In this section, basic concepts of specular X-ray and neutron reflectivity and off-specular x-ray scattering will be discussed in detail, along with the theoretical models used to explain the scattering phenomena. The procedures specific for each experimental set-up and measurement will be mentioned in each chapter.

2.2 Basic Principles

When radiation is incident on an interface between two materials, part of the energy is reflected at the interface and the other part is transmitted through it. Once the refractive indices of the two media are known, the geometry and the relative intensities of the reflected and refracted rays can be described by the principles of optics. For both x-rays and neutrons, the refractive index, n , of a condensed matter is, in general, slightly less than 1 and is given to a good approximation by:

$$n = 1 - \delta + i\beta \quad (2.1)$$

where δ is the real part and β is the imaginary part of the n .

For X-rays,

$$\delta = \frac{\lambda^2}{2\pi} r_e \rho_e \quad \text{and} \quad \beta = \frac{\lambda}{4\pi} \mu_x \quad (2.2)$$

where λ is the wavelength of the incident radiation, $r_e = 2.818 \times 10^{-15} \text{m}$ is the classical electron radius, ρ_e is the electron density of the material, and μ is the measured mass absorption coefficient.

We note that an analogous description of the index of refraction applies to the case of neutrons, namely

$$\delta = \frac{\lambda^2}{2\pi} \frac{b_n}{V} \quad \text{and} \quad \beta = \frac{\lambda}{4\pi} \mu_n. \quad (2.3)$$

where b_n is the scattering length of the material in a reference volume, V .

With $\delta > 0$ we find that $n < 1$, which leads to the phenomenon called total external reflection for incident angles α_i below the critical angle $\alpha_c = \sqrt{2\delta}$. For most polymers δ is of the order of 10^{-6} for both x-rays and neutrons. The imaginary part, β , arises only when the material is absorbing. For neutrons the absorption cross-

section density is sufficiently small that β can be neglected in most cases, except when the material contains isotopes of Li, B, Cd, or Gd. With CuK_α x-rays β for most materials is about 10^{-2} to 10^{-3} times δ .

The electron density, ρ_e can be calculated as,

$$\rho_e = \frac{\rho N_A \Sigma b_i}{MW} \quad (2.4)$$

where N_A is Avogadro's number, MW is the molecular weight of a reference volume of material, b_i , the scattering length for a single atom in the reference volume is identical to the atomic number, $b_i = Z_i$ (Z_i is the atomic numbers of the elements), when far from an absorption edge, and ρ is the mass density.

Neutrons detect the variation in neutron scattering length density (b_n/V). X-ray scattering length density varies in a monotonic fashion through periodic table. However, neutron scattering length does not. Isotopes which differ slightly in atomic number can have large difference in neutron scattering lengths. Neutron contrast can be provided by selective deuteration due to the particularly large difference between the scattering lengths of hydrogen ($b_H = -3.74 \times 10^{-15}$ m) and deuterium ($b_D = 6.67 \times 10^{-15}$ m). Neutron SLD is calculated:

$$\left(\frac{b}{V} \right)_n = \Sigma \frac{b_i}{V_i} = \frac{\rho N_A}{MW} \Sigma b_i \quad (2.5)$$

with b_i coherent scattering length of i th atom with a molecular volume V_i . For polymer systems the summations for b_i are most conveniently carried out over a repeat unit of the polymer.

When n varies through a sample, waves scattering from different elements of the sample interfere and result of the scattered spectrum is dictated by b/V or n over a distance probed. The shape of these features are defined by *differential scattering*

cross section, $d\sigma/d\Omega(q)$, which is the probability that a photon or a neutron impinging on the sample is scattered into a unit solid angle in the given direction (shown in Figure 2.1):

$$\frac{d\sigma}{d\Omega} = \frac{\text{number of particles scattered into a unit solid angle in a given direction per second}}{\text{flux of incident beam}}. \quad (2.6)$$

While n describes directly real space structure of a sample, $d\sigma/d\Omega$ describes scattering from that sample in reciprocal space.

Integrating the differential scattering cross section throughout the solid angle Ω gives the *total scattering cross section*:

$$\sigma_{total} = \int_{all\ directions} \left(\frac{d\sigma}{d\Omega}(q) \right) d\Omega, \quad (2.7)$$

which has dimension of area, as the word *cross section* implies.

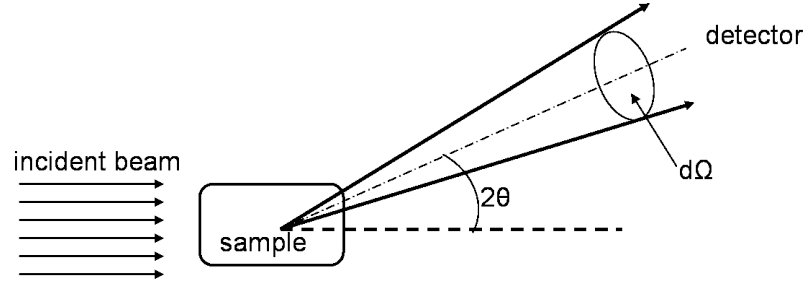


Figure 2.1: Basic geometry of scattering involving the incident plane wave, the sample, the scattered spherical wave, and the detector. 2θ is the detector angle with respect to incident beam direction.

If we take a simple system where we can assume that any incident wave interacts with, or is scattered by, the sample elements only once. For that kind of system, differential cross section is solved by taking the Fourier transform of the square of the b/V . For a two phase system with a sharp boundary, $d\sigma/d\Omega$ could be

written as:

$$\frac{d\sigma}{d\Omega}(q) = r_e^2(\Delta\rho_e)^2 \int_V \int_V e^{-iq(r-\acute{r})} dr d\acute{r} \quad (2.8)$$

where q is the dimension in reciprocal space, scattering wave vector, which is the change in the momentum of the wave vector of the beam after hitting and exiting the sample as shown in Figure 2.1. ($q = 4\pi \sin(\theta)/\lambda$, λ is the wavelength of the beam., q will be explored more elaborately in the next section.) Waves scatters from the

Since we are focused on surfaces and interfaces, it is better to transform volume integrals in Eq. 2.8 into surface integrals over the surface, S , dividing the two phases:

$$\frac{d\sigma}{d\Omega}(q) = r_e^2(\Delta\rho_e)^2 \frac{1}{q \cdot A} \int_S \int_S (dS \cdot A)(d\acute{S} \cdot A) e^{-iq(r-\acute{r})} \quad (2.9)$$

where A is an arbitrary unit vector in space and dS is the differential surface vector parallel to the surface normal. We can write the *differential cross section* separated into three terms:

$$\frac{d\sigma}{d\Omega}(q) = r_e^2(\Delta\rho_e)^2 S_T S_q \quad (2.10)$$

The first term is the square of the scattering length density difference between the two phases, $r_e^2(\Delta\rho_e)^2$, could be defined as contrast factor representing the scattering length density fluctuation in the system. Second term is the total interfacial area under illumination with $S_T = \hat{S}V$, where $\hat{S}$ is the interfacial area per unit sample volume. The third factor, S_q , is the structure factor which contains the form of the scattering and depends only on the interfacial structure, not the size of chemistry of the sample. From Eq. 2.10 several outcomes can be inferred. The form of the scattering is determined by the structure of the interface alone. The magnitude of the intensity determined will depend on S_T and contrast. S_T depends on illuminated volume and phase volume fractions, while the contrast will vary with the mass den-

sities and chemical compositions of the two phases. The features of $\rho_e(r)$ occurs at small r and could be seen at large q . Therefore, in order to study details of interfaces between phases one will need to measure data over a larger range of q .

2.3 Specular Reflectivity

At a sharp planar boundary between two homogeneous media of refractive indices, n_0 and n_1 , with the incidence occurring in the medium with $n = n_0$, portions of the radiation are both reflected and refracted in the plane of incidence, as shown in Figure 2.2. The angle θ of reflection is related to the angle of incidence, θ_0 , by *the law of reflection*:

$$\cos\theta_0 = \cos\theta \quad (2.11)$$

and the angle θ_1 of refraction is given by *Snell's law*:

$$n_0 \cos\theta_0 = n_1 \cos\theta_1. \quad (2.12)$$

In a medium of refractive index n , the wavelength is equal to λ/n and the magnitude of the wavevector $\mathbf{k}$ is equal to $2\pi n/\lambda$, where λ is the wavelength in vacuum. The two laws, (Eq. 2.11 and Eq. 2.12) state that the y component of the wave vector is invariant at the boundary on reflection and refraction.

In most cases the first medium is a vacuum or air so that n_0 is 1. Since n_1 is less than 1, in general, the refraction angle, θ_1 , is smaller than the incident angle θ_0 . As a consequence, at incident angles smaller than a certain angle, called the *critical angle*, θ_c , the radiation is totally reflected back into the medium 0 (air) in the absence of absorption in medium 1. The critical angle is thus given by:

$$\cos\theta_c = n_1 \quad (2.13)$$

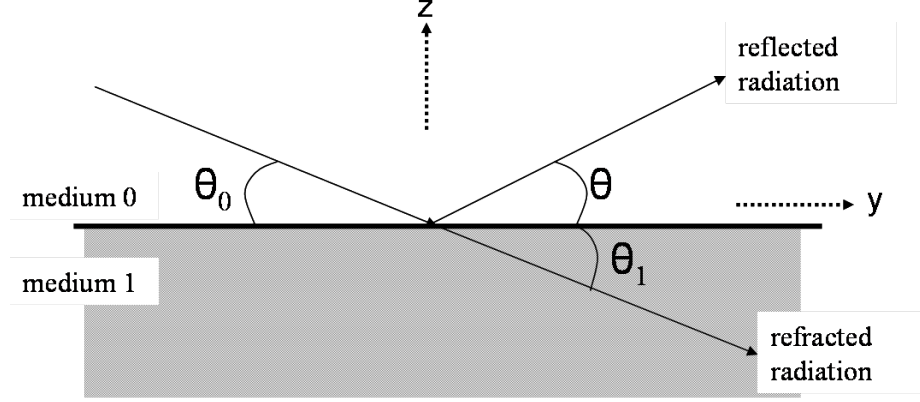


Figure 2.2: Geometry of reflection and refraction.

Since $\cos\theta = 1 - \theta^2/2 + \dots$ for small θ , within a good approximation:

$$\theta_c = \sqrt{2\delta}, \quad (2.14)$$

For both CuK_α X-rays and neutrons θ_c is on the order of milliradians.

The *reflectivity*, R , is defined as the ratio of reflected intensity to incident intensity. In the absence of adsorption, R is equal to 1 for incidence angles smaller than θ_c and it decreases rapidly with the perpendicular component of the incident wavevector, k_z , for angles larger than the critical angle. From Eq. 2.12 we can write:

$$n_0^2(1 - \sin^2\theta_0) = n_1^2(1 - \sin^2\theta_1) \quad (2.15)$$

Similarly from Eq. 2.13 we can write:

$$n_0^2(1 - \sin^2\theta_c) = n_1^2 \quad (2.16)$$

Taking the difference between Eq. 2.15 and Eq. 2.16 leads to

$$n_1^2 \sin^2 \theta_1 = n_0^2 \sin^2 \theta_0 - n_0^2 \sin^2 \theta_c \quad (2.17)$$

which can be written as

$$k_{z,1} = (k_{z,0}^2 - k_{z,c}^2)^{1/2} \quad (2.18)$$

where $k_{z,0}$ and $k_{z,1}$ are the z components of the wave vectors of the incident and refracted rays, each defined in the corresponding medium and $k_{z,c}$ is the value of $k_{z,0}$ when θ_0 is equal to θ_c .

In vacuum,

$$k_{z,0} = \frac{2\pi \sin \theta_0}{\lambda} \quad (2.19)$$

Reflectivity, R , is the absolute square of r , reflection coefficient, which is given by:

$$r = \frac{k_{z,0} - k_{z,1}}{k_{z,0} + k_{z,1}} \quad (2.20)$$

And R given by *Fresnel's law* is:

$$R = rr^* = \left| \frac{k_{z,0} - k_{z,1}}{k_{z,0} + k_{z,1}} \right|^2 = R_F(q_{z,0}) \quad (2.21)$$

where r^* indicates the complex conjugate of r and $q_z = 2k_{z,0}$ is the magnitude of the scattering vector in the direction perpendicular to the surface. This law is applies for both x-rays and neutrons. Substitution of Eq. 2.18 for $k_{z,1}$ in Eq. 2.21 leads to

$$R = \left| \frac{k_{z,0} - \sqrt{k_{z,0}^2 - k_{z,c}^2}}{k_{z,0} + \sqrt{k_{z,0}^2 - k_{z,c}^2}} \right|^2 \quad (2.22)$$

The plot of R with respect to q_z is plotted in Figure 2.3.

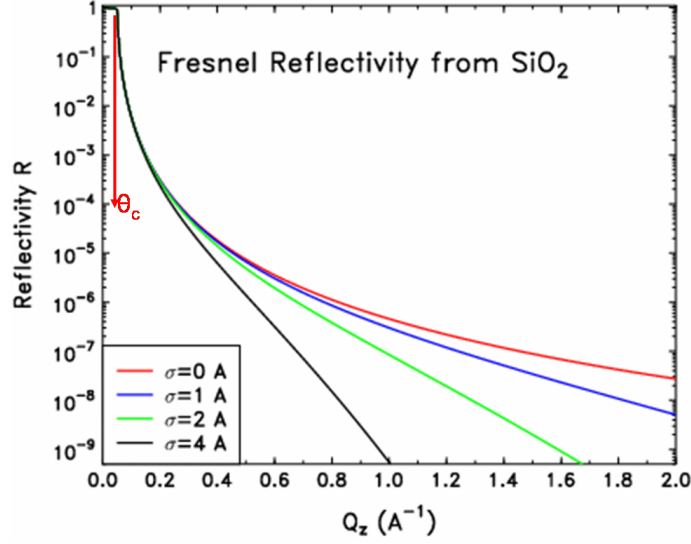


Figure 2.3: Specular Fresnel-reflectivity from SiO_2 surface with different roughnesses according to Eq. 2.22

For sufficiently high values of q dynamical effects can be ignored and a kinematical approximation is appropriate. In this case, for $k_{z,0} \gg k_{z,c}$ Eq. 2.22 can be approximated by

$$R = \left| \frac{1 - [1 - (k_{z,c}/k_{z,0})^2]^2}{1 + [1 - (k_{z,c}/k_{z,0})^2]^2} \right|^2 \cong \frac{1}{16} \left(\frac{k_{z,c}}{k_{z,0}} \right)^4. \quad (2.23)$$

For the ideal interface (no roughness), the tail of reflectivity curve decays as q^{-4} ($R \propto k_{z,0}^{-4} \propto q_{z,0}^{-4}$) for large q as in *Porod's law* for small angle scattering.

For a real interface only a portion of the beam is reflected in the way described by the above equations. This radiation reflected in the plane of incidence at $\theta_0 = \theta$ is referred as the specular beam. The portion that is not reflected specularly is scattered by surface or subsurface structure or absorbed. All the phenomena occurring under grazing incidence: specular reflection, grazing incidence scattering, absorption and fluorescence provide opportunities to learn about the sample's outer surface structure as well as interfaces within the sample. Information about those "buried" interfaces becomes available as the incident angle is increased above critical value.

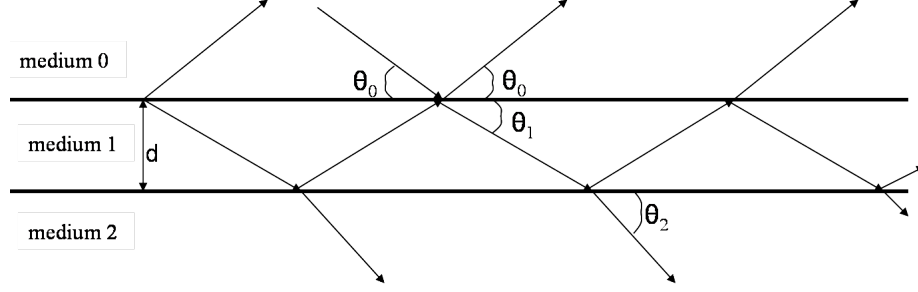


Figure 2.4: The reflected radiation observed consists of the rays reflected directly at the 0 – 1 interface as well as those that are transmitted from medium 1 to medium 0 after having been reflected at the 1 – 2 interface once, twice, etc.

When the film studied is deposited on a thick, flat substrate the reflected radiation will consist not only of rays reflected at the 0 – 1 interface, but also of rays transmitted from medium 1 to medium 0 after having been reflected at the 1 – 2 interface once, twice, etc. as shown in Figure 2.4. The overall sample reflectance is given by:

$$r = \frac{r_{0,1} + r_{1,2}\exp(2ik_{z,1}h)}{1 + r_{0,1}r_{1,2}\exp(2ik_{z,1}h)} \quad (2.24)$$

where $r_{1,2}$ and $r_{0,1}$ are reflection coefficients between substrate and the film and between the film and vacuum, respectively, and h is the film thickness. The reflectivity, R , which is calculated using Eq. 2.21, is simply:

$$R = rr^* = \frac{r_{0,1}^2 + r_{1,2}^2 + 2r_{0,1}r_{1,2}\cos(2k_{z,1}h)}{1 + r_{0,1}^2r_{1,2}^2 + 2r_{0,1}r_{1,2}\cos(2k_{z,1}h)} \quad (2.25)$$

Figure 2.5 shows the x-ray reflectivity for a film of 48 nm PS brush grown on a silicon substrate. The envelope of the curve is similar to that of one in Figure 2.3 calculated for the substrate only, but here a pronounced oscillation is superimposed. The interference between the radiation reflected from one interface and that from the other interface causes a series of maxima and minima to be observed. The maxima occur when the rays emerging from the 0 – 1 interface, after having been reflected

at the 1 – 2 interface one or more times, differ in phases by a multiple of 2π and interfere constructively. The oscillations are called “Kiessig fringes” and the spacing ($\Delta q_{z,1}$) of these fringes characterizes the thickness of the film as

$$h = \frac{2\pi}{\Delta q_{z,1}} \cong \frac{2\pi}{\Delta q_{z,0}} \text{ for } q_{z,0} \gg q_{z,c} \quad (2.26)$$

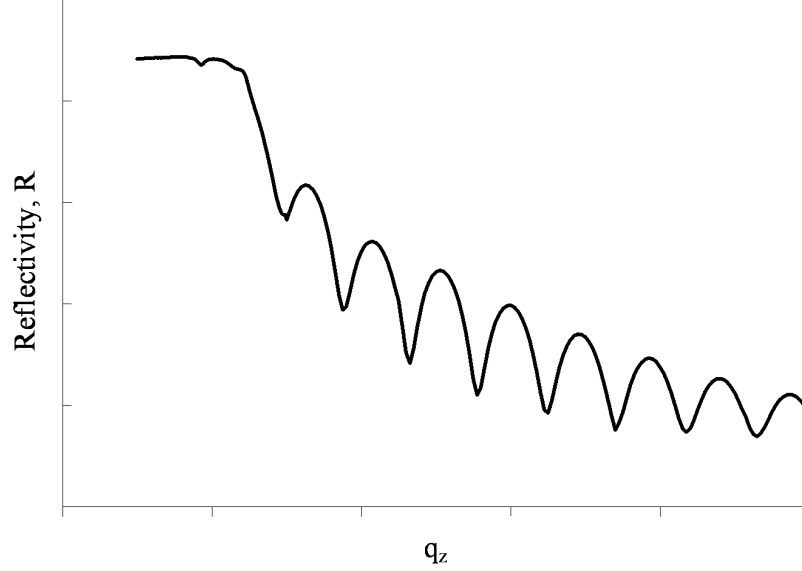


Figure 2.5: X-ray reflectivity for 48 nm thick PS brush grown on a silicon substrate.

The amplitude of the oscillations increases with the magnitudes of scattering length density jumps, $\Delta\rho$, at the air/film and film/substrate interfaces. The fact that the interfaces between the substrate and the film and between the consecutive polymer layers within the film are not infinitely sharp also influence the shapes of the fringes.

Reflectometry (XR, NR) considers only the specularly reflected radiation. A collimated beam hits to the surface with an angle θ_0 and the reflected beam is collected with a detector lying in the plane of incidence at an angle ϕ with respect to the surface that is set equal to θ_0 . The detector angle with respect to the incident beam direction

is 2θ . In this geometry, momentum transfer vector, $\vec{q}$ has only z component and only the lateral average of structural variations perpendicular to surface is probed. In a typical reflectivity measurement, reflected intensities are measured for a series of incident angles from nearly zero to a few degrees by varying θ and ϕ symmetrically.

By looking at the raw reflectivity data, information about the film thickness, characteristic spacing of periodic structures and approximate thickness of other key components of a films structure can be derived. Further and more detailed information, particularly on the interfacial profiles in the sample, the roughness values at each interface and the overall density profile, can be obtained only from a more detailed analysis. However, the structure of the thin film cannot be obtained by directly inverting the reflectivity data, due to the loss of phase information [143–145]. There are two primary techniques that are available for the analysis of specular reflectivity data. The first and the most common technique is to simulate a candidate model for the film structure and by varying the parameters of the model by means of a non-linear regression to obtain the best possible agreement between simulated and measured reflectivity. In the second method, a reduced reflectivity is considered to gain insight into the square of the electron density gradient's Fourier transform.

For the first method, there are three different calculational formalisms. In two of the formalisms most used, the continuous scattering length density profile is discretized, as shown in Figure 2.6, using N layers of homogeneous material, each of thickness, h_i , and electron density, $\rho_{e,i}$.

In the first calculation formalism, which is referred as *Parratt formalism*, the reflection and the transmission coefficients at each interface in the discretized structure are calculated recursively, starting with the layer/substrate interface. Using *Fresnel's law* (Eq. 2.21), the general recursive equation developed is:

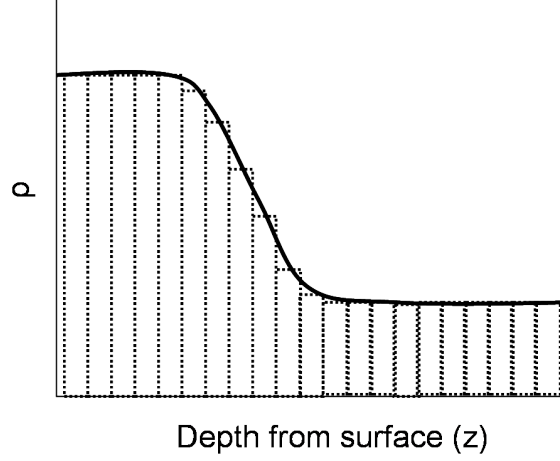


Figure 2.6: Gradual change in scattering length density (continuous line) and its approximation as a series of discrete steps.

$$r_{i-1,i} = \frac{r'_{i-1,i} + r'_{i,i+1} \exp(2ih_i k_{z,i})}{1 + r'_{i-1,i} r'_{i,i+1} \exp(2ih_i k_{z,i})}, \quad (2.27)$$

which involves the reflection coefficient $r'_{i,i+1}$ calculated from *Fresnel's law*. Eq. 2.27 is solved first for the $(N - 1)/N$ interface and then on up through the layers up to the air/sample interface. The overall reflectivity is obtained as the modulus of the air/top layer reflection coefficient. In the second calculation formalism, which is called the *optical transfer matrix formalism*, for any single layer, i , the layer optical characteristics can be concisely summarized in the transfer matrix, M_i , defined as:

$$M_i = \begin{bmatrix} \cos(k_{z,i} h_i) & \sin(k_{z,i} h_i)/k_{z,i} \\ -k_{z,i} \sin(k_{z,i} h_i) & \cos(k_{z,i} h_i) \end{bmatrix}. \quad (2.28)$$

The matrix M_i describes how the amplitude and its derivative of a wave propagating through layer i and reaching boundary $(i, i + 1)$ are related to the amplitude and derivative at the preceding boundary $(i - 1, i)$. The amplitude and its derivative of a wave at a boundary are continuous and this fact allows the construction of the

transfer matrix M for the whole stack of $N - 1$ layers sitting on top of a substrate by

$$M = \begin{bmatrix} m_{11} & m_{12} \\ m_{21} & m_{22} \end{bmatrix} = M_{N-1}M_{N-2}M \cdots M_2M_1. \quad (2.29)$$

The reflection coefficient, r , from the surface of the 0/1 interface is then obtained, in terms of matrix elements of M by

$$r = \frac{k_{z,0}k_{z,N+1}m_{12} + m_{21} - ik_{z,N+1}m_{11} + ik_{z,i}m_{22}}{k_{z,0}k_{z,N+1}m_{12} - m_{21} + ik_{z,N+1}m_{11} + ik_{z,0}m_{22}}. \quad (2.30)$$

The third formalism uses the *Born approximation*. In this approximation it is assumed that the scattered and reflected fields are always of negligible magnitude compared to incident beam. This approach is applicable for $q \geq 4q_c$ and for samples containing no large electron density gradients. The reflectivity averaged over the coherence of the beam is:

$$R(q_z) = R_f(q_z) \left| \frac{1}{\rho_s} \int_0^\infty dz \exp(iq_z z) \frac{\partial \rho(z)}{\partial z} \right|^2, \quad (2.31)$$

where ρ_s is a reference electron density of the substrate.

Reflectivity, R , can be defined in terms of total intensity while the scattering cross-section, $d\sigma/d\Omega$ is defined in terms of the flux [144]. In the case that $d\sigma/d\Omega$ has a specular part it is related to R as:

$$R = \frac{1}{L_x L_y \sin \theta_0} \int \left(\frac{d\sigma}{d\Omega} \right)_{spec} d\Omega \quad (2.32)$$

where $L_x L_y$ is the area of the reference plane surface about which the sample surface fluctuates. The factor $1/\sin \theta_0$ is for the change in flux at the surface as θ_0 is varied.

Normalized structure factor is:

$$S(q) \equiv \frac{d\sigma}{d\Omega} \frac{1}{r_0^2 (\Delta\rho_e)^2 L_x L_y} \quad (2.33)$$

By keeping in mind that in general the overall structure factor includes both specular and diffuse components, $S(q) = S_{spec}(q) + S_{diff}(q)$, reflectivity can be rewritten as:

$$R = \frac{r_0^2 (\Delta\rho_e)^2}{\sin\theta_0} \int S_{spec} d\Omega \quad (2.34)$$

2.4 Roughness Effects

In the real world, each interface shows deviations from ideal behavior. These deviations may be of two kinds. First, all surfaces show some roughness. That is, the interface is not planar, but rather the nominal height of the interface varies above and below the average height with location over the surface, as illustrated schematically in Figure 2.7 for a single dimension. While a more complete statistical description of the surface height is needed when discussing off-specular scattering, reflectivity measurements are only able to provide information on the laterally averaged variation in scattering length density with depth. Therefore, for the analysis of reflectivity curves it is often sufficient (and only possible) to characterize the rough interface with a single parameter. We choose as this parameter the root mean squared (rms) roughness, σ , defined as:

$$\sigma^2 = \langle (z(x, y) - \bar{z})^2 \rangle \quad (2.35)$$

where $z(x, y)$ corresponds to the distances between an averaged smooth interface, $\bar{z}$ and peak positions at the rough surface as shown in Figure 2.7.

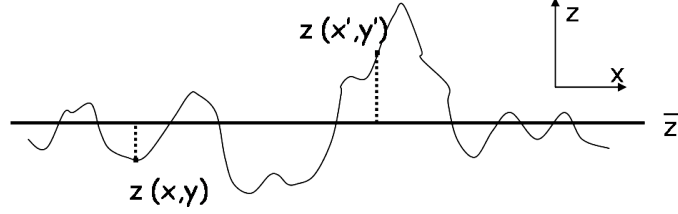


Figure 2.7: Sketch of a rough surface showing height variation with respect to the mean height $\bar{z}$.

The effect of this roughness on the reflectivity from a single interface can be handled in one of two ways. The computationally simplest approach is to just multiply the reflectivity from the ideally smooth interface with a factor that accounts for the roughness. For the special case of $q_{z,0} \gg q_{z,c}$ the expression for the reflectivity then has a particularly simple form:

$$R(q_{z,0}) \approx \frac{16\pi^2 r_0^2 (\Delta\rho_e)^2}{q_{z,0}^4} e^{-q_{z,0}^2 \sigma^2}. \quad (2.36)$$

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

$$R(q_{z,0}) = R_F(q_{z,0}) e^{-q_{z,0}^2 \sigma^2}, \quad (2.37)$$

where R_F is the Fresnel reflectivity.

When there are many interfaces in a film and these lie close together, the approach of using the simple multiplicative factor can lead to unphysical analyses of the reflectivity curves. In that case it is necessary to account for the fact that the roughnesses of neighboring interfaces can both influence the reflectivity from the material at a particular depth in the sample. This can be accounted for by noting that as far as reflectivity is concerned, an atomically sharp, but randomly rough interface presents the same laterally averaged scattering length density profile to the beam that

an interface of continuously changing SLD does. That is, a continuous profile such as that in Figure 2.6 may represent the effect of the roughness. The electron density changes as a step function for a smooth interface. A convenient form of continuous electron density profile to use to represent a randomly rough interface is that of the error function, so that $\rho_e(z)$ across the interface is given by:

$$\rho_e(z) = \rho_0 + (\rho_1 - \rho_0) \operatorname{erf}(z, \sigma) \quad (2.38)$$

where ρ_1 is the electron density of the film. The error function is defined as

$$\operatorname{erf}(z, \sigma) = \frac{1}{\sigma\sqrt{2\pi}} \int_{-\infty}^z \exp\left(\frac{-\varsigma^2}{2\sigma^2}\right) d\varsigma. \quad (2.39)$$

In this case, σ describes simultaneously the width of the fictitious gradient at the interface and the actual roughness. If the roughness of the film is somehow not well modeled by the symmetric erf function, some asymmetric function may be used instead. Reflectivity performed out to sufficiently high values of q_z is able to distinguish this sort of detail of the interface structure.

The second possible nonideality of an interface is that, in fact, the change in electron density at the interface is not modeled by a step function, but rather by a smooth, gradual change. This diffuseness can be modeled using the same profile discretization approach used to model the rough interface. In fact, reflectivity measurements alone are unable to distinguish interface diffuseness and interface roughness.

Both roughness or diffuseness generally reduce the amplitude of the Kiessig fringes and cause it to decrease with increasing $q_{z,0}$. However, if the roughnesses of two primary interfaces in a sample are well correlated, deep minima may still be observed. The observation of oscillations over a large $q_{z,0}$ range generally suggests a sample has uniform thickness and well-defined interfaces.

2.5 Off-specular Scattering

If one collects scattering data for scattering angles in the plane of the incidence which are not equal to the incident angle, or collects data out of the plane of incidence, this is referred to as an “off-specular” scattering experiment. Since in these measurements the scattering vector q has a nonzero component in the plane of the sample, information can be gathered about the lateral structure of the sample and its interfaces. The discussion of this kind of scattering can begin with that from a rough interface, but ultimately in this dissertation also in-plane structure within the film will be of importance.

One may visualize a rough interface as sketched in Figure 2.7, for which the height deviations $[z(x', y') - z(x, y)]$ with respect to average smooth interface is a Gaussian random variable. The distribution of this deviation depends on the relative position $(X, Y) = (x' - x, y' - y)$ and one may introduce a height difference correlation function $g(X, Y)$ which describes the correlation between the two heights $z(x, y)$ and $z(x' = x + X, y' = y + Y)$ on the surface as:

$$g(X, Y) = \langle (z(x, y) - z(x', y'))^2 \rangle = \langle (z^2(x, y) + z^2(x', y')) \rangle - 2 \langle (z(x, y)z(x', y')) \rangle \quad (2.40)$$

where the averaging is taken over the area coherently illuminated by the beam. We assume the surface to present the property of stationarity, i.e. the mean value of the square of the altitude does not depend on the position, so that $\langle z^2(x, y) \rangle = \langle z^2(x', y') \rangle = \sigma^2$. As a result

$$g(X, Y) = 2\sigma^2 - 2 \langle z(x, y)z(x', y') \rangle = 2\sigma^2 - 2C(X, Y) \quad (2.41)$$

where $C(X, Y)$ is the *height-height correlation function* defined as:

$$C(X, Y) = \frac{1}{L_x} \frac{1}{L_y} \int_{-\frac{L_y}{2}}^{\frac{L_y}{2}} \int_{-\frac{L_x}{2}}^{\frac{L_x}{2}} z(x, y) z(y + Y, x + X) dx dy, \quad (2.42)$$

L_x the width of the beam footprint on the sample, that is the dimension perpendicular to the beam direction, and L_y the length along the beam of the footprint.

2.5.1 Born Approximation

The simplest approach to the calculation of the scattering from a single rough interface is based on the *Born Approximation* [146]. This approximation, which is also known as *kinematic approximation* consists of taking the incident field in place of the total field as the driving field at each point in the scatterer. This approach is valid when the scattered wave amplitude is sufficiently small that the interaction between the incident and scattered waves can be neglected, which means in the case of the reflection geometry, that the multiple reflections are neglected. All the theories stating that the scattered intensity is given by the absolute square of the Fourier transform of the scattering length density distribution in the system are based on this assumption. With this approach, the contributions to the reflectivity curve by various features in the structure can be more easily understood and identified individually. However, results based on the *Born approximation* are valid only for weak interactions, that is when the incident angle is much larger than the critical angle θ_c , notably the approximation fails to predict total reflection.

In the *Born approximation*, *differential scattering cross section* is the Fourier transform of the square of the electron density difference as written in Eq. 2.8 and transferred into surface cross section by integrating over the surface, S , in Eq. 2.9.

We may write the *differential scattering cross section* by including the height deviations coming from the roughness of the surfaces :

$$\frac{d\sigma}{d\Omega}(q) = \frac{\rho_e^2 r_e^2 L_x L_y}{q_z^2} \int \int_S \exp(-\frac{q_z^2}{2} \langle (z(X, Y) - z(0, 0))^2 \rangle) \exp(i(q_x X + q_y Y)) dX dY \quad (2.43)$$

2.5.1.1 Ideally Flat Surfaces

For ideal flat surfaces $g(X, Y)$ is zero at the surface and the scattering cross-section simplifies to:

$$\frac{d\sigma}{d\Omega}(q) = \frac{\rho_e^2 r_e^2 L_x L_y}{q_z^2} \int \int_S \exp(i(q_x X + q_y Y)) dX dY \quad (2.44)$$

This integral is the Fourier transform of a constant so that:

$$\frac{d\sigma}{d\Omega}(q) = \frac{4\pi^2 \rho_e^2 r_e^2 L_x L_y}{q_z^2} \delta q_x \delta q_y, \quad (2.45)$$

leading to the following well-known expression for the reflectivity in the kinematic approximation:

$$R(\vec{q}) = \frac{16\pi^2 \rho_e^2 r_e^2}{q_z^4} q_z \gg q_{z,c} \quad (2.46)$$

This result is consistent with our understanding that the reflectivity for an ideally flat(smooth) surface is strictly specular.

2.5.1.2 Rough Surfaces without Cut-off

Surfaces with like many structure in nature such as clouds, mountains look similar on different length scales. These structures share the property of being fractals and such a behavior is called *self-affine*. Rough surfaces could be defined as *self-affine* where correlation length of the height fluctuations(ξ) is larger than the coherence length

with the beam at the surface. $g(R)$ is given by:

$$g(R) = 2\sigma^2(1 - \exp(-(R/\xi)^{2h})) \quad (2.47)$$

where h is the roughness exponent which is key parameter that describes the height fluctuations at the surface: small h produces very rough surfaces, and when h is close to 1 the surface is more regular.

If $R/\xi \ll 1$,

$$g(R) = 2\sigma^2\left(\frac{R}{\xi}\right)^{2h} \quad (2.48)$$

This function can be written as

$$g(R) = \frac{2\sigma^2}{\xi^{2h}} R^{2h} = AR^{2h} \quad (2.49)$$

The scattering cross-section yields:

$$\frac{d\sigma}{d\Omega}(q) = \frac{\rho_e^2 r_e^2 L_x L_y}{q_z^2} \int \exp\left(\frac{-q_z^2}{2} AR^{2h}\right) J_0(q_r R) R dR \quad (2.50)$$

with $q_r = \sqrt{q_x^2 + q_y^2}$ is the in-plane scattering wavevector and J_0 is the zero order Bessel function.

This equation has analytical solutions as:

$$\frac{d\sigma}{d\Omega}(q) = \frac{2\pi\rho_e^2 r_e^2 L_x L_y}{Aq_z^4} \exp\left(\frac{-q_r^2}{2Aq_z^2}\right) \text{ for } h=1 \quad (2.51)$$

$$\frac{d\sigma}{d\Omega}(q) = \frac{A\pi\rho_e^2 r_e^2 L_x L_y}{q_r^2 + \left(\frac{A}{2}\right)^2 q_z^4} \text{ for } h=0.5 \quad (2.52)$$

2.5.1.3 Rough Surfaces with Cut-off

For rough surfaces with a cut-off length ξ , the scattering cross-section is:

$$\frac{d\sigma}{d\Omega}(q) = \frac{\rho_e^2 r_e^2 L_x L_y}{q_z^2} \exp(-q_z^2 \sigma^2) \int \int_S \exp(q_z^2 C(X, Y) \exp(i(q_x X + q_y Y))) dX dY \quad (2.53)$$

It is possible to separate this expression into the specular and the diffuse off-specular components such as:

$$\frac{d\sigma}{d\Omega}(q) = \frac{d\sigma}{d\Omega}(q)_{spec}(\vec{q}) + \frac{d\sigma}{d\Omega}(q)_{diff}(\vec{q}) \quad (2.54)$$

where

$$\begin{aligned} \frac{d\sigma}{d\Omega}(q)_{spec} &= \frac{\rho_e^2 r_e^2 L_x L_y}{q_z^2} \exp(-q_z^2 \sigma^2) \int \int_S \exp(i(q_x X + q_y Y)) dX dY \\ &= \frac{4\pi^2 \rho_e^2 r_e^2 L_x L_y}{q_z^2} \exp(-q_z^2 \sigma^2) \delta q_x \delta q_y \end{aligned} \quad (2.55)$$

and

$$\frac{d\sigma}{d\Omega}(q)_{diff} = \frac{\rho_e^2 r_e^2 L_x L_y}{q_z^2} \exp(-q_z^2 \sigma^2) \int \int_S (\exp(q_z^2 C(x, Y) - 1) \exp(i(q_x X + q_y Y))) dX dY \quad (2.56)$$

Specular part of this equation similar to that of flat surface except that it is reduced by the $\exp(-q_z^2 \sigma^2)$ roughness factor.

2.5.1.4 Liquid Surfaces

On the surface of the low molecular weight organic liquids and low viscosity polymer solutions, capillary waves create a micro roughness that can be probed by XR. In capillary waves, the effect of gravity is much larger than that of surface tension. A characteristic feature of capillary waves is that their amplitudes are much smaller

than the wavelengths of the waves. Density-density correlations on the surface are long-ranged and ignoring finite size effects, $g(R)$ is expected to diverge for large R . So no true specular reflection is possible. The function $g(R)$ for capillary waves is given to good approximation by:

$$g(R) = 2\sigma^2 - BK_0(q_g R) \quad (2.57)$$

where $B = k_B T / \pi \gamma$ and γ is the liquid surface tension at temperature T and $K_0(X)$ is the modified Bessel function. The gravitational cut-off, q_g , is given by:

$$\kappa = \sqrt{\frac{\Delta \rho_m g}{\gamma}} \quad (2.58)$$

where $\Delta \rho_m$ is the mass density difference across the interface and g is the gravitational acceleration. The intrinsic roughness of the interface is found to be [147, 148]:

$$\sigma^2 = \frac{1}{4} B \ln \left[\frac{q_u^2 + q_g^2}{q_g^2} \right] \quad (2.59)$$

where q_u is the upper wave-vector cut-off, which is on the order of ϕ/d_m (d_m is the molecular diameter). In experiments, the length scale $1/q_g$ is not accessible due to resolution limits and one cannot readily separate the true specular reflectivity from diffuse scattering in the specular direction. Therefore, the measured roughness, σ_{eff}^2 will actually be larger than the intrinsic value, representing modes which scatter outside the resolution volume and defined as:

$$\sigma_{eff}^2 \approx \frac{k_B T}{2\pi \gamma} \ln \left[\frac{2q_u}{\Delta q_y} \right] \quad (2.60)$$

where Δq_y is the resolution in the q_y direction.

The gravitational cut-off (q_g) for bulk-liquid surfaces without a substrate is defined as $q_{l,c}$. The value of $q_{l,c}$ characterizes the fluctuations where lower than this cut-off the fluctuations on the surface are suppressed by the action of gravity. In other words, the wavelength, λ , of the surface fluctuations is limited so that $\lambda < \lambda_{max} = 2\pi/q_g$.

When there is a liquid film with a finite thickness, h , and interacts with the substrate with long range van der Waals interactions, the lower wave-vector cut-off ($q_{l,c}$) is dictated in combination with gravity and van der Waals interactions and given by:

$$q_{l,c}^2 = q_g^2 + q_{vdW}^2(h) \quad (2.61)$$

where q_{vdW} is van der Waals cut-off given by :

$$q_{vdW} = \sqrt{\frac{A_{eff}}{2\pi\gamma}} \frac{1}{h^2} \quad (2.62)$$

A_{eff} is the Hamaker constant that describes the interaction between the film and the substrate and surface tension, γ , is the tendency for the system to minimize interfacial area to minimize free energy. The length, $\sqrt{\frac{A_{eff}}{2\pi\gamma}}$, reflects the relative importance of these two effects and is usually in the range of 5 – 10 Å° for most liquids and polymers. $q_{l,c} \approx q_{vdW}(h)$ is a reasonable approximation for thin films with $h < 1000$ Å°. Variation of surface waves with thickness, h , are shown in Figure 2.8.

The effective specular reflectivity, R_{eff} , including diffuse scattering, can be calculated as:

$$R_{eff}^2 = R_F \exp[-q_{z,0}^2 \sigma_{eff}^2] \frac{1}{\sqrt{\pi}} \Gamma\left[\frac{1-\eta}{2}\right] \quad (2.63)$$

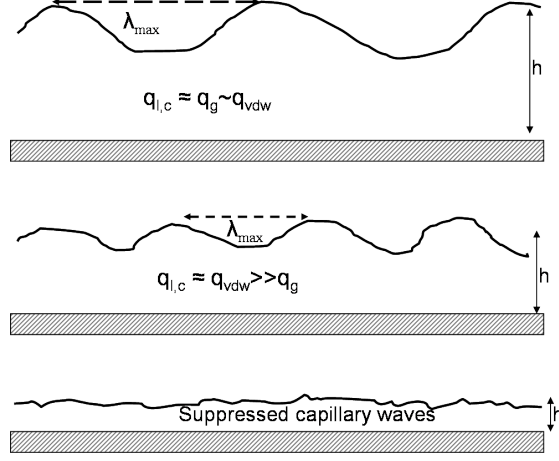


Figure 2.8: Schematic representative of capillary waves in the thin films of varied thickness, h . The influence of the constraints on the waves are represented by maximum wavelength, λ_{max} .

where

$$\Gamma = \frac{1}{2} B q_{z,0}^2 \quad (2.64)$$

where $\eta = B q_z^2 / 2$ and $\Gamma(X)$ is the gamma function. The factor $(1/\sqrt{\pi})\Gamma((1-\eta)/2)$, which comes from an integration over all q_y , differs from unity for large η .

For $q_x > q_{l,c}$, intensity of the diffuse scattering scales with a power law of $I(q_x) \sim q_x^{\eta-a}$. For liquids with capillary wave theory, a is equal to 1 and $q_{l,c}$ scales as h^{-2} . For thin films, suppression of the capillary waves occurs for sufficiently large values of wavelength, that is for values of wavevector, q_x , below a lower wavevector cutoff, $q_{l,c}$, due to interactions between the substrate and the surface. Schematic of different behavior of different films for log-log plot of intensity versus q_x are shown in Figure 2.9.

Wang *et al.* [149] studied the surface structure of quenched, spun-cast films of untethered polystyrene (PS) by diffuse X-ray scattering and found that the data could not be satisfactorily interpreted using capillary wave calculations assuming attractive van der Waals interactions between the substrate and the film. Suppression of surface

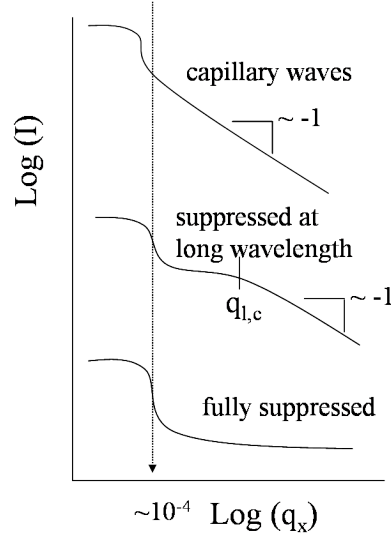


Figure 2.9: Representative plot of $\log(I)$ vs. $\log(q_x)$ for different types of films.

fluctuations for values of q_x below a lower wavevector cutoff, $q_{l,c}$ were observed. However, the exponent observed for the power-law scattering for $q > q_{l,c}$ was very low, implying an extremely large surface tension if the exponent was interpreted using capillary wave theory. They assigned these deviations to strong confinement effects even for film thicknesses considerably larger than the radius of gyration, R_g , of a chain. It has been demonstrated with different sorts of measurements that polymer films on substrates are in a strongly confined state due to interactions with the substrate surface. This effect is different when there is very thin free standing films with thicknesses below $2R_g$ and there is a finite size effect on those type of films [150]. Results of static off-specular scattering experiments published by Seo and co-workers [151] demonstrate that the wave vector dependence of capillary spectra for quenched thin polymer films is a function of chain length. For lengths, N , which are less than or close to N_e , the entanglement length, simple liquid-like scaling is observed. When N becomes much larger than N_e a Guiselin [152] type of “brush-like” behavior is observed where a layer of polymer chains adsorbed to a surface from a melt or con-

centrated solution. These authors found that for $d/R_g < 2$ there occurs an additional suppression of surface modes and the behavior of $q_{l,c}$ changes in a complex way with N . Li *et al.* [153] provided additional evidence that the chains closest to the substrate adsorb to the substrate in such a way that the viscosity of a film thinner than $2R_g$ is very large. The results of this pinning effect can be propagated to the surface of films thicker than $2R_g$ if other chains become entangled with the pinned layer.

For brushes situation changes, Fredrickson and co-workers [84] argues competition between an elastic restoring force at long wavelengths and a surface tension penalty at shorter wavelengths should lead to an energetically preferred wavelength of the order of brush thickness. Akgun *et al.* [121] shows that surface of free-radically polymerized homopolymer brushes are self-affine. They observed that the lateral correlation length varies as $\xi \sim h^{0.75}$ is reminiscent of the prediction of Fredrickson [84] in the limit of large surface tension that the wavevector of the most probable fluctuation in the brush should scale as $1/q^* \sim h^{0.75}$. The roughnesses of the PS brushes appear to follow power laws in the thickness of the brushes $\sigma \sim h^n$ with n having the value 0.41 ± 0.07 for unannealed PS brushes and 0.32 ± 0.02 for the annealed brushes, which is similar to those characterizing “kinetic roughening” in plasma deposited polymer films.

2.5.2 Distorted Wave Born Approximation

The *Born approximation* breaks down when the reflectivity becomes nearly unity, near critical angle for total external reflection. The distorted-wave born approximation (DWBA) can be a solution for that problem with the use perturbation theory on the exact solution of wave-equation for a smooth surface. The DWBA is a combination of a dynamical and kinematical treatment. It exactly takes into account refraction at smooth interfaces, while the scattering at lateral inhomogeneities is

treated kinematically. In this approach, it is accepted that excited beam present at the same time with the incoming field and those put together to do calculation.

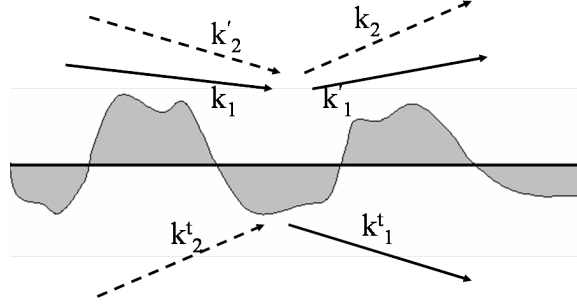


Figure 2.10: Schematic of a rough surface. The horizontal line is the average surface ($z=0$). The shaded regions are the regions of perturbation to a smooth surface. k_1 and $-k_2$ are incident wave-vectors, k'_1 and $-k'_2$ are reflected wave-vectors, k_1^t and k_2^t are the transmitted wave-vectors.

Let us consider the application of DWBA to a multi-layer. We start with the Helmholtz equation:

$$\nabla^2 \psi + k_0^2 \psi - V \psi = 0 \quad (2.65)$$

where ψ is the wave function(for neutrons) or the electron-field parallel to surface for x-rays, k_0 is the magnitude of the wave-vector in free space, V is the scattering potential which is:

$$V = k_0^2(1 - n^2) \quad (2.66)$$

which also can be written as:

$$V = V_1 + V_2 \quad (2.67)$$

where V_2 is regarded as perturbation on V_1 due to roughness as shown in Figure 2.10. k_1 is the incident on the surface and k'_1 is the wave-vector of the specularly reflected beam and k_1^t that of the beam transmitted into the medium. There is also time reversed state for a beam incident on the surface with wave-vector $-k_2$ where k'_2 is the incident wave-vector which is specularly reflected as k_2 and k_2^t is the wave-

vector in the medium which comes towards the surface and combines with wave k_2' to produce the time reversed wave k_2 . In DWBA, transmission functions for the incident radiation, $t_i(\theta_i)$, and scattered radiation, $t_f(\theta_f)$ are considered in the calculation of the scattering function. The functions $t_i(\theta_i)$ and $t_f(\theta_f)$ are given as:

$$t_i(\theta_i) = \frac{2k_{i,z}}{k_{i,z} + k_{z,i}^t} \quad (2.68)$$

$$t_f(\theta_f) = \frac{2k_{f,z}}{k_{f,z} + k_{z,f}^t} \quad (2.69)$$

where $k_{i,z} = k \sin \theta_i$, $k_{f,z} = k \sin \theta_f$, $k_{z,i}^t = nk \sin \theta_{t,i} = k(n^2 - \cos^2 \theta_i)^{1/2}$ and $k_{z,f}^t = nk \sin \theta_{t,f} = k(n^2 - \cos^2 \theta_f)^{1/2}$. To account for refraction, the perpendicular wave-vector transfer in the vacuum $q_z = k_{f,z} + k_{i,z}$ has been replaced by that in the sample medium, $q_{z,t} = k_{z,f}^t + k_{z,i}^t$. The diffusely scattered intensity I_{diff} from a single surface is given by

$$I_{diff} \sim |t_i(\theta_i)|^2 S(q) |t_f(\theta_f)|^2 \quad (2.70)$$

where the scattering function $S(q)$ is given as:

$$S(q) = \frac{(\Delta \rho_e)^2}{|q_{z,t}|^2} \exp \left\{ - \left[(q_{z,t})^2 + (q_{z,t}^*)^2 \right] \sigma^2 / 2 \right\} \times \int \int \left[\exp \{ |q_{z,t}|^2 C(r) \} - 1 \right] \exp(-iq_{||}R) dR \quad (2.71)$$

For $\theta_i \approx \theta_c$ or $\theta_f \approx \theta_c$ pronounced maxima are observed in the diffuse scattering. These maxima result from the transmission functions $t_i(\theta_i)$ and $t_f(\theta_f)$ and are called the Yoneda [154] peaks. When $\theta_i, \theta_f \gg 3\theta_c$, the factors $|t_i(\theta_i)|$ and $|t_f(\theta_f)|$ approach unity and $q_{z,t}$ approaches q_z so that the DWBA result reduces to that from the *Born approximation*.

2.6 X-ray Photon Correlation Spectroscopy

Synchrotron radiation was discovered half a century ago. After the invention of third-generation synchrotron in the last two decades, tremendous advantages of the coherent properties of x-rays were discovered. Here I will focus on the study of dynamics utilizing a recently developed time-dependent coherent x-ray scattering technique: x-ray photon correlation spectroscopy (XPCS).

2.6.1 Coherent Scattering and Speckles

When a non-ergodic sample is illuminated with coherent beam, of which phases of signals are correlated, variations in the surface cause scattered beam from individual elements to have more-or-less definite phase relationship with one another leading a pattern called “speckle” pattern. If the sample is ergodic with fluctuations occurring on a time scale much shorter than the integrated sampling time, the system undergoes many structural configurations during one sampling period, so that the time average is equivalent to the spatial ensemble average resulting in a smeared-out speckle pattern, which is also similar to the result of a scattering process with incoherent photons. Therefore, in order to reconstruct the absolute position-dependent structure with phase retrieval procedure for speckle patterns, a coherent (or at least partially coherent) source is required.

In a scattering experiment, with a finite sampling time in the detector, differential cross-section based on *Born approximation* can be defined as:

$$\frac{d\sigma}{d\Omega} = r_e^2 \int \int dr dr' \langle \rho(r) \rho(r') \rangle_T \exp(-iq(r - r')) \quad (2.72)$$

where $\langle \dots \rangle$ is the time average within the sampling period. Speckle patterns from light scattering is very common and well-known. The mostly widely known example

is Young's double slit diffraction experiment. However, to observe a speckle pattern with x-rays is much more challenging than those using lasers. Firstly, because it is necessary to use a partially coherent x-ray beam. Since most x-rays are generated from incoherent sources, where the the coherent volume is very small, the coherent intensity is usually ten orders of magnitude less than that from a typical optical laser. The emergence of high-brilliance third-generation synchrotron radiation sources brought a giant leap in source brilliance (the number of photons emitted per second per solid angle per source area per relative wavelength dispersion), making coherent x-ray scattering possible by sacrificing a large amount of photons using a tiny aperture opening in order to obtain a partially coherent beam. Secondly, the x-ray scattering cross-section is far smaller than for light scattering. As a result, the crucial aspect of an XPCS experiment is usually the signal-to-noise ratio (SNR). Thus, the source should be as brilliant as possible. The beamline optics should preserve the source brilliance. Sample with strong scattering and not easily damageable could be helpful to overcome those difficulties. The detector should collect as many x-rays as possible over as wide an angular range as possible, with an angular resolution sufficiently fine to resolve or nearly resolve x-ray speckle, on a time scale measurable with the samples interesting dynamics. Finally, when a CCD-base area detector is used, appropriate tools for data reduction, visualization and analysis must be created.

The first reported x-ray speckle pattern was obtained from the coherent x-ray diffraction of Cu_3Au [155]. Since then speckle patterns have been observed from many other systems, such as diblock copolymer films [156] and aerogels [157] that leads to the development of a new technique, coherent x-ray holography. That technique aims at an indirect imaging of buried nanoscale structures [158, 159]. With the new generations of x-ray sources, x-ray free-electron laser (XFEL) and energy recovery

linac (ERL), around the corner, more applications of coherent x-ray scattering will be explored.

2.6.2 Photon Correlation Spectroscopy

When a coherent beam is scattered from a disordered system and if the spatial arrangement of disorder changes with time, the speckle pattern changes leading to the time-dependent intensity variation at a particular point (q) in reciprocal space provides information on the dynamic properties at corresponding length scales ($2\pi/q$) within the system. This is the principle of photon correlation spectroscopy (PCS). Correlation spectroscopy with visible light, dynamic light scattering (DLS), has been well established and is a widely used technique and XPCS is an extension of DLS.

Compared to DLS, XPCS has an ability to study the dynamics on a much smaller length scale. And it can probe much slower time scales than the neutron spin echo technique can usually reach. It also allows a study of samples that are opaque to visible light, and the broadening problem of the wave vector due to multiple scattering in DLS can be resolved. Figure 2.11 shows the frequency and wave vector ranges accessible to XPCS compared with other frequently used techniques for the study of dynamics [160]. It typically measures the low frequency dynamics (10^6 Hz to 10^{-3} Hz) in a q range from typically $1 \times 10^{-3} \text{ \AA}^{-1}$ up to several $\text{\AA}^{-1}$.

In any XPCS measurement, the feasibility of the experiment will depend on whether it is possible to collect data of reasonable SNR on relevant time and length scales in the assigned experimental time. Jakeman [161] calculated the SNR for DLS by:

$$SNR = AI\Sigma(Q)W\exp(-W/\Lambda)\sqrt{T\tau_a}\sqrt{N} \quad (2.73)$$

where A is the optical contrast, that depends on the coherence of the incoming photons, and the detector characteristics, I is the incident intensity in photons/sec, $\Sigma(Q)$

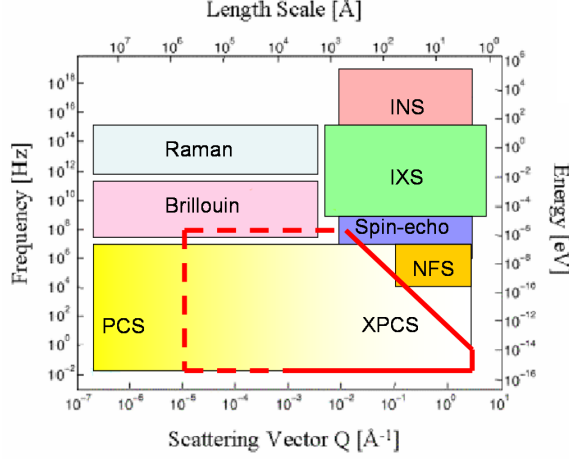


Figure 2.11: Frequency-scattering vector space covered by x-ray photon correlation spectroscopy (XPCS) and complementary techniques: photon correlation spectroscopy with visible coherent light (PCS), Raman and Brillouin scattering, inelastic neutron (INS) and x-ray scattering (IXS), neutron spin-echo and nuclear forward scattering (NFS).

is the differential scattering cross-section of the sample under study in units of one over length, T is the overall measurement time, τ_a is the accumulation time for each intensity measurements, N is the number of detectors that simultaneously collect data, W is the sample thickness and Λ is the attenuation length. Thus, SNR can be improved in the following ways:

- We can increase the measurement time, from Eq. 2.73 SNR improves with square root of T . With limited experimental time at synchrotron sources this approach is limited.
- We can increase the accumulation time, which in turn will limit the time scales we can probe. Since shortest time that is reachable is τ_a , by increasing this time scale can cause missing the relaxation times shorter than that.
- We may increase the incident intensity which is very expensive and causes beam damage.

- Scattering strongly depends on the structure, Porod law states $\Sigma(Q) \propto Q^{-4}$. We can increase the scattering intensity and SNR by decreasing the wave-vector probed but this will in turn limit the range of phenomena that can be studied.
- We can optimize AI by adjusting the beamline parameters which are collimating slit size, sample-to-detector distance, detector pixel size, X-ray energy.
- We can increase the number of independent simultaneous measurements by using an area detector increasing N .

Using a multi-pixel area detector, in principle, can greatly improve the performance of PCS methods. An area detector of a million pixels can collect a million times more photons, allowing measurements millions of times faster or allowing to study weakly scattering samples and shorter length scales.

The coherence of a photon beam has two components: transverse or lateral coherence and longitudinal or temporal coherence. For a synchrotron source of x-rays, with an approximately Gaussian intensity distribution, far from the source, the transverse “one-sigma” coherence lengths at the sample are $\xi = \lambda R / (2\pi\sigma_x)$ in the horizontal direction and $\zeta = \lambda R / (2\pi\sigma_z)$ in the vertical direction, where λ is the x-ray wavelength, σ_x and σ_z are the “one-sigma” source sizes in the horizontal and vertical directions, respectively, and R is the source-to-sample distance.

It is possible to create a partially-transversely coherent beam by aperturing any x-ray beam to have transverse dimensions that are on the order of the transverse coherence lengths. Only at high-brilliance third generation sources, however, do a sufficient number of photons for XPCS pass through such an aperture. The number of photons per second per unit solid angle from a source of brilliance B is the product

of the source area and the brilliance, or approximately $\pi B \sigma_x \sigma_z$. The transversely coherent flux is the number of photons that pass through the solid angle corresponding to the coherence lengths, i.e. $\pi \xi \zeta / R^2$. Thus, the transversely coherent flux is [162]:

$$\pi^2 B \sigma_x \sigma_z \xi \zeta / R^2 = B \lambda^2 / 4 \quad (2.74)$$

Eq. 2.74 shows that the more brilliant the source, the greater the transversely coherent flux. At Advanced Photon Source (APS) at sector 8-ID the brilliance is in the 10^{19} range at 6 keV.

There is also partial longitudinal coherence for XPCS in addition to the transverse coherence. The longitudinal coherence length of the beam is given by $\Lambda \cong \lambda(E/\Delta E)$, where E is the photon energy, and ΔE is the full-width-at-half-maximum (FWHM) of the energy spectrum. Partial longitudinal coherence requires that the optical path length difference (δ) between x-rays scattered from different parts of the sample should not be more than a few times Λ .

There are three different commonly used types of detection methods in scattering experiments such as filter, homodyne, heterodyne that is demonstrated in Figure 2.12 [163]. Filter method is used for studying relatively rapid molecular dynamic processes occurring on time scales faster than 10^{-6} sec [163]. The other two methods are used for slower processes.

In the homodyne method, also called as “self-beat” method, only the scattered beam is detected and correlated with itself. In heterodyne method reference beam, a small part incident beam separated before hits to the sample, is mixed with the scattered beam. In this method, the measured intensity as a function of time and

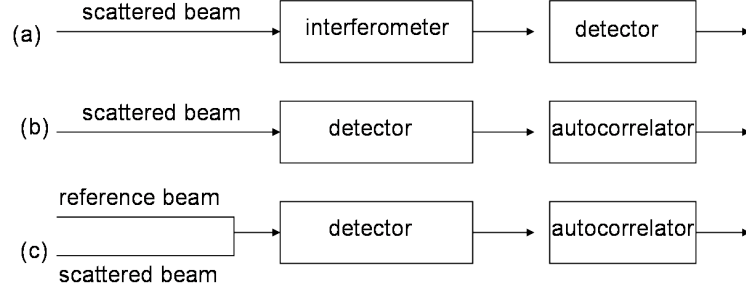


Figure 2.12: Schematic illustrations of detection methods in scattering experiments. (a) filter, (b) homodyne, and (c) heterodyne.

wave-vector transfer is defined as:

$$I(q, t) = |E_s(q, t) + E_r(q, t)|^2 = I_s(q, t) + I_r(q, t) + 2\text{Re}[E_s(q, t)E_r^*(q, t)] \quad (2.75)$$

where E_s and E_r are electric fields of scattered and reference beams, and I_s and I_r are the intensities of scattered and reference beam, respectively. By applying $g_r^{(1)}(q, t) = g_r^{(2)}(q, t) = 1$ intensity-intensity autocorrelation calculated as:

$$\begin{aligned} G(q, t) &\equiv \langle I(q, t')I(q, t' + t) \rangle \\ &= [\langle I_s(q, t') \rangle + \langle I_r(q, t') \rangle]^2 + 2 \langle I_s(q, t') \rangle \langle I_r(q, t') \rangle g_s^{(1)}(q, t) + \langle I_s(q, t') \rangle^2 [g_s^{(2)}(q, t) - 1] \end{aligned} \quad (2.76)$$

where $\langle \dots \rangle$ is the average over time t' , and $g_s^{(1)}(q, t)$ and $g_s^{(2)}(q, t)$ are the normalized first and second order correlation functions for the scattered electric field, respectively and written as:

$$\begin{aligned} g_s^{(1)}(q, t) &= \frac{\langle E_s(q, t')E_s^*(q, t' + t) \rangle}{\langle I_s(q, t') \rangle} \\ \text{and } g_s^{(2)}(q, t) &= \frac{\langle I_s(q, t')I_s(q, t' + t) \rangle}{\langle I_s(q, t') \rangle^2} \end{aligned} \quad (2.77)$$

Most XPCS measurements are done without a reference beam that gives the homodyne method with $\langle I_r \rangle \gg \langle I_s \rangle$ in Eq. 2.76.

The first and second order correlation functions are connected by the Siegert relation [164]:

$$g_s^{(2)}(q, t) = 1 + |g_s^{(1)}(q, t)|^2 \quad (2.78)$$

where $g_s(q, t)$ is proportional to electron density-density correlation as $g_s(q, t) \propto \langle \rho(q, t') \rho^*(q, t' + t) \rangle$ and $\rho(q, t') = FT[\rho(r, t)]$. Thus, $g_s^{(1)}(q, t)$ and $g_s^{(2)}(q, t)$ is proportional to time-dependent differential cross section of the sample.

$g_s^{(2)}(q, t)$ is usually written as :

$$g_s^{(2)}(q, t) = 1 + \beta |f(q, t)|^2 \quad (2.79)$$

where β is a factor represents the degree of spatial coherence of the scattered field and is usually written as the ratio of the coherent volume to the illuminated sample volume. Ideally $\beta = 1$. However, in real XPCS measurements with a partially coherent x-ray beam and non-zero detector, β is much less than 1. β is not sample-dependent parameter and not regarded as fitting parameter during the analysis. In Eq. 2.79, $f(q, t)$ is the normalized intermediate scattering function (ISF) and is written as:

$$f(q, t) \equiv \frac{S(q, t)}{S(q)} \quad (2.80)$$

where $S(q, t)$ is the ISF and $S(q)$ is the static structure factor given as:

$$\begin{aligned} S(q, t) &= \int \int dr'_1 dr'_2 \exp(-iq(r'_1 - r'_2)) \langle \rho(r'_1, 0) \rho^*(r'_2, t) \rangle \\ \text{and } S(q) &= \int \int dr'_1 dr'_2 \exp(-iq(r'_1 - r'_2)) \langle \rho(r'_1, 0) \rho^*(r'_2, 0) \rangle \end{aligned} \quad (2.81)$$

While probing bulk dynamics, $S(q, t)$ is related to the bulk density-density correlation function. For surface dynamics, the scattering contrast arises from the

electron density variations that depends on the surface profile so ISF is connected to the time-dependent surface height-height correlation function as:

$$S(q_{||}, t) = C(q_{||}, t) = \langle \delta_z(q_{||}, 0) \delta_z(q_{||}, t) \rangle \quad (2.82)$$

Langevin [165] measure the spectrum of liquid surfaces by using light scattering and found that it is consistent with the capillary wave theory. Since x-rays has two orders of magnitude smaller wavelength than light, it is applicable to use x-rays to probe surfaces, with a typical penetration depth of the evanescent wave field of less than ~ 5 nm. The presence of capillary waves on liquid surfaces at a broader range of length scale has been indirectly verified by measuring the capillary roughness defined in Eq. 2.59 by using x-ray reflectivity [166–168]. Sanyal *et al.* [148] showed that power-law behavior in diffuse scattering characteristic of the algebraic decay of in-plane height-height correlations at the surface dictated by capillary wave theory is verified on ethanol surface. However, these measurements capture the static time-averaged structure rather than the dynamics of the surface fluctuations. To investigate the dynamic properties of liquid surfaces, it is necessary to use time-dependent scattering measurements. To probe the dynamics occurring on very fast time scales, we need short measurement times which is impossible with conventional x-ray sources such as rotating anode that leads low intensity and low SNR. And use of coherent beam is also important. So third generation synchrotron sources are very suitable to overcome these restrictions in probing surface dynamics of liquid and polymer surfaces.

XPCS has shown the potential to impact several areas of statistical physics and provide access to a variety of dynamic phenomena. Among them are the time-dependence of equilibrium critical fluctuations and low frequency dynamics in dis-

ordered hard and soft condensed materials, or hydrodynamic modes in concentrated colloidal suspension. Surface dynamics of liquid crystal membranes [169–172], water surfaces [173,174], miscible binary fluids [175], molten polymer single layer films [6,7], bilayer films [34], metal/polymer nanocomposite thin films [176,177] or homopolymer brushes [178] which will be detailly explained in the following chapters are also studied by XPCS.

CHAPTER III

EXPERIMENTAL

3.1 Synthesis of Homopolymer and Diblock Copolymer Brushes

3.1.1 Materials

Styrene (Aldrich, 99%), deuterated styrene (d_8 -S, C/D/N Isotopes 98% Cambridge Isotope Laboratories N , N , N' , N'' , N'' -Pentamethyldiethylenetriamine (PMDETA, 99%), and ethyl 2-bromoisobutyrate (E2Br-iB, 98%) are passed through a column of activated basic alumina. CuBr (Aldrich, 98%) is purified as described in the literature [179]. Dodecyl trichlorosilane (DTS, Aldrich, 99%) is vacuum distilled prior to use. Anhydrous anisole (Aldrich), anhydrous toluene (Aldrich) is used as received. Silicon wafers (100) having (500 ± 50) μm thickness is purchased from the Semiconductor Processing Company.¹ All other reagents is purchased from either Aldrich or Fisher Scientific and used as received. Since NR measurements require substrates at least 6 cm in one dimension, bigger silicon wafers (60 mm x 35 mm x 0.5 mm) are used and the polymerizations are performed in a dry box. For x-ray measurements smaller wafers (15 mm x 30 mm x 0.5 mm) are enough.

¹Commercial materials, instruments and equipment are identified in this paper in order to specify the experimental procedure as completely as possible. In no case does such identification imply a recommendation or endorsement by the National Institute of Standards and Technology nor does it imply that the materials, instruments, or equipment identified are necessarily best available for the purpose.

3.1.2 Substrate Preparation

Silicon wafers (15 mm x 30 mm x 0.5 mm) were cleaned by treatment with a freshly prepared “piranha”² solution (70/30, *v/v*, concentrated H₂SO₄/30% aqueous H₂O₂) at 90 to 100°C for 1 h and were then rinsed with distilled water and dried with a stream of technical grade nitrogen.

3.1.3 General Procedure for Deposition of Surface Bound Initiator

A 20 mL glass vial is placed in oil bath, and a freshly cleaned silicon wafer is placed in the vial. The (11-(2-bromo-2-ethyl)propionyloxy)undecyltrichlorosilane is synthesized according to literature precedent [180] and utilized as a surface-bound initiator. For every 5 mL of anhydrous toluene, 0.1 mL of 25% by volume solution of the trichlorosilane initiator is added to the vial via syringe. The vial is sealed with a glass cap and heated at 60 °C for 4 h in a dry box. The silicon wafer is then removed, sequentially washed with toluene, ethanol and methylene chloride, and then dried in a stream of technical grade nitrogen gas. To vary grafting density, DTS is used as a spacer molecule. Since DTS is highly sensitive to air and humidity, initiator deposition is performed in a dry box. First DTS is deposited using various deposition times to yield different packing densities and then the empty spaces are back filled by depositing the trichlorosilane initiator. This procedure decreases the density of initiating sites on the substrate for the preparation of brushes with targeted lower grafting densities as shown in schematic in Figure 3.1. For bigger wafers, a 100 x 50 mm² crystallizing dish is used instead of a vial.

²Piranha etching consists of using hydrogen peroxide and sulfuric acid, which can be dangerous. Acid-resistant gloves, protective goggles, and lab coats must be worn when handling the piranha solution.

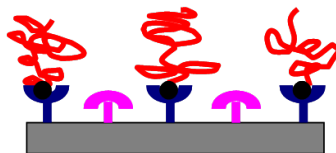


Figure 3.1: Schematic illustration of DTS, as spacer molecules in between initiator molecules.

3.1.4 Procedure for Surface ATRP from an Initiator Covered Silicon Substrate

Polystyrene (PS) and d-styrene (dPS) brushes (0.12 to 0.6) chains/nm²) are synthesized by atom transfer radical polymerization (ATRP). The general mechanism of ATRP is shown below:

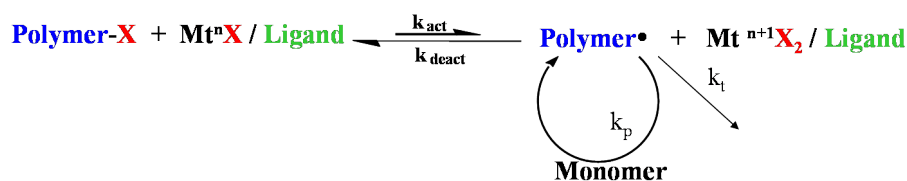


Figure 3.2: A general mechanism of ATRP.

X is halogen which is Br in our case and Mt is for metal which is Cu. L is a ligand and PMDETA is chosen as ligand for all ATRP reactions due to increased catalyst complex solubility of the multidentate amine ligands when employing copper metal (CuBr) as the ATRP catalyst. ATRP is based on a reversible halogen transfer between a dormant species, an added initiator or the dormant propagating chain end, and a transition metal complex in the lower oxidation state resulting in the formation of propagating radicals and the metal complex in the higher oxidation state with a coordinated halide ligand. The active radicals form at a rate constant of activation (k_{act}), subsequently propagate with a rate constant (k_p) and reversibly deactivate (k_{deact}), but also terminate (k_t). As the reaction progresses, radical termination is diminished as a result of the persistent radical effect, and the equilibrium is strongly shifted towards the dormant species ($k_{\text{act}} \ll k_{\text{deact}}$).

CuBr, anisole and monomer(styrene, d_8 -styrene or methyl acrylate) are added to a 100 mL Schlenk flask with a magnetic stir bar, sealed with a rubber septum and degassed by purging with technical grade nitrogen for 2 h. Three vacuum/purge cycles are applied to the flask and it is left under a nitrogen atmosphere. PMDETA is added to the mixture via syringe and the solution stirred at reaction temperature until it become homogeneous (~ 5 min). An initiator modified silicon wafer is placed in a separate 100 mL Schlenk flask and sealed with a rubber septum. The flask is degassed and back-filled with nitrogen at least three times and left under a nitrogen atmosphere. The solution is then transferred to the flask containing the silicon wafer via a cannula, followed by the addition of free initiator (E2Br-iB) via a syringe. The polymerization is allowed to proceed at (90-100) $^{\circ}$ C for a period of time depending on the thickness targeted, after which the silicon wafer is removed. The final concentrations are as follows: $[d_8-S]_0 = 3.9$ M, $[PMDETA]_0 = 25$ mM, $[CuBr]_0 = 12$ mM and $[Br-iB]_0 = 5$ mM, $[PMDETA]_0 = 25$ mM, $[CuBr]_0 = 12$ mM and $[Br-iB]_0 = 10$ mM. To remove untethered polymer chains, the silicon wafer is placed in a Soxhlet extractor and extracted exhaustively with tetrahydrofuran (THF) for 24 h followed by sonication in toluene for 2 hours. The brushes are annealed in high vacuum for 18 h at 150 $^{\circ}$ C to remove residual solvent. For synthesis done in dry box for bigger wafers, procedure is changed a little. Flask after PMDETA added is sealed transferred to the dry box along with the free initiator (E2Br-iB), silicon wafer and a 100x50 mm² crystallizing dish. An initiator-modified silicon wafer is placed in the crystallizing dish in the dry box. Polymerization solution is added to the crystallizing dish, followed by the usual procedure addition of free initiator and cleaning as explained above. The dish is covered with a piece of glass carrying a Teflon gasket on it to prevent evaporation of the solution.

The low concentration of initiator on flat surfaces causes an insufficient concentration of the deactivator to provide control during the surface ATRP reactions. Free initiator (ethyl-2-bromoisobutyrate, E2BriB) is added to the reaction solution to overcome this problem. The other advantage of using free initiator is that the free polymer in solution can be used to characterize the molecular weight and PDI of the grafted chains since the amount of tethered polymer on the silicon wafer is too small to degraft and analyze. The validity of equating the molecular weight of the free polymer in solution and that on the surface has been tested by various groups for all CRP techniques. Baum *et al.* [133] synthesize DCBs of PS, PMMA and poly(dimethylacrylamide) from a surface immobilized azo-initiator using RAFT. The free initiator they use is 2,2-azobisisobutyronitrile (AIBN). They compare the molecular weight of free polymer chains with that of the tethered polymer chains, by cleaving a homopolymer brush prepared on high surface area of non-porous silica. Their results shows that for homopolymer brushes of either PS or PMMA, both the number average molecular weight (M_n) and PDI were comparable for free polymer and degrafted polymer. Using the molecular weight and thermogravimetric analysis data, they find the initiator efficiency ranges from 0.15 to 0.19. Patten and co-workers [181] synthesize PS from silica nanoparticles using ATRP and they find that the M_n for degrafted chains is 46300 g/mol and the PDI was 1.29, whereas the M_n for free chains was 43800 g/mol and the PDI value was 1.22. In similar work by Hawker and co-workers shows that NMRP synthesized styrene on silica gel has a free polymer of M_n 48000 g/mol with a PDI of 1.20 and degrafted polymer has M_n =51000 g/mol and PDI=1.14. Kim *et al.* reports that the initiator efficiency for PMMA brushes grown on a flat substrate is 0.1, which is reasonably close to the value obtained by Brittain *et al.* [182]. As a result of these studies, there are two conclusions. First of them is that the initiator efficiency of the surface-initiated CRP

techniques is approximately 0.1. Second, the M_n and PDI of the free polymer give very good estimates of the M_n and PDI for the grafted polymer chains. Second one is especially important for calculation of molecular weight of the grafted brush chains and grafting density from the formula in Eq. 1.1.

3.1.5 Block Copolymerizations

To create a block copolymer brush, a second block was polymerized by ATRP in the same manner as the styrene, d₈–styrene or the MA homopolymer layers were polymerized. For example, the dPS-*b*-PMA brush was produced by first polymerizing the dPS block using d₈–styrene and then polymerizing the PMA block using methyl acrylate. After each polymerization, silicon wafer were cleaned and extracted to remove any untethered polymer before proceeding to the next polymerization. In Figure 3.3 there is an idealized schematic of a diblock copolymer brush (DBC) with a very sharp interface between two lamellar domains each rich in a particular block. This is a very common representation of “as-deposited” diblock copolymer brush in majority of papers.

The issue for the block copolymerization is the reinitiation of the second block from macroinitiator; first block. Reinitiation of the second block depends strongly on the concentration of “living” polymer chains. These “living” chains are the first block chains that still have halogen groups at their chain ends. A polymer chain could be dead during the polymerization of the first block if bimolecular radical coupling and disproportionation reactions occur predominantly. In a well-controlled ATRP, no more than 5% of the total growing polymer chains undergo termination during the initial, short, non-stationary stage of the polymerization. Matyjaszewski *et al.* [183] mentions that the rate of propagation (k_p) slows down considerably at high conversions. However the rate of any side reaction does not change significantly as

most of them are monomer concentration independent. Prolonged reaction times leading to complete monomer conversion may not increase PDI, but cause loss of end groups. Conversion must not exceed 95% to avoid end-group loss. In most of our studies especially for diblock copolymer synthesis, the conversion is kept under 70% in order to reduce the occurrence of termination reactions. By doing a reinitiation experiment, you may estimate the reinitiation efficiency. In a reinitiation experiment, first block is polymerized from SAM using the usual polymerization conditions. Thickness and molecular weight of this block are measured. Then, the homopolymer brush created in the first step is reinitiated with the same monomer using exactly the same conditions that have used in the first step. Thickness of the second block and the molecular weight are measured again. Comparison of these two blocks gives the reinitiation efficiency. Previous studies show that DCB contains about 10% homopolymer brush [184, 185] having repeat units the same as those in the first block of the block copolymers. Reinitiation experiments have been performed previously in our group with PS and it is found that 91% of the first polymer block reinitiates.

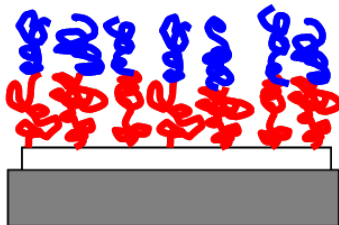


Figure 3.3: Idealized schematic of a diblock copolymer brush with a very sharp interface between the two lamellar domains, each rich in a particular block.

Throughout this thesis, DCBs will be called with the corresponding thickness values of each block. For example, dPS39-PMA6 indicates that the diblock brush has a 39 nm thick dPS layer next to initiator layer and 6 nm thick PMA layer next to air surface.

Scheme 3.4 illustrates the general ATRP “grafting from” approach used to synthesize dPS-b-PMA DCBs. To synthesize PMA-b-dPS DCBs, just the second and third steps change places in Scheme 3.1. Typical procedure of diblock copolymer brush synthesis requires the solution deposition of a bromoisobutyrate initiator onto a suitable substrate by self assembly techniques. The (11-(2-bromo-2-ethyl)propionyloxy)undecyltrichlorosilane is synthesized precedent and used as a surface-bound initiator. Then dPS and MA is grown by ATRP. By changing the monomers and sequences variety of DCBs can be synthesized.

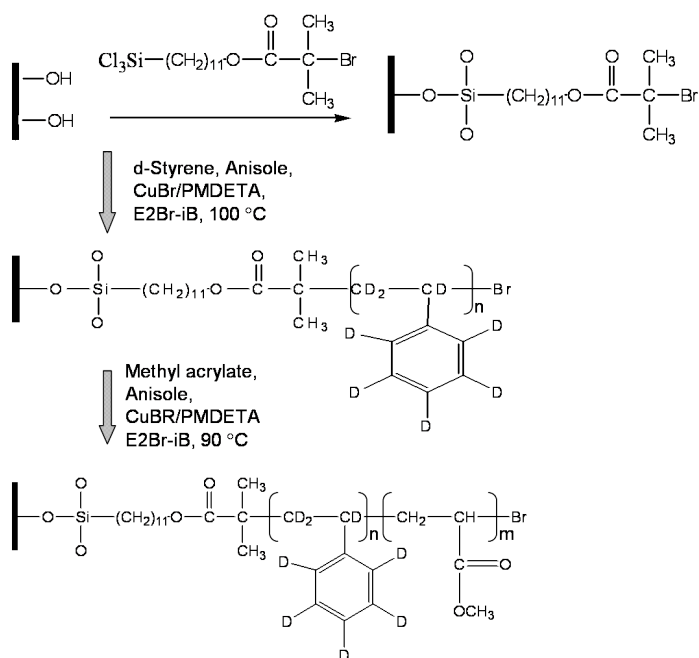


Figure 3.4: Synthesis scheme for dPS-*b*-PMA diblock copolymer brush.

Solution deposition of the initiator onto silicon substrate and ATRP of dPS and PMA on the surface was confirmed using FTIR, contact angle measurements and ellipsometry. Typical IR spectra of the all steps of DCB synthesis from ATR-FTIR is shown in Figure 3.5(taken from Bulent Akgun’s thesis). In the spectrum of surface immobilized trichlorosilane initiator, peaks at 2924 and 2858 cm^{-1} are assigned to the C-H stretching and CH_2 stretching vibrations, respectively, while the peak at 1726

cm^{-1} is assigned to the carbonyl stretching vibration of the ester group. Formation of homopolymer dPS brush is confirmed with an increase in layer thickness along with the appearance of peaks at 2273, 2195 and 2101 cm^{-1} which were attributed to the aromatic C-D stretching vibrations. The peaks that are assigned to initiator layer is still present in homopolymer brush spectra because the penetration depth of the IR beam ($\sim 0.5\text{ }\mu\text{m}$) is much larger than the thickness of the brush layer. Last spectra on top shows the PMA brush spectrum grown from dPS-Br macroinitiator. There are broad aliphatic C-H and CH_2 stretching peaks at 2952, 2925 and 2853 cm^{-1} and a sharp, large carbonyl peak at 1737 cm^{-1} .

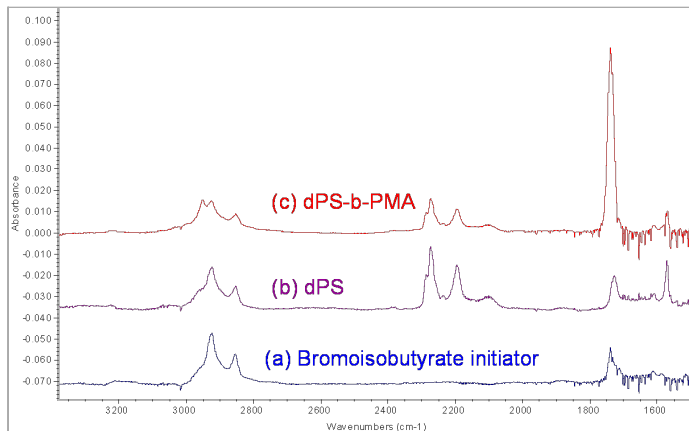


Figure 3.5: ATR-FTIR spectra of (a) bromoisobutyrate initiator, (b) homopolymer dPS brush, and (c) diblock copolymer brush of dPS-*b*-PMA.

3.1.6 Spin-coating

For bilayer films PS polymer films are spin-coated on brush grown silicon wafers. For spincoating, PS powders (purchased from Polymer Source Inc. and Pressure Chemical Company) of different molecular weights (MW) are dissolved in toluene and then spincoat on homopolymer brushes. According to the standard spin-coating procedure for PS films [186], desired film thicknesses were obtained by adjusting the concentration of PS in toluene and the spin-coating angular velocity.

3.2 Characterization Methods

FT-IR spectra....

Contact angles were determined using a Rame Hart NRL-100 goniometer equipped with a tilting base mounted on a vibrationless table. Advancing and receding contact angles of a 10 μ l drop were determined using the tilting stage method.

For quick thickness analysis ellipsometry measurements were performed on a Gaertner model L116C ellipsometer with a He-Ne laser ($\lambda = 632.8$ nm) and a fixed angle of incidence of 70° . For the layer thickness calculations the following refractive index values were used: 1.455 for silicon oxide, 1.508 for initiator layer, 1.589 for PS and 1.48 for PMA.

3.2.1 Neutron Reflectivity (NR)

NR is a very powerful technique that characterizes thin film structure in the direction perpendicular to the surface. In reflectometry, the ratio of specularly reflected intensity to incident intensity is measured for a thin film over a range of incident angles (θ) to yield a reflectivity curve. Information about the film thickness, microroughnesses at the interfaces, and scattering length density (SLD) profile for NR, can be obtained from the reflectivity curve. NR is a non-destructive technique for the investigation of interfacial structures “buried” inside the film due to the contrast that can be obtained through selective deuteration. Deuteration of one block in a bilayer system enhances the contrast between domains rich in differing blocks and makes the interfacial region visible to neutrons. The depth resolution of film structure with NR is of order 1 nm and is dependent on the range of scattering vector q_z ($|q_z| = 4\pi \sin\theta/\lambda$) over which data are collected. NR measurements were performed at the NG7 horizontal reflectometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research using a wavelength of 0.475 nm. The schematic of NG7 hori-

zontal reflectometer is shown in Figure 3.6. To maximize the intensity, the sizes of the collimating slits and detector slits were increased during the measurement as θ increased, keeping the relative resolution in q_z approximately constant ($\delta q/q \approx 0.04$). Data were corrected for both the varying slit size and background.

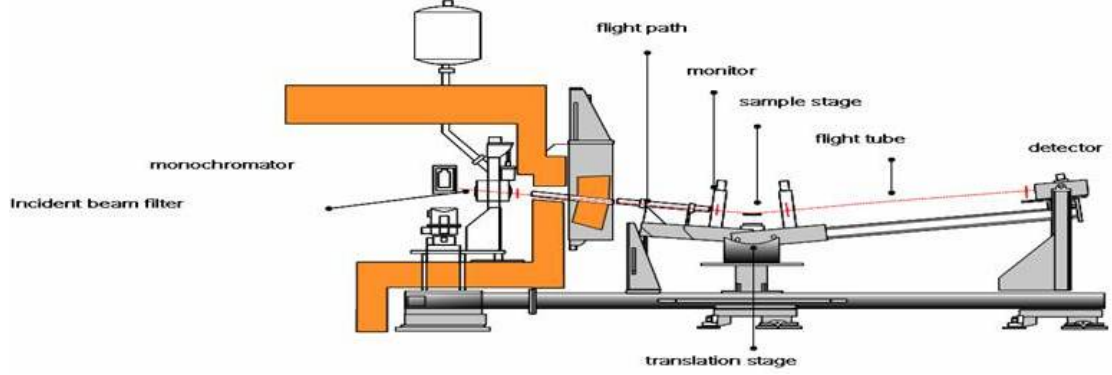


Figure 3.6: Schematic of the NG7 Horizontal Reflectometer at NIST Center for Neutron Research.

For swelling measurements of DCBs in different solvents special sample cell is designed and built as shown in Figure 3.7. Teflon trough (Figure 3.7(c)) is prepared with a 1 mm thick space for solvents and it is put upside down on a sample to cover the sample surface with solvent. Since wafers of the samples are too thin ($\sim 0.5 - 0.6$ mm) they are backed up with much thicker silicon wafer as shown in side-view of the cell in Figure 3.7(a). They are tightened and stabilized with two aluminium pieces, one on top and one at the bottom. Since there is a teflon piece on top of the sample, set-up of the measurement change as beam is coming from underneath the backup wafer and hits first to the backside of the sample and then goes in an order to silicon oxide layer, initiator layer, first block, second block and then to solvent.

For data analysis of NIST reflectivity measurements there is a software developed at the National Institute of Standards and Technology at the NIST Center for

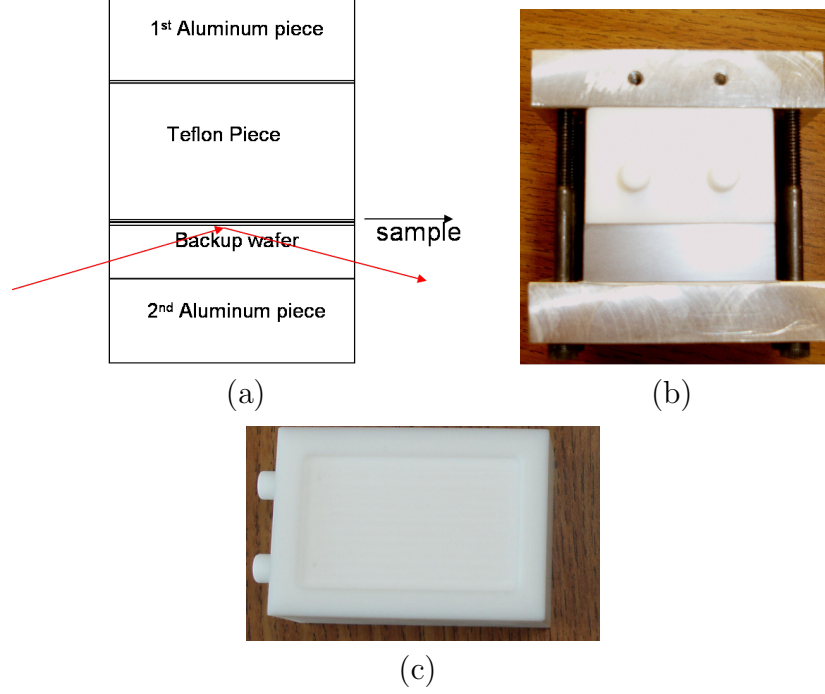


Figure 3.7: (a) Side-view schematic and (b) Photo of a sample cell for swelling measurements and (c) Photo of a teflon trough used in swelling cell

Neutron Research. *Reflred* allows to view NG-7 data files and reduce the raw data and then use the layer-based *reflfit* program to fit the reflectivity curve.

3.2.2 Grazing Incidence Small Angle X-ray Scattering(GISAXS)

Reflectivity is done in specular geometry where the direction of incident beam and reflected beam makes the same angles with respect to the normal of the surface. The specularly reflected intensity from a surface is generally lower than the theoretically calculated Fresnel reflectivity, R_F , because of the surface roughness. This decrease in intensity is due to scattering of the beam in off-specular directions where incident and exit angles are not equal. While specular reflectivity is sensitive in direction normal to the surface with an averaged lateral information, analysis of the off-specularly scattered intensity yields information about the lateral correlations and in-plane surface fluctuations. The schematic of scattering geometry showing both specular and off-

specular scattering is shown in Figure 3.8. For out-of-plane scattering an additional angle, Ψ , between the plane of incidence and the plane of detection must be specified. So as opposed the z -component of the wavevector transfer, there x, y, z components that are defined as:

$$q_x = k(\cos\theta_f \cos\Psi - \cos\theta_i) \quad (3.1)$$

$$q_y = k\cos\theta_i \sin\Psi \quad (3.2)$$

$$q_z = k(\sin\theta_i + \sin\theta_f) \quad (3.3)$$

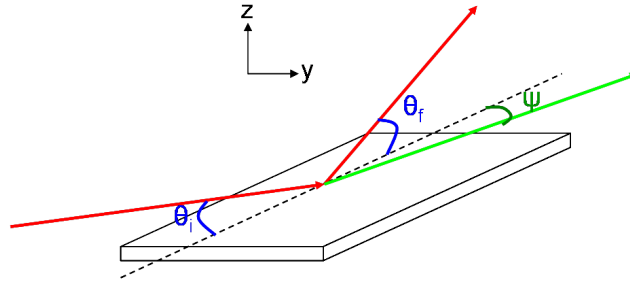


Figure 3.8: Schematic of a GISAXS scattering geometry. The angle of incidence is denoted with θ_i the exit angle with and the out-of-plane angle , θ_i with Ψ .

There are different types of off-specular scattering techniques that can be done such as transverse scans, longitudinal diffuse scan or detector scan.

Grazing Incidence Small Angle X-ray Scattering(GISAXS) which is the concern of this thesis, is a combination of specular and off-specular scattering. GISAXS combines interface sensitivity of the reflection geometry with sensitivity of small angle diffuse scattering to colloidal structure in lateral direction. It is a very powerful technique to investigate the structure of buried interfaces as well as the surface structure

in the plane of the sample. In GISAXS measurements, a fixed glancing incident angle is used, and scattering for a range of both q_z and q_y are collected using a 2-dimensional CCD detector. An incident angle is chosen between about half the critical angle α_c and several critical angles of the film material to make it surface sensitive. A beam stop has to be set-up to block intense specular beam to prevent beam damage on detector. The scattering geometry is thus relatively simple, and lends itself to study samples in in-situ environments. As the scattering intensity in the forward direction is high, real-time studies have become feasible. GISAXS provides information both about lateral and normal ordering at a surface or inside a thin film.

Schematics of GISAXS setup in at the 8-ID-E beamline at the Advanced Photon Source is shown in Figure 3.9. A monochromatic X-ray beam with a wavelength of 0.1675 nm is used. The beam quality was optimized using a set-up of high-quality entrance slits and a completely evacuated pathway. The beam had a vertical size of 50 μm and a horizontal size of 150 μm . The sample-to-detector distance was 1.975 m. Using a two-dimensional image plate detector with 150 μm pixel size and 1200x1200 pixel array, the scattered intensity was recorded at a fixed angle of incidence, α_i , of the X-ray beam onto the sample surface.

3.2.3 X-ray Photon Correlation Spectroscopy(XPCS)

XPCS measurements are carried out in Sector 8-ID-I at the Advanced Photon Source (APS), Argonne National Laboratory. The schematic of the set-up for XPCS is shown in Figure 3.10. A germanium (111) channel-cut double-bounce monochromator located 53 m from the source and adjustable slit system 40 cm upstream of the sample were used to prepare a coherent monochromatic x-ray beam with a wavelength of 0.16 nm. The beam is collimated to 20 x 20 μm^2 with defining slits and guard slits are used to remove the parasitic scattering. Samples were vertically mounted on top of a

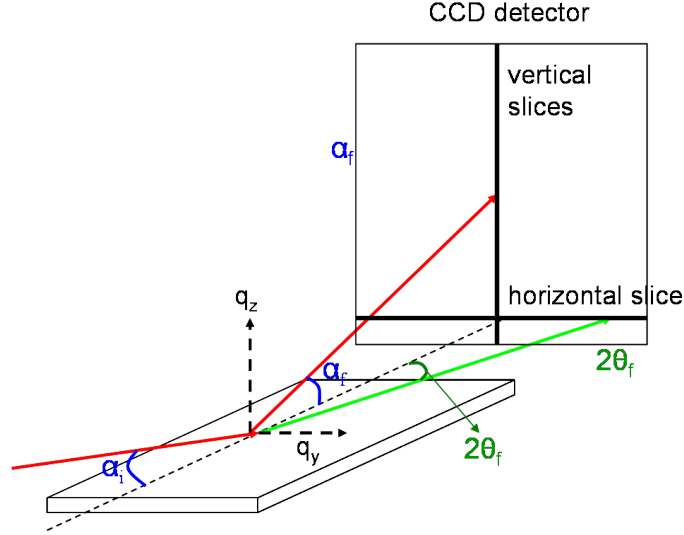


Figure 3.9: The schematics of GISAXS measurement. α_i is the incident angle and α_f is the exit angle with respect to film surface and $2\theta_f$ is the exit angle with respect to the plane of incidence. q_z is the scattering vector in the perpendicular direction and q_y is the scattering vector in the plane of the sample.

thermal-conducting copper stage assembled with heating elements and temperature controller sensors in a vacuum chamber. The incident angle during the XPCS data collection was usually fixed at $\alpha_i = 0.14^\circ$, below the PS critical angle ($\theta_c \approx 0.16^\circ$ at x-ray energy $E = 7.35$ keV), so that the penetration of the evanescent wave field intensity was limited to ~ 9 nm near the surface.

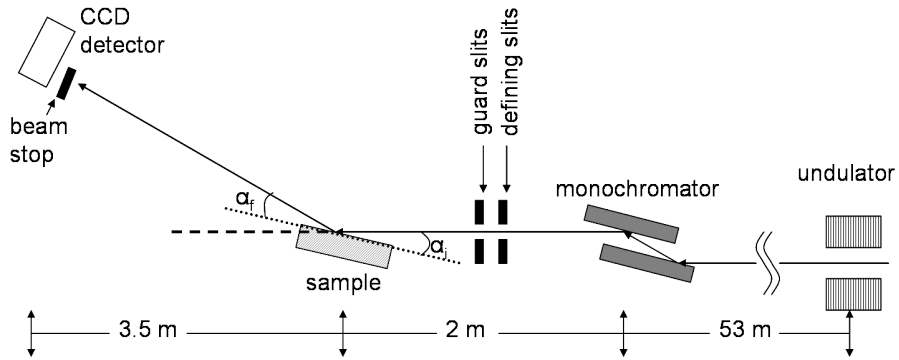


Figure 3.10: Experimental set-up for XPCS at Sector 8-ID-I at Argonne National Laboratory.

Figure 3.11 illustrates the scattering geometry in XPCS, where as opposed to sector 8-ID-I vertical sample mounting configuration, here the sample is schematized horizontally to show penetration depth. When arriving at the sample, the x-ray transverse coherent lengths were 7 and 90 μm in the horizontal and vertical directions. To give sufficient coherence, the horizontal coherent length of the beam is increased by a factor of about 400 because of the projection of the beam cross section in the grazing incidence geometry. The time-dependent scattered beam from the surface of the sample is collected by using a Princeton Instruments x-ray charged-couple device (CCD) mounted downstream. This CCD camera consists of a 1340 x 1300 pixel array with the effective size of each pixel 22.5 x 22.5 μm^2 . In a full-frame CCD mode, read out time is ~ 1.8 sec during which the beam was blocked with a front shutter synchronized with the CCD in order to save the sample. Due to environmental vibrations and beam stability issues, the maximum time span that XPCS on Sector 8-ID-I can reach is $\sim 10^3$ sec for reflection geometry, and $> 5 \times 10^3$ sec for transmission geometry.

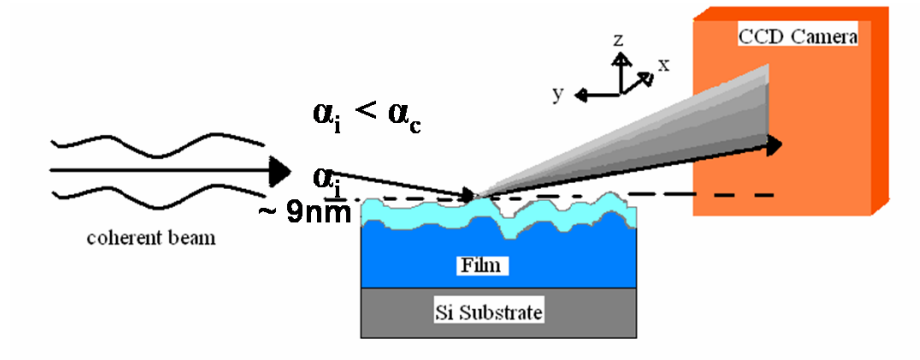


Figure 3.11: Geometry of Scattering and Wave-vector Transfer in XPCS

XPCS measures the normalized intensity-intensity time autocorrelation function, $g_2(q, t)$, defined as:

$$g_2(q, t) = \frac{\langle I(q, t')I(q, t' + t) \rangle}{\langle I(q, t') \rangle^2}; \quad t > 0 \quad (3.4)$$

where $I(q, t')$ refers to scattering intensity at the wave-vector q in reciprocal space at time t' , and brackets refer to the averages over time t' . The t denotes the time delay.

There are two modes of CCD camera to collect data; *full-frame* and *kinetics mode* [187]. In *full-frame*, whole area of the CCD camera can be used for a single exposure (Figure 3.12(a)). This method provides probing smaller length scales by reaching higher q ranges. Although the read-out time is 1.8 sec, it is still possible to achieve a time scale as fast as 30 ms, by means of the *kinetics mode* of the camera. Specifically, *kinetics mode* as shown in Figure 3.12(b) allows to take rapidly multiple successive exposures by using a fraction of the CCD camera. Here it is shown in the Figure 3.12(b) there are 13 fractions in a frame of CCD, which are called *slices*. After one exposure, that illuminated CCD image is subsequently shifted electronically into the illuminated parts of the CCD area for interim storage. The slices are read out as a full CCD frame after the acquisition of all slices, where the interval between slices are $\sim 50\mu s$. In doing so, a sequence of large images with poor time resolution can be effectively traded for a sequence of smaller slices but with improved time resolution. However, using only a small portion of the CCD in the *kinetics mode* narrows the probed in-plane wave vector range (and hence the length scales). Additionally, a very short pulse-like exposure may not guarantee enough scattered photons to provide sufficient SNR for the calculation of the intensity-intensity autocorrelation functions.

The procedure for an analysis is to determine the variation of the normalized intensity autocorrelation function, g_2 , versus time from a sequence of speckled patterns, which is well-known from DLS. However, in XPCS there is a challenge of the

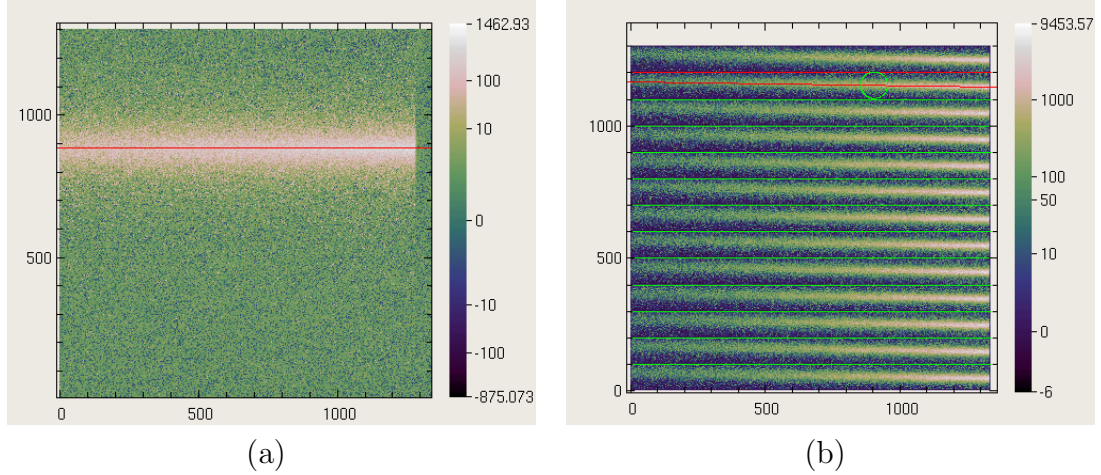


Figure 3.12: (a) Full-frame and (b) Kinetics mode feature of CCD camera.

low photon count rates encountered and data analysis takes place in the regime of short data batches. Before analysis, a few adjustments are needed to be made. Scattering patterns are retrieved from CCD detector as a time series of two-dimensional arrays. Saturated pixels are removed. Then, a sequence of CCD images in the absence of detector illumination with all other parameters being equal. This sequence of images so-called “dark frames” are used as a background subtraction to remove electronic noise. This dark frames exhibiting significant variations as a function of q , is subtracted on a pixel-by-pixel basis from every scattering pattern acquired.

To calculate the intensity-intensity correlation $\langle I(q, t')I(q, t' + t) \rangle$ for each pixel, a multi- τ correlation protocol is applied. In this protocol, the intensities of each pixel in several consecutive frames are averaged before long-delay correlations are evaluated. Thus, it improves the signal-to-noise ratio and logarithmically reduces the number of delays involved. The area detector measures intensities at multiple q 's simultaneously and then each pixel is mapped to a certain wave vector transfer value through simple geometrical configurations. By using a multi-speckle normalization procedure, the correlation functions can be normalized. Intensity is normalized in

a given pixel at a particular time by dividing intensity averaged across pixels of the same wave vector transfer, as well as the average over time, which improves the signal-to-noise ratio and provides more reliable correlation functions.

During dynamic measurements in XPCS, surface tension can be measured by surface diffuse x-ray scattering. The intensity of the scattering is related to the Fourier transform of the surface height-height correlation function $C(R)$, which is determined by the surface tension. According to the DWBA, the differential cross section is proportional to structure factor $S(q)$ which is given by:

$$S(q) \approx \frac{4\pi}{q_z^2 q_{||}^2} \exp(-q_z^2 \sigma^2) \left(\frac{r_0 q_{||}}{2\pi \exp(\gamma_e)} \right)^\eta \left[\frac{\Gamma(1 - \frac{1}{2}\eta)}{\Gamma(\frac{1}{2}\eta)} + \left(\frac{r_0 q_{||}}{2} \right)^2 \frac{\Gamma(1 - \frac{1}{2}\eta)}{\Gamma(1 + \frac{1}{2}\eta)} - \left(\frac{r_0 q_{||}}{2} \right)^{2-\eta} \frac{1}{1 - \frac{1}{2}\eta} \right] \quad (3.5)$$

where r_0 is the monomer size and can be taken as ~ 0.27 nm to prevent the divergence at large wave vectors. $S(q)$, in the limit of small q_z , becomes

$$S(q) \approx \frac{k_B T}{\gamma q_{||}^2} \quad (3.6)$$

For each value of q_z , the structure factor is plotted as a function of $q_{||}$, and the surface tension is obtained by fitting all these curves simultaneously to Eq.3.5.

One important issue for XPCS measurements is beam damage which can be controlled during measurements. There are different ways to check beam damage on the samples. One way is to measure reflectivity at the same point before and after measurement. Change in reflectivity curve can give a clue about the beam damage. The second method is comparison of the exposure times. If decreasing the exposure time makes a change in the autocorrelation functions, that could be due to long exposure time causing beam damage. Also we can compare the

exposure times for our samples with those for thin films of untethered chains. Our collaborators have studied hundreds of such films. They typically use exposure times of multiple minutes without damage. Of course, shorter exposure times are used at higher temperatures. In our work for both homopolymer brushes and bilayers of untethered chains spincoated on homopolymer brushes, exposure times mostly varied from 20 to 80 seconds or only a few minutes. Third and the strongest method is to check for changes in the correlation function with increasing exposure. This can be done by correlating different portions of the data set. Correlations for small numbers of frames show that those overlap with correlation functions calculated with more frames. If including any of the longest time frames (toward the end of the run) causes a systematic change in the correlation function, that could be due to damage and must be excluded. The remaining frames are the ones that are free of damage and is used to calculate relaxation times.

Another important issue is the relaxation of the paste that is used to improve thermal conductivity between the sample and heating block. The paste is a complex, viscoelastic material, with relaxation properties that depend on the thermal history. It has many different components some of which are lower molecular weight additive materials that can volatilize away in the vacuum, leaving a material that is still viscoelastic. These different components can show different relaxation times and if the sample that is probed has a much slower or comparable relaxation time with additives of the paste, resulting autocorrelation function could be misleading. This problem is demonstrated in Figure 3.13 that shows a bare silicon wafer run at room temperature with paste at its back side showed a paste relaxation at about 300 sec, while a bare silicon wafer run without paste at 60°C shows absolutely nothing up to 3000 seconds. This problem is overcome for homopolymer brushes by heating the samples to 230°C to remove lower molecular weight additive materials and then the XPCS

measurements are started. For bilayer films more stable paste with different components that doesn't show relaxation during the measurement is used. Relaxation time with additives of the paste, resulting autocorrelation function could be misleading. This problem is demonstrated in Figure 3.13 that shows a bare silicon wafer run at room temperature with paste at its back side showed a paste relaxation at about 300 sec, while a bare silicon wafer run without paste at 60°C shows absolutely nothing up to 3000 seconds. This problem is overcome for homopolymer brushes by heating the samples to 230°C to remove lower molecular weight additive materials and then the XPCS measurements are started. For bilayer films more stable paste with different components that doesn't show relaxation during the measurement is used.

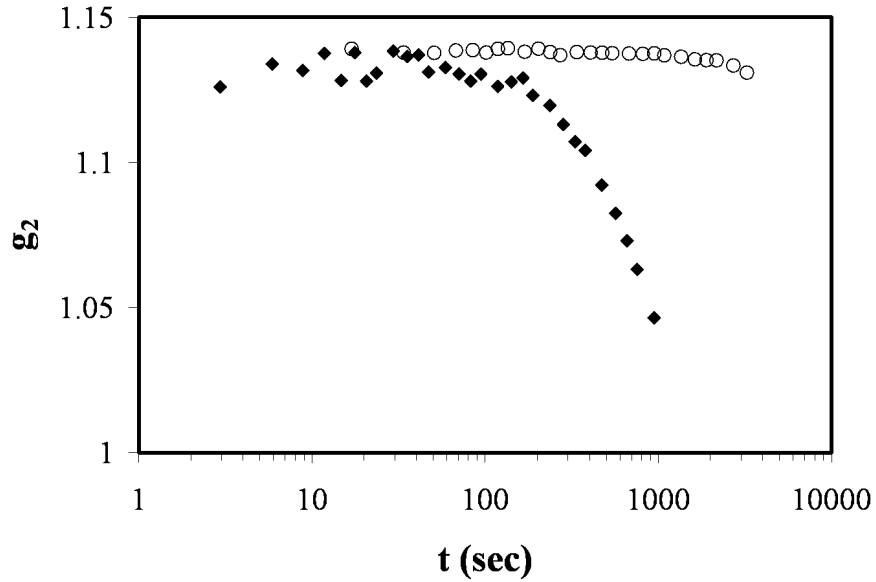


Figure 3.13: Intensity normalized time autocorrelation functions (g_2) as a function of delay time at $q_{||} = 2.9 \times 10^{-3} \text{ nm}^{-1}$ for a bare silicon wafer measured at room temperature with a paste (filled diamonds) and for a bare silicon wafer measured at 60°C without using paste (empty circles).

CHAPTER IV

INTERNAL STRUCTURE OF DIBLOCK COPOLYMER BRUSHES (DCBS) BY NEUTRON REFLECTIVITY

4.1 Experimental Study of Internal Structure of DCBs in “Dry” State

4.1.1 Internal Structure of DCBs in “as-deposited” State

As mentioned above in Chapter 1, diblock copolymer brushes (DCBs) have garnered enormous interest recently due to the observation that their surface character can be substantially altered by treatment with a solvent selective for one of their blocks. Zhao *et al.* [2] showed for the first time, using contact angle measurements and atomic force microscopy (AFM), that the surface of a polystyrene-*b*-poly(methyl methacrylate) (PS-*b*-PMMA) brush can be rearranged by changing the character of the solvent contacting the brush before it is dried. In their study, the advancing water contact angle of the surface of a PS-*b*-PMMA DCB (with the first block noted being that next to the substrate) can be changed from that characteristic of PMMA to that characteristic of PS by changing the solvent from dichloromethane, a good solvent for both polymers, to cyclohexane, a theta solvent at 35°C for the PS block ($M_n \sim 30k$) and a poor solvent for the PMMA block. They also demonstrated, using intermittent-contact mode AFM imaging, that the surface morphology changes after selective solvent treatment, forming a nanopattern at the surface. After this seminal paper, the surface rearrangement of diblock and triblock copolymer brushes have been studied by various authors using contact angle measurements, AFM, X-ray photoelectron spectroscopy (XPS), ATR-IR and ellipsometry. Sedjo *et al.* [132] synthesized the

same type of DCB of PS-*b*-PMMA using reverse ATRP and showed that the surface of a such brush reorganizes after treatment with selective solvent. Mathers and co-workers [114] synthesized polyisoprene-*b*-poly(ethylene oxide) DCBs by anionic polymerization and they proposed that the time allowed for the DCB to rearrange was not sufficient for the polar groups attached to the polymer backbone to reorganize, so the rearrangement of those DCBs was incomplete. Other groups [134–138] studied the surface rearrangement and the efficiency of switching for various monomers [136], block lengths [138], and temperatures [137]. Tomlinson [134] and Xu [138] studied the effect of block lengths on DCBs when they were treated with different types of solvents. Tomlinson *et al.* formed an orthogonal gradient DCB by the solution draining method. When the DCBs were treated with an A-selective solvent, the increase in the size of the “A” block caused an increase in the micellar core size and finally the brush formed a bicontinuous morphology. With increasing length of the “B” block, the micelles become less laterally confined. In a similar manner Xu *et al.* showed that there is a threshold thickness for the “B” block over which the surface composition cannot be driven by an A-selective solvent because the “A” block chains are not long enough to totally cover the “B” block chains. Both Tomlinson and Xu drew those conclusions by looking at scanning probe microscope images, but such images are unable to resolve the internal structure of DCBs. There was one experimental study by Devaux and co-workers [188] that probed the structure of a dense DCB. They studied, using neutron reflectivity, the swelling behavior of highly stretched PS chains grown on a silicon surface. In the case of very dense brushes (>1.0 chain/nm²) in good solvent, the highest volume fraction ever measured for polymer chains leads to a significant reduction of the swelling capacity of the layer and a noticeable deviation from classical brush scaling laws.

Theoretical work has been reported for the internal structure of DCBs that are in contact with a solvent good for both polymer blocks [189], or a solvent selectively good for one of the polymer blocks [141, 142, 190]. A variety of well-ordered structures with variations in composition in the plane of the DCBs, such as “onion”, “garlic” and “dumbbell” structures, have been predicted for low grafting density brushes and compatible polymer blocks ($\chi \approx 0$), using both scaling arguments and 2D SCF lattice calculations [141, 142], and Monte Carlo simulations [190]. These studies predict very rich phase behavior for DCBs in solvent, with the predicted morphology depending on the volume fraction (f) of one block, Flory-Huggins exchange interaction parameter (χ) between solvent and polymers, and molecular weight or length (N) of the chains. The authors have suggested that the structures that emerge from 2D SCF calculations should have cylindrical geometry. Gersappe *et al.* [190] showed that there is a lateral phase separation in an “AB” block copolymer brush forming well-defined domains rich in “A” and “B”, while brushes of random and alternating copolymer chains do not show lateral phase separation. Ferreira *et al.* [189] and Heine *et al.* [191] focused on DCBs in the melt state. Heine *et al.* [191] pointed out that the interface between the A-rich and B-rich domains will be sharper when the DCB is “dry”. Yin *et al.* [192] has done a simulated annealing study of the morphologies of block copolymer brushes in selective solvents. They observed that various morphologies can be induced by varying the solvent selectivity, polymer grafting density and block lengths, which is in good agreement with Zhulina’s simulations. Recently, Wang *et al.* [193] have investigated the microphase separation of A-*b*-B DCBs in selective solvents by single-chain-in-mean-field (SCMF) simulations. They obtained morphology diagrams in terms of the fraction of the A block (f), and grafting density (σ) in different solvents.

None of the earlier experimental studies on the rearrangement behavior of DCBs can solve the internal structure or mechanism of surface rearrangement, since the techniques they have used (contact angle measurements, AFM and XPS), are not sensitive to the internal structure in either the in-plane or normal directions. Additionally, there has been no theoretical study that considers the equilibrium structure of strongly stretched chains (with high grafting density ($\sigma = 0.6$ chains/nm²)) with incompatible polymer blocks in a solvent, especially in selective solvent. The structure of homopolymer brushes under melt conditions and in good solvents have been studied extensively and are well understood. In this part of the thesis, we focus on the internal structure of DCBs in the as-deposited state and their swelling behavior in selective and good solvents. We use NR for our study of DCB internal structure because NR can probe the structure all the way through the brush with high resolution in the direction perpendicular to the surface. Information about the film thickness, microroughnesses at the substrate/film and air/film surface and neutron scattering length density (SLD) profile, can be obtained from the reflectivity curve. NR is the superior non-destructive technique for the investigation of interfacial structures “buried” inside the film due to the larger contrast that can be obtained through selective deuteration. The depth resolution of film structure with NR is between 0.1 and 1 nm and is dependent on the range of scattering vector, q , over which data are collected. Deuteration of one component in a DCB enhances the contrast between domains rich in differing blocks and makes the interfacial region visible to neutrons in a way not generally possible with X-rays.

We have mentioned above that the phase behavior of diblock copolymer chains and DCBs depend on different parameters such as f , χ and N . The combined parameter χN is more helpful for classifying behavior, where χ represents the magnitude of enthalpic contributions to the system’s free energy depending on how

χ is defined and calculated and the magnitude of entropic contributions are reflected by N . As shown in Figure 4.1, block copolymer chains of near symmetric composition and large N order in the bulk for values of χN of order 10. Due to the influence of composition fluctuations, the value of χN above which ordering occurs, $(\chi N)_{\text{disorder} \rightarrow \text{order}}$, is even larger for smaller values of N for which fluctuations become important. The value of $(\chi N)_{\text{disorder} \rightarrow \text{order}}$ also increases as one moves away from symmetric composition. Previous NR investigations on DCBs in our group [194], have shown that the internal brush structure depends strongly on the block sequence and the value of χN .

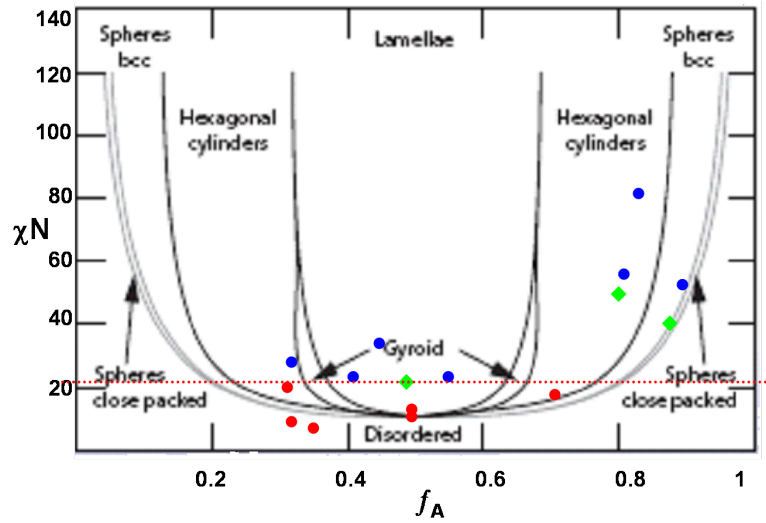


Figure 4.1: Schematic diblock copolymer phase diagram: f_A : volume fraction of A block. Known equilibrium mesophases are spheres, cylinders, gyroid, and lamellae, as well as the disordered (homogeneous) state at small χN values. Symbols (blue, red and green) on the diagram shows the samples listed in Tables 4.2 and 4.3 with corresponding χN , f values.

Since the PS-*b*-PMA block copolymer has not been widely studied, there is no published value of χ . For making rough comparisons to the behavior expected in the bulk we have thus estimated the value of χ from solubility parameter arguments.

Table 4.1: Solubility Parameters(δ (J/cm^3)^{1/2}) of Polymers and Solvents

Name	Exp. (*10 ⁻³) ^a	Hansen (*10 ⁻³) ^b	van Krevelen and Hoftyzer (*10 ⁻³) ^b
Styrene	17.6-19.8		
Methyl acrylate	20.1-20.7		
Methyl methacrylate	18.8-26.2		
Isoprene	16.2-20.5		
Cyclohexane	17.20	16.63	15.85
Acetone	20.05	19.98	18.29
Dichloromethane	19.50	20.18	20.83

^a Experimental values [195].

^b Calculated. [195]

At this level of approximation the exchange interaction parameter χ_{AB} is given by:

$$\chi_{AB} = \frac{V_r}{RT}(\delta_A - \delta_B)^2 \quad (4.1)$$

where δ_i is the solubility parameter of species i , V_r is the reference volume of a polymer segment and R is the universal gas constant. Values of solubility parameters calculated for PS, PMA and the solvents used in this work using a group additivity calculation, as described by van Krevelen, are compared in Table 4.1 with experimental values from the literature and values for two other polymers, poly(methyl methacrylate) (PMMA) and polyisoprene (PI), for which the interaction parameter with PS has been measured experimentally.

Rather than calculating the value of $\chi_{PS-b-PMA}$ simply using Eq. 4.1 we estimate it from the published values of $\chi_{PS-b-PMMA}$ and $\chi_{PS-b-PI}$. The value of $\chi_{PS-b-PMMA}$ has been determined as 0.041 at 298 K by a small-angle neutron scattering [196]. The value of $\chi_{PS-b-PI}$ has been measured by small-angle X-ray scattering as 0.14 at 298 K [197]. Using a constant reference segment volume for all values of χ , ratios of the relative magnitudes of $\chi_{PS-b-PMA}$, $\chi_{PS-b-PMMA}$ and $\chi_{PS-b-PI}$ can be calculated as:

$$\chi_{PS-b-PMA}/\chi_{PS-b-PMMA} = (\delta_{PS} - \delta_{PMA})^2/(\delta_{PS} - \delta_{PMMA})^2 = 64 \quad (4.2)$$

$$\chi_{PS-b-PMA}/\chi_{PS-b-PI} = (\delta_{PS} - \delta_{PMA})^2/(\delta_{PS} - \delta_{PI})^2 = 0.22 \quad (4.3)$$

We thus expect that a good estimate of $\chi_{PS-b-PMA}$ should be considerably larger than the value of $\chi_{PS-b-PMMA}$ (0.04) and somewhat smaller than that for $\chi_{PS-b-PI}$ (0.14). We choose a value of 0.1 for $\chi_{PS-b-PMA}$ because it lies between these experimentally known bounds even though it does not satisfy either Eq. 4.2 or 4.3. Estimates of χN are included in Table 4.2 and Table 4.3. Here in our experiments, we don't consider the effect of χ and it is kept constant and same for all samples. The red, blue and green symbols on phase diagram of diblock copolymer blends in Figure 4.1 shows the corresponding spots of our listed samples according to their χN and f_A values in which A is taken as PS. We investigated that how the diagram changes when chains are tethered which is discussed below.

4.1.2 Internal Structure of DCBs for $\chi N \leq 23$

It has been found [194] that when $\chi N \leq 23$, a model of two layers with smooth interfacial gradient provides a good description of the data for DCBs of PMA-*b*-dPS and dPS-*b*-PMA which is represented with red circles on Figure 4.1. The neutron

Table 4.2: Properties of Diblock Copolymer Brushes for PMA-*b*-dPS and dPS-*b*-PMA series

Sample	$M_{n,PMA}^a$ (kg/mol)	$M_{n,dPS}^a$ (kg/mol)	N_{PMA}	N_{dPS}	h_{PMA}^b (nm)	h_{dPS}^b (nm)	χN
PMA2- <i>b</i> -dPS4	1.8	5.7	21	51	2	4	17.2
PMA6- <i>b</i> -dPS5	4.8	5.7	55	51	6	5	10.6
PMA7- <i>b</i> -dPS2	4.8	5.7	55	29	7	2	8.4
PMA8- <i>b</i> -dPS2	6.6	3.2	76	29	8	2	10.5
dPS5- <i>b</i> -PMA2	3.9	5.1	46	49	2	5	9.5
dPS14- <i>b</i> -PMA3	5.7	14.5	66	139	3	14	20.5
dPS15- <i>b</i> -PMA4	8.6	14.5	100	139	4	15	23.9
dPS15- <i>b</i> -PMA6	8.2	19.6	95	188	6	15	28.3
dPS11- <i>b</i> -PMA8	11.1	11.7	130	104	8	11	23.4
dPS14- <i>b</i> -PMA9	12.8	119.9	152	191	9	14	34.3

^a Number averaged molecular weights were measured using GPC for free chains in solution created at the same time the brush was synthesized.

^b Thickness (h) values are from NR for the first two samples. The rest are from ellipsometry measurements.

Table 4.3: Physical Properties of Diblock Copolymer Brushes for Highly Asymmetric PMA-*b*-dPS and dPS-*b*-PMA series

Sample	$M_{n,PMA}$ (kg/mol) ^a	$M_{n,dPS}$ (kg/mol) ^a	N_{PMA}	N_{dPS}	h_{PMA}^b (nm)	h_{dPS}^b (nm)	χN
PMA10–dPS3	12	14	124	127	10	3	25
PMA5–dPS24	4.0	38.5	46	343	5	24	39
PMA9–dPS27	8.6	43.5	100	388	9	27	48
dPS39–PMA6	5	50	57	45	9	27	51
dPS43–PMA9	9	50	107	45	9	43	56
dPS54–PMA25	12	76	68	139	25	54	81

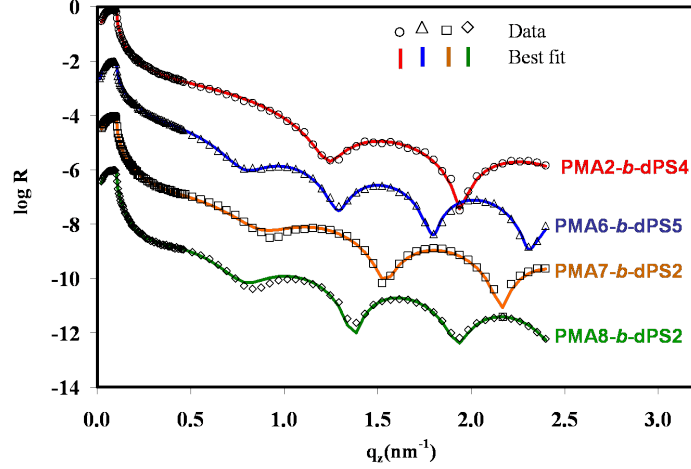
^a Number averaged molecular weights were measured using gel permeation chromatography (GPC) for free chains in solution created at the same time the brush was synthesized.

^b Thickness (h) values are from NR.

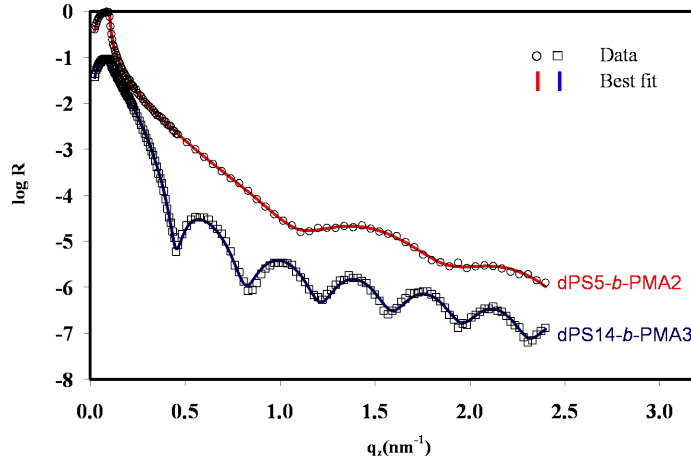
reflectivity(data points) and best fit(solid lines) curves for samples for which a two layer model could be used are shown in Figure 4.2(a) for PMA-*b*-dPS and in Figure 4.2(b) for dPS-*b*-PMA. In this two layer model, the brush structure consists of a bottom layer of one SLD, a top layer of a second SLD, and an interface between the layers created by convoluting the step change in SLD between layers with a Gaussian of appropriate width. Roughnesses at the other interfaces are modeled by convolution with appropriate Gaussian functions as well. In other words, for these series of samples a purely lamellar structure model is used even though most of the films have asymmetric composition. This suggests that the effective fields resulting from tethering to the substrate, the affinity of PMA for the substrate and the affinity of dPS for the air surface serve to force these brushes to form lamellar structures, even though equivalent, untethered diblock molecules might not do so in a bulk melt. In the SLD profiles as shown in Figure 4.3, it is observed that for the PMA-rich

layer (bottom or top) a value of SLD is obtained which is higher than the SLD value calculated for pure, bulk PMA melt at bulk density(1.15 g/cm^3) that is represented by the lower bold line. Also, the value of SLD obtained for the dPS-rich layer (top or bottom) is lower than the SLD calculated for pure dPS at a density characteristic of a bulk melt (1.14 g/cm^3) that is represented by the upper bold horizontal line. There are four possible explanations for this behavior. First, there could be substantial mixing of the two types of blocks in both layers. Secondly, the density of the brush might be markedly less than that of the corresponding polymers in the bulk. This seems unlikely and does not explain the high SLD of the PMA-rich layer. Thirdly, it is possible that when the second block was synthesized, reaction initiated not only at the end of the first blocks, but also at some sites remaining on the surface of the substrate, since only 10 percent of the initiator molecules initiate the polymerization at the first polymerization step. Finally, only 85-90% of the homopolymers reinitiate to yield block copolymer. Thus, our DCBs contain approximately 10% homopolymer brush of the “bottom” block.

The model can be elaborated to the extent that we have considered explicitly both the SiO_x on the substrate and the initiator layers. The thickness of the oxide layer is $1.2 \pm 0.2 \text{ nm}$, and the thickness of the initiator layer varies from 1.3 nm to 2 nm. The thickness of the initiator layer expected from a calculation based on the chemical structure is 2.1 nm, whereas NR measurements done on a sample consisting of only an initiator layer on a substrate yields an experimental thickness of 1.9 nm. When the thickness of the initiator layer in the model is lower than 1.9 nm, this may indicate that the grafting density of the initiator layer is lower than the maximum possible, and therefore the layer is not close packed. The presence of a loosely-packed initiator layer should not affect the final properties of the brushes significantly, so



(a)

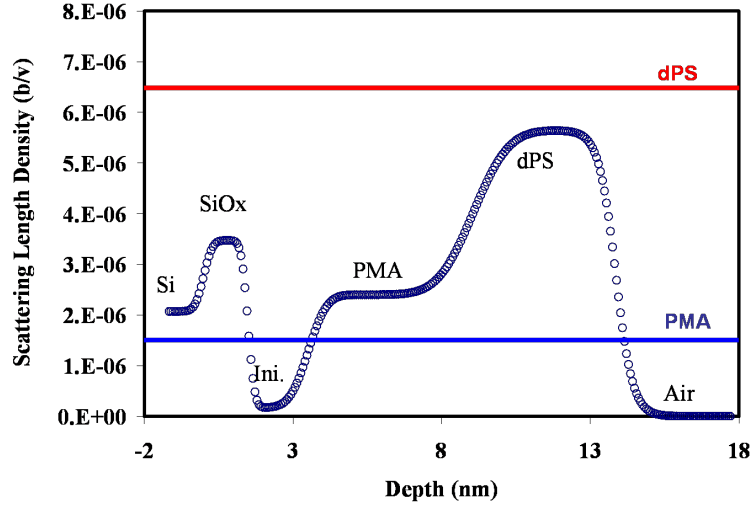


(b)

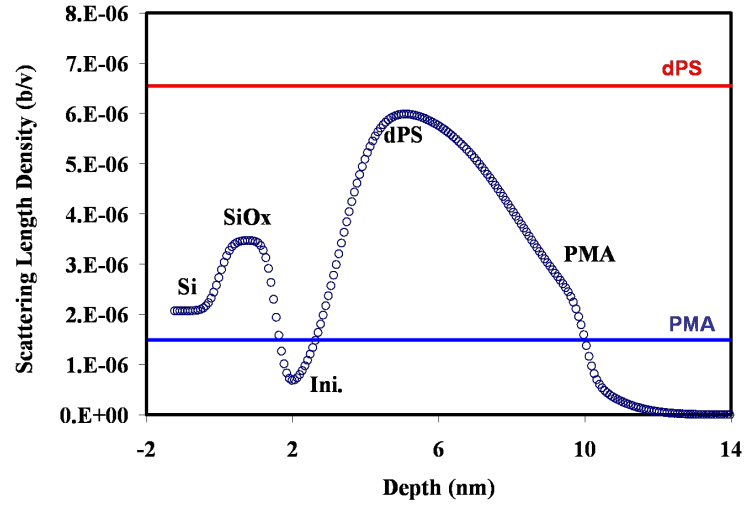
Figure 4.2: (a) The neutron specular reflectivity (open symbols) and best fit model curve are plotted as a function of wavevector in the direction normal to surface, q_z , for (a) a series of PMA-*b*-dPS and (b) the two dPS-*b*-PMA brushes indicated, fit using a two-layer lamellar model. Adjacent curves have been shifted vertically for clarity.

long as the density of initiator sites is still large enough that it substantially exceeds the grafting density of the polymer chains.

Changing the sequence in which the blocks are synthesized changes the balance among the different forces dictating the interface structure. PMA has a slightly higher surface energy (41.8 dyn/cm at 293 K) than does the dPS (40 dyn/cm at 293K), and it has a higher affinity for the substrate. Thus, it may be expected that



(a)



(b)

Figure 4.3: The scattering length density as a function of depth for (a) the PMA6-*b*-dPS5 and (b) for dPS5-*b*-PMA2 as an example samples. The text markings on the plots approximately identify the material to which that portion of the SLD profile corresponds. For example “dPS” refers to that part of the sample that is rich in dPS, not necessarily pure dPS. The upper bold line represents the calculated SLD value expected for bulk, pure dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower bold line is that for bulk, pure PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$).

even when the dPS block is tethered to the substrate, there will be some gain for the system by replacing some PMA segments at the air surface with dPS segments. Fig-

ure 4.2(b) shows the specular NR curves for dPS5-*b*-PMA2, for which χN has a value of about 9.5 and dPS14-*b*-PMA3, for which $\chi N = 20.5$. The data from both samples have been modeled using the a two layer lamellar model used for the PMA-*b*-dPS brushes which are represented by green diamonds in Figure 4.1. The thicknesses of the oxide and the initiator layer were the same as used to fit the data from the PMA-*b*-dPS series. Both data sets were fit with values of the normalized sum of squared errors of less than 0.5. The SLD depth profile for dPS5-*b*-PMA2 is given in the Figure 4.3(b). The final SLD profile does not exhibit two well-defined layers, and exhibits an interface of large width between the polymer layers. As with the thinnest PMA-*b*-dPS brush, the thinnest dPS-*b*-PMA brush contains chains that would probably not be ordered if they were not tethered. The important difference between the SLD profiles found for the brushes with dPS on the bottom and those with PMA on the bottom is that the width is larger for the dPS-*b*-PMA samples. The affinities of the dPS block for the air surface and PMA block for the substrate interface causes greater mixing than in the case of PMA-*b*-dPS samples. dPS5-*b*-PMA2 has an interface width of 4.2 nm and 60% of the film is composed of polymer/polymer interface.

Experimental interface width can be calculated in two different ways: For the first calculation method, the SLD profile is first converted to a profile of volume fraction of dPS or PMA. The composition profile in the neighborhood of the interface between the two polymer layers for PMA7-*b*-dPS2 is shown in Figure 4.4(a). There are substantial fractions of dPS segments in the PMA-rich layer and PMA segments in the dPS-rich layer. The interfacial width is calculated using Helfand's [5] convention (Fig. 4.4(b)). A tangent to the composition profile is drawn at the depth at which the composition lies halfway between its values in the two layers and extended to intersect horizontal lines corresponding to the compositions of the two layers. The projection of the distance between these intersections onto the depth axis is the

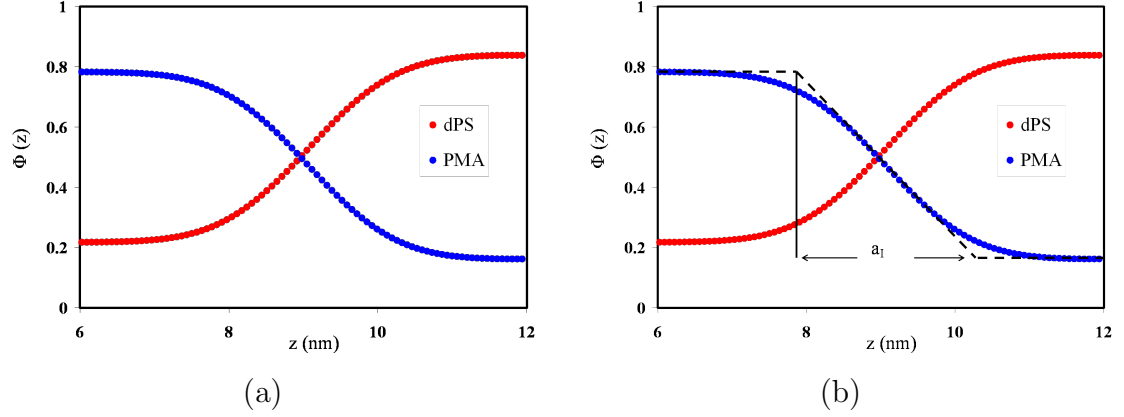


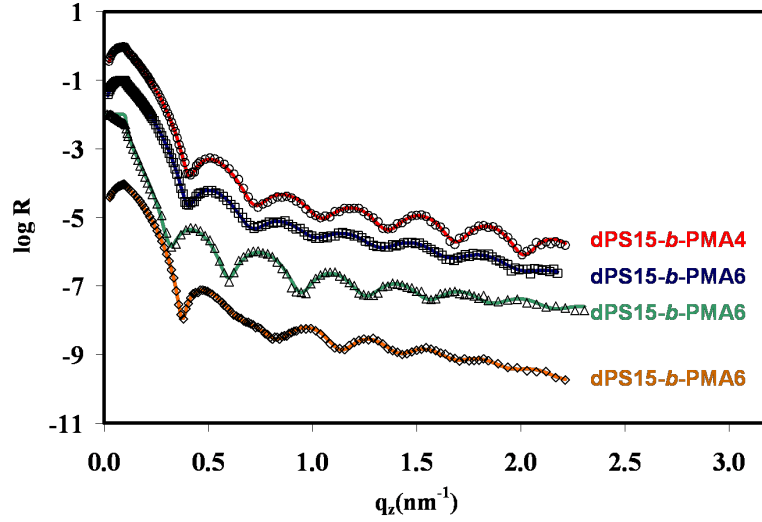
Figure 4.4: (a) The compositions of dPS(pink) and PMA(blue), expressed as volume fractions, as a function of depth, in the region of the internal interface, for PMA7-*b*-dPS2 sample. Curves are derived from SLD profile of the sample. (b) Calculation of interface width using Helfand convention [5].

interface width a_I . Another way of calculating interface width, which is used for our samples mentioned here, is to model the shape of the interfacial profile using the convolution of a Gaussian distribution with a step function. The value of full width at half maximum ($FWHM$) for the error function provides another measure of interface width. The value of $FWHM$ may be calculated by multiplying σ_{rms} by $\sqrt{2\pi}$. The interface width calculated using Helfand's convention and calculated from the latter method are almost identical. The experimental interface widths are compared in Table 4.4 with estimates from a theory of immiscible homopolymer blend interfaces which will be explained further in the following text. For the PMA-*b*-dPS series the interface width, a_I , between the polymer domains varies from 2 to 3.3 nm. For dPS5-*b*-PMA2, the value is 4.2 nm and when χN increases up to 20.5, which corresponds to the sample dPS14-*b*-PMA3, and which is the point where two-layer model no longer applies, the interface width increases up to 8.4 nm.

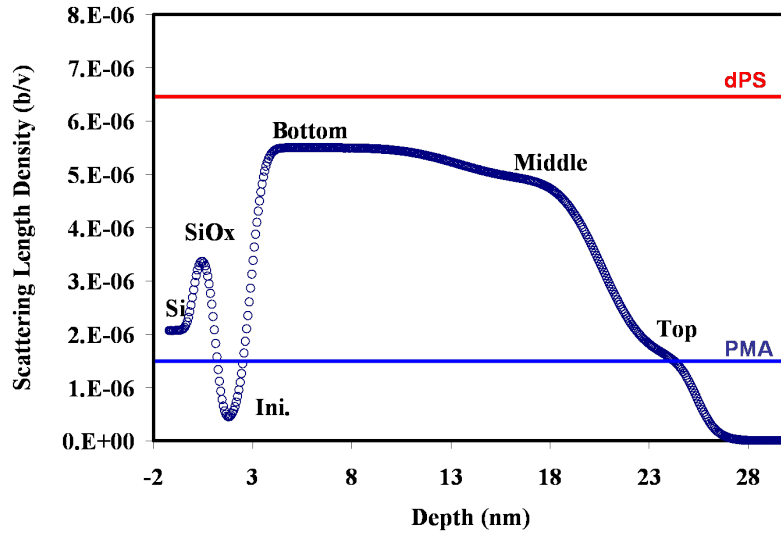
Table 4.4: Comparison of Theoretical and Experimental Interface Widths

Sample	$a_{I,exp1}$ (nm)	$a_{I,exp2}^a$ (nm)	a_∞ (nm)	$a_{I,th}$ (nm)	$(h/R_g)^2 / \chi N_{(DCB)}$	$(h/R_g)^2 / \chi N_{(PMA)}$	$(h/R_g)^2 / \chi N_{(PS)}$
PMA2-<i>b</i>-dPS4	2.2±0.4	-	1.8	2.4	0.77	0.99	0.69
PMA6-<i>b</i>-dPS5	2.4±0.8	-	1.8	2.6	1.18	1.28	1.07
PMA7-<i>b</i>-dPS2	3.3±1	-	1.8	2.6	1.26	1.75	0.54
PMA8-<i>b</i>-dPS2	2.0±0.5	-	1.8	2.6	1.0	1.2	0.54
dPS5-<i>b</i>-PMA2	4.2±0.5	-	1.8	2.5	0.65	0.21	1.36
dPS14-<i>b</i>-PMA3	8.4±1.4	-	1.8	2.7	0.84	0.22	1.32
dPS15-<i>b</i>-PMA4	4.2±1.9	5.5±1.2	1.8	2.8	0.76	0.17	1.51
dPS15-<i>b</i>-PMA6	5.8±1.8	6.6±1.0	1.8	2.8	0.65	0.39	0.83
dPS11-<i>b</i>-PMA8	4.9±1.4	5.4±2.5	1.8	2.8	0.74	0.42	1.28
dPS14-<i>b</i>-PMA9	5.5±2.8	4±0.8	1.8	2.8	0.55	0.4	0.7

^a For the samples fitted by three layer model there are two polymer/polymer interfaces. $a_{I,exp1}$ stands for the interface between the bottom and middle polymer layer and $a_{I,exp2}$ stands for the interface between middle and top polymer layers.



(a)



(b)

Figure 4.5: (a) Neutron specular reflectivity data (open symbols) and best fit model curves (solid curves) as a function of q_z for a series of dPS-*b*-PMA brushes fit using three-layer lamellar models. Adjacent curves have been shifted vertically by an arbitrary amount for clarity. (b) The SLD as a function of depth for the dPS14-*b*-PMA9 sample, for which the data have been fit using a three layer model. The bottom layer is 10 nm thick, the middle layer is 8 nm thick and the top layer is 5 nm thick. The upper bold line represents the calculated SLD value expected for bulk, pure dPS of high molecular weight and the lower bold line is that for bulk, pure PMA.

4.1.3 Internal Structure of DCBs for $23 < \chi N \leq 34$

Reflectivity data from samples with $\chi N \geq 23$ could not be fit using a two layer model; instead a three-layer model had to be used which is represented as blue circles in the phase diagram in Figure 4.1. The additional layer is located at the center of the film. The NR curves for these samples and the corresponding fits using three-layer models are given in Figures 4.5(a) and 4.5(b), respectively. The thicknesses for the oxide and initiator layers are the same as used with samples for which the two-layer model worked. The SLD of the additional layer lies between the SLD values of the d-PS rich layer and PMA-rich layer and closer to the value of dPS rich layer. There is no obvious trend in the variation of the SLD of the additional layer with the brush thickness and composition. The SLD value for the dPS-rich layer next to the substrate is similar to that seen for the two-layer models. The thicknesses obtained from NR are 10, 8 and 5 nm for the bottom, middle and top “layers” for the dPS14-PMA9 sample (Figure 4.5(b)).

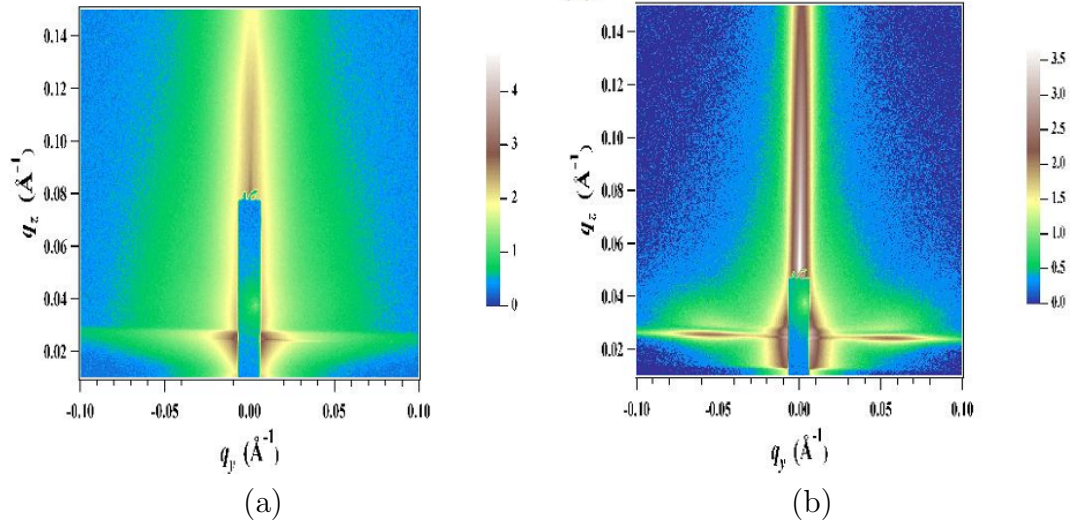


Figure 4.6: GISAXS data for (a) PMA8-*b*-dPS2 and of a (b) PMA14-*b*-PS20 DCBs. PMA14-*b*-PS20 has longer blocks and $\chi N = 29.5$. Intensity is plotted in color as a function of α_f (incident angle) and $2\theta_f$.

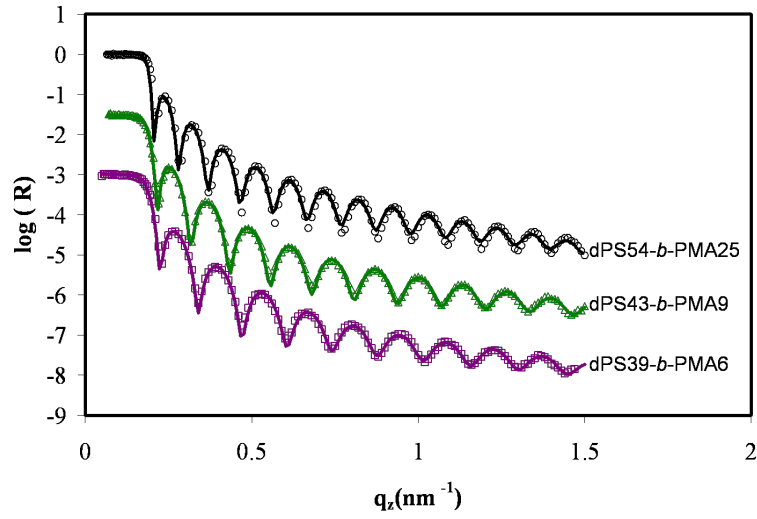
The existence of a third layer may be checked using 2D GISAXS measurements. The GISAXS data set from each of the samples with $\chi N \geq 23$ contained weak correlation peaks at nonzero values of q_y , indicating that the structure within the brush was not uniform in the plane of the sample. In Figure 4.6 there are representative images for the samples without correlation peaks and with correlation peaks. Figure 4.6(a) shows the 2D GISAXS pattern for the PMA8-*b*-dPS2 sample contains no remarkable scattering features to the left or right of the plane of incidence, which intersects the detector at the center of the image. This indicates that the structure of the PMA8-*b*-dPS2 brush is uniform along the y direction in the plane of the sample, even though it has a highly asymmetric composition. For the same diblock copolymer in bulk, one would expect to find dPS-rich spheres or cylinders in a PMA-rich matrix, since the volume fraction of dPS is 0.28. The GISAXS data pattern shown in Figure 4.6(b) belongs to a thicker sample (PMA14-*b*-dPS20) with a $\chi N = 29.5$ and shows scattering peaks to the left and right of the center. These indicate the presence of an in-plane liquid-like structure. The lateral correlation lengths, ξ of the in-plane structures were determined from the widths of the peaks using the Debye-Scherrer relation $\xi = 2\pi/\Delta q_y$, where q_y corresponds to the full width at half maximum. The value of ξ varies from 17 to 20 nm for these four samples. The position of the correlation peak gives the domain-domain distance of the in-plane structure and this spacing varies from 10 to 14 nm. Thus the ordering is limited to nearest neighbor correlation; there is no long-range ordering. NR cannot resolve the lateral variations in SLD corresponding to this structure, but it is sensitive to the laterally average structure. One feature of this laterally separated structure that the NR analysis gives us is the height of the laterally separated domains in the middle of the film. These domains appear not to extend through the entire thickness of the brush, but

rather the NR data indicate that there is a laterally uniform layer at the air surface and at the substrate interface.

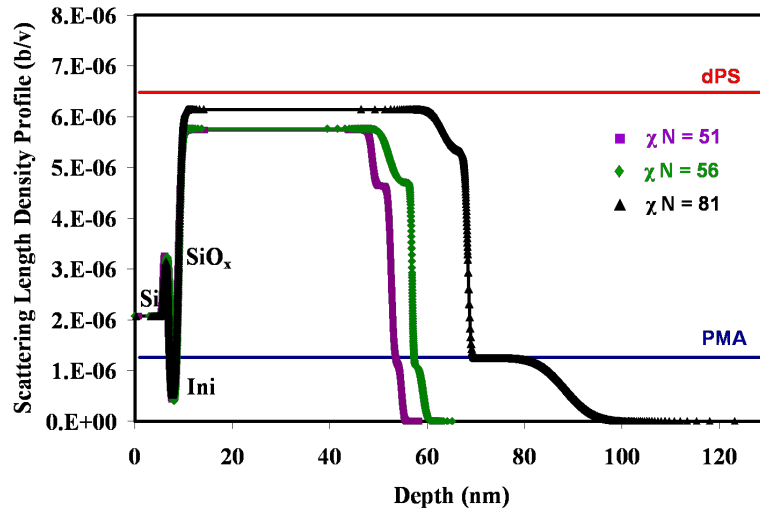
4.1.4 Internal Structure of Highly Asymmetric DCBs with High χN

For DCBs with still higher block lengths, the SLD profiles are similar to those observed for DCBs with $23 \leq \chi N \leq 34$. Properties of these samples are listed in Table 4.3. NR data (open symbols) and best fits (solid lines) curves with three layer model are shown in Figure 4.7(a) for dPS-*b*-PMA samples with χN values of 51, 56 and 81 and Figure 4.7(b) shows corresponding SLD profiles for those DCBs. There is a dPS-rich bottom layer with SLD value close to that of bulk, pure dPS and a top PMA-rich layer with a SLD very close to that calculated for bulk PMA. This suggests that on top there is a layer of almost pure PMA. This presence of this nearly pure PMA layer stands in contrast to the structure of the DCBs with three-layer structure already discussed, in which there is a mixture of PMA and dPS segments in the top layer. The reason for the difference is the difference of grafting densities of the top layers for the two sets of samples. For the previous samples, the PMA layer grafting density is half that of the bottom dPS layer grafting density. However, for these three samples, the grafting density calculated for the PMA layer is almost the same as that of the dPS-rich layer. Thus, a denser packing of PMA chains leads to a layer of mostly PMA chains, decreasing the unfavorable contact with dPS chains. In the three layer model, there is a layer with a SLD between those of the dPS-rich and PMA-rich layers, but the corresponding SLD value is quite close to that for the dPS-rich layer, implying that the layer in the middle of the film has a substantial majority of dPS chains (Figure 4.7(b)).

Changing the sequence of the blocks in highly asymmetric DCBs, from dPS on the bottom to PMA on the bottom, changes the structure markedly. As mentioned



(a)



(b)

Figure 4.7: (a) Neutron specular reflectivity (open symbols) and best fit model curves are plotted as a function of wavevector in the direction normal to the surface, q_z , for a series of dPS-*b*-PMA samples with χN values of 51 (purple), 56 (green) and 81 (black). Adjacent curves have been shifted vertically for clarity and (b) SLD profiles for corresponding DCBs.

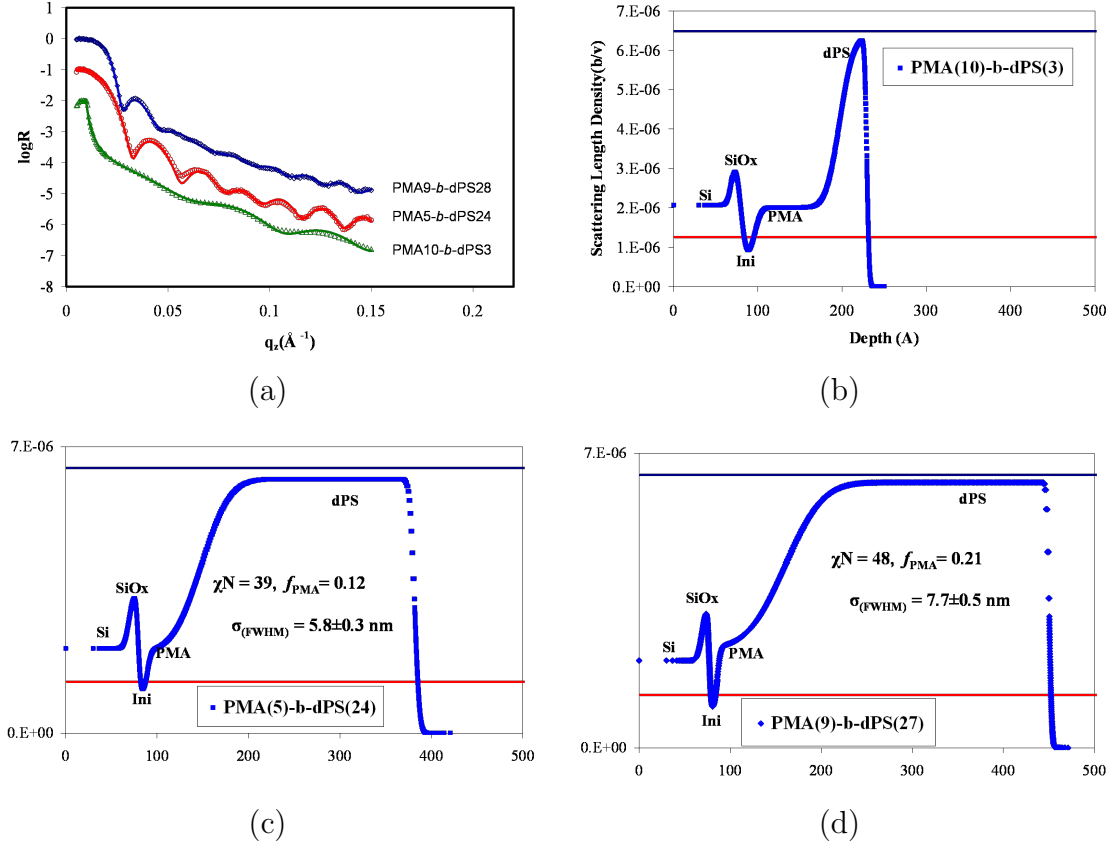


Figure 4.8: (a) Neutron specular reflectivity (open symbols) and best fit model curves are plotted as a function of wavevector in the direction normal to the surface, q_z , for a series of PMA-*b*-dPS samples with χN values of 25 (green), 39 (red) and 48 (blue). Adjacent curves have been shifted vertically for clarity and (b) SLD profiles for corresponding DCB of PMA10-*b*-dPS3 (c) PMA5-*b*-dPS24 and (d) PMA9-*b*-dPS27. Labels show values of χN and PMA fraction and $FWHM$ values mentioned here are obtained from *refit*.

in the Table 4.3 for the first three samples of the PMA-*b*-dPS series, the values of χN , are 25, 39 and 48, respectively. Above it was shown that PMA-*b*-dPS DCBs with χN values in the range of 30 to 70 show in-plane ordering. We have also mentioned above that a three layer model captures the structure of DCBs when there is large incompatibility between the blocks and the value of χN is higher than 23. So for these asymmetric samples of PMA-*b*-dPS listed in Table 4.3, we expect to get best fits to the NR data using the three-layer model. However, we get better fits when

we model our structure with two-layer models. Figure 4.8 shows the NR data and best fit model curves for three PMA-*b*-dPS samples. Figure 4.8(b) gives the SLD profile for the sample with $\chi N = 25$, obtained using a model of the brush structure consisting of a bottom layer of SLD value higher than that calculated for bulk PMA, a top layer of SLD close to that of bulk dPS and a finite interface width ($FWHM$) between these two PMA-rich and PS-rich layers which is 3.1 nm for this sample. The fact that the SLD of the layer next to air is nearly equal to that for pure dPS for all three samples is remarkable when one compares with the behavior seen in brushes with short, PS top blocks. For $\chi N = 39$ as shown in Figure 4.8(c), $FWHM$ becomes 5.8 nm and when χN reaches 48, $FWHM$ reaches 7.7 nm. The increase in interface width with increase in χN seen here is counter to what is expected in lamellar structures in block copolymers, because larger χ values lead to narrower interfaces. We haven't done GISAXS measurements on these highly asymmetric PMA-*b*-dPS samples. However, a previous study in our group [198] found that the GISAXS data sets for PMA16-*b*-dPS27 with a $\chi N = 39$ and PMA18-*b*-dPS54 with a $\chi N = 58$ both contained correlation peaks. Thus, the apparent increase in interface width with χN observed here could be due to the lateral ordering in the middle of the film. It may be that the ordering in the middle of the film is not quite sharp enough to be resolved with NR as a distinct third layer, rather can be adequately modeled, for purposes of the explaining the NR data, with simply a rather large interface width.

4.2 Theoretical Study of Interfacial Widths in “Dry” State DCBs

4.2.1 Scaling and Self-Consistent Field (SCF) Theory for Interfacial Widths in DCBs

In order to explain the interfacial widths observed experimentally, we present here a scaling theory and SCF calculations for the interfacial width in a DCB, developed by

Prof. David Wu. To better understand the dominant forces determining the width in a DCB, we first review the cases of an immiscible blend and a free diblock copolymer.

The width of an interface between immiscible blocks has been well studied in both blends of homopolymers and block copolymers. Experiments have shown that the widths observed for high molecular weight polymers are of the order of 3 to 8 nm [129, 199–201], which is consistent with the predictions of the Helfand-Tagami theory [5, 202, 203] which uses a SCF calculation to derive an expression for the interfacial width, for the case of infinite molecular weight polymers ($N \rightarrow \infty$) with equal statistical segment lengths, b ,

$$w = a_\infty = \frac{2b}{\sqrt{6\chi}} \quad (4.4)$$

where χ is the Flory interaction parameter between monomers of type-A and type-B. The proportionalities in this relationship for a blend of immiscible homopolymers can be understood using a simple scaling argument [9], in which the width is determined by a balance of chain conformational entropy and the free energy of mixing. Namely, the interfacial region is spanned by an excursion of one chain, i.e. a “blob”, say composed of N_w type-A monomers, into the region rich in type-B monomers. These fluctuations will have energy of order $k_B T$. Since the energetic penalty of having N_w type-A monomers in a B-rich region scales as $N_w \chi k_B T$, this implies $N_w \approx 1/\chi$. Inside this blob, since the interaction energy is less than $k_B T$, the conformations can be considered to be Gaussian, and thus the size of this excursion is $w \approx \sqrt{N_w} b \approx b/\sqrt{\chi}$, which is consistent with the Helfand expression up to prefactors. Furthermore, since each blob corresponds to an excess of energy on the order of $k_B T$, and occupies area $N_w/(\rho w)$, where ρ is the monomer density, the surface tension scaling is given by the ratio of the two, $\gamma \approx k_B T \rho w / N_w \approx k_B T \chi \rho w$. Substituting for the width gives

$\gamma_{AB} \approx \rho b \sqrt{\chi} k_B T$, which likewise agrees up to prefactors with the Helfand-Tagami expression [202, 203] for polymers having (nearly) equal statistical segment lengths.

$$\gamma_{AB} \approx \rho b \sqrt{\chi/6} k_B T \quad (4.5)$$

Using Eq. 4.4 with a value of averaged statistical segment length, b , of 0.71 nm appropriate for PMA and dPS yields a value for a a_∞ of 1.83 nm. This value is smaller than the experimentally measured a_I values in this work. This is to be expected, not only due to the difference between immiscible homopolymer interfaces and bulk and grafted diblock copolymer interfaces, but also because interface fluctuations due to capillary waves have been ignored in the Helfand-Tagami calculation. The effective interface width measured by NR represents a convolution of the intrinsic width and a broadening due to fluctuations [204–206] in the position of the nominal interface. A proper comparison must account for these fluctuations. For untethered chains, the mean-square displacement of the interface from its average position, $\langle(\Delta z)^2\rangle$, is given by [204]

$$\langle(\Delta z)^2\rangle = k_B T \ln(\lambda_{max}/\lambda_{min})/2\pi\gamma_{AB} \quad (4.6)$$

where λ_{min} and λ_{max} are the minimum and maximum wavelengths of the fluctuations, and γ_{AB} is the interfacial tension between immiscible homopolymers. Using the value of $b = 0.71$ nm and a value of $1/\rho_0 = 137 \text{\AA}^3$ we obtain an estimate of 2.75 dyne/cm for the interfacial tension between PS and PMA homopolymers at 25°C. To estimate the values of λ_{max} and λ_{min} we turn to the theoretical work of Fredrickson and coworkers [84] on surface fluctuations in grafted brushes. They argued that surface fluctuations (which are Rayleigh waves) with wavelengths greater than the film thickness are strongly suppressed due to the cost of chain stretching. Very short wavelength modes are also suppressed due to the action of surface tension. Thus,

there is a preferred fluctuation wavelength that should be on the order of equilibrium brush height. We take λ_{max} to be the total brush thickness, which varies from 6 to 11 nm for samples in the PMA-*b*-dPS series or 7 to 23 nm for samples in the dPS-*b*-PMA series. The value of λ_{min} is expected to be close to the intrinsic interface width and we adopt a value of 1 nm. With these assumptions we find $\langle(\Delta z)^2\rangle^{1/2} \approx 0.8$ nm. Convolution of a Gaussian distribution of interface positions with a step function profile gives an error function profile with an interface width, $a_{fluc.}$, of $\langle(\Delta z)^2\rangle^{1/2}$. Thus the interface width ascribed to interface fluctuations is about 2 nm. The overall interface width, $a_{I,th}$, is then predicted to be

$$a_{I,th}^2 = a_{\infty}^2 + a_{fluc.}^2. \quad (4.7)$$

which is listed in Table 4.4 for all the samples.

For the case of dry bulk diblock copolymers, in principle one needs to consider the possibility that chain stretching may affect the interfacial width, since the tendency towards microphase separation acts to stretch the polymer chains away from the interface. Indeed, in the strong-stretching limit, each block of a polymer chain can be considered as effectively tethered to the interface, similar to a brush. The degree of stretching, or equivalently, the areal density of chains at the interface, is given then by a competition between the free energy of the stretched chain, favoring less highly stretched chains, and the interfacial free energy, favoring more strongly stretched chains which occupy less area. This balance leads to a chain extension, corresponding to the microphase domain spacing

$$d \approx \left(\frac{\gamma_{AB} b^2 N^2}{\rho k_B T} \right)^{1/3} \quad (4.8)$$

where N is the number of monomers in a block [9]. From the equation that gives the grafting density (Eq. 1.1), $d/\sigma = N/\rho$ and Eq. 4.8 can be converted to areal density of chains,

$$\sigma = \left(\frac{\gamma_{AB} b^2 \rho^2}{N k_B T} \right)^{1/3}. \quad (4.9)$$

Despite the potential for chain stretching to play a role, for large χN ($\chi N \geq 20$), the interfacial widths in bulk untethered block copolymers predicted by the same SCF approach and observed experimentally are only slightly larger, or nearly the same, as the interface widths from the Helfand-Tagami expressions above (Eq. 4.4) for a blend of immiscible homopolymers. [129,202,203] We will see below that this is a result of the fact that a system of free diblock copolymers adjusts its interfacial areal chain density to minimize free energy, and in so doing, the portion of a chain spanning the width of the interface always has stretching energy less than $k_B T$, and is thus largely unaffected in size by the chain stretching.

4.2.2 Stretched Interface Scaling Regime

Turning now to the case at hand of the internal interface of a dry DCB, one sees that a key difference with the free block copolymer is that the grafting density is fixed, and the free energy cost of stretching cannot be compensated by an areal dilution of chains. As a result, a block copolymer can be in a state of greater stretching when covalently grafted compared to when it is untethered. The size of a tension blob, i.e. the length of chain for which the stretching energy is on the order of $k_B T$, is given by $\xi \approx \sqrt{g}b$. The number of monomers on the tension blob, g , is given by the relation $(N/g)\xi \approx d$, expressing the fact that on scales larger than ξ , the chain conformation is stretched into a line of tension blobs, [207] giving

$$g \approx \left(\frac{N b^2}{d} \right) \approx \left(\frac{\rho b}{\sigma} \right)^2 \approx N / \left(\frac{d}{R_g} \right)^2 \quad (4.10)$$

and

$$\xi \approx \left(\frac{Nb^2}{d}\right) \approx \left(\frac{\rho b^2}{\sigma}\right) \approx \left(\frac{R_g}{d}\right)R_g. \quad (4.11)$$

The interface still consists of fluctuations of the monomers of one block into the other, and we might expect that these excursions are not strongly dependent on the tension in the polymer, particularly in the limit of long chains. Then, as before, we expect that the number of such monomers is $N_w \approx 1/\chi$. This therefore leads to two scaling regimes: (i) $N_w < g$, for which the monomers in the interface are unstretched, corresponding to the conventional Helfand-Tagami regime with $w \approx b/\sqrt{\chi}$, and (ii) $N_w > g$, for which the portions of a chain in the interface exceed a tension blob and thus assume a stretched conformation, corresponding to a new *stretched interface* regime. In this stretched interface regime, the interfacial width is given by

$$w \approx \left(\frac{N_w}{g}\right)\xi \approx \left(\frac{N_w}{N}\right)d \approx \frac{d}{\chi N} \approx \frac{\sigma}{\chi \rho} \quad (4.12)$$

In contrast to the Helfand regime, where the interfacial width scales as $\chi^{-1/2}$ and is independent of areal chain density, in the stretched interface regime the interfacial width scales as χ^{-1} and is proportional to the areal chain (grafting) density, σ . Note that the independence from molecular weight is maintained since $d \propto N$. However, the threshold for crossing over into the stretched interface regime can be expressed as

$$N_w > g \text{ or } w > \xi \text{ or } (d/R_g)^2 > \chi N \text{ or } \left(\frac{\sigma}{\rho b}\right)^2 > \chi. \quad (4.13)$$

For example the interface is expected to be stretched when the square of the ratio of brush height to R_g is large compared to χN . We see that larger grafting densities favor stretching, whereas larger χ values favor narrow interfaces that even-

tually are narrow enough that the stretching energy of chains there can be neglected. These results are summarized in Figure 4.9.

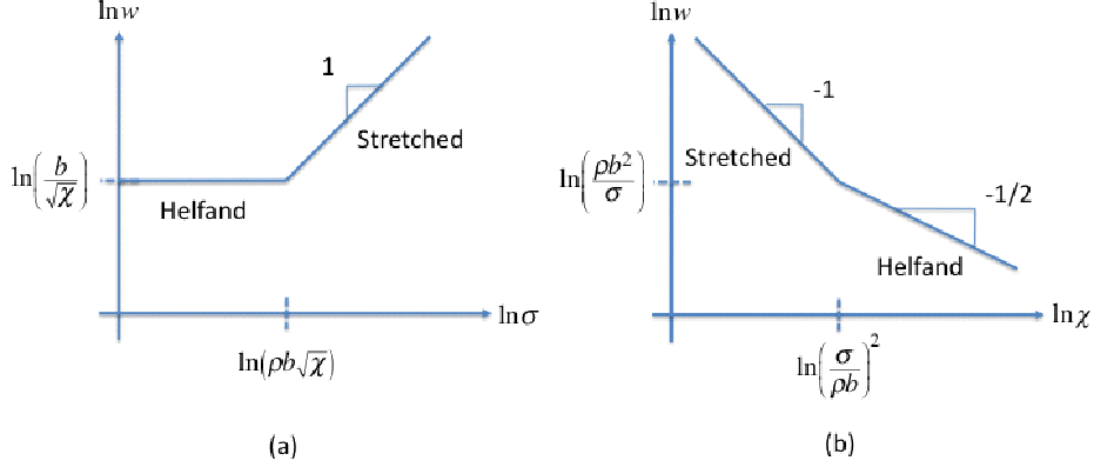


Figure 4.9: Scaling of interfacial width (w) versus (a) grafting density (σ) and (b) Flory χ parameter, showing the crossover from the Helfand regime to the stretched interface regime.

This analysis allows us to see why the stretched interface regime is not normally accessible in free block copolymer systems, but is instead limited to DCBs. For a free block copolymer to enter the stretched interface regime, the grafting density would have to satisfy $(\sigma/\rho b)^2 > \chi$. Using the expression above for σ in free diblocks and $\gamma \approx \rho b \sqrt{\chi} k_B T$ for the interfacial tension, we find that the criterion for stretched interfaces in free block copolymers reduces to $\chi N < 1$. This is incompatible with the significantly higher values of $\chi N > 10$ needed for microphase separation, and thus when microphase separation is seen, the interfaces will be in the Helfand regime.

We tested these scaling ideas against SCF calculations of DCBs with varying brush parameters. The DCB interaction free energy was modeled as

$$W[\rho_A(z), \rho_B(z)]/k_B T = \int \frac{1}{2} \nu [\rho_A(z) + \rho_B(z) - \rho]^2 + \chi \rho_A(z) \rho_B(z) dr \quad (4.14)$$

with ν an adjustable compressibility parameter and the intrinsic conformations of the diblock chains taken to be Gaussian. This leads to a self-consistent solution for the density field for A-monomers

$$\rho_A(z) = \sigma \frac{\int_0^{fN} dt q(z; t) q^\dagger(z; t)}{\int dz q(z; N) q^\dagger(z; N)} \quad (4.15)$$

and similarly for $\rho_B(z)$, where f is the fraction of monomers which are A-type. The reduced propagators $q(z; t)$ and $q^\dagger(z; t)$, starting from the grafted chain end and the free end, respectively, satisfy the modified diffusion equations

$$\begin{aligned} \frac{\partial q(z; t)}{\partial t} &= \frac{b^2}{6} \frac{\partial^2 q(z; t)}{\partial z^2} - \mu(z; t) q(z; t), \\ \mu(z; t) &= \begin{cases} \mu_A(z) & 0 \leq t \leq fN \\ \mu_B(z) & fN \leq t \leq N \end{cases} \end{aligned} \quad (4.16)$$

in the chemical potential fields $\mu_K(z) = \delta W / \delta \rho_K(z)$, with $K = A \text{ or } B$ and δW is the change in free energy. The grafting condition at one end only is enforced by the initial conditions $q(z = 0; t = 0) = 1, q(z \neq 0; t = 0) = 0$ and $q^\dagger(z; N) = 1$, and the boundary conditions $q(z < 0; t) = q^\dagger(z < 0; t) = 0$ and $q(z > L; t) = q^\dagger(z > L; t) = 0$ define a box with walls at $z = 0$ and $z = L$. To mimic the effects of cohesion in a dry brush, the box length L was taken to be the expected height h of a brush having a density equal to that of a melt, with a compressibility parameter ν taken large enough that the density profile is fairly flat. A separate comparison was done with a strictly incompressible SCF theory that produced consistent results. Details of the calculation method can be found in elsewhere [191].

Figure 4.10 shows the SCF results for the interfacial width versus grafting density, Flory χ parameter, and number of monomers. Overall, there is quite good

agreement with the predictions of the scaling theory, which neglects variations in chain extension both between chains and along a single chain. The width shows a clear crossover from grafting density independence in the Helfand regime to a width that increases with grafting density. Likewise, the dependence on the Flory χ parameter shows a break between two slopes, which are close to the predicted scaling slopes of -1 and -1/2. Finally, as expected according to the scaling theory, there is negligible dependence on the molecular weight throughout both Helfand and stretched interface regimes.

4.2.3 Comparison Between Experiment and Theory

In order to make comparison with theory, we estimate stretch ratios, of $(h/R_g)^2$ to χN , to determine which brush samples may be close to or in the stretched interface regime. From the SCF calculations and within uncertainties, we would expect the crossover to the stretched interface regime to occur at values of stretch ratio around 0.2 to 2. As mentioned above, the relative stretching is non uniform in a brush, and tends to be stronger near the grafting point than near the free end, and so Table 4.4 lists values of this ratio for each block as well as for the brush taken as a whole. The stretch ratio of the grafted block (0.7 - 1.75) clearly shows stronger stretching than in the free block (0.17-1.07), while the range for the brush taken as a whole was from 0.55 to 1.26, with the largest values occurring for the samples PMA7-*b*-dPS2 and PMA6-*b*-dPS5. For each sample, the experimentally measured interface widths are listed along with, as a reference, the Helfand widths and Helfand widths corrected for fluctuations in Table 4.4.

Of the four brushes with grafted PMA blocks, the two samples with the largest stretch ratio do in fact show the greatest ratio of experimental widths to the Helfand widths corrected for capillary fluctuations, as shown in Figure 4.11. Of the

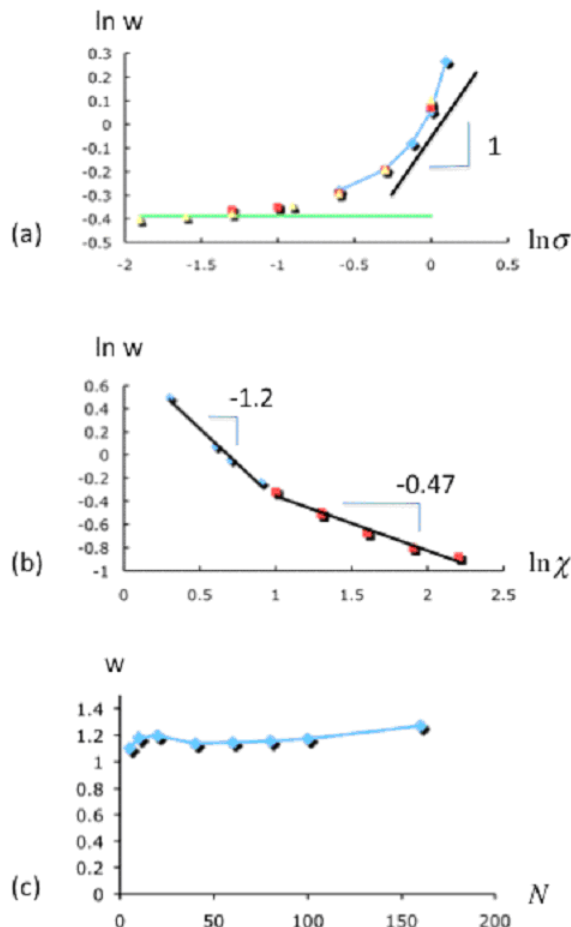


Figure 4.10: Results of SCF calculations for the interfacial width, w , versus (a) grafting density (σ), (b) Flory χ parameter, and (c) number of monomers N . The lines in (a) illustrate the expected slopes from scaling; the lines in (b) are best linear fits whose slopes are displayed.

samples with grafted dPS blocks, it should be noted that only dPS5-*b*-PMA2 and dPS14-*b*-PMA3 were well described by a single interface, with the interface width for dPS14-PMA3 being strikingly large. (As discussed below, the remaining samples have more complicated structures that are three-dimensional.) With the samples for which dPS is grafted to the substrate, it is more difficult to establish a trend, since there are only two points. However, we can make two observations. First, the ratios of experimental to theoretical interface widths for these samples are much higher

than for the samples in which the PMA block is grafted. Secondly, this ratio of experimental to theoretical width does increase with stretch ratio, and much more sharply than for the brushes with PMA grafted to the substrate. We conjecture that the sequence of blocks in the chain is extremely important. Since the dPS block is preferred at the surface the block sequence in PMA-dPS samples leads more readily to well-defined lamellar structures. In dPS-*b*-PMA samples the drive to place dPS segments at the surface leads to much broader interfaces.

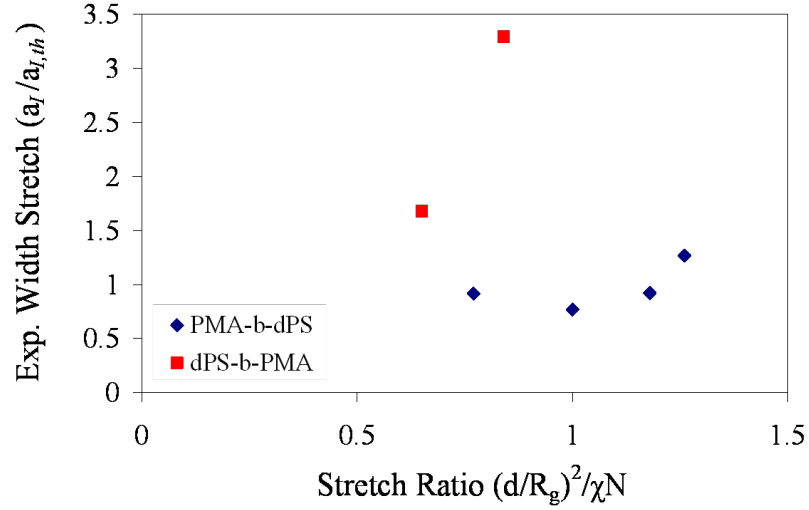


Figure 4.11: Segment density of PMA (filled circles) and dPS (empty circles) as a function of depth for the PMA6-*b*-dPS5 brush calculated using SCF theory. Grafting density for the diblock was taken to be 0.7 (chains/nm²) and that for the PMA and dPS homopolymers 0.1 (chains/nm²).

While the calculated Helfand interface widths corrected for fluctuations, $a_{I,th}$, are generally in the same range as experimental values of a_I for the PMA-*b*-dPS series, they are noticeably lower than experiment for the dPS-*b*-PMA series. Since the dPS blocks are attached to the substrate, but dPS is enthalpically preferred at the air surface, the two blocks mix more than they would otherwise, broadening the interface. The cost for dPS chains to stretch away from the tethering sites is compensated by the reduction in surface tension accomplished by putting dPS segments at the

surface. A possible contributing factor towards explaining the discrepancy between the experimental and theoretical a_I values is that the theoretical calculations do not take into account the existence of additional interfaces on either side of the interface of central interest. Details of these other interfaces have the effect of imposing additional biasing fields on the polymer chains in the brush.

Direct comparison between experiment and SCF theory calculations using experimental parameters have been attempted for two samples: dPS5-*b*-PMA2 and dPS14-*b*-PMA9. As explained below, two approximate methods were used to model the sharp surface of a dry brush. In the first approach, the polymer was assumed to be at the bulk density resulting from cohesive forces, and this constrains the brush height. Density fluctuations are accounted for by a compressibility factor. This was the approach taken in Ref. [191], and can account for tethering and additional effects at the substrate and air interfaces through the use of effective surface potentials. In the second approach, the DCB is considered to be in the presence of nonpreferential solvent. The interface width is obtained as a function of the interaction parameter between the solvent and the block copolymer. The dry brush case is taken to be the limit of poor solvent. However, since the calculation becomes more difficult as the solvent quality becomes poorer, the value of interface width for the case of the dry DCB is obtained by extrapolation (calculation performed by Prof. Qiang Wang at Colorado State University). The two methods of accounting for the behavior of a dry DCB produce consistent values of the interfacial width.

Here we compare the experimentally measured values to interface widths calculated with SCF theory [191] using the first approach, which accounts for the tethering at the substrate interface, but does not attempt to capture the differing affinities of the two blocks for the substrate and air interfaces. Another feature of the actual sample captured in this calculation is the existence of grafted homopolymer in

the brush. We have assumed for purposes of this calculation that the DCB contains about 10% homopolymer brush [185] having repeat units the same as those in the first block of the block copolymers. The segment density depth profiles for PMA and dPS calculated using parameters characteristic of the PMA6-*b*-dPS5 sample are shown in Figure 4.12. The overall grafting density has been taken as 0.8 chains/nm² and the grafting density of the diblock chains as 0.7 chains/nm² (i.e. only 7 of 8 chains of the first block synthesized are assumed to reinitiate.) The value of interface width (defined according to Helfand's convention [5]) derived from Figure 4.12 is 4.0 nm. The SCFT using the nonselective solvent gives an equivalent extrapolated interface width. This is larger than the experimentally observed value of 2.4 ± 0.8 nm.

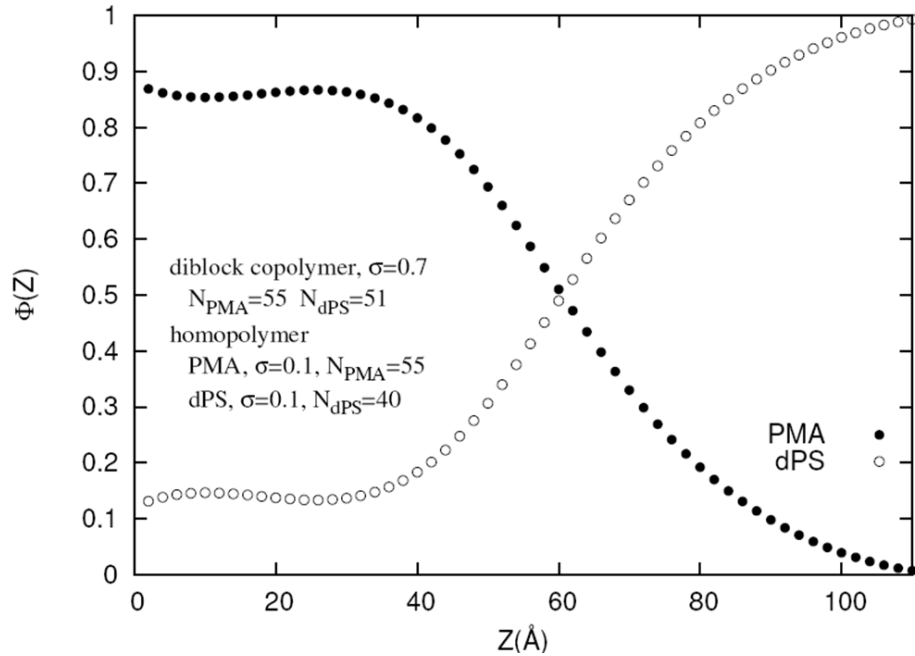


Figure 4.12: Plot showing positive correlation between the ratio of observed interfacial width to the Helfand width, and the stretch ratio $(h/R_g)^2/(\chi N)$ for PMA-*b*-dPS DCBs, in qualitative agreement with the scaling theory.

In fact, the calculation is insensitive to the order in which the blocks are located in the chains, so that an interface width of 4 nm is found from an SCF

theory calculation also for the corresponding brush with the PS block tethered to the substrate. In the calculation it is assumed that the dPS segregates preferentially to both air and substrate interfaces. The failure of the SCFT to pick up the key dependence of interface width on identity of the block tethered to the substrate can be remedied by adding pertinent surface tension values to the calculation. This extension is beyond the scope of the current work.

The interface widths found by the second SCF theory method for dPS5-*b*-PMA2 and by the first SCF theory method for dPS14-*b*-PMA9 are the same: 4 nm. The experimental interface width for dPS5-*b*-PMA2 (4.2 ± 0.5 nm) is consistent with the interface width obtained by SCFT. It is very difficult to make comparisons between theory and experiment for samples that have in plane ordering such as dPS14-*b*-PMA9. SCF theory calculations are still in progress and we believe the SCF theory results will be improved by adding differing affinities of the two blocks for the substrate and air interfaces.

The most meaningful comparisons, however, will require 3-D calculations. The SCF theory described here assumes that the brush structure is laterally homogeneous. GISAXS measurements have shown, though, that the sample dPS14-*b*-PMA9 is not laterally uniform. In fact, in general the internal structure of brushes with thickness $h \geq 19$ nm cannot be described by one dimensional models that account only for layering in the z-direction. Rather, a 3-D model of internal structure is required.

It may not be thickness that determines whether a 3-D structure is formed by the brush. For a series of brushes in which the grafting density is held constant chain length N increases with thickness. Thus, the thicker brushes are those with larger values of the parameter χN , which measures the propensity of the diblock chains to order into domains. Presumably, at low values of χN a lamellar geometry can

be imposed on the ordered material by tethering to a flat substrate and the penalty against curvature imposed by the polymer/air interface, even if the composition of the chain is far from symmetric. Once χN becomes large enough (> 23) the drive to reduce contacts between unlike segments is sufficient to force the formation of curved interfaces within the brush, despite the planar geometry imposed at the top and bottom interfaces. The observation of 3-D structures in this case has been confirmed by GISAXS studies which were already explored in the thesis of Bulent Akgun [198].

To conclude, in this part of the “dry” state structure of DCBs, neutron reflectometry measurements have revealed the details of the internal structure of dPS-*b*-PMA and PMA-*b*-dPS DCBs. For the brushes with dPS and PMA blocks, which are characterized by a moderate block-block χ parameter, sufficiently thin brushes adopt a lamellar internal morphology even when the chain composition is quite asymmetric. This layering results from the effective biasing fields imposed by the tethering, the affinities of each block for a given interface and the van der Waals interactions of the polymers with the substrate. For brushes characterized by values of $\chi N \approx 7$ -22 each layer in the lamellar structure contains a substantial volume fraction of each block. The width of the internal interface for PMA-*b*-dPS samples is equal to that expected in an ordered bulk mesophase of an untethered analog of the brush chain, whereas it is greater for dPS-*b*-PMA samples than for untethered chains. This is due to the affinities of the two blocks for opposite interfaces and this feature was not considered by previous theories. For brushes with sufficiently high values of χN (> 23), the internal structures in the as-deposited DCBs can no longer be represented with lamellar models, but rather in-plane variations in the composition must be considered. For DCBs with still higher block lengths ($50 > \chi N > 23$), the profiles are still shows three layer model. However, changing the sequence for highly asymmetric DCBs, better fits are obtained with two layer model. χN values, the

increase of interface width χN , and correlation peaks observed with GISAXS peaks suggest that the ordering in the middle layer of the film is not quite sharp enough to be observed by NR as a distinct third layer but modeled with a large interface width.

Consideration of a scaling theory for the interface width in DCBs provides some insights. Specifically, it identifies two regimes in the dependence of interface width on grafting density and on χ . For lower grafting density interface width is weakly dependent on σ . When σ is sufficiently high to cause strong stretching, the interface width increases markedly with grafting density. When χ is small, the interface width varies as χ^{-1} . For large χ , the exponent is about -0.5 as anticipated by Helfand. Interface width is mostly independent of N . Comparisons show qualitative consistency between the experimental trends in interface width and those predicted by a scaling theory, but a more rigorous validation would require further careful measurements. A particular characterization challenge is the unambiguous identification of the grafting density. This issue is further complicated by the possibility that polymerization of some of the second block is initiated on the grafting surface while attempting to grow it from the living ends of the first block. Moreover, there is currently a limited range for the control of grafting density. An alternate route to test the stretched interface regime is to use blocks with smaller values of χ . Larger values of χ will also aid in mapping out the crossover from the classical Helfand regime to the stretched interface regime.

SCFT calculation of the interface width for a sample with PMA tethered to the substrate estimates an interface width larger than the experimental width, while an analogous calculation for a sample with the dPS block tethered to the substrate agrees well with experiment for dPS5-*b*-PMA2.

4.3 Swelling Behavior of DCBs

Zhao *et al.* [2] showed for the first time, using contact angle measurements and atomic force microscopy (AFM), that the surface character of DCBs can be substantially altered by treatment with a solvent selective for one of their blocks. However, the surface characterization techniques they used are only very sensitive to the structural changes at the topmost layer. They offered speculations about the internal structures based on the results from those techniques. Another limitation of their work was that the DCBs were exposed to solvents, then taken out from the solvent, dried with nitrogen and the characterization with AFM or contact angle measurements done in the dry state. However, upon rapid removal of the sample from its solvent bath and the concomitant rapid evaporation of solvent from the brush surface and interior, the brush may vitrify into a non-equilibrium morphology if one or both of the blocks can vitrify. To what degree the dry morphology is templated by the “wet” morphology is not known. In other words, to date, neither the “as-deposited” structure nor the “switched” structure has been established. The mechanism of the surface rearrangement remains to be elucidated as well. Clarifying the structures of the “as-deposited” states in the previous sections was the first step to understanding and controlling of surface rearrangement. The second step is to elucidate the structure of DCBs when swollen with solvent. For swelling measurements we used the special cell described in Chapter 3 and shown in Figure 3.7. Measurements were done *in-situ* using this cell in the NG7 reflectometer at NIST.

Solvents used for swelling were selected by considering the chemical structures and solubility parameters of the two blocks. The heat of mixing varies approximately with the square of the difference of solubility parameters $((\delta_p - \delta_s)^2$, where δ_p is the solubility parameter for polymer, and δ_s that for the solvents). When the solubility

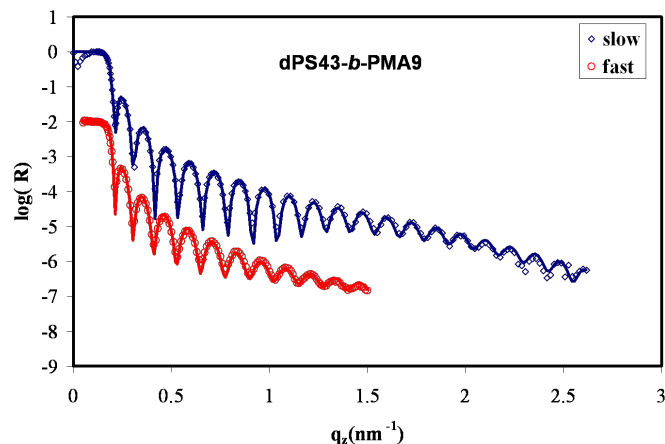
parameters of polymer and solvent are nearly equal, polymer and solvent will be miscible. Homologues and chemically similar compounds are generally miscible (though in the case of polymer/polymer mixtures very subtle differences in monomer shape can lead to immiscibility). Solubility parameter values for the polymers and solvents we used are shown in Table 4.1. Solvents for switching experiments were chosen so that DCBs of A-*b*-B were treated with a solvent that is a good or theta solvent for the “A” blocks and a non-solvent (poor) for the “B” blocks. Cyclohexane is a theta solvent for PS and poor solvent for PMA at room temperature, which makes it a selective solvent for a PS-*b*-PMA DCB. Acetone, on the other hand, is a good solvent for PMA and a poor solvent for PS and therefore selective for PMA-*b*-PS. Dichloromethane is a good solvent for both blocks. Deuterated solvents were used for *in-situ* measurements of swelling because the labelling offers a good neutron scattering contrast between the solvent and the chains.

Zhao *et al.* [2] presented two ways of swelling of DCBs in selective solvent. In the first path, “fast” swelling, they immersed the sample in cyclohexane at 35°C for 1 h and removed from solvent, dried under air and did contact angle and AFM analysis. For the second path, “slow” swelling, the sample was immersed in a mixture of dichloromethane and cyclohexane at 35°C for 30 min. Half of the mixed solvent was replaced with an equal volume of pure cyclohexane and the sample allowed to remain the solvent mixture of new composition for 30 min. at 35°C. This procedure was repeated until the ratio of cyclohexane to dichloromethane was $> 99.5 : 0.5$ (v/v). The sample was treated in each solvent composition for 30 min. at 35°C. They found that with the first path, the surface became relatively rough, with the rms roughness changing from 0.7 nm to 1.8 nm. However, with the second path the rms roughness increased much more to 13 nm, and an ordered structure was created on the surface. They observed that there was an array of “bumps” on the surface, and

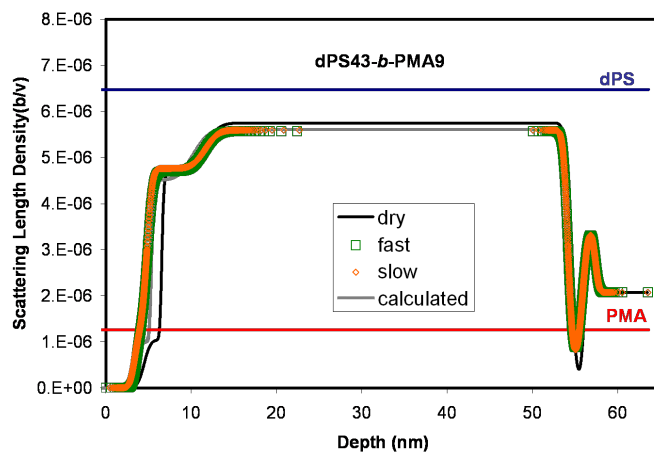
they conjectured that the “bumps” were associated with micelles with an ellipsoidal shape. They speculated that this is a result of the PS block forming a layer around a collapsed PMA core. This speculation about the internal structure, which was based on AFM and contact angle measurements was not elaborated for either state. Thus, we want to investigate first the internal structures after both fast and slow swelling before we consider *in-situ* study of the swollen structure that exists next to liquid solvent.

To observe if there is a difference in the internal structure of DCBs depending on the way in which the DCB is swollen, we did NR measurements of the DCBs in the dry state after “fast” and “slow” swelling as done in Zhao’s work. For a DCB of PS43-*b*-PMA9, NR curves and SLD profiles are shown for the different states in Figures 4.13(a) and 4.13(b). The first observation is that the three layer model still captures the data even after solvent treatment for both cases. Both ways of solvent swelling give a structure very similar to that after annealing. Secondly, the thickness increase after solvent treatment is 2.4%. Since these were measured ex-situ this increase is due to residual solvent remaining in the brush.

The dashed curve is a hypothetical SLD calculated based on the observed thickness increase with an assumption that solvent is equally distributed among the layers. This calculated profile is very similar to the experimental data after solvent treatment which means that solvent is nearly equally distributed through the sample. For the bottom, dPS-rich layer, the calculated SLD value matches the SLD value observed for the dPS-rich region SLD of after swelling structure. The SLD of the middle layer is just slightly higher than that in the calculated SLD which means there are more deuterated PS chains in that layer because with hydrogenated solvent, an increase in SLD is only possible with addition of dPS chains. These could be dPS chains from the dPS-rich region that are incorporate into the domains while the



(a)

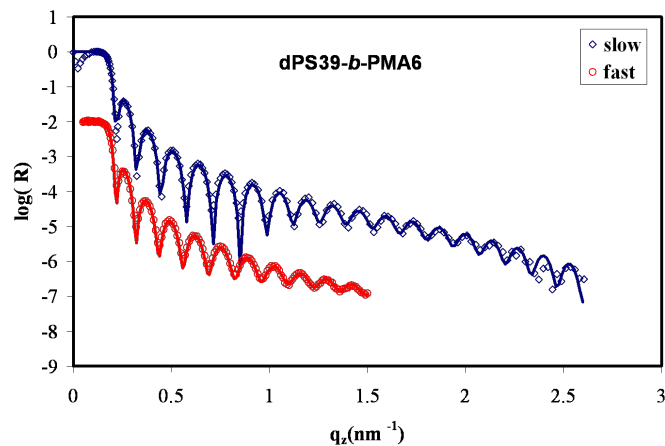


(b)

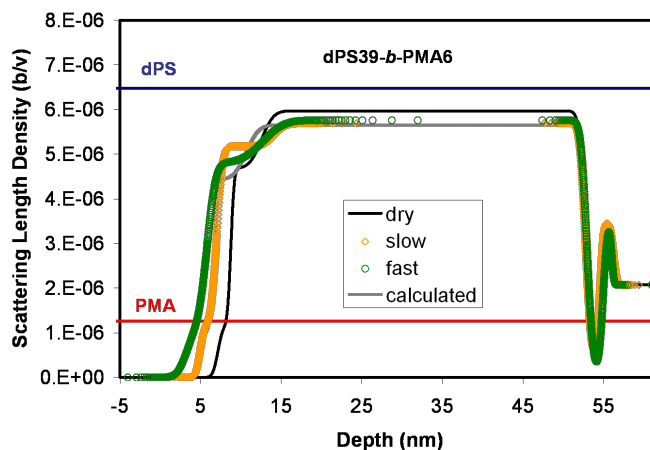
Figure 4.13: (a) Neutron specular reflectivity (open symbols) and best fit model curves as a function of q_z , dPS43-*b*-PMA9 in the dry state after “slow” (blue) and “fast” (red) swelling in d-cyclohexane. (b) The neutron SLD as a function of depth for dPS43-*b*-PMA9 in the dry state after annealing (black solid curve), after “fast” swelling (green square), after “slow” swelling (orange diamond). Dashed curve corresponds to a hypothetical SLD, calculated assuming that the solvent is equally distributed among the layers. The upper blue line represents the calculated SLD value expected for bulk, pure, high molecular weight dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower red line is that for bulk, pure, high molecular weight PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$)

structure is swollen. The transition in SLD to the top PMA-rich layer is broader than in the hypothetical profile with uniform solvent distribution. Thus, the PMA-rich layer is not as distinctly defined after the DCB has been swollen as it is in the annealed dry state. Instead, the interface disappears and the PMA-rich layer mixes into the broad interface for the solvent treated structure.

For the PS39-*b*-PMA6 DCB, the structures after “fast” and “slow” solvent treatments are different, as shown in Figure 4.14(a) and 4.14(b). Even the thickness increases for the two states are different. These are 9.1% and 5.4% after the “fast” and “slow” treatments, respectively, the solvent retention in this sample is much higher. As in the figure for the previous sample, the dashed curve is the hypothetical SLD based on a 5.36% thickness increase due to solvent distributed uniformly through the sample. First, we make some observations on the dry structure. The SLD in the dPS-rich region for the dry sample is once again substantially below that for pure high molecular weight dPS. It is about the same as for the dPS43-*b*-PMA9 sample. The interface between the middle and top layer is quite sharp and the top, PMA-rich layer is quite thin. The general shape of the SLD profiles for the two samples are quite similar. Then we consider comparison of the structures after swelling and removal from solvent with the hypothetical uniform swelling SLD. The SLD for the dPS-rich region in the hypothetical profile matches with that of the dPS-rich region “slow” solvent treatment. After both the “fast” and “slow” solvent treatments, the middle layer has higher SLD than in the annealed state structure, and the middle layer is broader. This is similar to what is seen in the dPS43-*b*-PMA9 sample. However, the middle layer is thickened more with swelling for this sample. The dPS chains in the bottom layer apparently swell and extend and more segments from those chains are incorporated into middle layer after swelling. The interface between the middle layer and the thin, PMA-rich layer is sharper after the “slow” solvent treatment than after



(a)



(b)

Figure 4.14: (a) Neutron specular reflectivity (open symbols) and best fit model curves as a function of q_z , for dPS39-*b*-PMA6 in the dry state, and after “slow” (blue) and “fast” (red) swelling in *d*-cyclohexane. (b) The neutron SLD as a function of depth for dPS39-*b*-PMA6 in the dry state after annealing (black solid curve), after “fast” swelling (green circle), after “slow” swelling (orange diamond). Dashed curve corresponds to a hypothetical SLD, calculated assuming that the solvent is equally distributed among the layers. The upper blue line represents the calculated SLD value expected for bulk, pure, high molecular weight dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower red line is that for bulk, pure, high molecular weight PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$)

the “fast” treatment. After the “fast” solvent treatment the interface between the middle and top layers disappears and the PMA-rich layer is no longer distinguishable from the air interface. These studies show that the “middle” layer, where the SLD is consistent with domains rich in one block in a matrix rich in the other block, persists after swelling, even though the top layer becomes less distinct with swelling. It is unlikely that in the short time available during the rapid solvent removal (as the sample taken out of the beaker) the segments of the two blocks could demix to sharpen the interface to its equilibrium dimension. Likewise, it is unlikely that domains favored in the solvent-free state could form during the rapid solvent removal. If there are domains present after the collapse, they were probably present in some form when the brush was swollen. To what degree the dry morphology is templated by the “wet” morphology in liquid solvent before solvent evaporation is difficult to determine. To determine that we need to see the structure next to solvent with in-situ swelling measurements.

NR curves and SLD profiles for two dPS-*b*-PMA brushes measured *in situ* while swollen with liquid d-cyclohexane are shown in Figures 4.15 and 4.16, respectively. The SLD profiles from the dry films have been reproduced here for convenience of comparison. They appear flipped horizontally because now the medium through which the neutron beam comes is with silicon substrate. We note once again that the SLDs of the dPS-rich regions do not quite reach up to the value expected for pure dPS, indicating that about 0.3 volume fraction of the bottom layer is PMA homopolymer or PMA block in the dry brush. There is a very thin layer of PMA next to the air. The SLDs of the dry states reach zero where they come to the air surface (right side of the plot). However, the SLDs of the d-cyclohexane treated DCBs end at a very high value of SLD which is the SLD of d-cyclohexane ($b/V=6.67 \times 10^{-6} \text{ \AA}^{-2}$) because the DCBs are sitting next to pure d-cyclohexane. When a DCB is swollen

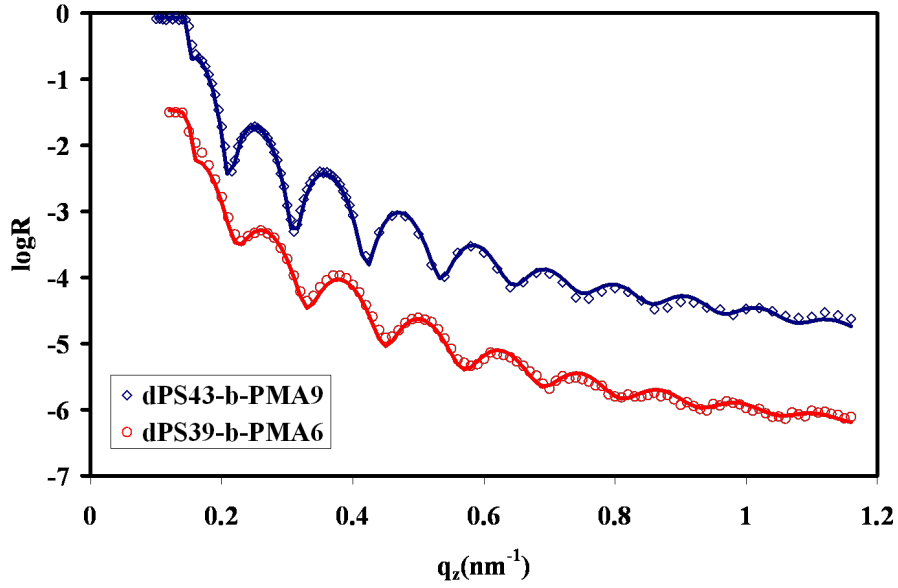
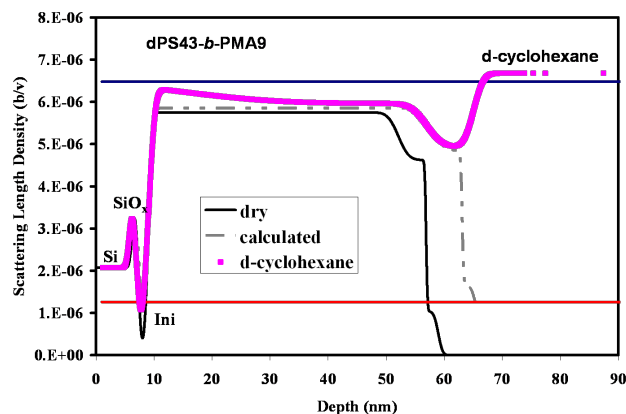
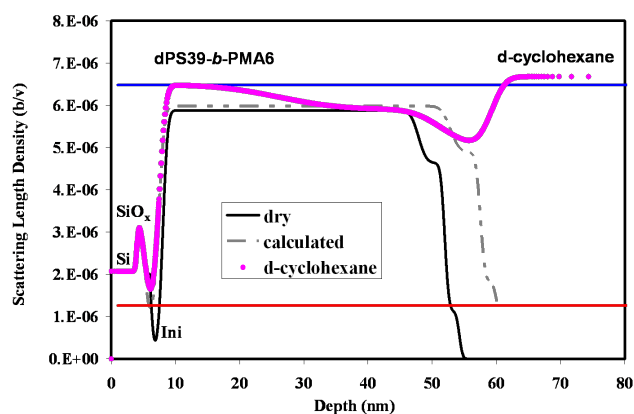


Figure 4.15: Neutron specular reflectivity (open symbols) and best fit model curves as a function of q_z , for dPS43-*b*-PMA9 (blue) and dPS39-*b*-PMA6 (red) DCBs measured in situ in contact with liquid d-cyclohexane after 6 hours of equilibration. Adjacent curves have been shifted vertically for clarity.

with d-cyclohexane, a three layer model is still needed to fit the data, but the layer configuration is totally different than that of the dry structure. When swollen with d-cyclohexane, the dPS-rich layer has a uniform SLD which can be described by imagining that the layer is split into two layers with a broad transition from the SLD of the one layer to the SLD of the other. Then one must envision a third layer at the surface. All through the brush the SLD increases due to the presence of solvent. The greater increase in SLD of the dPS-rich region next to the substrate means that the solvent goes there preferentially. The differential in swelling in different parts of the dPS-rich region indicates that although the SLD in the entire dPS-rich region can be modeled as uniform when the DCB is dry, the structure may not be the same all the way through that region. What is clear at this point is that the NR data can be much better fit using a model with nonuniform SLD in the dPS-rich region. However,



(a)



(b)

Figure 4.16: The neutron SLD as a function of depth for (a) dPS43–*b*–PMA9 and (b) dPS39–*b*–PMA6 in the dry state (black curve) and next to *d*–cyclohexane (pink data points). The text markings on the plot approximately identify the material to which that portion of the SLD profile corresponds. The upper blue line represents the calculated SLD value expected for bulk, pure dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower red line is that for bulk, pure PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$)

the exact form of the profile in that region and the reason for that profile shape are still not entirely clear. The profile shapes shown here fit the data well, but the fact that the SLD next to the substrate surface is imagined to be larger than the SLD closer to the PMA-rich layer is difficult to explain, particularly for the dPS39-PMA6 sample. In that case the modeling suggests that the SLD of the “upper” part of the

dPS-rich layer does not change at all with contact with solvent, implying that that part of the brush does not swell at all. This seems unphysical. However, the ease with which different portions of the chain swells is expected to be different due to the fact that in swollen homopolymer brushes the chains do not stretch uniformly along their length. However, the behavior of homopolymer brushes might lead us to expect the portion of the dPS block farther from the substrate to swell preferentially. We do know that even though cyclohexane is a better solvent for PS than for PMA, it is not a good solvent for PS at the temperature under which the in-situ NR measurements were made. Cyclohexane is a good solvent for PS at 35°C. The theta temperature for dPS in d-cyclohexane should be close to that, but probably slightly different. The *in-situ* swelling measurements were done at room temperature around 21°C, so d-cyclohexane is a mediocre solvent for the dPS segments. The dashed gray lines in Figures 4.16(a) and 4.16(b) denote the SLD profile to be expected if the solvent were uniformly distributed in the film and the film were sitting next to air. The comparison between the fitted SLD and the hypothetical SLD is different for the two samples. For dPS43-*b*-PMA9 sample the shape of the interface between the dPS-rich region and PMA-rich region inferred from the data is close to that expected for uniform swelling. For the dPS39-*b*-PMA6 sample it is not. The current best fit shows a broadening of the interface between the dPS-rich region and PMA-rich region as compared to the hypothetical uniform solvent distribution. The reason for that difference could be that the amount of PMA grafted to the substrate at the time of reinitiation is higher for dPS43-*b*-PMA9 than for dPS39-*b*-PMA6. Thus, the dPS chains in the dPS43-*b*-PMA9 sample are already more stretched in dry state at the substrate than in the case of the dPS39-*b*-PMA6 sample. Solvent doesn't affect that part as much as it does for dPS39-*b*-PMA6. Then we would not expect the dPS chains to stretch as much with contact with d-cyclohexane for the dPS43-*b*-PMA9

sample. The middle and top layer of the dry state structure become mixed in the swollen state because absorption of solvent screens the enthalpic interactions between the PS and PMA blocks and reduces the effective value of χ between blocks.

The total thickness change when in contact with d-cyclohexane is 12% and 14% for dPS43-*b*-PMA9 and dPS39-*b*-PMA6, respectively. Based on earlier studies of scaling behavior [66, 69], one expects the thickness of the brush to vary linearly with chain length N or the grafting density σ (i.e. $h \propto N\sigma$). In a good solvent, the chains adopt more extended conformations by stretching and lose conformational entropy and $h \propto N\sigma^{1/3}$. We have highly dense DCBs with σ around 0.6 chains/nm² and the chains are highly extended, even in the dry state. During swelling with a selective solvent, the two parts of the diblock chain will strike different balances between stretching and contact between the chain and solvent. Considering the combined effects of extending the dPS chains to allow more d-cyclohexane into the bottom portion of the brush, less swelling of the PMA chains, and the high grafting density of the DCBs, low degree of swelling (14%) observed is reasonable. The swelling of the dPS-rich layer is 10% and 13% for dPS43-*b*-PMA9 and dPS39-*b*-PMA6, respectively. Our studies on PS homopolymer brushes show that high density PS brushes in cyclohexanes stretch to give thickness increase of about 50% (data not shown). We conjecture that the lesser swelling of the dPS-rich layer here is due to two effects. First, PMA chains grafted both on the dPS block (desired), also on SiO_x in between dPS chains (undesired). This would both limit further stretching due to the greater effective grafting density, and it would make it less enthalpically favorable for the solvent to go into the dPS-rich region. Secondly, the connection of the dPS block to a solvophobic block results in a higher penalty for the dPS chain swelling here. As the dPS chains swell, the entropic restoring force would tend to pull up into the

dPS/cyclohexane region the PMA block to which the dPS block is attached. This would be unfavorable.

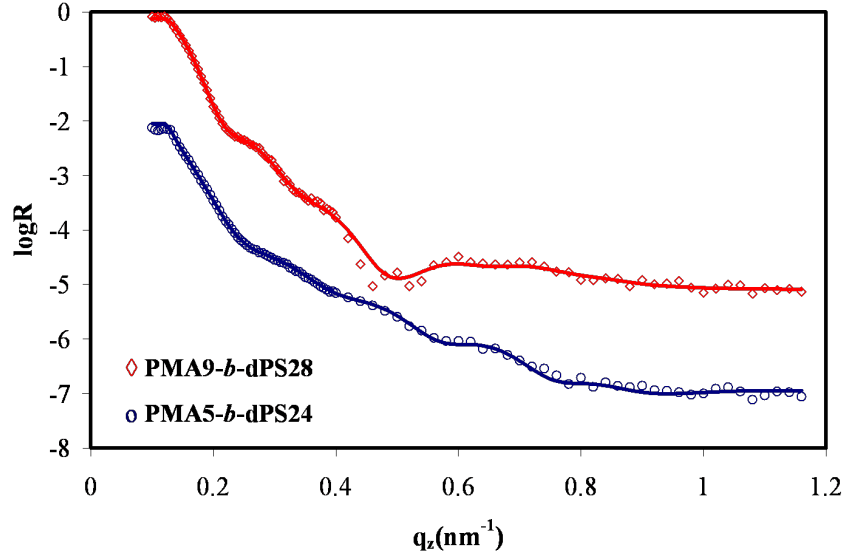
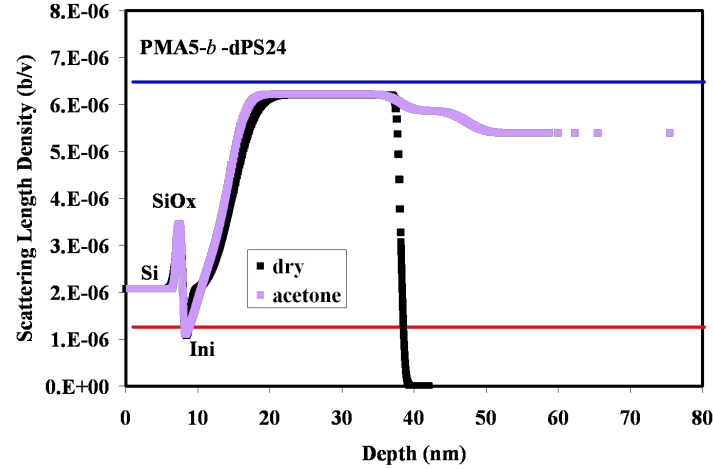
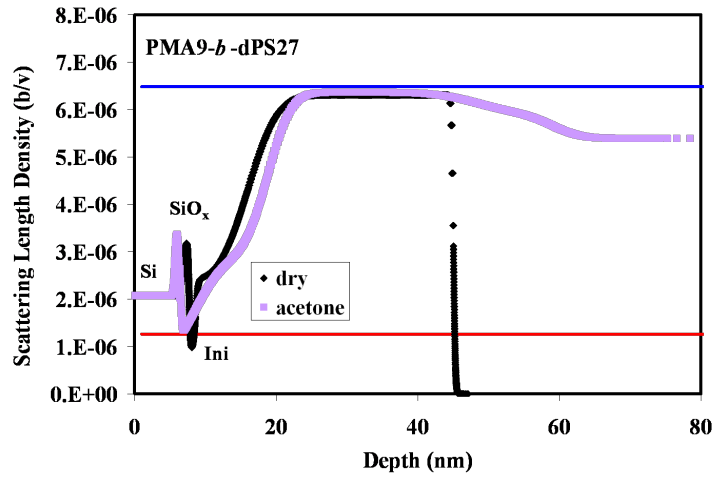


Figure 4.17: Neutron specular reflectivity (open symbols) and best fit model curves are plotted as a function of wavevector q_z , for PMA5-*b*-dPS24 (blue) and PMA9-*b*-dPS27 (red) DCBs measured *in situ* in contact with liquid d-acetone after equilibration. Adjacent curves have been shifted vertically for clarity.

The selective solvent swelling behavior of DCBs with a PMA block grafted on a substrate are shown in Figures 4.17, 4.18 and 4.19. In the dry DCBs the region rich in PMA is quite narrow and not well defined, due to the highly asymmetric compositions of the chains. On the other hand, the large dPS block allows the SLD in the dPS-rich region to attain nearly the SLD characteristic of bulk dPS. This may be partly due to the fact that at the time of reinitiation, some dPS is grafted to the substrate surface. We note that the SLD of the PMA-rich layer is substantially above the value expected for pure, high molecular weight PMA. Since the molecular weight of the PMA block is low, in fact the SLD expected for the pure PMA block would be slightly lower than the horizontal line, so clearly there are dPS chains tethered beside the PMA blocks tethered to the substrate. Since the PMA-rich layer is so thin, these



(a)



(b)

Figure 4.18: The neutron SLD as a function of depth for (a) PMA5-*b*-dPS24 and (b) PMA9-*b*-dPS27 in the dry state (black) and next to d-acetone (purple). The text markings on the plot approximately identify the material to which that portion of the SLD profile corresponds. The upper blue line represents the calculated SLD value expected for bulk, pure dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower red line is that for bulk, pure PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$)

dPS chains grafted to the surface extend out far beyond the PMA-rich layer and contribute substantially to the dPS-rich layer. The SLD profiles for the d-acetone treated DCBs end on the right (in the solvent) at a value of SLD consistent with

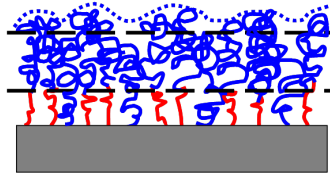


Figure 4.19: Schematic of a swollen PMA-*b*-PS DCB next to d-acetone.

that calculated for d-acetone, which is $5.67 \times 10^{-6} \text{ \AA}^{-2}$. This is lower than the SLD of bulk dPS. In contrast to the behavior seen with the cyclohexane swollen dPS-*b*-PMA DCBs, fitting the data from PMA-*b*-dPS DCBs next to d-acetone, requires a three-layer model. The thickness increase when in contact with d-acetone is 41% for PMA9-*b*-dPS27 and 31% for PMA5-*b*-dPS24. The lower overall swelling for PMA5-*b*-dPS24 is because that sample contains a smaller fraction of PMA. In the swollen state profile, there is a thin, PMA-rich layer near the substrate. Then there is a middle dPS layer which shows no change in b/V or thickness, consistent with the fact that d-acetone is a very poor solvent for dPS. On top, there is third layer with a value of SLD that suggests that region contains a mixture of dPS and solvent. A change occurs next to the initiator layer when these brushes are next to d-acetone. The PMA-rich layer becomes less well defined, even for PMA5-*b*-dPS24. Since the PMA-rich layer is much thinner in PMA5-*b*-dPS24 than in PMA9-*b*-dPS27, the PMA-rich layer loses its identity and mixes in with the interface between the PMA-rich and dPS layer. This could be due to swelling of the initiator chains along with PMA chains upon exposure to acetone. Such swelling is probable because the initiator SAMs for these samples have thicknesses of about $17 \text{ \AA}$. If the SAM were as dense as possible (all-extended chains) the thickness should be $21 \text{ \AA}$, which shows that they are not all-extended and could extend more. However, not all SAM chains swell upon contact with acetone. There are definitely some dPS chains grown directly from the initiator layer. And the unswollen, collapsed dPS chains grafted to the SAM chains are long

enough to prevent the swelling of the initiator chains to which they are attached. This combined behavior of initiator chains drawn up by swollen PMA chains and restrained by collapsed dPS chains could be the reason for the broader interface with the PMA-rich layer in the presence of d-acetone. The unchanged thickness and b/V of the middle dPS layer are due to the high density of dPS chains in that layer. This high density of PS chains are due to summation of chains grafted on PMA and on directly to the initiator layer as shown in the schematic Figure 4.19 of swollen highly asymmetric PMA-*b*-dPS chains during exposure to d-acetone. In the SLDs in Figures 4.18(a) and 4.18(b) there is an additional layer next to the d-acetone reservoir which has an SLD profile through the layer similar to the SLD profile one would see for a swollen homopolymer brush. It is not possible that there is a very thin layer on the surface that contains enough PMA chains to lead to substantial swelling. The PMA chains are not long enough to stretch up to surface and the SLD value in that region is high enough to represent a mixture of dPS and acetone. This could be due to a nonuniformity of chain lengths manifesting itself next to the poor solvent. dPS chains attached to swollen PMA chains sitting next to collapsed dPS chains could make a bumpy surface due to height variations. The presence of “bumps” is much more likely than the extension of longer dPS chains out into d-acetone because dPS doesn’t swell in the poor solvent. NR, however, cannot distinguish between the presence of a bumpy interface here and a diffuse interface. Acetone swelling measurements on PMA-*b*-dPS DCBs show that acetone could be a good selective solvent to cause switching, but the lengths of the chains in the DCB are also very important to achieve the change of surface characteristics from those of one type of polymer to those of another. The bottom block chains should be much longer than the top block chains to be able to stretch enough and cover the unswollen top block chains.

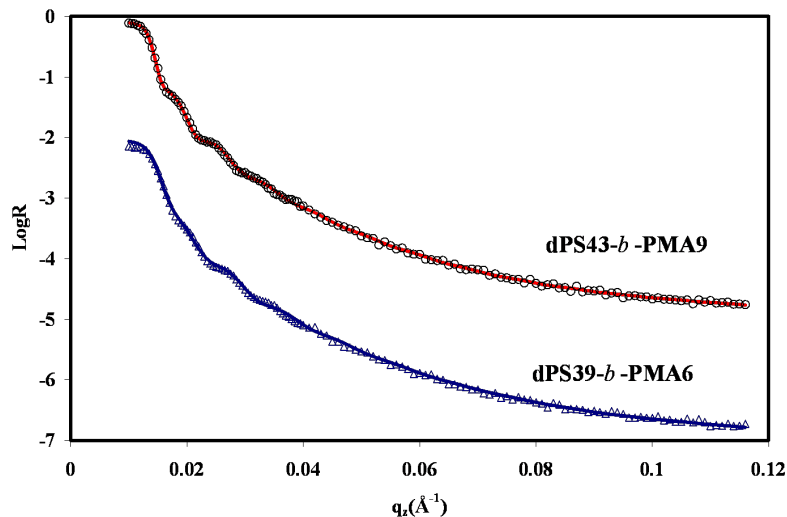
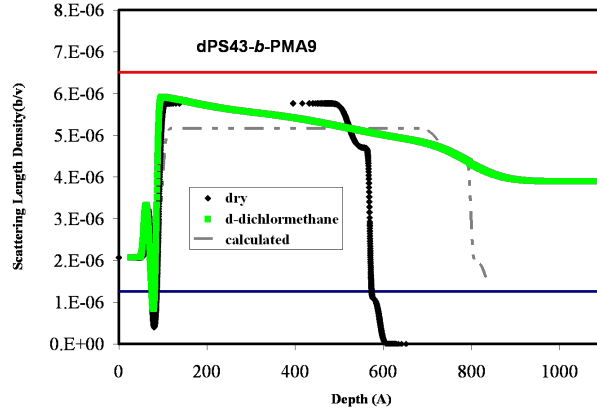
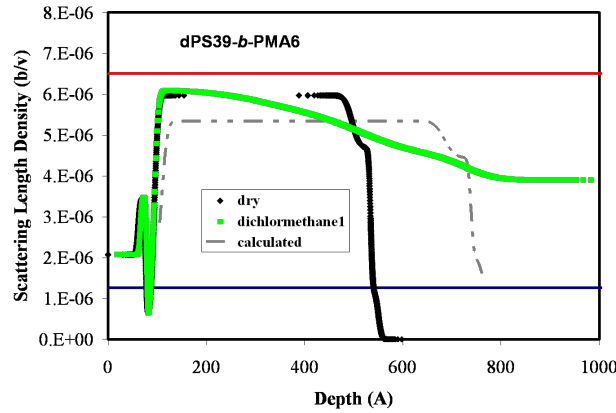


Figure 4.20: Neutron specular reflectivity (open symbols) and best fit model curves are plotted as a function of wavevector q_z , for dPS43-*b*-PMA9 (red) and dPS39-*b*-PMA6 (blue) DCBs measured *in situ* in contact with liquid d-dichloromethane after equilibration. Adjacent curves have been shifted vertically for clarity. χ^2 of the fits for dPS54-*b*-PMA25 and dPS43-*b*-PMA9 are 4.5 and 3.6, respectively.

Asymmetric DCBs were also swollen with dichloromethane. This solvent was picked with the intent that it should be a good solvent for both blocks. The neutron reflectivity curves for two DCBs, dPS43-*b*-PMA9 and dPS39-*b*-PMA6, having large dPS blocks attached to the substrate with smaller PMA blocks as the second block are shown in Figure 4.20 and the SLD of these DCBs are shown in Figure 4.21. These curves are somewhat more difficult to fit, but from visual inspection of the NR data alone the experienced user can infer that some sharp interface or interfaces have been “smeared” or made broader by exposure to the good solvent. The reflectivity curve and SLD profile for one DCB next to d-chloromethane in which the block sequence has been reversed are shown in Figure 4.22. There are clear distinctions in the dry state between the SLD profiles for the brushes having PMA grafted to the substrate and that for the case in which dPS is grafted to the substrate. When PMA is on the bottom the SLD profile has nearly pure dPS for the dPS-rich layer in the dry state. If



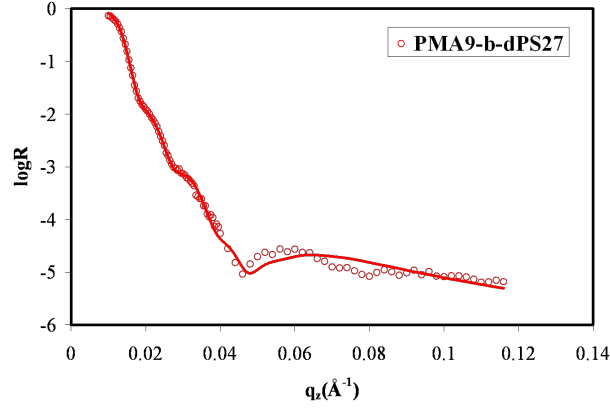
(a)



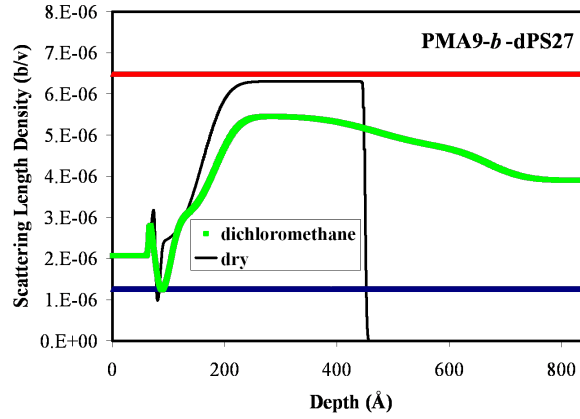
(b)

Figure 4.21: The neutron SLD as a function of depth for (a) dPS43-*b*-PMA9 and (b) dPS39-*b*-PMA6 in dry state (black) and next to d-dichloromethane (green). The dashed gray lines are hypothetical SLDs calculated assuming the solvent is equally distributed among the layers. The upper red line represents the calculated SLD value expected for bulk, pure dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower blue line is that for bulk, pure PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$)

dPS is on the bottom, the b/V for the dPS-rich region is considerably lower. However, once the brushes are swollen next to dichloromethane the structures of the three brushes are more similar. The models used for fitting the d-dichloromethane swollen DCBs have three layers for both the case of PMA-*b*-dPS and the case dPS-*b*-PMA. However, in all three cases the interfaces between pairs of layers used in the models are



(a)



(b)

Figure 4.22: (a) Neutron specular reflectivity (open symbols) and best fit model curves are plotted as a function of q_z for a PMA9-*b*-dPS27 next to d-dichloromethane. (b) The corresponding SLD as a function of depth. The upper red line represents the calculated SLD value expected for bulk, pure dPS ($b/V = 6.48 \times 10^{-6} \text{ \AA}^{-2}$) and the lower blue line is that for bulk, pure PMA ($b/V = 1.26 \times 10^{-6} \text{ \AA}^{-2}$)

very broad, so no distinct layers are seen. The overall shape of the SLD is approaching that which one expects for a homopolymer in good solvent, which is a parabolic shape with a tail. This makes sense. In the limit of a solvent that is very good for both blocks and small incompatibility between the blocks the brush should swell like a homopolymer brush except for the complication of the mixture of homopolymer and

diblock copolymer both grafted at the initiator layer. This leads to a stretching along the chains that is somewhat different than in a narrow polydispersity homopolymer brush. The swelling by good solvent of both blocks diminishes very strongly the effective value of χ between the two blocks. In fact, from basic Flory-Huggins theory of ternary mixtures one expects the effective χ between the two blocks in the presence of solvent to vary as $\chi(1 - \phi)$, where ϕ is the volume fraction of solvent. For dPS43-b-PMA9 and dPS39-b-PMA6, the overall swelling of the DCB with d-dichloromethane is 46% and 43%, respectively. For PMA9-b-dPS27 DCB, the overall swelling with d-dichloromethane is 58%. For homopolymer PS brush ($\sigma = 0.5$ chains/nm²) in good solvent, toluene, thickness increases approximately 50% (data not shown).

In conclusion, the swelling behavior of DCBs was studied using both *ex-situ* and *in-situ* swelling measurements. For *ex-situ* swelling measurements the samples were immersed in the solvent, removed and measured dry. *Ex-situ* study showed that for dPS-*b*-PMA DCBs, a three layer structure model still captured the essential features of the data even after treatment with cyclohexane, a solvent selective for dPS. In the model the top PMA layer is not distinct but the middle layer which we believe to contain domains rich in PS chains, persists even after swelling. Domains most probably were present in the brush when it was swollen and are present after collapse after drying. However, *in-situ* swelling measurements show that the internal structures of brushes next to solvent are totally different than the dry structure. For those measurements, highly asymmetric DCBs were used with cyclohexane, a selective solvent for dPS, acetone, a solvent selective for PMA and a dichloromethane, a good solvent for both blocks. It was observed that the structure of a swollen DCB depends on many different parameters such as solvent quality, ratio of chain lengths of the blocks, block sequence and the degree of reinitiation during the synthesis procedure. For highly asymmetric dPS-*b*-PMA samples, the *in-situ* swelling measurements were

done at room temperature around 21°C, so d-cyclohexane is a mediocre solvent for the dPS segments and poor solvent for PMA. For those samples, even though the chain lengths of dPS were long enough to stretch and cover the solvophobic PMA chains, no clear rearrangement was observed. On the other hand, for PMA-*b*-dPS brushes, acetone was a good solvent for PMA chains and poor solvent for dPS chains at room temperature. Since the block lengths of the dPS chains were much larger (4 and 7 times) than those of the PMA chains, the dPS chains collapsed and sat on the short swollen PMA chains, forming a bumpy surface next to the solvent. In the future, more work should be done with DCBs of various block lengths to clearly observe surface rearrangement. When DCBs are swollen with a solvent good for both blocks, DCBs behave similarly to homopolymer brushes, but the structure model retains the three layer form, and with a parabolic profile superposed on it with much broader interfaces between layers so that no distinct layers are seen.

CHAPTER V

SURFACE DYNAMICS OF THIN FILMS OF HOMOPOLYMER BRUSHES AND BILAYERS OF UNTETHERED CHAINS ON HOMOPOLYMER BRUSHES

5.1 Capillary Waves on “Untethered Chain” Films

The reason that “switching” of brushes is of interest is that being able to simply alter the properties of a polymer film by tethering the chains to form a brush could be very useful. So far, we have focused on the static or time-averaged structure of the brush, but, in fact, the dynamic properties of the surfaces of brushes are also important for some applications. Dynamic properties may play a role in such diverse physical phenomena as wetting, adhesion, lubrication, tribology, colloid stabilization, and conformational response to changes in environment. Their importance notwithstanding, dynamical properties of brush surfaces have not yet been probed much either theoretically or experimentally. Before getting into a detailed analysis of the surface dynamics of brushes, it is necessary to appreciate what is currently known about the surface behavior of corresponding liquid films of chains that are untethered.

The dynamics of liquid surfaces have been of great interest for more than a century. Liquid interfaces are constantly being deformed by thermal stimulations in the form of waves. The propagation of waves on the liquid surface depends on the liquid properties in a way expressed by a *dispersion relation*, which is a relation between the energy of a system and its momentum. The *dispersion relation* relates the angular frequency (ω) to the wave number (k). In general the *dispersion relation*

takes the form of a power law, $\omega \approx q^\alpha$, where the value of the exponent α changes with the types of waves present.

The surface modes on simple, pure liquids have been extensively studied and are well understood [208–211]. For the simple liquids, these waves are typically of small amplitudes (of order $10\text{\AA}$), which are much smaller than their wavelengths, which are of order $10\text{ }\mu\text{m}$ and propagate as capillary waves called *ripplons*. The propagation of these waves is controlled by the surface tension (γ) and their temporal damping by the liquid viscosity (η) [212]. For capillary waves, the resonant frequency of the surface waves, w , is proportional to $q^{3/2}$.

Polymer solutions have both a frequency-dependent viscosity, and a nonzero, frequency-dependent shear modulus. It has been shown theoretically that in such a viscoelastic polymer solution, several types of surface modes can exist [213]. These modes can be capillary waves, overdamped waves or *Rayleigh elastic waves*. As viscosity increases, the damping of the capillary waves becomes so large that all the modes become over-damped, and one reaches the regime which is called *over-damped capillary waves*. *Rayleigh waves* occur when the surface wave behavior begins to be controlled by elasticity as well as viscosity and is dictated by a competition between viscosity and elasticity. The force which tends to restore the surface flatness, the “restoring force”, is dominated by elasticity which increases with concentration. The resonant frequency of the surface waves, w , for the case of *Rayleigh waves* is proportional to q .

Recently [6, 7] it has been demonstrated that at temperatures far above the glass transition temperature, T_g , the surface height fluctuations on a film of undiluted, untethered polymer chains of film thickness greater than $4R_g$, where R_g is the unperturbed chain radius of gyration, can be understood using the over-damped capillary wave theory for viscous liquid surfaces. The characteristic over-damped relaxation

time of a single-layer film of untethered chains with a non-slip boundary condition is found to be:

$$\tau_{nonslip}(q) \simeq \frac{2\eta H}{\gamma q F} \quad (5.1)$$

where h is the thickness of the film and

$$H = \cosh(qh)^2 + (qh)^2 \quad (5.2)$$

and $F = \sinh(qh)\cosh(qh) - qh$.

With a perfect slip boundary condition the relaxation time changes to:

$$\tau_{slip}(q) \simeq \frac{2\eta \cosh(qh)\sinh(qh) + qh}{\gamma q \sinh(qh)^2} \quad (5.3)$$

In both Eqs. 5.1 and 5.3 one can divide both sides of the equation by thickness, h , to create relationships between the scaled quantities $\tau_{nonslip}(q)/h$ and qh , and between $\tau_{slip}(q)/h$ and qh . In both cases the scaled relaxation time is proportional to η/γ . This means that at a certain temperature, the behavior of the capillary waves on films with different thicknesses are related by simple scaling and plots of τ/h vs. qh should collapse onto a single master curve as shown in Figure 5.1.

For appropriately annealed spuncast films with various thicknesses ($h = 84, 170, 177, 312.5$ nm), but identical polystyrene (PS) molecular weight ($MW = 123$ kg/mol, hence $R_g = 9.4$ nm), the scaling relations between τ/h and normalized wave vector, qh , predicted by the theory of overdamped capillary waves, as identified in Eq. 5.1, have been verified [6]. The data shown in Figure 5.1 were obtained from an analysis of X-ray Photon Correlation Spectroscopy data. The directly measured quantities are 2-D static scattering patterns in the form of I vs. $q_{||}$. The intensity-intensity autocorrelation functions, g_2 , are calculated from the data. These g_2 functions can

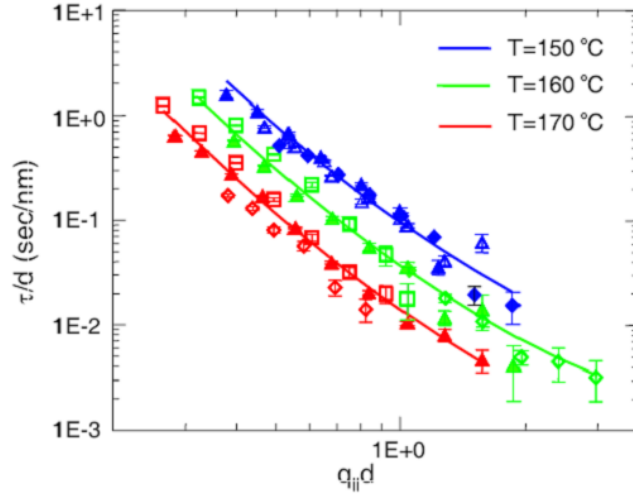


Figure 5.1: Plot demonstrating the universality of the behavior of overdamped capillary waves on films of untethered polystyrene chains of $M_w = 123\text{k g/mol}$ and thicknesses 84 nm (squares), 170, 177 nm (triangles), and 312.5, 318, 333 nm (diamonds) at three temperatures. Solid lines are fits to Eq. 5.1.

be fit well with a stretched exponential relationship:

$$g_2(q_{||}, t) = 1 + \beta \exp(-2(t/\tau)^\alpha) \quad (5.4)$$

where β is the coherent contrast, $\tau = \tau(q_{||})$ is the relaxation time for the equilibrium surface height fluctuations, and α is the stretching exponent. It is found that $\alpha = 1$ provides a good description of the data, even for these viscoelastic fluids, except in certain temperature regions [214].

Kim *et al.* [6] found that the relaxation time decreases as the wave-vector ($q_{||}$) probed gets bigger, as shown in Figure 5.2, because smaller asperities relax faster than do larger ones. Figure 5.3 shows how the relaxation time constants decrease with increasing temperature and thickness of the film. The fact that the surface dynamics depend on film thickness demonstrates that, although the measurements are sensitive only to surface motions, those motions in turn depend on flow throughout the film,

which is consistent with the assumptions of the continuum model of capillary wave theory.

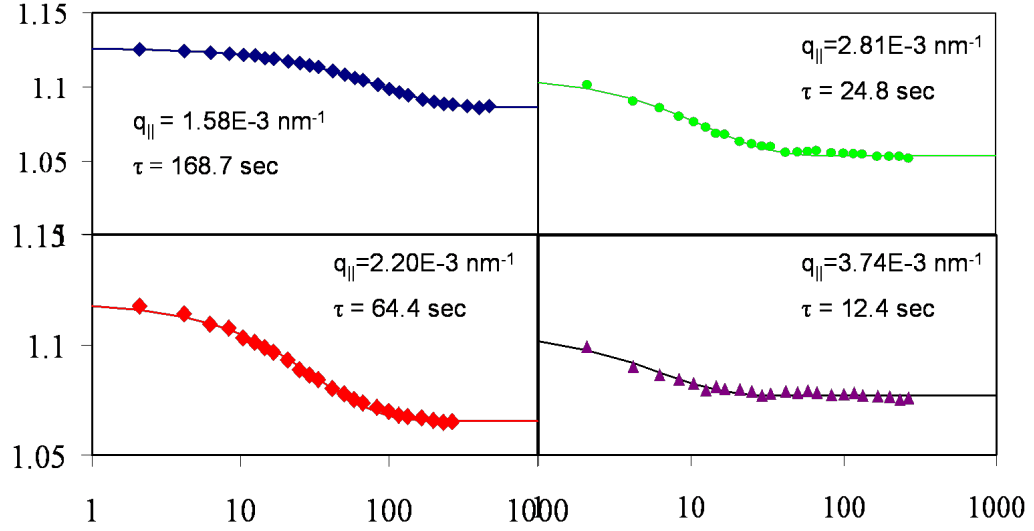


Figure 5.2: Autocorrelation functions at four different values of in-plane wave vectors ($q_{||}$) measured on a PS film of $MW = 2.2k$ g/mol and thickness 45 nm at 110°C (symbols), compared with fits to Eq. 5.4 with $\alpha = 1$ (solid lines).

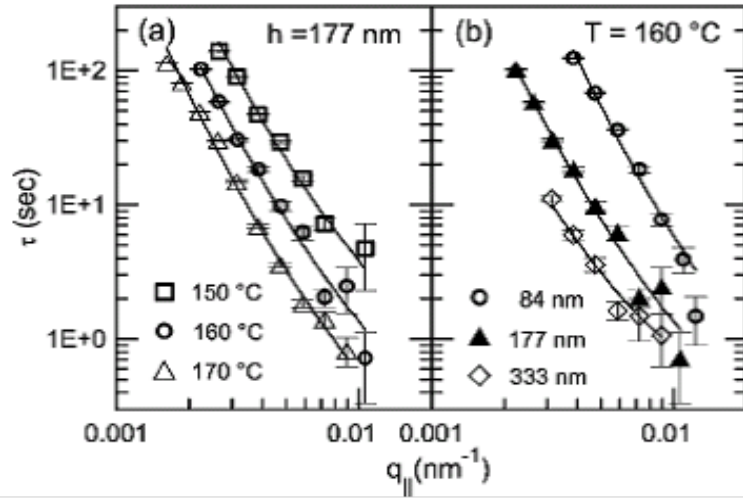


Figure 5.3: (a) Measured relaxation time τ vs in plane wave vector $q_{||}$ for the 177 nm thick PS film at 150°C (squares), 160°C (circles), and 170°C (triangles). (b) τ vs $q_{||}$ at 160°C for films of thickness 84 nm (circles), 177 nm (triangles), and 333 nm (diamonds) [6].

Time constants can be plotted as a function of $q_{||}$ and Eq. 5.1 fit to the data points to obtain a value of η/γ . A value of surface tension can be extracted from the static surface diffuse scattering collected when the XPCS data are collected, and then viscosity can be calculated. Kim *et al.* [215] compared the viscosities they calculated from XPCS in this way with published [216] bulk viscosity values for PS measured with rheometry. They obtained good agreement for molecular weights 30 to 290 kg/mol and temperatures at least 50°C above the glass transition temperature (i.e. far from the glass transition). However, the viscosities obtained from films of chains having 400 kg/mol and 650 kg/mol chains were lower values than the bulk viscosities.

Analysis of follow-up XPCS experiments on films of PS untethered chains of thickness comparable to $2R_g$ found fluctuation relaxation behaviors that differed significantly from those of films of thicknesses $> 4R_g$ [7]. Those authors rationalized these results by arguing that pinning of the chains closest to the substrate creates behavior that is somewhat “brush-like”, displaying suppression of the surface dynamics. The resulting changes in the characteristic surface relaxation time were successfully captured by a model of a viscous liquid film modified to account for a film elastic modulus, μ , in the equations for characteristic time, $\tau_{nonslip}(q)$,

$$\tau_{ve}(q_{||}) \cong \frac{\tau_{nonslip}(q_{||})}{1 + \tau_{nonslip}(q_{||})(\mu/\eta)} \quad (5.5)$$

and for the static fluctuation spectrum, $S(q)$

$$S(q) = \frac{k_B T}{\gamma q^2 + 2\mu q \frac{H}{F}} \quad (5.6)$$

There are two asymptotes of the viscoelastic surface dynamic model defined in Eq. 5.5: (i) $\tau_{ve}(q_{||})$ reduces to $\tau_{nonslip}(q_{||})$ when $\tau_{nonslip}(q_{||}) \ll \eta/\mu$, which corresponds to the purely viscous model previously described for a free liquid surface without elastic effects. (ii) $\tau_{ve}(q_{||}) \approx \eta/\mu$ when $\tau_{nonslip}(q_{||}) \gg \eta/\mu$, which corresponds to states in which the viscoelasticity is strongly manifested.

The g_2 functions from the XPCS measurements of Jiang *et al.* [7] are shown in Figure 5.4 for PS untethered chains of various thicknesses. The surface dynamics get slower when the thickness of the film is decreased to $2R_g$. It has been shown that the viscoelastic model defined in Eq.5.5 gives much better fits than the viscous liquid model expressed in Eq. 5.1. In $1R_g$ films, no surface dynamics are observed in the window of time and wave-vector experimentally available. The fact that g_2 of the $1R_g$ film is above unity and not at 1 means that there is a signature of a static surface or at least a surface with extremely slow dynamics. This might be due to the fact that the number of adsorption points per chain is larger in $1R_g$ films than in $2R_g$ films, which would make the lateral displacement of chains required for surface fluctuations more thermodynamically unfavorable.

In recent work by Tsui *et al.* [217,218], they describe an alternative methodology and interpretation for data from PS thin films. They measured the power spectral density (PSD) of surfaces with AFM and then watched the evolution of the PSD with time. They observed nonliquidlike behavior when the annealing time of the film was less than the relaxation time of the capillary wave mode. The fact that relaxation times of capillary wave modes are often on the order of days and even years means that insufficient annealing time may cause the nonliquidlike behaviors. They also measured the change in surface dynamics of PS transition and found that they did not observe any change of behavior with thickness, h , in the range of $= 2R_g$, $4R_g$, to $8R_g$. This result favors the insufficient annealing to be the cause of the ob-

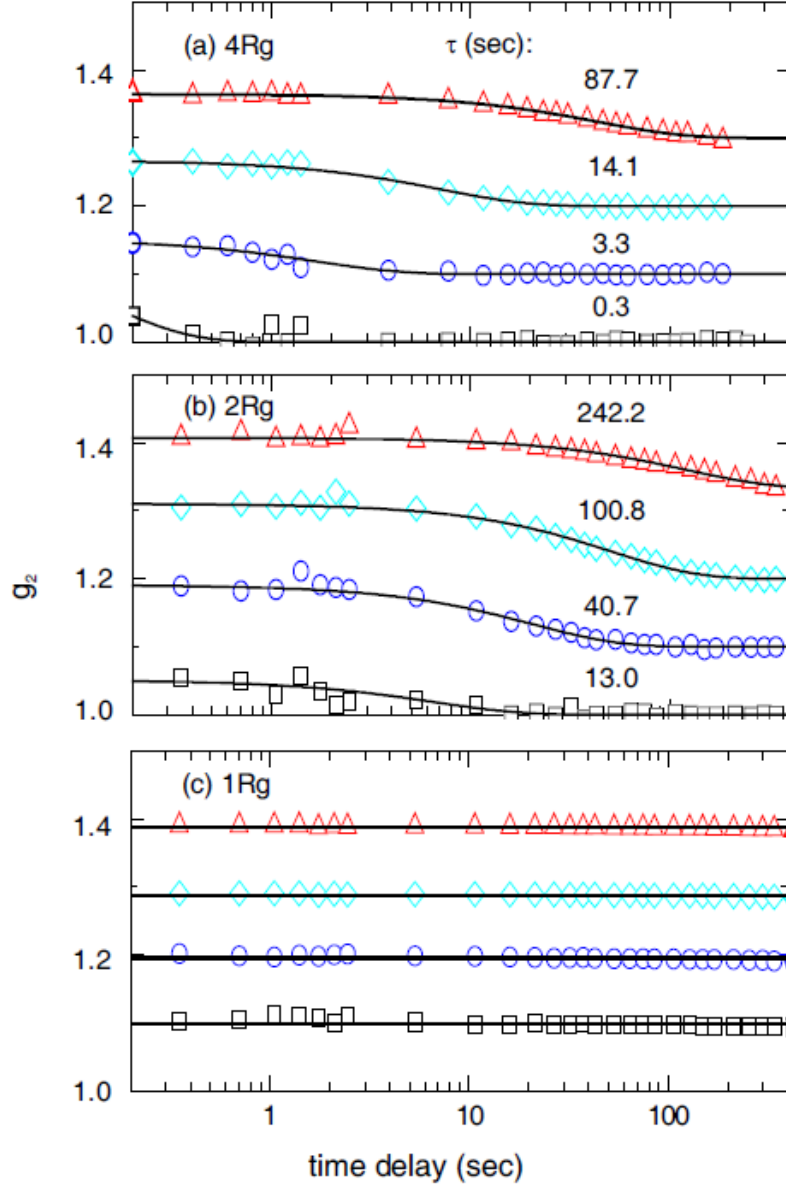


Figure 5.4: Intensity-intensity autocorrelation functions obtained from PS films of $M_w = 123\text{k g/mol}$ and thickness (a) $4R_g$, (b) $2R_g$ and (c) $1R_g$ at 195°C at four in-plane wave vectors $q_{||} = 3.3$ (red Δ), 5.4 (cyan $\diamond$), 7.7 (blue $\bigcirc$) and 10 (black $\square$) $\times 10^{-3} \text{ nm}^{-1}$. Solid lines are the best fits to Eq.5.4 with $\alpha = 1$. The fitted relaxation time constants for $4R_g$ and $2R_g$ films are shown next to the curves. For clarity the curves are shifted vertically [7].

served nonliquidlike behaviors as opposed to previously suggested strong pinning of the polymer chains to the substrate.

5.2 Surface Dynamics of “Dry” Homopolymer Brushes

These studies by Jiang *et al.* [7] suggested that even though the chains in $2R_g$ or $1R_g$ films are not purposely grafted, the chain segments may be confined and pinned onto the substrate in such a way that the films behave like brushes with much slower dynamics. The question arises now how chains behave when they are purposely and chemically tethered to the substrate. No full theoretical treatment of the surface dynamics of densely grafted brushes has been published. Thermodynamic theories [84, 219, 220] that draw on an analogy with an elastic layer predict that if chains are covalently end-grafted with a distance between tethering points smaller than R_g of the unperturbed chain, the resulting stretching from Gaussian conformations in the “polymer brush” leads to dramatic changes in film surface dynamics. For surface modes with wavelengths, $\lambda = 2\pi/q$ much larger than the equilibrium brush height, h_0 , the entropic cost to stretch the chains the necessary amounts varies strongly with $q_{||}$ so that modes with $\lambda \gg h_0$ are predicted to be suppressed. Competition between an elastic restoring force at long wavelengths and a surface tension penalty at shorter wavelengths should lead to an energetically preferred wavelength of the order of h_0 . Fredrickson *et al.* [84] further argue that while the fluctuation spectrum of equal-time correlations is governed only by thermodynamics, what may be observed in time-resolved scattering measurements is very sensitive to two time scales of motion of the surface elastic waves. One time scale is the wave frequency of the Rayleigh-like surface modes, ω . The second is a time τ_r for entanglements in a melt brush to relax. Those authors remark that theoretical work by Obukhov and Rubinstein [221] suggests that τ_r is a very large time that grows at least exponentially with the length of the brush chains. In practical situations it could be that $\omega \gg \tau_r^{-1}$ and the chain entanglements are unable to relax during the time required for a wave to travel a distance of order

$2\pi/q_{\parallel}^*$. The observation, in static scattering measurements, of correlation between the roughnesses of the top and bottom interfaces of a diblock copolymer brush [222] and a self-affine structure at the surface of homopolymer brushes [121] has offered indirect evidence that long wavelength fluctuations are suppressed in densely grafted brushes [121], but it remains to demonstrate this suppression directly with a measurement of surface dynamics.

The collective dynamics of polydisperse ($M_w/M_n \approx 2$) “wet” (solvent swollen) polymer brushes synthesized by conventional free radical polymerization has been studied using evanescent wave dynamic light scattering with visible light [223–226]. These experiments revealed that fast cooperative diffusion is characteristic of the good solvent regime, whereas in a theta solvent fast diffusion is accompanied by a slower mode. To study surface dynamics of melt (“dry”) brushes, however, smaller length scales must be reached. In our work we investigate the surface dynamics of brushes (Table 5.1) using XPCS and the results are presented throughout the following part of the chapter.

That the fluctuations at the surface of a film of polystyrene chains are remarkably altered by tethering is clear from the comparison in Figure 5.5 in which $g_2(t)$ at $q_{\parallel} = 5.3 \times 10^{-3} \text{ nm}^{-1}$ is plotted for two films at temperatures far above T_g : a 26 nm thick film of tethered PS chains with $\sigma = 0.6 \text{ chains/nm}^2$, and a 29 nm thick film of untethered chains made by spin casting, drying, and annealing. The surface relaxation for the film of untethered chains is clearly observed and fitting with a single exponential (Eq. 5.4 with $\alpha = 1$), yields a relaxation time of 32 s. In contrast, g_2 for the brush is greater than unity (baseline) and exhibits no relaxation within the experimental window. The fact that the value of g_2 remains above unity reflects that there is structure at the surface of the brush, but this structure does not relax, on the length scale probed, in the time window investigated. Data collected at much

Table 5.1: Physical Properties of Samples

Sample	h^a (nm) ± 0.2	M_n^b (kg/mol)	Pdi (M_w/M_n)	σ^c chains/nm ²	d^d (nm) ± 0.03	R_g^e (nm)	h/R_g
PS-9	9	10 $\pm$ 0.5	1.02	0.6 $\pm$ 0.03	1.4	2.8 $\pm$ 0.1	3.2 $\pm$ 0.1
PS-21	21	95 $\pm$ 5.7	1.64 $\pm$ 0.027	0.13 $\pm$ 0.05	0.3	9.2 $\pm$ 0.4	2.3 $\pm$ 0.1
PS-26	26	28 $\pm$ 1.4	1.03	0.6 $\pm$ 0.03	1.3	4.6 $\pm$ 0.2	5.6 $\pm$ 0.2
PS-37	37	123 $\pm$ 6.1	1.62 $\pm$ 0.023	0.19 $\pm$ 0.01	2.3	9.4 $\pm$ 0.5	4 $\pm$ 0.2
PS-39	39	34 $\pm$ 1.7	1.16	0.6 $\pm$ 0.04	1.3	4.9 $\pm$ 0.2	8.0 $\pm$ 0.3
PS-48	48	50 $\pm$ 2.5	1.09	0.6 $\pm$ 0.03	1.3	6.0 $\pm$ 0.3	8.0 $\pm$ 0.4
PS-67	67	107 $\pm$ 5.4	1.56 $\pm$ 0.030	0.39 $\pm$ 0.03	1.6	8.8 $\pm$ 0.4	7.6 $\pm$ 0.4
PS-101	101	95 $\pm$ 5.8	1.64 $\pm$ 0.027	0.6 $\pm$ 0.05	1.3	9.2 $\pm$ 0.5	11.6 $\pm$ 0.6
PnBA-30	30	25 $\pm$ 1.3	1.20	0.8 $\pm$ 0.04	1.1	3.6 $\pm$ 0.2	8.3 $\pm$ 0.5

^a Thickness (h) values from XR.

^b Number averaged molecular weights measured using gel permeation chromatography (GPC) for free chains in solution created at the same time the brush was synthesized.

^c Grafting density (σ) is calculated using $\sigma = N_A \rho h / M_n$, where M_n is the number average molecular weight, N_A is Avogadro's number and ρ is the bulk mass density.

^d Distance between the anchoring points.

^e Radius of gyration for corresponding unperturbed chain.

shorter times for the 26 nm thick brush in this figure and for the 48 nm thick brush in Figure 5.7 demonstrated that there was no relaxation at times as short as tenths of a second. If the brush had a surface relaxation on this length scale with single exponential shape and a relaxation time of ca. 10000 s, at least the beginning of the relaxation would be visible within this time window. Thus if fluctuations exist at the surface for this length scale their relaxation time has been increased by at least three orders of magnitude by the tethering of the chains.

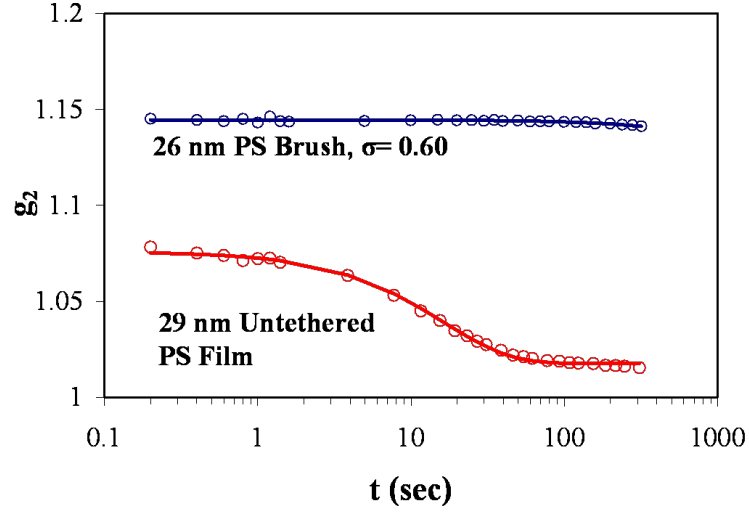


Figure 5.5: Intensity normalized time autocorrelation function vs. delay time at $q_{||} = 5.3 \times 10^{-3} \text{ nm}^{-1}$ for a 26 nm thick PS brush ($M_n = 28 \text{ kg/mol}$) with $\sigma = 0.6$ chains/ nm^2 (blue), 29 nm thick film of untethered PS chains ($M_n = 65 \text{ kg/mol}$) (red) measured at 170°C .

Comparison of line cuts through the speckle patterns of a brush sample and a film of untethered chains, shown in Figure 5.6, also makes clear that the brush surface has structure that is static over the time scales investigated. Error bars in Figure 5.6 represent ± 1 “standard deviation”. A line cut averaged over 441 seconds at the beginning of a measurement for brush PS-21 shows detailed structure arising from scattering of the coherent beam. The same line cut averaged over the same period of time (or number of frames) at the end of the run (126 s later) shows the

same detailed scattering pattern, to within experimental uncertainty. In contrast, the same line cut made for the data from a film of untethered chains and averaged over 280 s (100 frames) is simply flat within the uncertainties because the surface structures relax within that period of time.

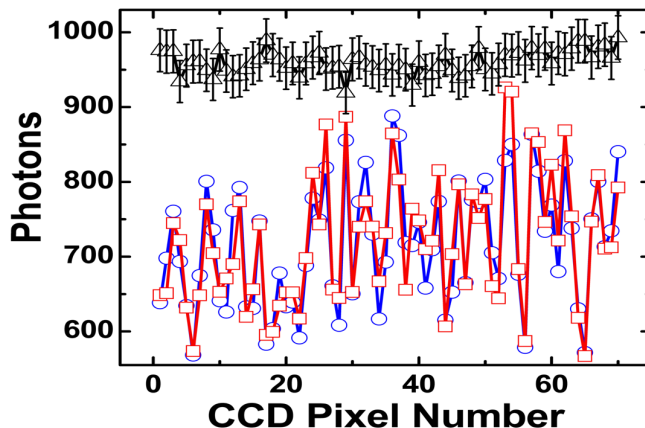


Figure 5.6: Comparison of speckle data for a brush and a film of untethered chains for $q_{||} = 0.01 \text{ nm}^{-1}$. Bottom curves: Photons as a function of CCD pixel along a line in the speckle patterns measured for brush PS-21: averaged over the first 441 seconds, or 70 frames (open circles) and averaged over last 441 seconds (open squares). Error bars are given as square root of the photon counts (i.e. ± 25 to 30). Top curve (triangles): Same, but for 100 nm thick film of untethered 36k PS chains at 150°C averaged over 280 s (100 frames) and shifted up by 150 photons for clarity. Error bars are given as square root of the photon counts (i.e. ± 30 to 32).

This alteration of surface fluctuations when passing from the film of untethered chains to the brush is seen for five different thicknesses of brush, 101, 48, 39, 26 and 9nm, as shown in Figure 5.7. The thickness (h), calculated grafting density (σ), molecular weight, distance between anchoring points (d), R_g and h/R_g values for the samples measured with XPCS are shown in Table 5.1. The thicknesses of brushes for which no surface relaxations were seen correspond to values of h/R_g from 3 to 11.6. These values are much larger than those h/R_g values for which Jiang et al. [7] found suppression of surface fluctuations in films of untethered chains. It would be interesting to test the behavior of still thicker brushes, but it is not currently possible

to make thicker brushes with chains of molecular weight as well controlled as for the brushes studied here. Even to reach the thickness of 101 nm required relaxing the molecular weight control (polydispersity $M_w/M_n = 1.64$) relative to our standard ATRP synthesis protocol ($M_w/M_n = 1.05 - 1.3$).

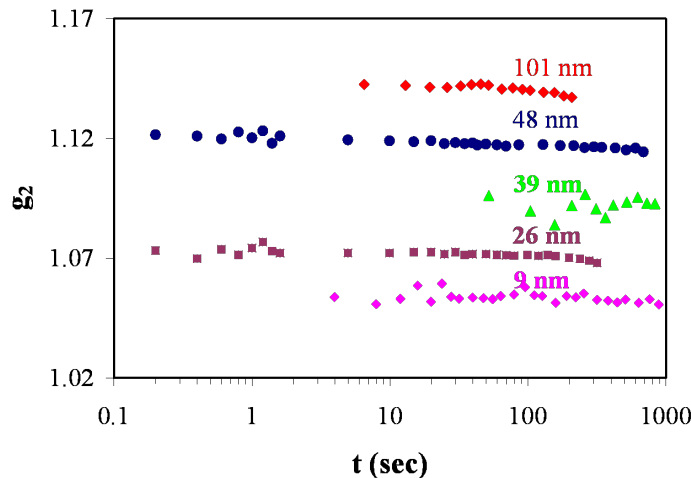


Figure 5.7: $g_2(t)$ at $q_{||} = 3.4 \times 10^{-3} \text{ nm}^{-1}$ for brushes of thickness 101, 48, 39 and 26 nm. $g_2(t)$ for the 9 nm thick PS brush was measured at $q_{||} = 3.1 \times 10^{-3} \text{ nm}^{-1}$. For the 26 and 48 nm brushes data were collected at much shorter times. The contrast is similar for all four samples. The data for the 48 nm film has not been offset, but for clarity the other curves have been vertically offset by 0.065(101nm), -0.015 (39nm), -0.095 (26nm), and -0.03 (9nm), respectively. Measurements were done at 230°C except for 101 nm brush (225°C).

To decrease the effect of tethering and see if a cross-over to a regime where a relaxation of brushes could be identified, we decreased the grafting density of the brushes. Decreasing grafting density is achieved by putting spacer silane molecules among the initiator molecules as explained in more detail in 3, Experimental section. Since decreasing the grafting density diminishes the brush thickness for a particular molecular weight chain, to reach comparable thicknesses with lower grafting densities, longer reaction times are needed. This causes a loss of control of the molecular weight for very low grafting densities, which would require very long reaction times. Also, the molecular weights for brushes with the same thickness but different grafting densities

will be different. With these limitations, the lowest grafting density (σ) we reached in this series of experiments was 0.12 chains/nm². In Figure 5.8 correlation functions from three PS brushes with different grafting densities are shown: a 21 nm thick film of tethered PS chains with $\sigma = 0.12$ chains/nm², a 37 nm thick film of tethered PS chains with $\sigma = 0.19$ chains/nm² and a 67 nm thick film of tethered PS chains with $\sigma = 0.39$ chains/nm². Comparison of these three samples presents one challenge, and one expects a slowing of the surface relaxation with decrease in thickness, even apart from effects of covalent tethering. However, the main point is that we observe no relaxation in the experimental window of XPCS for grafting densities down to 0.12 chains/nm² for readily attainable molecular weights.

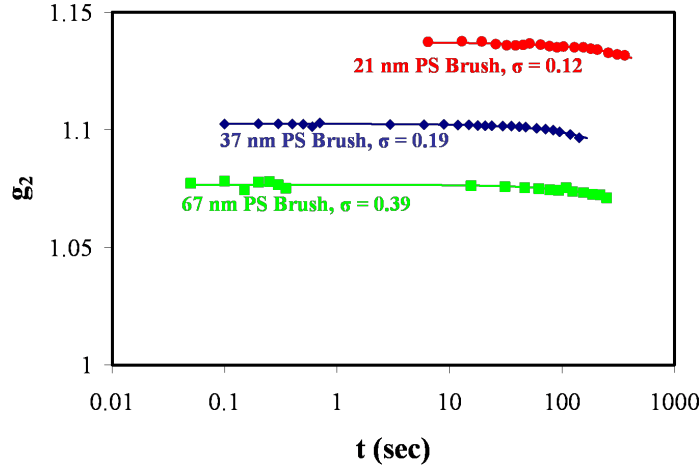


Figure 5.8: $g_2(t)$ vs. time at $q_{||} = 5.38 \times 10^{-3} \text{ nm}^{-1}$, $4.78 \times 10^{-3} \text{ nm}^{-1}$, $4.92 \times 10^{-3} \text{ nm}^{-1}$ for brushes of thicknesses(nm)/grafting density (chains/nm²) 21 (0.12), 37 (0.19), and 67 (0.39), respectively. For clarity the curves have been vertically offset by 0.04(21nm), 0.03 (37nm), and -0.02 (67nm), respectively. Measurements were done at 200°C except for the 21 nm film at 225°C.

The XPCS data provide information on surface fluctuations with characteristic wavelengths over a range of length scales, according to the range of $q_{||}$ probed. No relaxation was seen at any of the length scales investigated. Figure 5.9 presents

$g_2(t)$ for five values of $q_{||}$ for which reasonable statistics were obtained, corresponding to a range of length scales from 620 nm to 3100 nm.

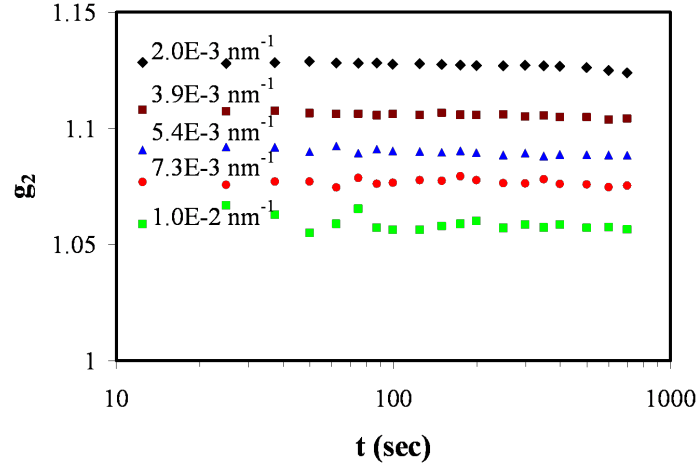


Figure 5.9: $g_2(t)$ for the 39 nm thick PS brush at 190°C at $q_{||} = 0.002, 0.0039, 0.0054, 0.0073$, and 0.01 nm^{-1} . The data for the $q_{||} = 0.0039 \text{ nm}^{-1}$ film has not been offset. For clarity, the other curves have been vertically offset by -0.01 (0.002 nm^{-1}), -0.01 (0.0054 nm^{-1}), -0.015 (0.0073 nm^{-1}), and -0.035 (0.01 nm^{-1}), respectively.

No relaxation was seen for any brush at any temperature investigated, as highlighted by Figure 5.10, which presents data for the PS-48 brush at temperatures up to 230°C. The highest temperature is about 130°C above the T_g of untethered chains of the same molecular weight ($T_g \sim 100^\circ\text{C}$). For the PnBA-30 brush no surface relaxation was seen for temperatures up to 170°C above the T_g of untethered chains, which is $\sim -50^\circ\text{C}$, so the phenomenon is also not peculiar to PS brushes.

All of these observations may be compared with the predictions of Fredrickson *et al.* [84] and Milner *et al.* [219] that long wavelength surface modes should be suppressed. Unfortunately, the scattering intensity falls off so quickly with $q_{||}$ that even at this state-of-the-art facility it is not currently possible to reach the values of $q_{||}$ comparable to $2\pi/h$ where relaxations are predicted to become evident. One anticipates that for sufficiently large h/R_g as the grafting density is decreased one should

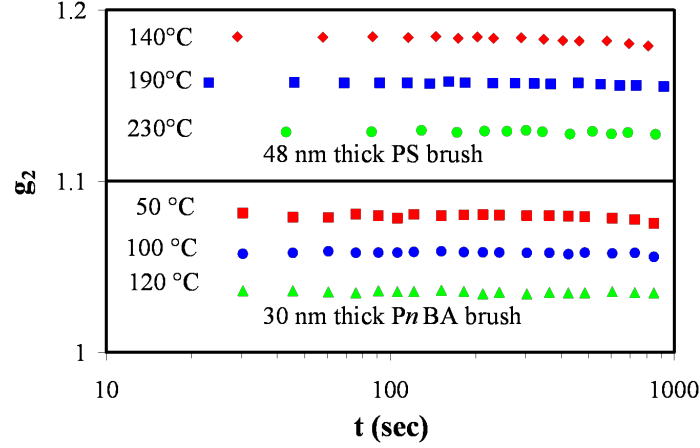


Figure 5.10: Autocorrelations for (top) a 48 nm thick PS brush at 3 temperatures, and for (bottom) a 30 nm thick PnBA brush. For clarity, curves for the PS brush have been offset by 0.07 (140°C), 0.04 (190°C) and 0.018 (230°C); curves for the PnBA brush have been offset by -0.08 (50°C), -0.07 (100°C), and -0.12 (120°C).

begin to see surface relaxation in the experimental time and $q_{||}$ window. However, for a grafting density of 0.12 chains/nm² ($h/R_g = 2.3$) still no relaxation is observed.

Application of Eq. 5.5 to the brushes suggests that their viscosities could be very high. Fredrickson *et al.* [84] estimate the zero-frequency shear modulus, μ_0 , of a brush to be:

$$\mu_0 = \frac{3k_B T \nu \sigma^2}{b^2} \quad (5.7)$$

where k_B is the Boltzmann constant, (1.38×10^{-16} gcm²/s²K), T is the equilibrium temperature in K , ν is the volume of a monomer, σ is the grafting density, and b is the segmental length. According to this formula, the modulus for the brushes with grafting density of 0.6 chains/nm² changes from 2 to 2.6 MPa as the temperature increases from 100 to 230°C. For brushes with lower grafting density (0.12 chains/nm²) the predicted modulus becomes 0.1 MPa at 230°C. For the brushes with high grafting density these values are approximately three orders of magnitude higher than the values of moduli estimated by Jiang *et al.* [7] for thin films of untethered chains. If

the viscosity of the brush were the same at 170°C as that of the 65 kg/mol chains in the 29 nm film of untethered chains in Figure 5.5, Eq. 5.5 would predict the surface relaxation time to be in the order of 0.01 seconds, which is too short to be seen in the XPCS experiment. For the relaxation time of a film of this molecular weight to be so large that it falls beyond the XPCS window on the high side, the viscosity would have to be at least 5 orders of magnitude higher than that of a corresponding film of untethered chains.

It is certain that the suppression or freezing of fluctuations seen here is not due to an increase in the T_g of the film for several reasons. First, we note that the temperature range we probe reaches up to 130°C above the bulk T_g of PS and 170°C above the bulk T_g of PnBA. Secondly, the temperature range probed is also much bigger than the magnitude of changes in T_g that have been reported by anyone [227, 228] to occur when chains are tethered in a brush. Thirdly, we have measured the shift in T_g for one of the brushes in this series and find that it is very small.

Due to a lack of consensus in the literature on the matter of shifts in T_g caused by the tethering in brushes, the topic bears some brief discussion. There have been various studies on the T_g of polymer brushes, but there is still no clear consensus about how T_g of a brush may differ from that of an analogous film of untethered chains. The determination of T_g in thin films can be done by several techniques, including positron annihilation lifetime spectroscopy [229], optical waveguide spectroscopy [230], Brillouin light scattering (BLS) [231–233] or particle embedding technique [234–237], ellipsometry [238–245], and X-ray reflectivity [246–251]. Using evanescent wave spectroscopy Prucker *et al.* [230] found the T_g ’s of free-radically polymerized PMMA of polymer brushes of high grafting density to decrease as the brush thickness decreased from 200 nm to 3 nm. Fukuda and coworkers [227] reported that 15-25 nm thick densely grafted PMMA brushes exhibit a value of T_g roughly 20°C

above that of bulk PMMA. However the strong interaction that PMMA segments have with the hydroxyl groups of the oxide layer, which might be the cause of the elevated T_g for PMMA brushes, is not present for PS chains. Tate *et al.* [228] found an elevation of 25°C for a 43 nm thick endgrafted PS chains. The best comparison between our situation and literature results can be made with the study of Tsukruk *et al.* [252]. They synthesized brushes using the same technique, ATRP, and their grafting densities were as high as ours. Tsukruk *et al.* directly measured the heat dissipation and thermoelastic response within the brush layer using a scanning probe technique. On the basis of their measurements they argued that the T_g of a densely grafted brush of poly(styrene-co-2,3,4,6-pentafluorystyrene) is the same as that in the bulk.

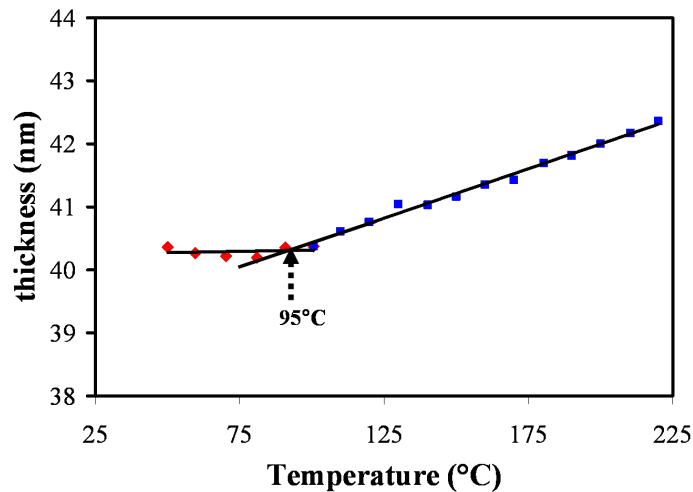


Figure 5.11: Thickness vs. temperature for 42 nm PS brush. The intersection of linear fits to two regimes of data indicates T_g .

An alternative method to determining the T_g of a brush is to measure the brush thickness as a function of temperature and note in a plot of thickness vs. temperature two regions of differing thermal expansion. The value of T_g is taken as the temperature of the intersection between linear fits to the data in these two regions,

as shown in Figure 5.11, which presents data for 42 nm thick PS brush considered in this work. The intersection occurs at $95 \pm 5^\circ\text{C}$, which is within a few degrees of the value of T_g in the bulk at a molecular weight of 40k g/mole.

In summary, XPCS measurements have revealed that the surface fluctuations seen in a particular time and $q_{||}$ window for films of untethered chains are absent on homopolymer brushes with grafting densities in the range of (0.12 to 0.6) chains/ nm^2 . In fact no relaxation at all can be observed in the time and wave vector space currently accessible. This is consistent with thermodynamic theories [84, 219, 220] to the degree that they anticipate fluctuations should be suppressed on the brush. However, whether the fluctuations are truly suppressed or rather slowed dramatically is not yet clear because the surface does have some sort of structure. This remarkable change in surface dynamics is more profound than that seen in ultrathin films of untethered chains and is a result of covalent tethering. The ability to alter surface dynamics by tethering could be used to tailor wetting, friction, and adhesion of polymer surfaces.

5.3 Surface Dynamics of Homopolymer Films on Chemically Identical Homopolymer Brushes

This remarkable change of surface dynamics of molten brushes brings a question if swelling a brush with short chains makes the surface mobile and moves the surface dynamics into the measurement window of XPCS. Naively one could imagine two scenarios occurring in that circumstance. The first scenario could be that short chains are equally distributed through the brush and provide swollen brush chains at the surface. The second scenario could be the partial penetration of short chains into the brush with a layer of short chains sitting atop the brush. The latter scenario with short chains of chemically identical polymer brings to the fore the issue of wetting

properties for which tethering could be crucial for stability of the film. This scenario has been extensively studied both experimentally and theoretically.

It has been demonstrated [253–257] that the wetting of polymeric films can be very different from those of simple liquids. Many polymeric films are unstable at temperatures above T_g , and dewet from substrates such as silicon wafers. Reiter [255,256] identified the three stages of dewetting process in thin films as (i) formation of holes, (ii) merging of holes and (iii) formation of droplets, and showed that the hole spacings scale with film thickness. Zhao et al. [257] demonstrated that the dewetting is dependent on the thickness of the film and the film dewets if its thickness is smaller than the radius of gyration of unperturbed chains, R_g .

It is vital to understand the mechanism and control of such surface instabilities. Various approaches to controlling dewetting have been proposed, including using additives [258–261] or chemical treatments [262–265]. An alternative approach is to create a new substrate surface by tethering the polymer chains to the substrate. It has been demonstrated that a partial wetting surface can be changed into a completely wetting surface by grafting to the substrate chains that are chemically identical to those in the melt [24,263,266]. However, grafting chains to the substrate is not always helpful. Sometimes addition of a grafted layer promotes dewetting. Maas *et al.* [8] combined experimental and theoretical SCF investigations of the wetting behavior of a 5 nm thick PS melt on top of a PS brush with M_n in the range of 1-10⁴ kg/mol with an increasing grafting density on a silica substrate and constructed the wetting phase diagram as shown in Figure 5.12. At zero or low σ , the films are always unstable because enthalpic interactions between the untethered PS and substrate are less favorable than enthalpic interactions among the chains. Contact between the substrate and PS melt chains occurs easily. In this *allophobic* region, the film has too many unfavorable contacts with the substrate to be stable. At higher σ , stable films

appear, and there is a region of complete wetting in the phase diagram for a wide range of free chain molecular weights. When σ is much higher, *autophobic* partial wetting is found. In narrow regions around the transition between the major regions yet other behavior is observed where the brush/melt interaction can be complicated.

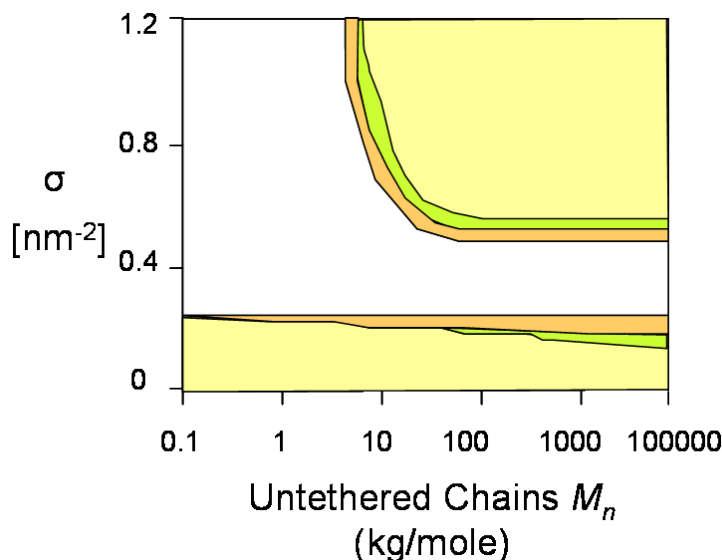


Figure 5.12: Wetting phase diagram of a untethered PS chains of varying M_n onto a PS brush of varying grafting density σ after annealing 12 days at 145°C under reduced pressure, redrawn from reference [8]. The initial film thickness in all experiments is $5 \text{ nm} \pm 0.1 \text{ nm}$. White area corresponds to complete wetting regime. Yellow areas of low and high σ s are for the aliphobic and autophobic regimes, respectively. Orange and green areas are regions for intermediate regimes where sample shows “hills” or “hills and holes”, respectively.

Liu et al. [24] reported that autodewetting of PS films occurs on a lamellar diblock copolymer surface when the ratio of the molecular weight of the free chain and the chemically identical top block of the lamellar substrate, $\alpha \equiv N_h/N_b$ is greater than 5. However, when $\alpha < 5$, the homopolymer completely wets the surface. It has been further investigated that PS thin films dewet from chemically identical grafted brushes much differently than they dewet from solid substrates [25–27]. They synthesized PS brushes with “grafting to” approach with grafting densities ranging from 0.0025 to

0.2 chains/nm². For brushes with a thickness of 20-35 nm no dewetting of the PS film occurs, while considerably thicker (high grafting density) or thinner (low grafting density) PS brushes lead to dewetting of the PS top layer.

The first theoretical predictions of wetting behavior of free chains on brushes by Leibler [28] were based on a strong stretching-theory that provided expressions for the scaling of the brush/homopolymer interface width, ($w_{b/h}$), with grafting density: $w_{b/h} \propto \sigma^{-1/3}$ and the scaling of interfacial tension, $\gamma_{b/h}$, with σ : $\gamma_{b/h} \propto \sigma^{1/3}$. Later, Shull [29] demonstrated, by more accurate self consistent field theory (SCFT) calculations, that the wetting/dewetting boundary occurred near $\alpha \approx 1$. In another theoretical study, Gay [30] showed that for high grafting densities and high molecular weight melts, for which partial wetting occurs, the melt chains penetrate into the brush over a distance that is small compared to the brush thickness. MacDowell [31] calculated an effective interface potential and found that at low grafting densities, the melt dewets; at intermediate grafting densities the liquid of free chains wets the brush. On further increasing the grafting density, dewetting (autophobicity) is encountered.

Using SCFT, Matsen [32] attributed the wetting/dewetting transitions to the change of interfacial tension between the brush layer and the free polymer layer. Khanna et al. [33] measured the temperature dependence of this interfacial tension with contact angle measurements and came up with an extremely small and negative excess interfacial entropy. This is in sharp contrast with liquid surfaces and interfaces between different liquids and reveals how large the discrepancy between experiments and theory can be when the compressibility of the polymer melt is not taken into account.

All of these studies have focused on the thermodynamics of free chain/brush interfaces, but still very little is known experimentally of the molecular level structure of these interfaces and the dynamics of the interfaces. These are very important,

however, to understanding the mechanisms of interfacial wetting, friction, adhesion and coating stability. Hu *et al.* [34, 35] investigated using XPCS the dynamics at polymer/polymer interfaces for the case of two immiscible polymer melts. They considered a thin PS film on top of a poly(4-bromo styrene) (PBrS) film. Due to high X-ray contrast between PS and PBrS, both the dynamics of the polymer/polymer interface, and the dynamics of the air/polymer interface were accessible. They observed that the top PS interface with vacuum shows two relaxation modes, while the buried polymer/polymer interface shows a single mode. The slow mode relaxation time of the top interface is wave-vector independent and the relaxation time of the fast mode is shorter than the relaxation time of the surface of a corresponding, thick PS homopolymer layer on a rigid substrate. They modeled the dynamics of these “bilayers” by assuming that the PBrS remains immobile on time scales involved, within the substrate layer and a thin, low viscosity mixed layer exists between the PS and PBrS melts, and a uniform PS layer lies on top of the mixed layer. Henle *et al.* [36] investigated with theory the effects of viscoelasticity and interfacial slip on the relaxation dynamics of the capillary waves of single layer films and melt/melt bilayer supported films. Their results account for Hu *et al.*’s observation of a wavevector-independent decay rate of a slow mode at the top surface of PS/PBrS bilayer films.

In this work, we consider the dynamics of the surface of a film of untethered PS chains on a PS brush and how the unusual dynamics of the brush may influence the dynamics of the free chains atop it. These structures we also refer to as “bilayers”, for convenience, but they are distinct from the melt/melt bilayers already mentioned above. To create the bilayers we spincoat PS untethered chains on PS polymer brushes. We considered first low molecular weight untethered chains (2.2 kg/mol) that cannot entangle with the brush chains and then increased the molecular weight of untethered chains to 7, 9, 20 and then 40 kg/mol. Throughout this

dissertation, bilayers are identified using a notation similar to that used for identification of the DCB samples. Each sample name contains the thickness of the brush and the thickness of the layer of untethered chains originally spincoated on top of the brush, and whether a given component of the bilayer is conventional PS or perdeuterated PS (dPS). The thicknesses of bilayers used in the sample names were measured with ellipsometry. Thickness values obtained from NR or XR are listed in Tables 5.3, 5.4, 5.5, 5.7. Physical properties of brushes used in bilayers are listed in Table 5.2. For example, the sample designation “PS37-dPS18” identifies a bilayer with an 18 nm thick film of untethered dPS spincoated on a 37 nm thick PS brush. Bilayer samples with untethered chains of M_n of 2200 g/mol and measured relaxation times at a chosen in-plane wavevector ($q_{||}$) are listed in Table 5.3.

Placing a PS brush between a film of untethered PS chains and the substrate on which it sits dramatically alters the dynamics of the film surface. Samples were not annealed in a separate oven before the XPCS measurement, but rather were annealed on the XPCS sample stage in an aluminum chamber under high vacuum before and during the dynamics measurements. When temperature was changed before a measurement, the sample was heated in the chamber and then equilibrated at the desired temperature over a total time of about an hour. Reflectivities were measured at each temperature before and after measurement to check for beam damage as well as to see if the structure changed while XPCS data were being measured. The data we present here were checked and any frame found to be distorted by beam damage removed. DSC curves of the PS ($M_n = 2000$ g/mole) and dPS ($M_n = 2200$ g/mole) chains used are shown in Section 7 in Figures 7.8 and 7.9 and the corresponding T_g s were found to be 64.5°C and 68°C, respectively. The experiments were run at T values very close to and above the T_g of the brush. However, these temperatures are substantially above the T_g of the free chains (2.2k) lying on the top surface where we probe surface dy-

Table 5.2: Physical Properties of Brushes Used in Bilayers to do XPCS and Neutron Reflectivity

Sample	h^a (nm) ± 0.2	M_n^b (kg/mol)	Pdi (M_w/M_n)	σ^c chains/nm ²	d^d (nm) ± 0.03	R_g^e (nm)	h/R_g
XPCS Samples							
PS-79	79	83	1.26 $\pm$ 0.016	0.6	1.3	7.7	10.2
PS-76	76	76	1.24 $\pm$ 0.017	0.6	1.3	7.4	10.3
PS-72	72	95	1.64 $\pm$ 0.027	0.6	1.2	8.2	12.3
PS-40	40	47	1.1 $\pm$	0.5	1.4	5.8	6.7
PS-21	21	21	1.02 $\pm$ 0.01	0.6	1.3	3.9	5.3
PS-41	41	123	1.6 $\pm$ 0.023	0.2	2.3	9.4	4
PS-18	18	96	1.3 $\pm$ 0.021	0.11	2.9	8.3	2.2
NR Samples							
PS-22	22	22	1.03 $\pm$ 0.021	0.6	1.28	4.03	5.45
PS-40	40	34	1.03 $\pm$ 0.014	0.7	1.17	4.95	8.07
PS-52	52	45		0.7	1.17	5.66	9.17
PS-70	70	73	1.21 $\pm$ 0.031	0.6	1.3	7.3	9.6
PS-25	25	62	1.05	0.25	1.99	6.7	3.75

^a Thickness (h) values from XR.

^b Number averaged molecular weights measured using gel permeation chromatography (GPC) for free chains in solution created at the same time the brush was synthesized.

^c Grafting density (σ) is calculated using $\sigma = N_A \rho h / M_n$, where M_n is the number average molecular weight, N_A is Avogadro's number and ρ is the bulk mass density.

^d Distance between the anchoring points.

^e Radius of gyration for corresponding unperturbed chain.

Table 5.3: Properties of Bilayers and Relaxation Times Measured (τ) with XPCS

Sample [*]	PS72-dPS27	PS79-dPS33	PS76-dPS45	PS44-dPS43	PS21-dPS42	PS41-dPS46	PS18-dPS62	PS18-dPS162	2.2k spuncast
h_u^a (nm)	27	33	50	46	44	50	70	102	43
h_b^a (nm)	72	79	76	40	21	41	18	18	--
σ^b chains/nm ²	0.5	0.6	0.5	0.5	0.6	0.2	0.11	0.11	--
τ (90°C)(sec) ^c		>10000		642	456	>10000	718	41.9	210
τ (100°C)(sec) ^c		>10000	303	110	36	>10000	95.6	4	23
τ (110°C)(sec) ^c		>10000		11	9				3.1
τ (120°C)(sec) ^c	>10000	>10000	8.8		1.4	>10000			0.7

^{*} All of the untethered chains listed in this table have M_n of 2.2k g/mol.

^a Thickness (h) values from XR.

^b Grafting density (σ) is calculated using $\sigma = N_A \rho h / M_n$, where M_n is the number average molecular weight, N_A is Avogadro's number and ρ is the bulk mass density.

^c Relaxation times (τ) obtained at $q_{||} = 4.5 \times 10^{-3} \text{ nm}^{-1}$.

namics. Figure 5.13 shows the relaxation time constants (τ) as a function of in-plane wave vectors, $q_{||}$, at 100 °C for a 45 nm thick PS film of 2.2k chains on a silicon wafer from which the native oxide has been etched using hydrofluoric acid. Also shown are the relaxation times at the same temperature for three samples for each of which a PS film of 2.2k chains was spuncast onto a densely grafted ($\sigma=0.5-0.7$ chains/nm²) brush using conditions such that after spinning (without drying in vacuum) the thickness of the overall sample (brush+free chains), as determined by X-ray reflectivity, was approximately 45 nm greater than the thickness of the brush itself. It is difficult to state precisely a thickness for the layer that was spun on for reasons that will become clear below. It is important to keep in mind that when the solution for spincoating the film is placed on top of the brush, at least some of the brush will certainly be swollen by the good solvent in the solution. Since the solvent is rapidly removed by spinning right after the solution is spread on the brush, one imagines the brush may not have time to be swollen to an equilibrium state before it collapses again upon solvent removal. However, it is reasonable to suppose that some interpenetration of casting solution (i.e. solvent + short polymer) into the brush occurs during spin casting.

The brush thicknesses vary from 21 to 40 to 76 nm. For each sample and value of $q_{||}$ the relaxation time was obtained by fitting the discrete data points for g_2 , the autocorrelation function, with the single exponential decay function shown in Eq. 2.79. The only assumption made in obtaining the relaxation times was that the surface dynamics could be well-characterized using a single exponential functional form. This was found to be an excellent assumption for all the data. There was no evidence of stretched exponential or multi-exponential forms. The relaxation times for the different samples can first be compared without reference to any model for the

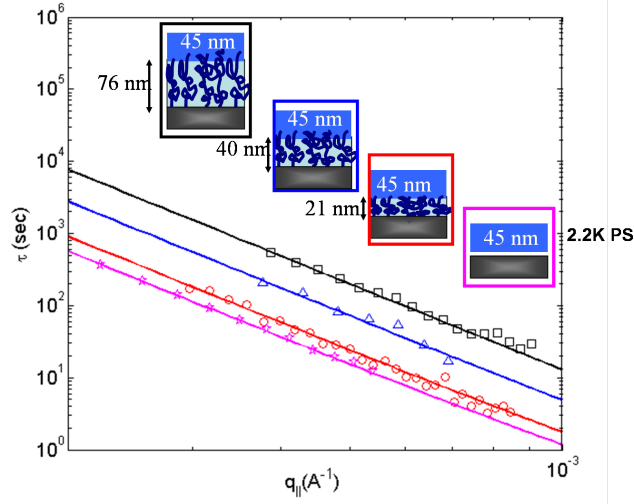


Figure 5.13: Relaxation times (τ) at 100°C for 45 nm thick film of untethered PS chains deposited on Si wafer(stars), and brushes with $\sigma = 0.5 - 0.6$ chains/nm² and thicknesses of 21 nm (circles), 40 nm (triangles), and 76 nm (squares). Curves represent least-squares fits based on Equation 5.1. A schematic of corresponding bilayers are shown as insets.

surface dynamics and so we consider first just the data points without the continuous curves (fits) that also appear in the plot.

When a 21 nm thick brush is interposed between the silicon and the 45 nm thick layer of free chains, the surface relaxation time of the film of free chains increases by a factor of two. Since the data points for different samples fall on essentially parallel curves on the plot, this factor is independent of wave-vector, or, correspondingly, the length scale of the surface fluctuations. When the brush thickness increases to 40 nm and 76 nm, the relaxation times increase by factors of, respectively, 5 and 14 relative to the film on a bare silicon substrate. We attempt to quantitatively model the experimental data by starting with the simplest model one can imagine, that of a single layer of viscous fluid on a rigid substrate with a non-slip boundary condition. That is, we assume that the brush surface is not moving, and that overdamped capillary waves on top of the layer of free chains can be described by the hydrodynamic

continuum theory of Jaekle [267]. This means that we assume there is a single layer atop the brush which is uniform in structure and in viscosity through its depth, as shown in Figure 5.14. In fact, one can readily imagine that the interface between the free chain layer and the brush is more complicated than that, with a region of finite depth in which the rheology of the sample varies from that characteristic of free chains (low viscosity) to that characteristic of the brush (potentially extremely high viscosity). However, we ignore the likely complexity and consider how far we may go in obtaining the ability to predict the surface dynamics using this simple picture. Consider the data for a single sample and a single temperature. In order to calculate the relaxation times from the model one must specify two parameters: the ratio of the viscosity of the top layer to the surface tension of the top layer (η/γ) and the thickness of the top layer. We assume that there is indeed a layer of some thickness next to the air that consists, to a good approximation, of pure free chains. In this case we may assume that the value of η/γ is the same for all the samples in Figure 5.13. For the 45 nm film on silicon we know the thickness precisely from reflectivity measurements, so for that sample we fix the value of h and by fitting the overdamped capillary wave model (which we know to be appropriate) to that data, we obtain the value of η/γ . Once η/γ is known the model can be fit to each data set using a film thickness as a fitting parameter. The thickness is the thickness of a (potentially fictitious) layer that has the same surface dynamics as the sample of potentially much more complicated structure. The solid curves in Figure 5.13 denote model fits obtained in this way. One observes that the model curves do an excellent job of capturing the shapes of the data sets.

The dynamic behavior predicted by the hydrodynamic continuum theory has the property that when the relaxation times normalized by film thickness (τ/h) are plotted as a function of dimensionless wavevector ($q_{\parallel}h$), as in Figure 5.15, data from

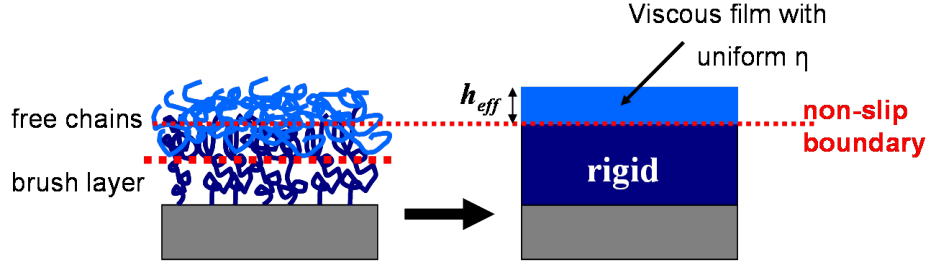


Figure 5.14: A schematic of a bilayer on the left and the representation of the model used to fit the XPCS data on the right.

various film thicknesses, but at the same temperature, must all fall onto a single curve. Thus, the data from different bilayers collapse onto universal curves because we have imposed the requirement that the effective viscous layer at the surface must have the same value of η/γ , no matter what the underlying brush is. This collapse is found for these data using a value of η/γ for the top layer, which corresponds at 100°C to a viscosity of 8.3×10^3 Pa.sec when the value of surface tension for pure 2.2k chains is taken to be 34.9×10^{-3} N/m as interpolated from data in ref [268]. (We assume the polymer material at the surface is pure 2.2k chains and that the surface tensions of PS and dPS are indistinguishable within our uncertainties.) This viscosity is close to the bulk viscosity for 2.2k PS chains (4.8×10^3 Pa.sec) calculated by double interpolation of literature values [216] and it is in good agreement with the viscosity value obtained for thin PS films by Zhang *et al.* using XPCS [214].

The effective thicknesses of the untethered chain layers found by this modeling process are 36 nm for the bilayer on the 21 nm brush, 27 nm for the bilayer on the 40 nm brush, and 16 nm for the bilayer on 76 nm brush. How might one understand these “effective” layer thicknesses, each of which is less than the thickness of the layer that was originally spun on? The interpretation that suggests itself most readily is that in each case some of the chains from the layer of free chains have penetrated into the brush, resulting in the overlayer being thinner than what it would have been

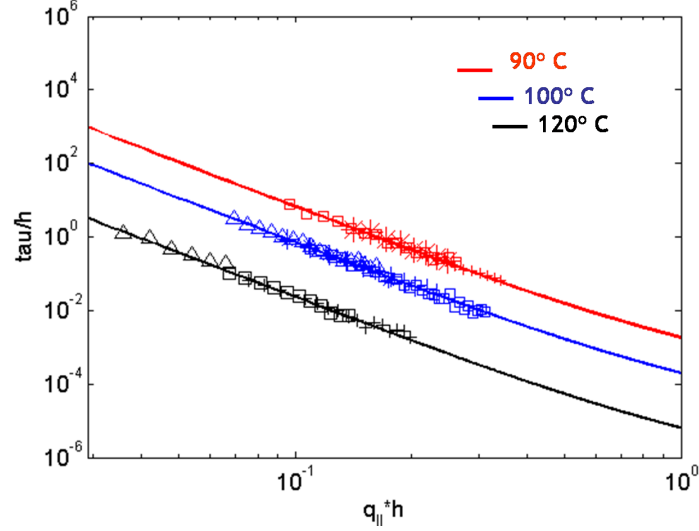


Figure 5.15: τ/h vs $q_{\parallel}h$ at 90°C (red), 100°C (blue), and 120°C (black) for bilayers of 2.2k PS chains on Si wafer(plus), and on 21 nm (squares), 40 nm (stars), 76 nm (triangles) thick brushes with $\sigma = 0.5 - 0.6$ chains/nm². Data from samples with different thicknesses of effective top layer collapse onto universal curves.

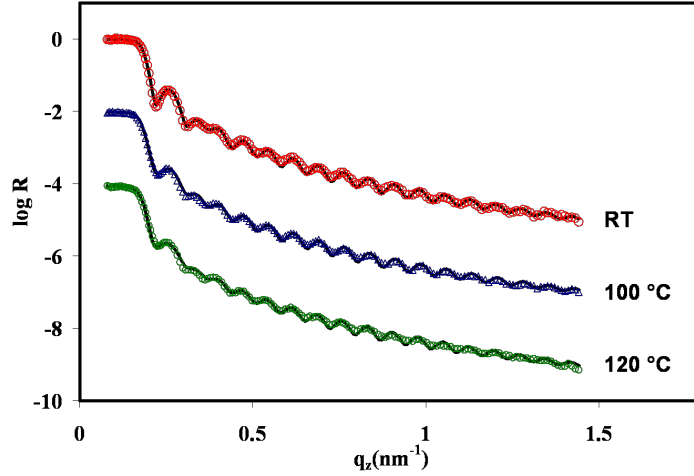
if the interface between free chains and brush were sharp. The free chains that have penetrated into the brush, though of very low molecular weight and therefore essentially like solvent molecules from a dynamics point of view, must not have plasticized the underlying brush sufficiently to cause appreciable interfacial fluctuations at the brush/free chain interface. The brush continues to act essentially as a rigid substrate. In the case of the layer on the 21 nm brush, 9 nm of the thickness increase achieved by spinning on the film remains unaccounted for after fitting to find the thickness of the effective top layer (i.e. 45 nm - 36 nm = 9 nm). This suggests that there must be a region in the sample, at least 9 nm in depth, which can be characterized neither as pure (or nearly pure) free chains nor as original brush. For the bilayer on the 40 nm thick brush this unaccounted for region is about 16 nm in depth, and for the 76 nm brush it is 29 nm in thickness. We speculate that the untethered chains in this region that contains both brush chains and free chains does not contribute to the sample surface dynamics. If our simple picture is sufficient, it is the portion of the free chains

that do not penetrate into the brush that determines the surface dynamics behavior; what the swollen brush does is irrelevant because we assume it is rigid, even though swollen.

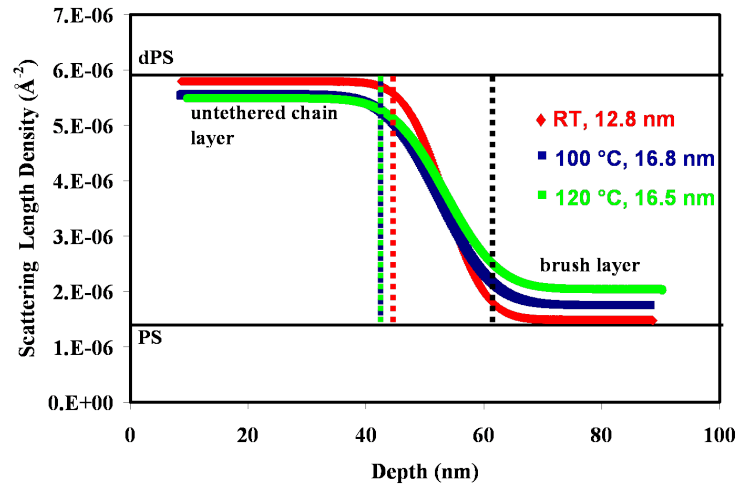
A critical experimental test of this simple, one layer theory for explaining the bilayer behavior is to measure the actual structure of the bilayer using NR, which can distinguish different types of chains using deuterium labeling. It is important to note also that in order for the model to be used to predict the surface dynamics of a sample for which no XPCS measurements have been done one must somehow determine experimentally the effective thickness of the top layer. This may be possible with NR. Unfortunately it was not possible to measure with NR precisely the same samples as had been measured with XPCS. For XPCS measurements, since the beam size is very small (beam dimensions were $20 \times 20 \mu^2$), samples of brushes grafted from 12 mm x 15 mm wafers are big enough to be used in XPCS. However, for NR, bigger wafers are needed because the beam width is around 35 mm and the area illuminated at small incident angles is greater than the size of the sample. So it is better to have bigger wafers to avoid this troublesome geometric effect. To do that, other samples were made that very nearly matched the bilayers studied with XPCS. The bilayer samples used for NR measurements are listed in Tables 5.2, 5.4 and 5.7. Figure 5.16 shows NR curves and the scattering length density (SLD) profiles at different temperatures for a bilayer of a 40 nm, high density brush and free chains sufficient to increase the overall film thickness by 45 nm. The fits were obtained using a structure model of the film structure consisting of a bottom layer of one SLD, a top layer of a second SLD, and an interface between the two layers created by convoluting the step change in SLD between layers with a Gaussian of appropriate width. Following this chapter, the interface widths mentioned here are the values of full width at half maximum of the Gaussian convolution functions obtained from best fit curves.

Roughnesses at the other interfaces were modeled by convolution with appropriate Gaussian functions as well. For all the bilayer films, such a model captures all the key features of the reflectivity curves. In order to picture the structure, schematic of the structure with corresponding SLD profile layers are shown in Figure 5.17. In order to make clear certain features of the SLD profiles, the plots contain horizontal reference lines corresponding to two important theoretical SLD values for pure materials. The upper bold line marks the experimentally determined value of SLD for the pure deuterated 2.2k g/mole dPS. This value was not available in the literature, and so was measured using NR. NR data collected from “as-deposited” spun cast film of 2.2 k dPS at three temperatures appear in Figure 5.18(a) and the corresponding SLD profile for one temperature in Figure 5.18(b). The SLD values found for all temperatures are shown in the table in the inset of Figure 5.18(b). The mass density inferred from the SLD value at 100°C is 1.1 g/cm³. This is 3.5% lower than the literature value for asymptotic value of density of high molecular weight dPS.

Several observations can be made about the SLD profiles shown in Figure 5.16(b). First, the best fit model for the room temperature (RT) data involves a value of SLD for the dPS-rich layer that is slightly less than that measured from the film of pure 2.2k dPS. This suggests that there could be some hydrogenous chains from the brush in this layer but the amount is 8% at RT based on the comparison of SLD value with that of film composed of pure untethered chains. Secondly, with increase of temperature, the SLD of the dPS-rich layer decreases more. While the mass density, and therefore SLD would be expected to decrease with temperature, since the measured values of SLD for pure 2.2k dPS do not change that much, it seems that more of the brush chains (23%) must be stretching into the free chain layer. Our third observation is that the value of SLD for the PS-rich layer at RT is almost same as the SLD value for pure PS at bulk density at room temperature.



(a)



(b)

Figure 5.16: (a) Neutron specular reflectivity (open symbols) and best fit model curves (solid lines) as a function of wavevector in the direction normal to the surface at q_z at RT (red), 100 °C (blue) and 120 °C (green) and (b) the scattering length density as a function of depth for the bilayer with 40 nm high density brush ($\sigma = 0.6$ chains/nm²) for the case in which addition of the free chains has increased the overall film thickness by 45 nm. Dashed vertical lines denote the extent of the interfacial regions for the three samples as specified by $fwhm$. The legend links each curve color with the temperature and interface width.

Table 5.4: Properties of Bilayers Measured with NR

Sample [*]	h_b^a (nm)	h_u^a (nm)	σ^b chains/nm ²	$fwhm^c$ (nm)25°C	$fwhm^c$ (nm)80°C	$fwhm^c$ (nm)90°C	$fwhm^c$ (nm)100°C	$fwhm^c$ (nm)110°C	$fwhm^c$ (nm)120°C
PS40-dPS20	37	18	0.7	10	14.6		15.9		15.2
PS40-dPS45	36	47	0.7	12.8			16.8		16.5
PS40-dPS60	37	66	0.7	10.6	15		16		
PS22-dPS45	25	46	0.6	6	8		9		9
dPS52-PS50	48	46	0.7	9.7	14.9		15.8		14
PS70-dPS45	75	40	0.6	22			27		26
PS30-dPS30	34	30	0.6	9.5	13	12	12	14	
PS25-dPS45	28	41	0.25	16	21		20		19

^{*} All of the untethered chains listed in this table has M_n of 2.2 kg/mol.

^a Thickness (h) values from NR.

^b Grafting density (σ) is calculated using $\sigma = N_A \rho h / M_n$, where M_n is the number average molecular weight, N_A is Avogadro's number and ρ is the bulk mass density.

^c $fwhm$ is the full width at half maximum of the Gaussian function used to define the interface between two layers in a model of structure to calculate the reflectivity .

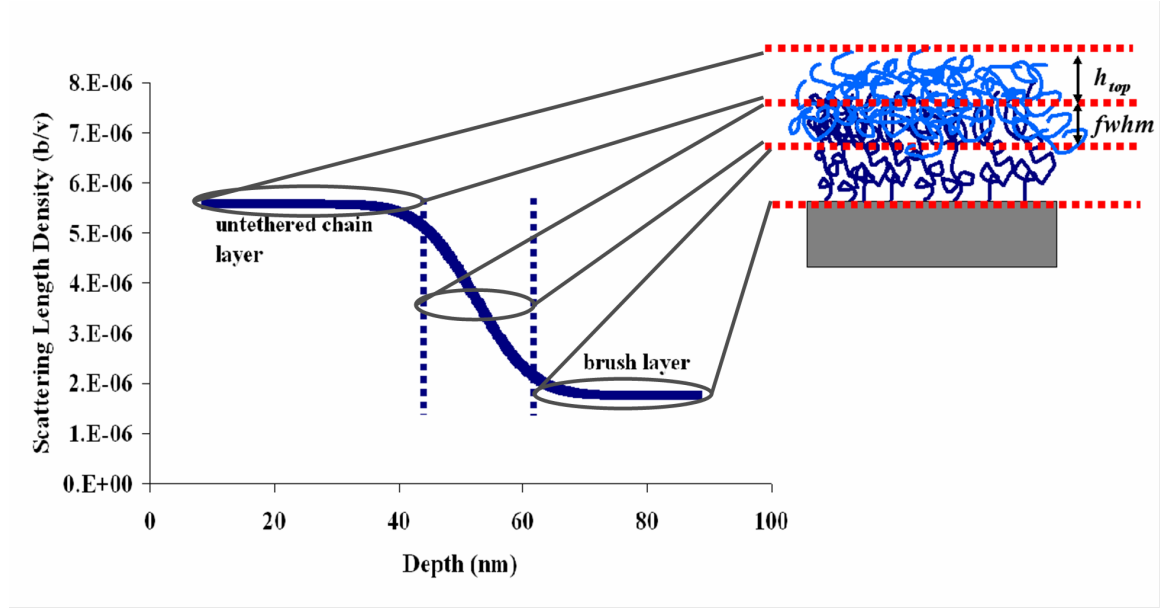
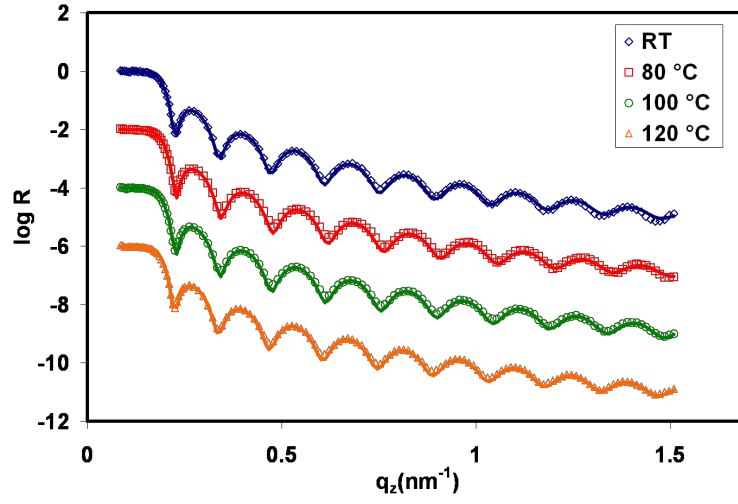
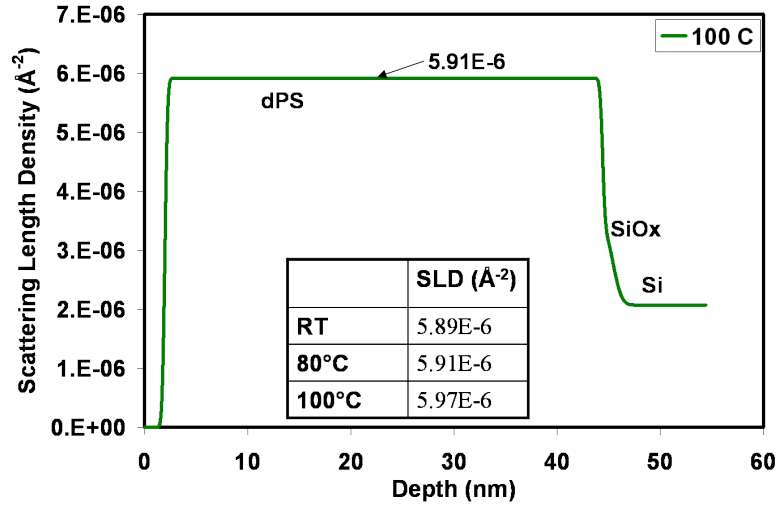


Figure 5.17: The scattering length density profile of the bilayer shown as a blue curve in Figure 5.16(b) and the corresponding layers are shown in the schematic of the structure.

Thus, the base of the brush appears to be essentially unchanged by the presence of the dPS chains on top of the brush. Increasing the temperature causes an increase of the brush layer's SLD apparently by incorporation of a small fraction (4.5% at 100°C and 9.5% at 120°C) of dPS free chains into the PS brush layer. The final general, and most important, observation is that there is an interface of finite width between these two layers. The interface width ($fwhm$) increases from 12.8 nm at RT to 16.5 nm at 100°C. The change with further heating to 120°C is within the uncertainty of the interface width determination. This behavior of change of interface width at 80°C and remaining constant within the uncertainties with further increase of temperature is consistent for all bilayers with 2.2k g/mole free chains on top. With increase of free chain molecular weight to 20k or 40k g/mole, change in $fwhm$ occurs at around 100°C which will be shown later in the text. This shows that the T_g of the free chains is very important for determining the interface behavior. Above T_g of bulk PS of



(a)



(b)

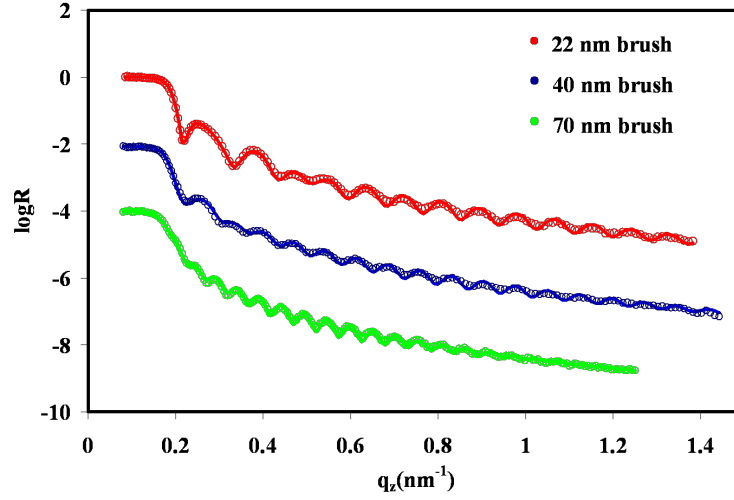
Figure 5.18: (a) Neutron specular reflectivity (open symbols) and best fit model curves (solid lines) as a function of wavevector in the direction normal to the surface at q_z at room temperature (RT) (blue), 80°C (red), 100°C (green) and 120°C (orange) and (b) the representative scattering length density as a function of depth for 100°C of 40 nm 2.2k dPS free chains spun on Si wafer.

Table 5.5: Interface Widths and Comparison of Top Layer Thicknesses of XPCS and NR

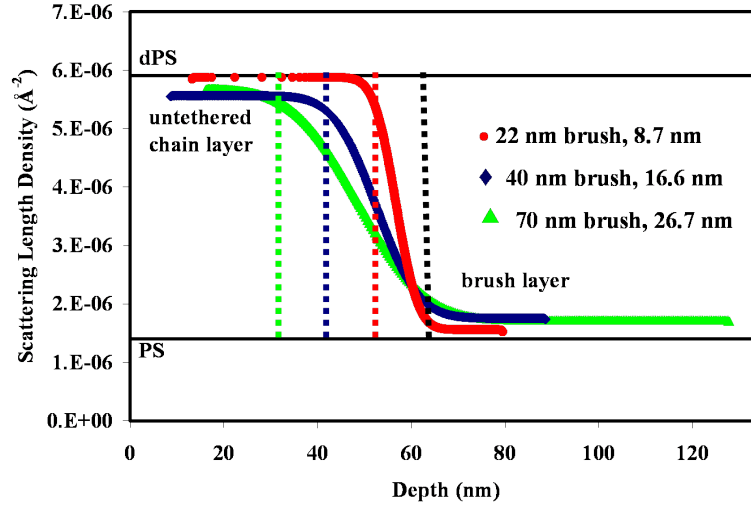
XPCS				NR				
name	h_b	h_u	h_{eff}	name	h_b	h_u	$fwhm$	h_{top}
					22	45	8.7	36
21d45	21	45	36	match 21	21	45	8.8	36.2
					40	46	16.6	28
40d45	40	43	27	match 40	40	43	15.8	27.2
					70	45	26.7	9
76d45	76	45	16	match 76	76	45	29.2	15.8

2.2k ($\approx 67^\circ\text{C}$), chain motions across the interface increases, they adjust the interface width at a value that the increase of temperature does not change it anymore.

The length over which the untethered chains interpenetrate the brush markedly are denoted approximately by vertical dashed lines in Figure 5.19b. Gay [30] and Leibler [28] anticipate two regimes of interpenetration behavior depending on whether the wetting of the brush is partial or complete. For all three bilayers the degree of polymerization of the untethered chains, P , is less than $(N/\sigma)^{0.667}$, where N is the number of segments in a brush chain and σ is the number of chains grafted in an area b^2 , with b being the segment length. This corresponds to Gay’s “short chain” regime. Complete wetting is expected and the interpenetration length, λ , defined as the distance over which a linearly varying is found, is expected to be $bN/\sigma P$. Our comparison with Gay’s predictions is limited in two ways. First, the actual composition profile is an error function, not linear. Secondly, Gay’s expressions are given only to within a numerical prefactor. For purposes of comparing experimental and theoretical “interpenetration lengths” we need to get the values of two times of the



(a)



(b)

Figure 5.19: (a) Neutron specular reflectivity (open symbols) and best fit model curves (solid lines) as a function of wavevector in the direction normal to the surface at q_z at 120°C and (b) the scattering length density as a function of depth for bilayers on 22 nm (red), 40 nm (blue) and 70 nm (green) high density brushes ($\sigma = 0.6$ chains/ nm^2) for the case in which addition of the free chains has increased the overall film thickness by 45 nm. Dashed vertical lines denote the extents of the interfacial regions measured as $fwhm$, with the black line used for all three samples. The legend links each curve color with the brush layer thickness and and corresponding interface widths for each bilayer.

Table 5.6: Interface Comparison of Theory with Our NR Results

h_b^a (nm)	M_n^b (brush) (kg/mol)	N	M_n (untethered chains) (kg/mol)	P	h_u (nm)	Scaling Theory λ (nm)	$2 \times fwhm$ (nm)	Exp./ Theory
22	23	217.2	2.2	19.6	45	33.2	17.4	0.52
40	34	328.4	2.2	19.6	46	50.2	33.2	0.66
70	74	706.2	2.2	19.6	45	107.9	53.4	0.50

^a Thickness (h) values from XR.

^b Number averaged molecular weights measured using gel permeation chromatography (GPC) for free chains in solution created at the same time the brush was synthesized.

full width at half maximum ($fwhm$). We assume that this interpenetration length may be reasonably compared with Gay’s value for a linear profile. In the bilayer with the 22 nm thick brush, the experimental interpenetration length is 17.4(8.7x2) nm and the theoretical value 33 nm, so the ratio of experimental to theoretical is about 0.5. The interpenetration length increases with brush thickness as predicted by Gay and Leibler, as shown in Table 5.6 and values of the ratio of the experimental to theoretical values are 0.56 ± 0.1 .

We next ask how the thicknesses of the top layer of nearly pure 2.2k chains seen by NR compare with the effective thicknesses of the top, mobile layer implied by our modeling of the XPCS data. The calculation of the NR top layer thickness, which involves a judicious choice of the boundary between “interface” and “top layer”, is illustrated in Figure 5.20 for the case of the thinnest brush studied by NR. Since the $fwhm$ interface width underestimates the width of the region in which SLD differs appreciably from the SLDs of either dPS or pure brush, especially for thicker brush

bilayer, we wish to consider the top layer as one in which the SLD hardly deviates from that of pure dPS.

Figure 5.19 shows NR curves and the scattering length density (SLD) profiles for bilayers of untethered PS chains on 22 nm (red), 40 nm (blue) and 70 nm (green) thick high density brushes ($\sigma = 0.6$ chains/nm²) for the case in which the overall sample thickness was increased by 45 ± 1 nm when the untethered chains were spun on. The structures seen in these three samples should be very close, though not identical, to the structures of the films studied with XPCS where the comparison details of the samples are shown in Table 5.5. The interface width increases with the thickness of the brush. When the untethered PS chains are on top of the 22 nm thick PS brush, the interface width ($fwhm$) is 9 nm. In the Figure 5.20 this width corresponds to the distance between the black dotted line and red dotted line. A nominal thickness for the top layer thickness can be calculated by measuring from the center of the polymer/air interface to the boundary between the top layer and interface region. For the bilayer with the 22 nm brush this top layer is 36.5 nm thick. In Figure 5.19(b) interface widths for all three samples are denoted by vertical dashed lines. When the brush thickness increases to 40 nm the interface width becomes ca. 17 nm and the thickness of layer on top becomes about 28 nm. Finally, when the brush is 70 nm thick, the interface width becomes 27 nm and the “top” layer thickness becomes 8.5 nm. It is critical to observe that these “top layer” thicknesses, since they are defined beginning at a point within the interfacial zone corresponding to the top edge of the $fwhm$, rather than beginning where the SLD has fully attained the value characteristic of the top layer in the structural model, are larger than the thicknesses of the free chain-rich regions for which the SLD is uniform. That is, these “top” layer thicknesses are actually for a region that is not fully uniform in composition (or viscosity) with depth. However, that nonuniform part of the layer is thin.

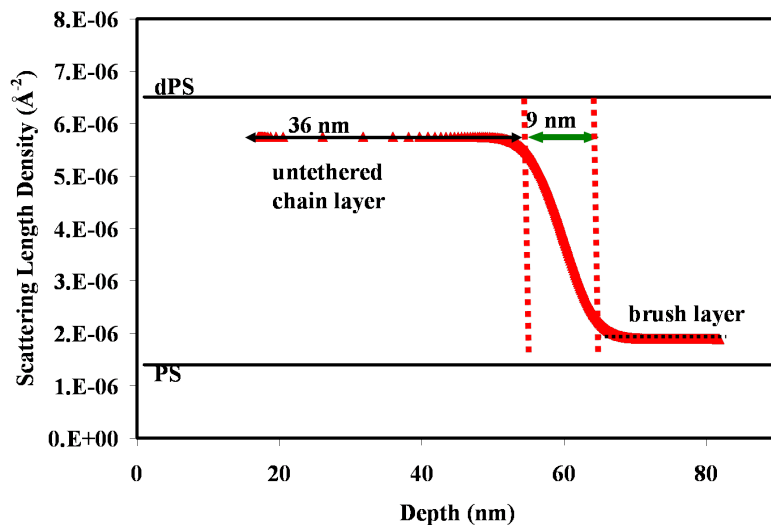


Figure 5.20: Interface width ($fwhm(9\text{ nm})$) and effective “top” thickness (36 nm) is shown details on the scattering length density profile of a bilayer of 22 nm high density ($\sigma = 0.5\text{ chains/nm}^2$) brush for the case in which addition of the free chains has increased the overall film thickness by 45 nm given in Figure 5.19(b).

The NR study actually represents more than just a determination of the structure of the samples measured with XPCS. It investigates a scientific question of interest on its own, which is how the free chains penetrate into a brush. Once the polymer brush and untethered chains are in contact, they adjust the penetration depth to minimize the overall system free energy. For convenience we can consider our “system” to be a volume including the entire brush and the entire layer of free chains. The elements of the bilayer structure that potentially change as the system seeks an equilibrium state are i.) the interfacial width, ii.) form of the interfacial profile, iii.) concentration of free chains in the brush below the interfacial zone, and iv.) concentration of brush chains in the “top” layer above the interfacial zone. The system free energy is adjusted essentially by balancing two effects. Penetration increases combinatorial entropy; on the other hand the penetration causes extra stretching of the brush chains that brings with it an entropic cost in elastic free energy. The

most apparent manifestation of this balancing is the increase in interface width with increase in brush thickness. When the brush thickness is larger, the percentage increase in stretching of brush chains is smaller to achieve the same penetration depth. Therefore, at a given penetration depth the stretching penalty for mixing is smaller with the thicker brush.

These “top” layer thicknesses observed experimentally with NR can now be compared with the “effective” thicknesses from the single viscous layer analysis of the XPCS data. In order to make a precise comparison, some interpolations of values must be done since the layer thicknesses in the NR samples do not correspond exactly to the layer thicknesses in the XPCS samples. It proves to be convenient that the change of the *fwhm* with brush thickness appears to be linear and a 1 nm increase in brush thickness is accompanied by a 0.35 nm increase in interface width. Since *fwhm* does not change with untethered chain layer thickness(a fact explored below), we do not need to correct our interface widths for differences in the untethered chain layer thicknesses between the NR and XPCS samples. In Table 5.5 the comparison of the top layer thicknesses inferred from the XPCS and NR results is facilitated by listing numbers for three types of samples: real XPCS samples, real NR samples, and fictitious NR samples with brush thicknesses identical the brush thicknesses in the corresponding XPCS samples. For the fictitious comparison samples, values for IW have been interpolated, where necessary from experimental values obtained from the samples that were measured.

Comparison of the top layer thicknesses inferred from the two techniques can now be done using the values of h_{eff} (from XPCS) in the fourth column of Table 5.5 and values of h_{top} in column nine. We may think of the values of h_{top} as “structural” thicknesses of the top layer, while values of h_{eff} are “dynamical” thicknesses of the top layer. Since the interface widths are not quite large enough to

account for the full transition of SLD from one layer to another, the thicknesses shown in column nine actually correspond to layers that are not entirely uniform, but have a small region of somewhat higher viscosity at the edge adjacent to the brush. Since such a region would slow the top surface fluctuations, the “structural” thicknesses would be expected to be slightly higher than the “dynamical” thicknesses, if anything. For the thinnest brush, the effective thickness of a 2.2k chain layer pertinent for the surface dynamics and the thickness seen by NR of the bilayer is the same. The relative difference between “dynamical” thickness and the “structural” thickness is slightly larger for the thicker brush, for two reasons:

Firstly, as the brush thickness grows, the rate of change in composition with depth in the beginning of the interpenetration region becomes more gradual. The precision of measurement of τ is such that the relative composition of short chains and brush chains must change substantially before the resulting difference in viscosity can be sensed by the modeling of the XPCS data. That is, as observed above, in order to detect with modeling the presence of a separate, mobile layer containing mostly 2.2k chains and a fraction of tethered chains, the viscosity would have to differ from that of the top layer by 5 or 6 orders of magnitude. However, at a depth in the sample at which the viscosity actually becomes that large, the material is, with respect to the experimental window of the technique, no longer mobile. Put another way, the depth at which the derivative of the composition profile of highly mobile 2.2k chains changes rapidly is determined by XPCS. For the 76 nm thick brush, the first 10 nm of the interpenetration region has a viscosity sufficiently similar to that of pure 2.2k chains that it contributes to the effective layer thickness dictating the relaxation rate of the surface fluctuations.

The second reason for greater relative difference between “effective” and observed layer thicknesses for higher brush thickness is a result of fact that the amount

of 2.2k chains spun on was held constant as brush thickness increased. As the fraction of the 2.2k chains that penetrate into the brush grows larger, the thickness of the layer left on top drops. Thus, the depth of the region inside the swollen brush over which the concentration of 2.2k chains (and thus viscosity) varies gradually becomes more and more significant in comparison to the thickness of the top layer.

So the most sensitive measurement one can do for determining if some part of the swollen brush is contributing to the surface relaxation time is to measure bilayers in which the layer of untethered chains spun onto the brush is thin enough to completely penetrate into the brush so that no free chains are left on the brush. This is the only way with a dPS on PS system to study the dynamics of the swollen brush interface directly because there is insufficient contrast at the interface between brush and free chains for the XPCS to resolve the dynamics. Therefore, fixing brush layer thickness and grafting density, we decreased the thickness of the layer of free chains. Fixing brush thickness and grafting density should fix the interpenetration between the brush and untethered chain layer. Thus, decreases in the amount of free chains should lead to decreases in the free chain layer thickness effective for the surface dynamics. In Figure 5.21 the intensity-intensity normalized time autocorrelation functions for these three samples with 76 nm brushes in which the amount of free chains spun onto the brush was decreased. For the first sample the overall sample thickness increase with addition of free chains was 45 nm thick. For the other two the thickness increase was 33 and 27 nm, respectively. For the sample with 45 nm of free chains added (sample already studied above) the full relaxation of the surface fluctuations falls within the XPCS measurement window and the best fit using a single exponential yields a relaxation time of 5 s at 120°C. For bilayer samples with 33 and 27 nm increase due to untethered chains, the surface fluctuations become so slow that they move outside the time and $q_{||}$ range of our XPCS experimental setup at

120°C. Films of 2.2k chains on rigid silicon substrates do have surface relaxation times in the XPCS experimental window, so clearly the surface fluctuations have been altered dramatically again by interaction with the brush, but we must once again use insights from NR to reveal what sort of structure is present. We do not have measurements from exactly these samples, but we do have NR measurements for a series of bilayers in which the thickness added by spinning on free chains is decreased while brush thickness and density are held constant. The SLD profiles for bilayers of 40 nm thick, high density dPS brushes are shown in Figure 5.22. These three samples correspond to adding 20 nm, 45 nm and 60 nm of untethered PS chains on the brush. The interface widths for these three samples are almost the same around 16 nm. If the interface width remains the same for these samples implies, the effective “top” layer thickness must decrease as h_u decreases. If the interface width is constant at 17 nm under these conditions, then the layer outside the brush must be 28nm and 3nm in thickness for these two cases. That means that the sample PS40-dPS20 is a very good approximation to a sample in which the surface of the brush has been swollen, but there is very little residue of free chains on top. In this case very similar to PS76-dPS27 of XPCS sample even thinner on top, indeed, although the surface of the brush has been plasticized, as evidenced by the fact that the 2.2k chains have gone a substantial distance into the brush, the surface relaxation of the brush would not be sped up enough to come into the XPCS experimental window.

It has been shown both theoretically [66, 269] and experimentally [31] that the grafting density of the brush strongly affects the mixing between the untethered chains and brush chains. The grafting density of the brush is an important factor since by just varying it one can obtain mushroom like structure or strongly stretched chains. MacDowell [31] demonstrated that the variation in grafting density of the brush affects the wetting of a brush by chemically identical untethered chains on

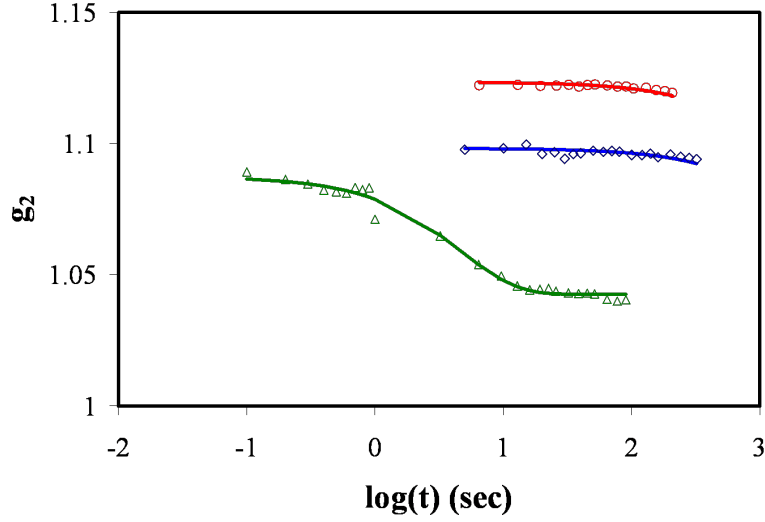


Figure 5.21: Intensity-intensity time autocorrelations at $q_{||} = 4.9 \times 10^{-4} \text{ \AA}^{-1}$ and at 120°C for bilayer samples 76 nm thick PS brush ($\sigma = 0.5 \text{ chains/nm}^2$) on which have been spun cast untethered PS chains sufficient to increase the total sample thickness by 27 nm (circles), 33 nm (diamonds), and 45 nm (triangles).

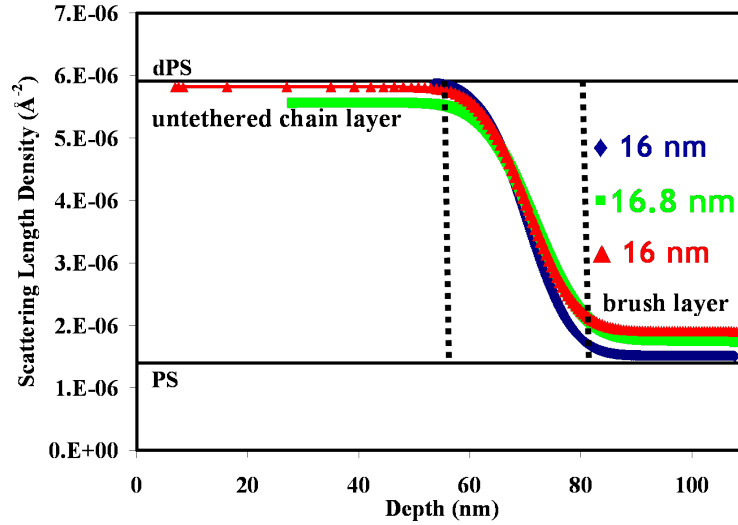


Figure 5.22: The scattering length density as a function of depth at 120°C for bilayers of 40 nm high density ($\sigma = 0.5 \text{ chains/nm}^2$) brushes for the case in which addition of the free chains has increased the overall film thickness by 20 nm (blue), 45 nm (green) and 60 nm (red). Labels show the interface widths for the corresponding bilayers.

top. The effect of grafting density on the relaxation of surface height fluctuations was investigated by preparing samples with the same h_u and h_b but with different grafting densities. The surface relaxation for a film of untethered chains on a dense (0.5 chains/nm²) 44 nm thick brush in the case that 45 nm of chains is spun on is clearly observed in Figure 5.23. In contrast, no relaxation is observed within the XPCS time and length scale for a bilayer with a brush with σ of 0.2 chains/nm² and 45 nm of free chains spun on top. When the brush chains are sparsely grafted, there is space for untethered chains to penetrate into the brush appreciably without stretching the brush chains to a very highly stretched state. When the brush chains are densely grafted, they form layer which can accommodate the interpenetration of free chains only by very high stretching of the brush chains. Thus, if the amount of free chains spun onto the brush is sufficient to leave a layer of free chains on top, for the brushes with lower grafting densities, the effective thickness of the untethered chain layer is lower than that of the layer on the high grafting density brushes.

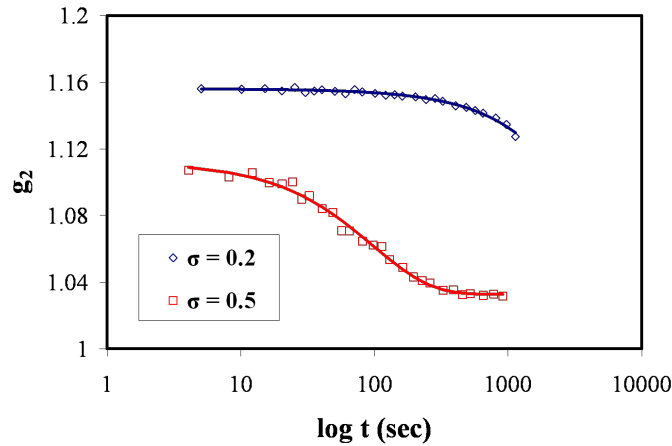


Figure 5.23: Measured time constant τ vs in-plane wave vector $q_{||}$ at 90°C for bilayers of 41(44) nm PS brush of $\sigma = 0.2$ (diamonds) and 0.5(squares) chains/nm² for the case in which addition of the free chains has increased the overall film thickness by 45 nm.

The increase in penetration depth with decreasing grafting density can be readily tested by NR measurements. SLD profiles of two bilayer samples made by spinning 50 nm of untethered dPS chains on top of a high density brush of 22 nm thickness and low density brush of 25 nm thickness after annealing for 6 hours at 100°C are shown in Figure 5.24. The interface width for the bilayer sample with grafting density ($\sigma = 0.5$ chains/nm²) is 9.7 nm. Decreasing the grafting density to 0.2 chains/nm², increases the interface width by a factor of 2.5 and *fwhm* becomes 24.2 nm. This penetration depth increase causes a decrease in effective thickness of the free chain layer on top and leads to very slow surface height fluctuations. We also note that in the case of lower grafting density the SLD in the bottom layer is larger, suggesting that some small fraction of chains may penetrate through to the substrate surface, or that there are some holes in the brush (see discussion of AFM images below). The SLD in the layer of free chains is also somewhat lower in the case of the low grafting density brush. This could be due to a small fraction of long brush chains that extend up into the free chain layer, or a small number of holes in the top layer that does not occur on the denser brush.

Both XPCS and NR provide only laterally averaged information on the sample surface. They do not evidence directly the presence of lateral variations in structure or dynamics. Therefore it is important to check on some issues with the bilayer films using a complementary technique such as Atomic Force Microscopy, which does have lateral resolution. One of these issues is the stability of the films and the potential for dewetting. According to the wetting phase diagram in Figure 5.12 we are in the regime of complete wetting even for 2.2k untethered chains. To be sure about complete wetting of the untethered chains on the brush layer, we did AFM measurements on some of the bilayers to observe the surface topography. Images shown here are representative images of more samples measured giving similar results and rms

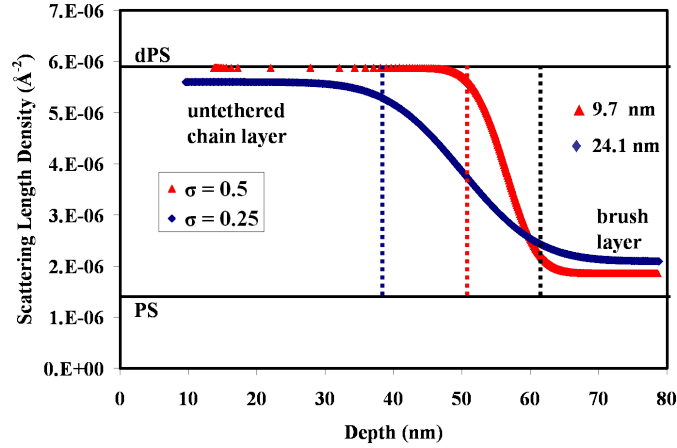


Figure 5.24: The scattering length density as a function of depth at 100°C for bilayers of 22 nm high density ($\sigma = 0.5$ chains/nm²) (red) and 22 nm low density ($\sigma = 0.2$ chains/nm²) (blue) brushes for the case in which addition of the free chains has increased the overall film thickness by 50 nm. Labels show the interface widths for corresponding bilayers.

roughnesses are the average roughnesses of images taken at least at 3 different spots on the surface of the sample. Figure 5.25(a) shows AFM topography images taken before and after XR exposure to the surface of a bilayer of 40 nm PS brush for which the addition of untethered chains has increased the overall film thickness by 43 nm. The surface rms roughness from a 15 μm x 15 μm AFM image before heating and X-ray exposure is 0.37 $\pm$ nm. After heating this increases substantially to 1.8 $\pm$ nm. The roughness value at the air surface obtained from NR at 100°C for a bilayer of 40 nm brush on which has been spun cast untethered PS chains sufficient to increase the total sample thickness by 46 nm is 1.6 $\pm$ 0.3 nm. Since the bandwidths of these two techniques are different and NR averages over a much larger area on the surface, this difference is reasonable. There is not a significant pattern of widespread dewetting such as holes, droplets or islands in either image. After XPCS measurement at higher temperatures with a cycle of 80°C-90°C-100°C-120°C with an annealing time of $\sim$ 30 min at each temperature, the surface gets much rougher, which is the effect

of temperature. The roughness does not change much after spinning free chains onto the brush but the roughness does increase after XPCS measurements. The XPCS measurements were done at higher temperatures and then the sample cooled down to room temperature. The surface structure measured with AFM is the structure quenched from 120°C and reflects the effects of thermally stimulated fluctuations of larger amplitude thus a higher surface roughness.

We also consider a comparison of surface topography of a bilayer with that of the underlying brush with no untethered chains atop. Figure 5.25(b) shows an image of the surface of only the brush layer (on the left) and the surface after untethered chains have spun on the same brush (on the right) and measured with XPCS with a heating cycle of 80°C-90°C-110°C-120°C with an annealing time of ~ 30 min at each temperature. After spinning on a layer of free chains and heating while taking XPCS measurements, no dewetting is seen. There is a low density of holes, defects, in the bilayer before XPCS measurement. After heating to higher temperature for some time the holes associated with such defects are somewhat larger and also contribute to the increased roughness of 1.7 ± 0.06 nm. Images were taken from 5 different spots and they are all consistent in terms of the density and heights of the spots. The high features have heights of 5 to 21 nm. We conjecture that this is due to the relaxation of the ATRP conditions to get thicker, 79nm brush. This is done by addition of monomer second time to increase the thickness of the brush more. It could be that a few chains grow much more than the others and then the “extra” chain balls up in a globule sitting on the brush causing holes and bumps on the surface. They become more prominent after spinning on the 2k chains and heating.

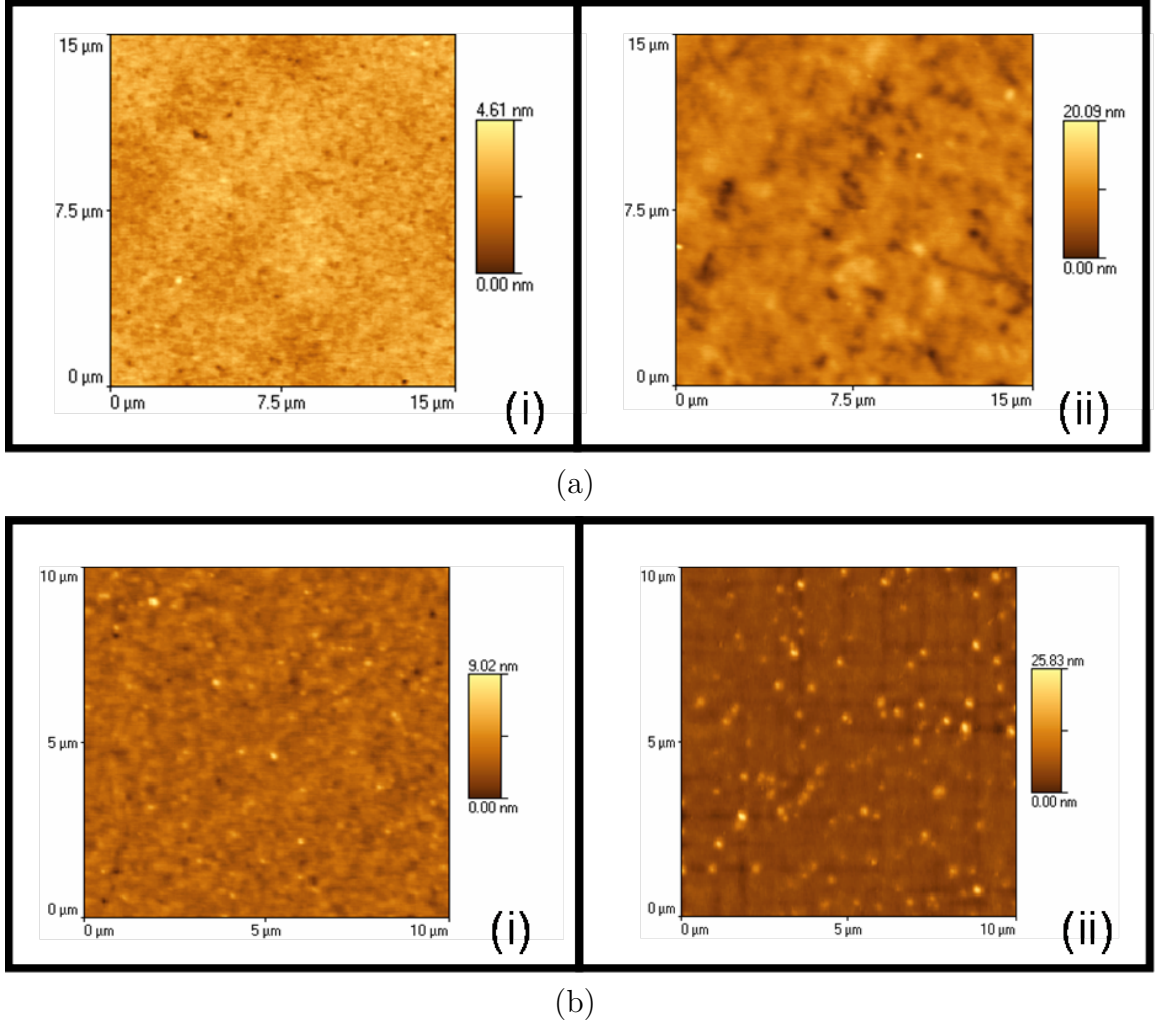


Figure 5.25: (a) (i) AFM image of 45 nm 2.2k g/mole untethered chains on 44 nm PS brush with $\sigma = 0.53$ chains/nm² right after spinning before annealing and (ii) after XPCS measurements with a heating cycle of 80°C-90°C-100°C-120°C. (b) AFM image of 79nm PS brush with $\sigma = 0.6$ chains/nm² before spincoating. (ii) AFM image of the same brush with a 33 nm thick layer of 2.2k g/mole untethered chains on top after XPCS measurements with a heating cycle of 80°C-90°C-110°C-120°C.

5.3.1 Trial of Different Models to fit the Bilayer XPCS Data

The single layer model with a non-slip boundary does a good job of fitting the XPCS data. However, attempts were made to fit the data using models provided by Henle *et al.* [36] that envision either a single layer of Newtonian fluid with slip boundary at the

interface, or bilayers of two Newtonian fluids or a Newtonian fluid on a Maxwellian viscoelastic layer.

Henle shows that when there is a single Newtonian layer with non-slip boundary at the substrate interface, there occur two modes of relaxations, changing depending on the value of qh . When a significant amount of slip occurs between the fluid and the solid interface an intermediate relaxation mode occurs along with the other two modes. As shown before within our XPCS data range, our data fits one of the modes of the single Newtonian layer model with non-slip boundary condition. When slip is incorporated into the model, the model definitely cannot capture the data, as shown in Figure 5.26. The viscosities and surface tension values used in the slip boundary model ($\lambda = 0.01h$) are the same as those used for non-slip boundary model (Figure 5.13).

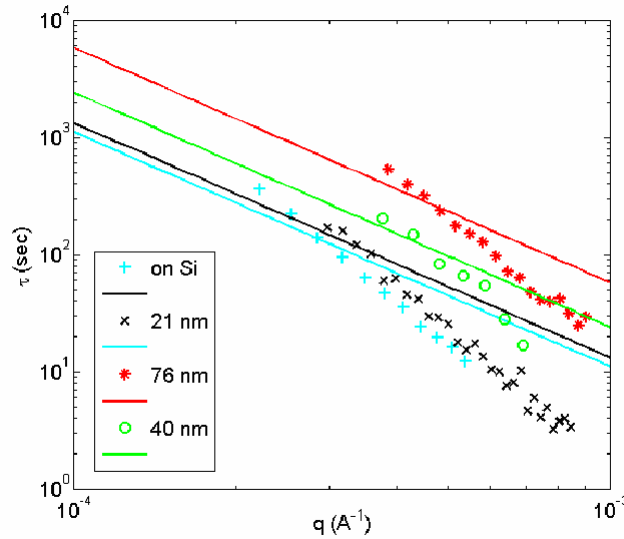


Figure 5.26: Relaxation times(τ) at 100°C for 45 nm thick film of untethered PS chains deposited on Si wafer(plus), and brushes with $\sigma = 0.5 - 0.6$ chains/nm² and thicknesses of 21 nm (cross), 40 nm (circles), and 76 nm (star). Curves represent least-squares fits based on single layer Newtonian model with a slip boundary.

We now turn to double layer models as illustrated in the schematic in Figure 5.27. The bottom and the top fluid layers have viscosities η_1 , η_2 , surface tensions γ_1, γ_2 and thicknesses h_1 , h_2 , respectively. The total thickness is $h = h_1 + h_2$. For simplicity Henle consider the possibility of slip at only the fluid/fluid interface and no slip at fluid/substrate interface.

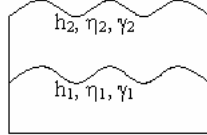


Figure 5.27: Schematic illustration of two fluid layers of thicknesses h_1 , h_2 , viscosities η_1 , η_2 and surface tensions γ_1, γ_2 . 1 and 2 correspond to bottom and top layers, respectively.

Henle predicted that there should be two normal modes when both layers are Newtonian fluids. In the presence of either small ($\lambda = 0.01h$) or large slip length ($\lambda = 10h$) at the fluid/fluid interface these modes have q -dependent decay rates. One of these modes is a fast mode dominating at the air surface while at the buried interface the slow mode dominates. We have tried to fit our data using Henle's two Newtonian fluid model by varying the thicknesses and viscosities of the layers.

In the model the thickness of the bottom Newtonian layer was assumed to be equal to the thicknesses of the brush layer (21, 40, 76 nm), and the thickness of the top layer was taken as the thickness of the effective layer (36, 27, 16 nm) obtained from single layer fitting. Viscosities of the layers are kept constant (8×10^3 Pa.sec). Calculated relaxation times from the model are compared to the experimental ones in Figure 5.28. The first observation we make is that the q -range we explore with XPCS is really limited (symbols in the figure are data points) and covers a very small portion of the whole spectrum over which different q -dependent behaviors are observed. Secondly, even though the model predicts two modes, one at the air surface

and one at the fluid interface, we can only measure the fast mode at the air surface using XPCS due to the strong X-ray contrast available there. It is clear from the figure that this kind of model does not capture the experimental data. As shown in 7 in Figures 7.1, 7.2, 7.3, the autocorrelation functions of bilayers reach to the baseline of the range of 1.02-1.05. If there is a second, slower relaxation that is out of our window we would expect the baseline not to reach 1.0.

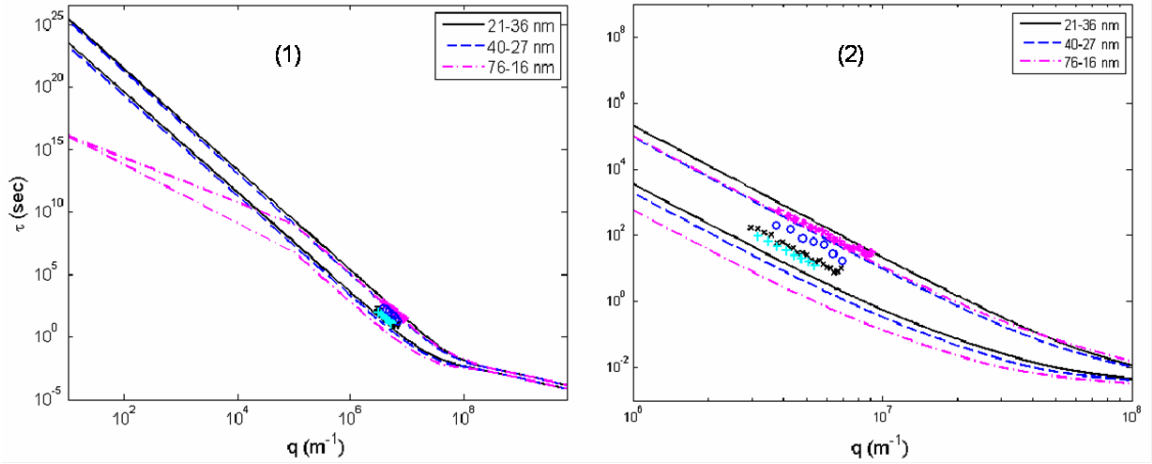


Figure 5.28: (1) τ vs q for a double layer system with a buried Newtonian layer and an upper Newtonian layer together with (2) a zoom-in plot, using thicknesses of layers $h_1 = 21, 40, 76$ nm and $h_2 = 36, 27, 16$ nm and same viscosity for both layers $\eta_{1,2} = 8 \times 10^3$ Pa.sec for all three bilayer models. Symbols correspond to our data points measured by XPCS.

Fixing the viscosities for the bottom and top layers to the same value is certainly not a good approximation since previous work [178] has indicated that the polymer brushes are immobile within the time and length scales of the XPCS measurements, perhaps due to the viscosity of the brush being orders of magnitude larger than viscosity of the corresponding untethered chains. Therefore, the calculations were performed in which the bottom layer viscosity was varied while keeping the top layer viscosity and thickness constant and the results shown in Figure 5.29. When viscosity difference between the two layers gets larger, the relaxation time difference

between the two modes of the model gets bigger, with more prominent changes occurring in the slow mode relaxations. A given increase in the viscosity difference between layers causes different effects when the layers have different thicknesses. The thicker the top layer and higher the viscosity difference between the layers, the slower the slow mode relaxation gets. The fast mode (upper surface) relaxations of the two Newtonian layer model matches with our XPCS data as long as the viscosity difference between the bottom and top layers is at least two orders of magnitude or larger.

The best model fit for our data with the fast mode of the two Newtonian layer model is shown in Figure 5.30. For the bilayer with thickest bottom layer the model has a better fit when the viscosity difference between the two layers is at least 3 orders of magnitude while for the other two thinner samples a difference of 6 orders of magnitude or larger is needed to get a good fit. This suggests that the mixing of the two layers is more pronounced for the sample with the thickest brush leading to a much thinner layer of pure untethered chains, on top of the brush. If the top layer thickness is decreased by a factor of about two (9 nm) to be consistent with the NR analysis for the thickest brush, the fast mode of the two Newtonian model fits the data when the viscosity difference between the layers is 2 orders of magnitude as shown in Figure 5.31.

It is more conceptually attractive to use the interfacial width, instead of brush thickness, as the thickness of the bottom layer thickness, since we do not expect that the pure brush is mobile. Using a top layer thickness of either 9 nm or 16 nm for the bilayer with the thickest brush, and a viscosity difference of 6 orders of magnitude the fast mode of the relaxation fits the XPCS data well, as shown in Figures 5.32(a) and 5.32(b).

To investigate the effect of bottom layer thickness we have tried different thicknesses by keeping the top layer thicknesses and both layers' viscosities constant.

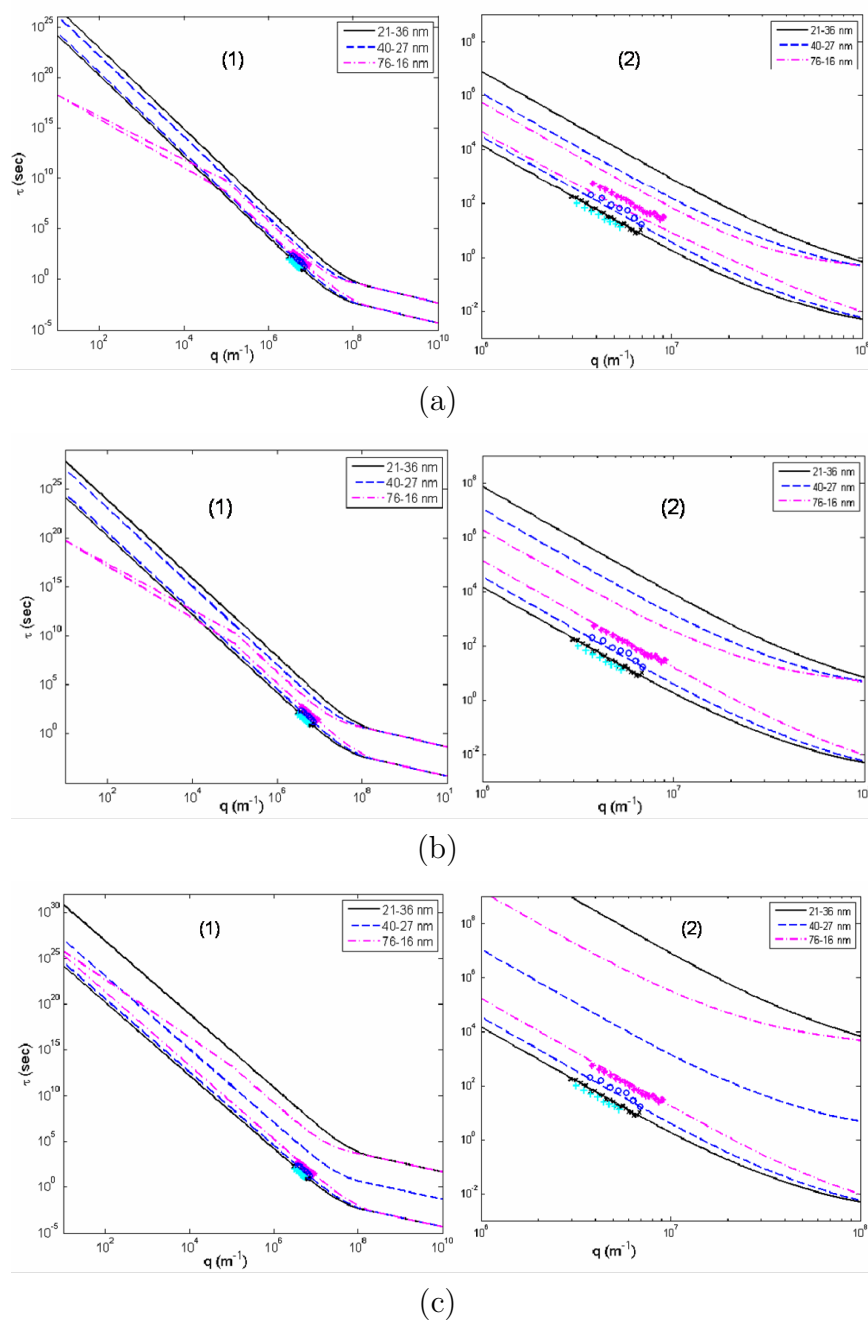


Figure 5.29: τ vs q for a double layer system with a buried Newtonian layer and an upper Newtonian layer, using bottom layer thicknesses of $h_1 = 21, 40, 76$ nm and viscosities $\eta_1 =$ (a) 8×10^5 (b) 8×10^7 (c) 8×10^9 Pa.sec, respectively. Top layer thicknesses are taken as $h_2 = 36, 27, 16$ nm, respectively and $\eta_2 = 8 \times 10^3$ for all three cases. Symbols correspond to our data points measured by XPCS. (The plots on the right side (2) are zoom-in plots of the left hand side plots (1))

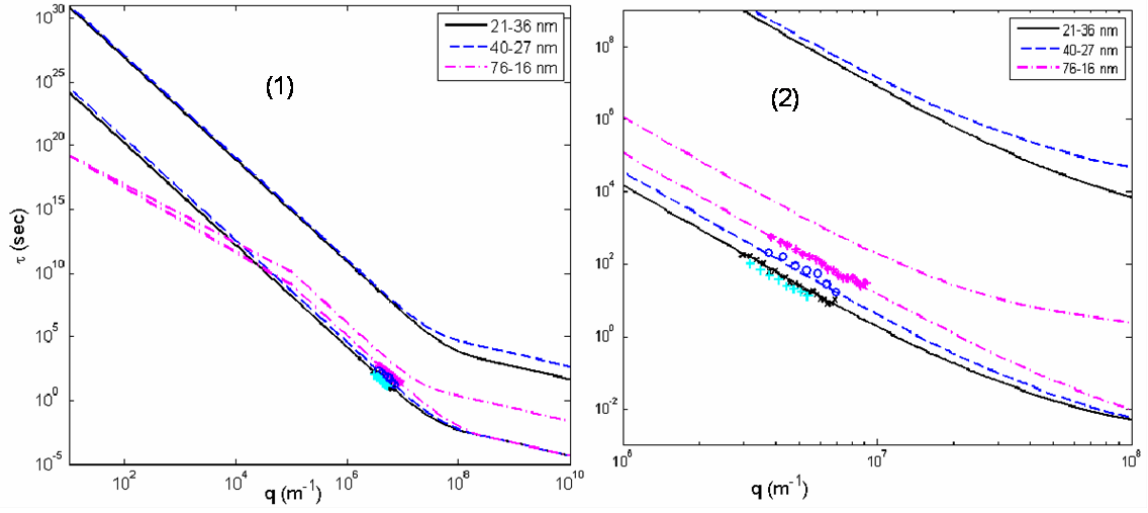


Figure 5.30: (1) τ vs q for a double layer system with a buried Newtonian layer and an upper Newtonian layer with (2) a zoom-in plot, using thicknesses of layers $h_1 = 21, 40, 76$ nm and $h_2 = 36, 27, 16$ nm. Viscosities of the layers are $\eta_2 = 8 \times 10^3$ and $\eta_1 = 8 \times 10^9, 8 \times 10^9, 4 \times 10^6$, respectively. Symbols correspond to our data points measured by XPCS.

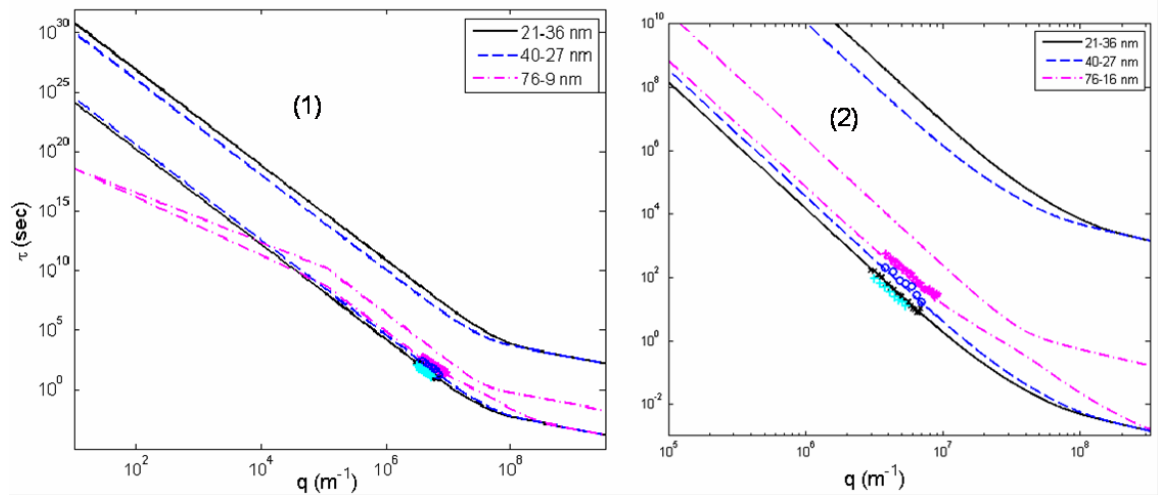


Figure 5.31: (1) τ vs q for a double layer system with a buried Newtonian layer and an upper Newtonian layer with (2) a zoom-in plot, using thicknesses of layers $h_1 = 21, 40, 76$ nm and $h_2 = 36, 27, 9$ nm. Viscosities of the layers are $\eta_2 = 8 \times 10^3$ and $\eta_1 = 8 \times 10^9, 8 \times 10^9, 9 \times 10^5$, respectively. Symbols correspond to our data points measured by XPCS.

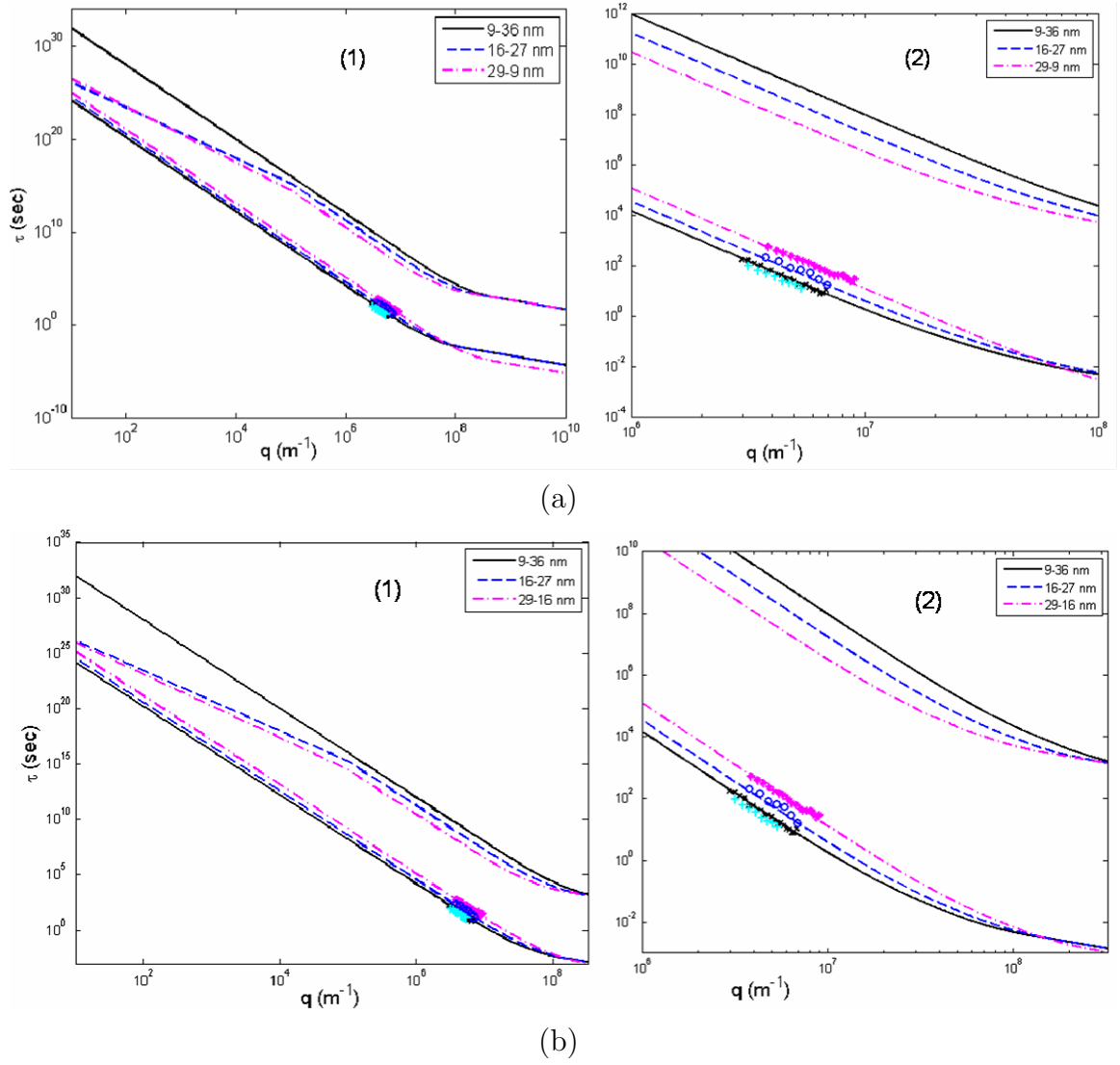


Figure 5.32: (1) τ vs q for a double layer system with a buried Newtonian layer and an upper Newtonian layer (2) with a zoom-in plot, using thicknesses of layers (a) $h_1 = 9, 16, 29$ nm and $h_2 = 36, 27, 9$ nm and (b) $h_1 = 9, 16, 29$ nm and $h_2 = 36, 27, 19$ nm viscosities of the layers are $\eta_1 = 8 \times 10^9$ and $\eta_2 = 8 \times 10^3$ same for all bilayers. Symbols corresponds to the our data points measured by XPCS.

We have varied the thickness of the bottom layer from 10 nm to 100 nm. When the same thickness is taken for the bottom layer for all three samples, the slow mode relaxation times become very nearly the same for the three choices of upper layer thickness. As shown in Figure 5.33, increasing the thicknesses of the bottom layers speeds up the slow mode at the interface by for all the samples. On the other hand, the fast mode relaxations on the surface still captures our XPCS data for any thickness of the bottom layer.

All of these models show that if we assume a two Newtonian layer system, the viscosity of the bottom layer should be at least three orders of magnitude higher than that of the top layer. While theorists anticipate that the brush should, in fact, be modeled as a viscoelastic layer [84], the data collected here can be rationalized by contenting ourselves with a model having a bottom layer thickness that high enough. However, it is interesting to consider a model in which bottom layer is a Maxwell fluid, in order to understand what sort of behavior such a model predicts and what range of q one would need to cover in order to experimentally reveal if the bottom layer has an elastic component to its behavior. The Maxwell fluid is the simplest model for a viscoelastic material. This approach introduces two rheological parameters for the Maxwell layer, the transient modulus, E , and the stress relaxation time of the medium, τ_s . For simplicity, Henle analyzed this system with stick boundary conditions at all interfaces. The Maxwell fluid itself has two decay rates, and each rate has two major scaling regions: a q -dependent region and a q -independent region. Such a double layer system has both those features of a Maxwell fluid as well as those of a Newtonian fluid, so that all four decay rates contribute to the relaxations at both top and buried interfaces. Similarly as with the two-Newtonian layer model trials, here different models with various layer thicknesses, viscosities, and bottom

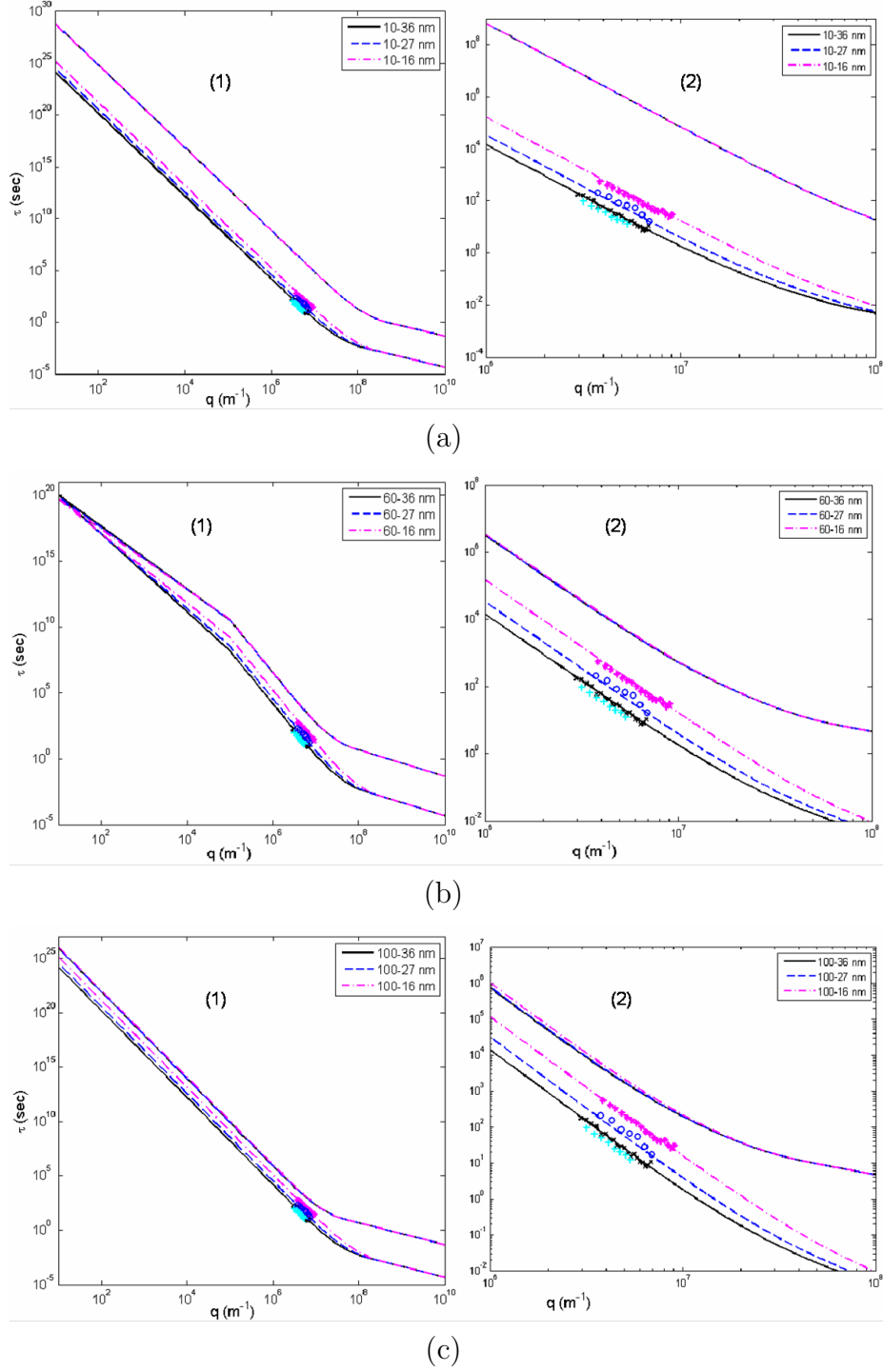


Figure 5.33: (1) τ vs q for a double layer system with a buried Newtonian layer and an upper Newtonian layer with (2) a zoom-in plot, using thicknesses of layers $h_2 = 36, 27, 16$ nm and (a) $h_1 = 10$ nm (b) $h_1 = 60$ nm and (c) $h_2 = 100$ nm. The viscosities of the layers are $\eta_1 = 8 \times 10^6$ and $\eta_2 = 8 \times 10^3$ for all bilayers. Symbols corresponds to our data points measured by XPCS.

layer transient modulus and stress relaxation time have been used to find the best fit of our XPCS data.

As shown by the comparisons to relaxations times calculated from such models fits in Figures 5.34, 5.35, 5.36, there are both similarities in behavior of the decay rates to that seen for the two Newtonian layer models and distinct differences. In particular, with the model having the Maxwellian bottom layer there are regions of q -independent behavior combined with q -dependent rates. In Figure 5.34 viscosity difference between layers is set to three orders of magnitude to be able to fit data points with the fast mode relaxation curve. The stress relaxation time of the Maxwellian bottom layer has been varied from 10 seconds to 10^5 seconds. In all cases the faster relaxation modes of the models fit the data points. The effect of stress relaxation is observed in the slower (buried layer) modes and particularly in regions where those slower modes are strikingly q -independent.

If the thicknesses and viscosities of the layers are kept the same as those models used in Figure 5.34 and the stress relaxation times of the bottom Maxwellian layer is set as 1000 seconds in all models, when the transient modulus of the bottom layer varied from 1 to 10^5 Pa, the fast modes of the models still fit the data well. However, a change becomes apparent when the value of E_1 becomes 10^3 Pa. The single continuous curve describing the slower modes splits into two curves with different rates. When E_1 becomes 10^5 Pa, the split becomes more clear with increases in the relaxation times of both branches of the q -independent behavior.

Changing the top layer thickness of the bilayer with the thickest brush (76 nm) to 9 nm to match the untethered chain thicknesses measured by NR, to be able to fit the XPCS data for the bilayer with the thickest brush, the viscosity difference between the layers needs to be set to at least five orders of magnitude. Increasing the viscosity difference of that model to 7 orders of magnitude (Figure 5.36.(2)),

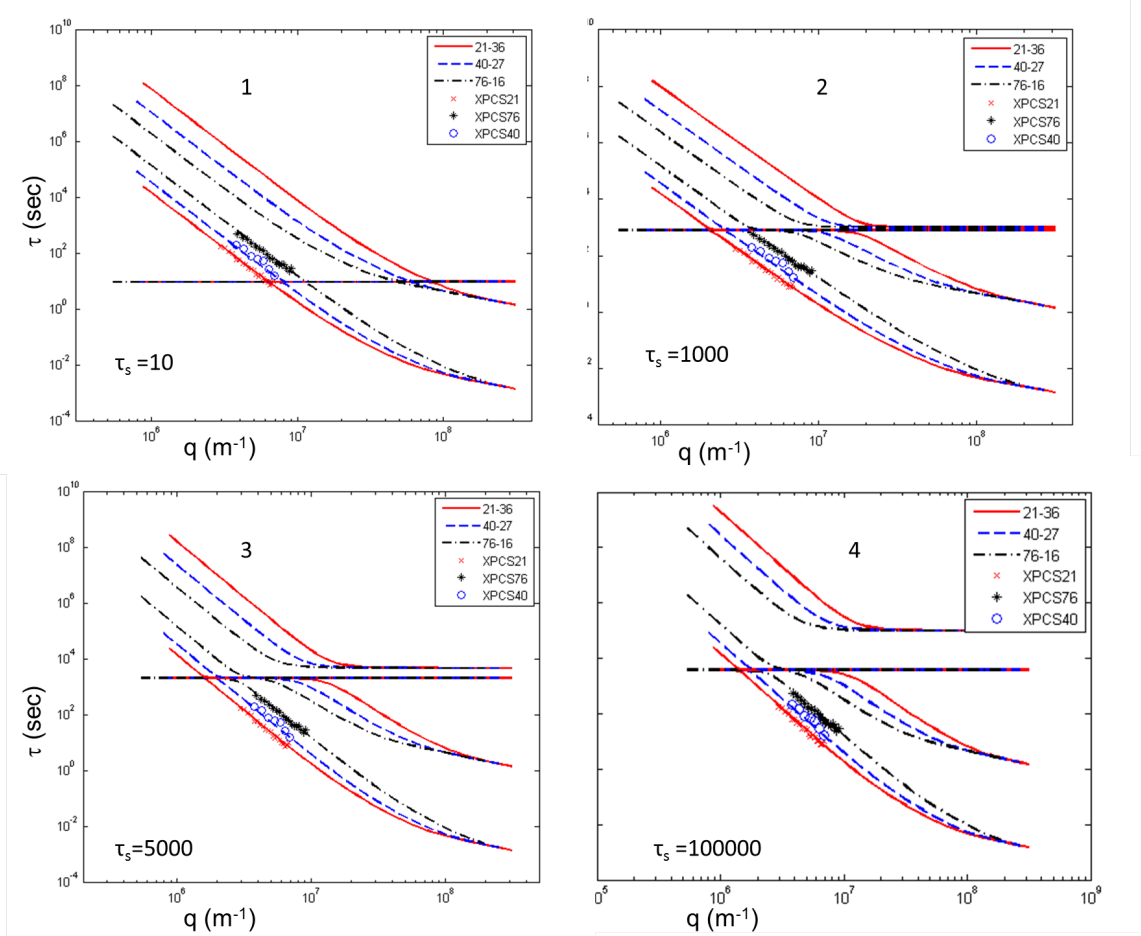


Figure 5.34: τ vs q for a double layer system with a buried Maxwell layer and an upper Newtonian layer with thicknesses of layers $h_1 = 21, 40, 76$ nm and $h_2 = 36, 27, 16$ nm and viscosities of the layers are $\eta_1 = 8 \times 10^6$ and $\eta_2 = 8 \times 10^3$. E of the Maxwell layer is taken to be the same for all three bilayer samples and equal to 8×10^3 Pa and τ_s of the Maxwell layers is taken to be (1)10, (2)1000, (3)5000, (4)100000 sec. Symbols corresponds to our data points measured by XPCS.

the faster modes of the model still fits our data. The difference is observed in the q -independent and q -dependent parts of the slower modes of the bilayer with the thickest brush layer. If the τ_s of the Maxwell layers is reduced from 10^5 sec. to 10 sec. (Figure 5.36.(3),.(4)) for each model, the faster mode still fits our data.

If, instead of the brush thickness, we use the interfacial width as the thickness of the bottom layer and we use either 9 nm or 16 nm for the top layer thickness of

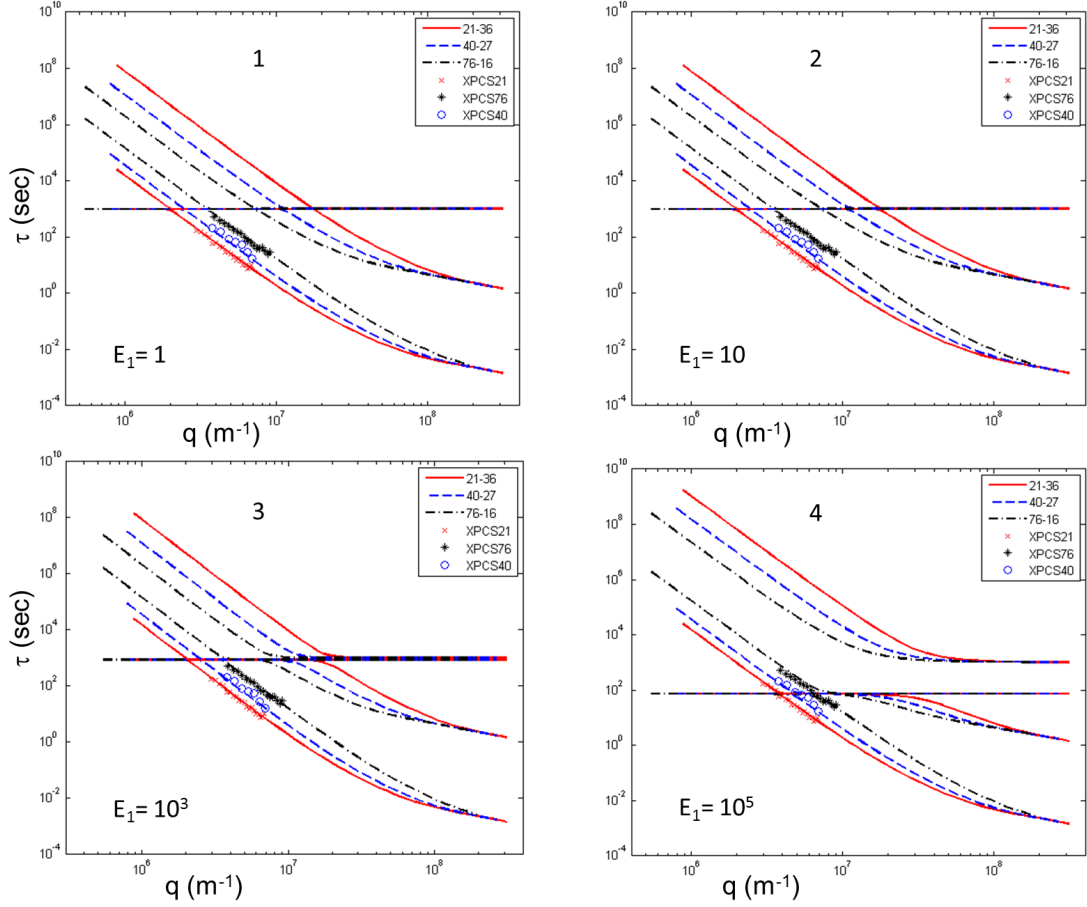


Figure 5.35: τ vs q for a double layer system with a buried Maxwell layer and an upper Newtonian layer with thicknesses of layers $h_1 = 21, 40, 76$ nm and $h_2 = 36, 27, 16$ nm and viscosities of the layers $\eta_1 = 8 \times 10^6$ and $\eta_2 = 8 \times 10^3$. The value of τ_s for the Maxwell layers is taken same for all three layers and is equal to 1000 sec and E_s of Maxwell layers are (1)1, (2)10, (3) 10^3 , (4) 10^5 Pa. Symbols correspond to our data points measured by XPCS.

the bilayer with thickest brush, the fast modes of the relaxations still fits the XPCS data well, as shown in Figure 5.37. This collection of Figures show that taking the Maxwellian layer thickness as either the brush thickness or the interface width does not affect the behavior of the relaxations of central interest.

All of these more complicated models offered no better fits, but the fitting process did provide a bound on the viscosity of the swollen brush. In order to obtain

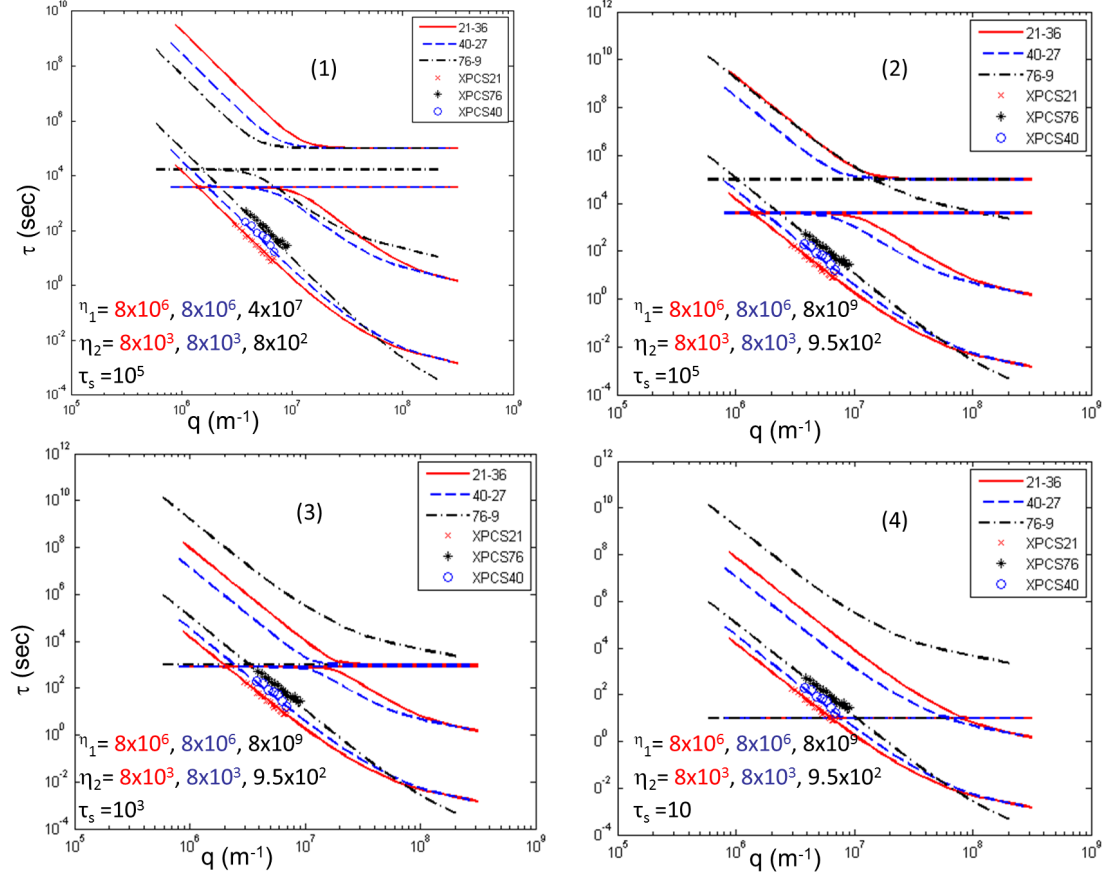


Figure 5.36: τ vs q for a double layer system with a buried Maxwell layer and an upper Newtonian layer using thicknesses of layers $h_1 = 21, 40, 76$ nm and $h_2 = 36, 27, 9$ nm and $E_1 = 2 \times 10^3$ for all models. Viscosities of layers and τ_s of Maxwell layers are labeled in the figure. Symbols correspond to our data points measured by XPCS.

a fit with either of these models having a sluggish, but mobile swollen brush layer underneath the top layer, the viscosity of the swollen brush layer must be 5-6 orders of magnitude greater than the viscosity of the top layer. This is consistent with the contention that the bottom layer is immobile on the length and time scales of the XPCS measurements. One may distinguish between hydrodynamic continuum models involving one and two layers only at relatively high values of $q_{||}$ not readily attained at 8-ID-I, as shown by Zhang *et al.* [270] .

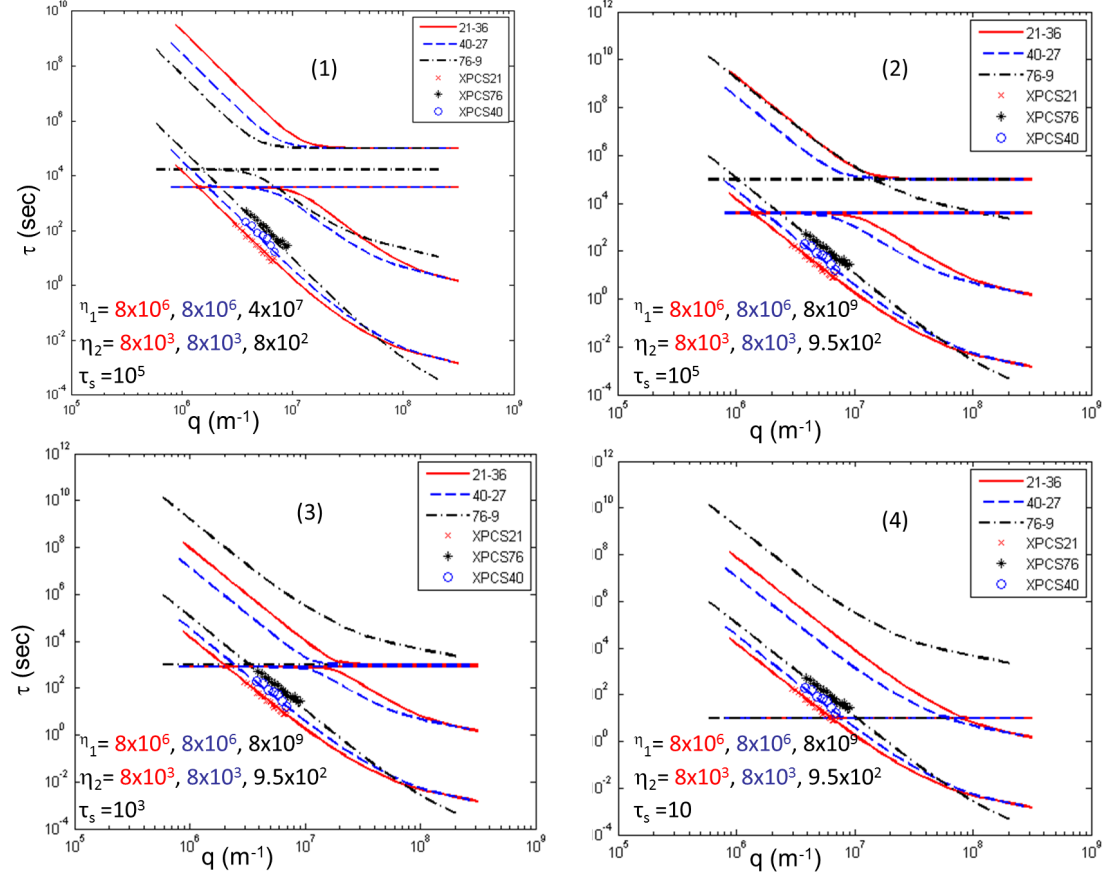


Figure 5.37: τ vs q for a double layer system with a buried Maxwell layer and an upper Newtonian layer using thicknesses of layers $h_1 = 9, 16, 29$ nm and $h_2 = 36, 27, 16$ nm and $E_1 = 2 \times 10^3$ for all models. Viscosities of layers and τ_s of Maxwell layers are labeled in the figure. Symbols corresponds to the our data points measured by XPCS.

5.3.2 Effect of Molecular Weight of Untethered Chains on Interface Width of Bilayer Films

One anticipates that when the molecular weight of the free chains is increased, the dynamical interactions with the underlying brush can become more complex, since entanglements can enter the picture. In order to identify the most important regions of parameter space to investigate with XPCS measurements we have considered how the interface width varies with free chain molecular weight using NR measurements.

While differing in detail, both theoretical [29,30,271] and experimental [24, 25,28,272] studies done to date show that penetration of free chains into chemically identical polymer brushes depends on degree of polymerization of the free chains. Leibler *et al.* [28] theorized that when $N_u < N_b$ (where N corresponds to length of chains, number of repeating units of chains of untethered and brush layers), there is a complete penetration of free chains into the brush, and for $N_u > N_b$, they predicted partial penetration. By partial penetration they mean penetration of very long chains is limited because the penalty of stretching of the brush chains becomes greater than the entropy gain upon mixing if the entire long chains are incorporated into the brush. In this case only short sections of long chains penetrate into the brush. This slight penetration leads to a surface tension at the polymer/brush interface with a negative spreading coefficient that causes partial wetting. Leibler calculated the penetration depth, $\lambda \equiv a\sigma^{-1/3}N_b^{1/3}$, for $N_u > N_b^{2/3}\sigma^{-2/3}$, where a is the monomer size. As a continuation of Leibler's study, Gay [30] presented a theoretical study and found that for small free chains ($N_u < N_b^{2/3}\sigma^{-2/3}$), although wetting is complete as predicted by Leibler, penetration is partial with associated partial wetting with penetration depth of $\lambda = a\sigma^{-1}N_bN_u^{-1}$. For $N_u < N_b^{2/3}\sigma^{-2/3}$, although wetting is complete, penetration is still partial. In the case of short free chains, the penetration length is a decreasing function of molecular weight of free chains. For sufficiently long free chains, penetration does not depend on the molecular weight of free chains.

To test the effect of free chain molecular weight on interpenetration, we studied the penetration into the brushes of chains with different lengths. The samples used are listed in Table 5.7 with the interface widths observed with NR for multiple temperatures. Selected SLD profiles are shown in Figures 5.38, 5.39, and 5.40, while the trends in interface width with free chain molecular weight are summarized in Figures 5.41 and 5.42. We remark briefly first on the development of the interface width

Table 5.7: Properties of Bilayers with Untethered Chain Layer of Higher Molecular Weight

Sample	h_b^a (nm)	h_u^a (nm)	M_n^b (g/mol)	σ^c chains/nm ²	$fwhm^d$ (nm) RT ^e	$fwhm^d$ (nm) 100°C	$fwhm^d$ (nm) 120°C	$fwhm^d$ (nm) 150°C
PS40-dPS47	35	48	20k	0.7	6.4	6.4	7.5	8.8
PS340-dPS47	35	48	40k	0.7	6.4	7	8	
dPS48-PS53	44	53	9k	0.7	6.5	10.5	10.5	
dPS48-PS53	44	53	20k	0.7	5	7.7	7.3	6.8
dPS48-PS53	45	53	40k	0.7	4.4	6	6.5	6.8
PS70-dPS40	72	52	20k	0.6	10	14.5		
PS70-dPS40	72	52	40k	0.6	9.7	13.5	12.7	12.7
PS22-dPS50	23	50	40k	0.6	5.3	6.6		
PS25-dPS48	20	47	7k	0.25	14.6	19		
PS25-dPS48	20	47	20k	0.25	7.61	12	12	12
PS25-dPS48	21	48	40k	0.25	7.3	8	11	11

^a Thickness (h) values from NR.

^b M_n values of untethered PS chains

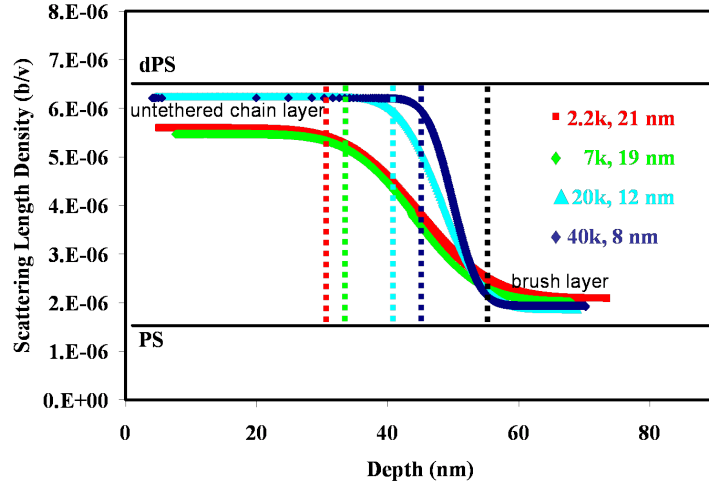
^c Grafting density (σ) is calculated using $\sigma = N_A \rho h / M_n$, where M_n is the number average molecular weight, N_A is Avogadro's number and ρ is the bulk mass density.

^d Roughness between brush-untethered chain layers obtained by *reflfit*.

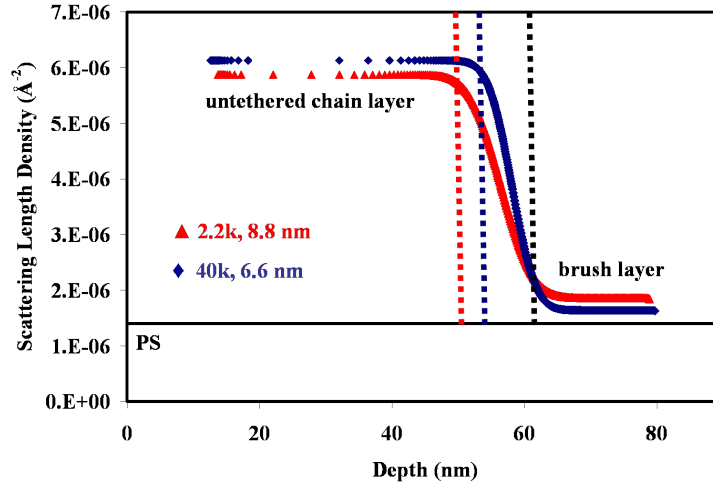
^e RT for room temperature.

with temperature for the samples with higher free chain molecular weight. Although the T_g 's of the 7k, 9k, 20k, and 40k chains are 88, 91, 97, and 99°C, respectively, a finite interface width is observed already at RT for all the samples, even though room temperature is below the T_g of the free chains in all cases. The establishment of this “initial” interface is apparently enabled by the brief presence of solvent during the spin-casting, just as for the case of the 2.2k free chains. As we see from bilayers with free chains with M_n 2.2k, interface width changes when the sample is heated above T_g of free chains. We expect that the samples are more sluggish to reach equilibrium at a given temperature as free chain molecular weight goes up. However, for all but one sample (PS36-dPS47 with 20k), the interface width increases significantly with heating to 100°C. Heating to still higher temperatures (with 6 h annealing times) generally had little effect on the interface width, even for those samples for which the temperature was increased to 150°C. Therefore, in the remainder of the discussion of these results we focus on data measured at 100 and 120°C.

Figures 5.38 shows the SLDs of bilayers of 22 nm high and 25 nm low grafting density brushes for the case in which addition of the free chains has increased the overall film thickness by 50 nm. We note first that the interface width is a decreasing function of molecular weight of the free chains (M_n), independent of the underlying brush layer. However, the rate at which interface width decreases with an increase in M_n of free chains drops as M_n increases, as shown in Figure 5.41. When 2.2 kg/mol untethered PS chains are on top of the 22 nm thick PS brush with $\sigma = 0.25$ chains/nm², the interface width is 21 nm. When the M_n of the chains is 7, 20 and 40 kg/mol, the interface widths becomes 19 nm, 12 nm, and 8 nm, respectively. We also note that the SLD of the dPS-rich layer of free chains increases with an increase of M_n of free chains. The increase is more pronounced for higher molecular weight of free chains. There are at least two causes for this. First the mass density of dPS



(a)



(b)

Figure 5.38: The scattering length density as a function of depth at 100°C for bilayers of (a) 25 nm thick low density ($\sigma = 0.2$ chains/nm²) and (b) 22 nm thick high density ($\sigma = 0.5$ chains/nm²) brushes for the case in which addition of the free chains of various M_n has increased the overall film thickness by 50 nm. Labels show the interface widths for bilayers with corresponding M_n of free chains.

increases with M_n , just as it does for PS ([273]) and while the mass density changes markedly between 2k and 7k, it has nearly leveled off by about a value of M_n of 30k. A second effect could be the degree to which brush chains extend up into the layer of tethered chains. For the smaller free chains there may be more stretching of the brush through the layer of untethered chains. On the bottom of the sample, the change in SLD of the brush layer with M_n is quite small. In fact, the SLD at the base of the brush appears to be slightly increased relative to the SLD of pure PS, by the presence of a few dPS chains brush in the bottom of the brush, but this contribution hardly changes with M_n of the free chains. Figure 5.38(b) shows the effect of M_n for the equivalent bilayer with high grafting density brush ($\sigma = 0.5$ chains/nm²). The interface width decreases with increase of M_n . However, the decrease is much less pronounced than that for the bilayer with low grafting density brush. In this very thin high density brush, the brush chains are so densely grafted that they are already stretched and even a significant increase in M_n of free chains is not enough to result in a dramatic decrease in the interface width, in contrast to the case of the lower grafting density brush. With 2.2 kg/mol free chains on the high density 22 nm thick brush, an 8.8 nm interface width is observed, while increasing of M_n up to 40 kg/mol decreases the interface width only down to 6.6 nm.

Further data on the effect of M_n of free chains on the interface width of bilayers are shown in Figures 5.39 and 5.40. Figure 5.39 shows the SLD profiles of bilayers of the untethered chains with M_n of 2.2, 9, 20 and 40 kg/mol on 70 nm thick high density brush. The trend is clear from the plot in Figure 5.42 and is quite consistent with the behavior seen for the 52 nm thick brush. Bilayers in which the deuterated species was the brush, rather than the free chains, were also studied. Data from these samples are shown in Figure 5.40 for a 52 nm thick perdeuterated brush

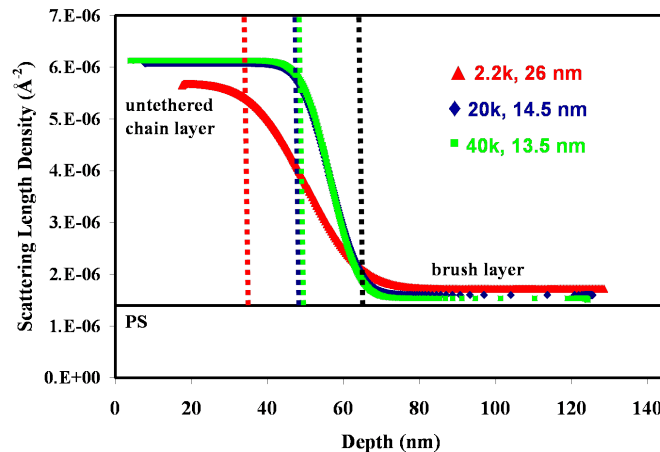


Figure 5.39: The scattering length density as a function of depth at 100°C for a bilayer of 70 nm high density ($\sigma = 0.5$ chains/nm²) brushes for the case in which addition of the free chains of M_n 2.2 (red), 20 (blue), and 40 (green) kg/mol has increased the overall film thickness by 45 nm. Labels show the interface widths for corresponding bilayers.

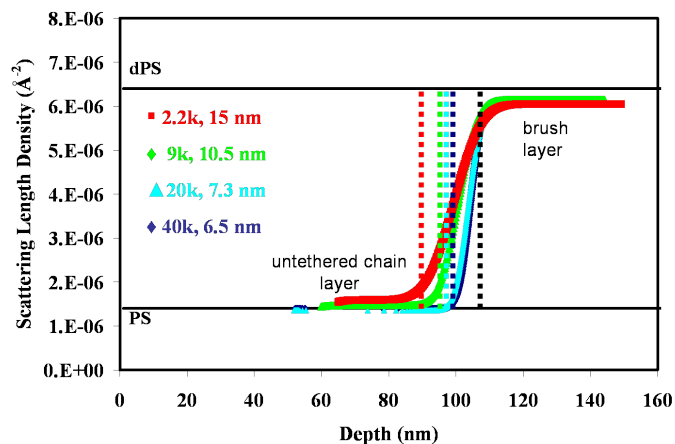


Figure 5.40: The scattering length density as a function of depth at 120°C for a bilayer of 52 nm high density ($\sigma = 0.5$ chains/nm²) brushes for the case in which addition of the free chains of M_n 2.2 (red), 9 (green), 20 (cyan), and 40 (blue) kg/mol has increased the overall film thickness by 50 nm. Labels show the interface widths for corresponding bilayers.

layer with 2.2, 20 and 40 kg/mol untethered chains. Since the brush layer is thinner, the interface widths are narrower, but vary with chain M_n in the same way.

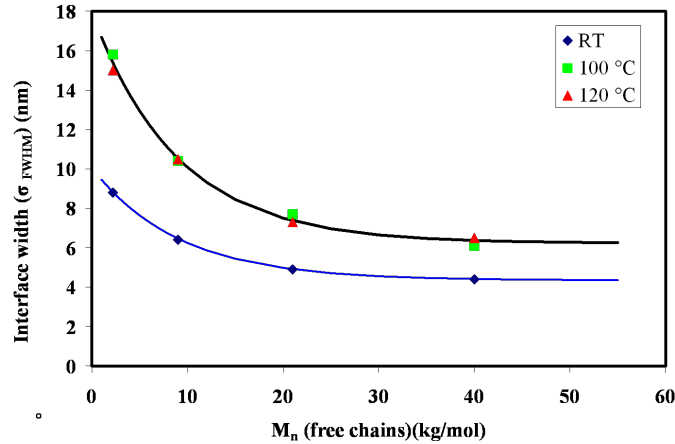


Figure 5.41: The interface width as a function of M_n of free chains at RT, 100°C, and 120°C for bilayers of 52 nm high density ($\sigma = 0.5$ chains/nm²) brushes for the case in which addition of the free chains has increased the overall film thickness by 50 nm. Solid lines are the best fits with exponential decay function.

Figure 5.41 summarizes the effect of M_n on the interface widths of the bilayers for different temperatures for a bilayer of 52 nm thick high density ($\sigma = 0.5$ chains/nm²) brush for the case in which addition of the free chains has increased the overall film thickness by 50 nm. The interface width vs. M_n could be fitted with an exponential decay function as shown by the solid lines. At three temperatures, the bilayers show the same general behaviors except that for the temperatures higher than the T_g of 2.2 kg/mol PS chains, the interface widths are higher. However, the data at 100°C, and 120°C fall onto a single curve.

The change in interface width with M_n is shown in Figure 5.42 for bilayers containing 22 nm, 40 nm and 70 nm thick high density brushes ($\sigma = 0.6$ chains/nm²) for the case in which addition of the free chains has increased the overall film thickness by 45 nm. The interface width is highest for the bilayer using the thickest brush. The value of interface width for the lowest molecular weight decreases as brush thickness is decreased down to almost the value of the baseline of the exponential decay function

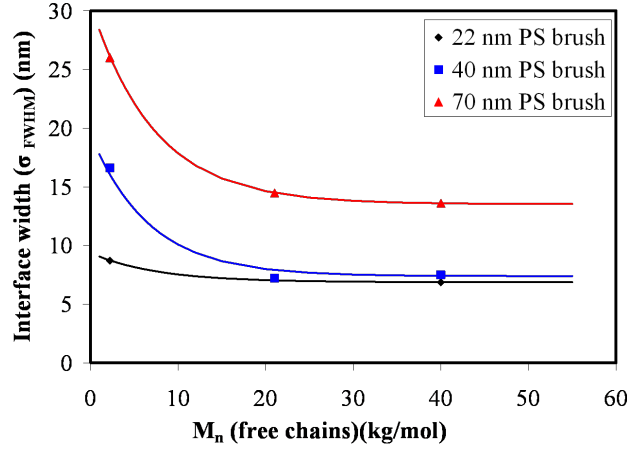


Figure 5.42: The interface width as a function of M_n of free chains at 100°C for bilayers of 20 nm (black), 40 nm (blue) and 70 nm (red) high density ($\sigma = 0.5$ chains/nm²) brushes for the case in which addition of the free chains has increased the overall film thickness by 45 nm. Solid lines are the best fits with exponential decay function.

when the brush thickness is 22 nm. The interface width for the bilayer with the thinnest brush layer is almost M_n independent.

In summary, first, we observed that the relaxation of surface height fluctuations of spun cast PS chains on a PS brush is dramatically slower compared to the relaxation of the same PS chains on a bare silicon surface. A model of a single layer of viscous fluid on a rigid substrate with a non-slip boundary condition does an excellent job of capturing the shapes of the data sets. Calculated thicknesses from the model that are “effective” for the observed surface dynamics are found to be decreasing with increasing brush layer thickness (h_b). The structural model obtained from NR consists of a bottom layer of one SLD, a top layer of a second SLD, and an interface between these two layers. The interface width is an increasing function of h_b . Secondly, the “top” layer thicknesses observed with NR found to be same within the uncertainties as the “effective” thicknesses from the single viscous layer analysis of the XPCS data. Thirdly, as the grafting density of the brush is reduced by a

factor of two, the surface dynamics of the spun cast chains become very slow and no longer observable. NR results showed that this is due to an increase in penetration depth and a decrease in “effective” layer thickness of the free chains on top. Finally, an exponential decrease of the interface width with increase in free chain molecular weight (M_n) is observed. Since brush chains with high grafting density are already stretched, even an increase in M_n of the free chains by a factor of 20 results in a decrease in the interface width of only a factor two.

CHAPTER VI

CONCLUSION

To understand the internal structures of the “dry” and the swollen or the surface rearranged structure of DCBs of PS-*b*-PMA and PMA-*b*-dPS, NR measurements have been performed. The dry state structure strongly depends on the value of χN , and the sequence in which the polymer blocks have been synthesized. For all DCBs studied when $\chi N \leq 23$, they adopt lamellar structures. For dPS-*b*-PMA brushes with $\chi N > 23$, and sufficiently asymmetric composition, a third layer must be included in the model to describe the NR data. The inclusion of third layer is consistent with the presence of a lateral ordering in the center of the brush, as evidenced by correlation peaks in grazing incidence small angle scattering (GISAXS) data from these samples. When PMA blocks synthesized next to the substrate, and with $\chi N > 23$, two-layer model does a good job of capturing the data. However, there occurs an apparent increase in interface width with χN due to the lateral ordering in the middle of the film. The lateral ordering in the middle of the film may be diffuse in the direction normal to the surface and can not be resolved with NR as a distinct third layer, rather can be adequately modeled, for purposes of the explaining the NR data, with simply a rather large interface width.

In-situ NR measurements of highly asymmetric DCBs in selective solvents show that the swollen DCB structure depends on solvent quality, the ratio of chain lengths of the polymer blocks, block sequence of DCBs and the reinitiation effects during the synthesis of the blocks. For highly asymmetric dPS-*b*-PMA samples,

cyclohexane which is a poor solvent for PMA and theta solvent for PS used as a selective solvent and measurements were done at a temperature (21°C), which is close to the transition between being theta and poor solvent for dPS. For those samples, even though the chain lengths of dPS were long enough to stretch and cover the solvophobic PMA chains, no clear observation of rearrangement observed. On the other hand, for PMA-*b*-dPS brushes, acetone was a good solvent for PMA chains and poor solvent for dPS chains at room temperature but block lengths of dPS chains were much larger (4 and 7 times) than that of PMA chains and they collapsed and sit on short swollen PMA chains. In future, more work should be done with DCBs of various block lengths. When DCBs are swollen with a solvent good for both blocks, DCBs behave similarly to homopolymer brushes, but the model of data fit conserves the three layer structure, and establishes a parabolic profile with much broader interfaces in between layers so no distinct layers are seen.

XPCS investigation showed that within the range of time (0.2 -1100 s) and length scale (0.6-3 μm) studied, no relaxation of fluctuations of the brush surfaces are detectable. This is true for PS brushes of thicknesses of 9 - 101 nm and high grafting density (≥ 0.5 chains/nm²) at temperatures up to 130°C above bulk T_g . Even reduction of the grafting density from 0.6 to 0.1 chains/nm² does not bring the relaxation into the measurement window.

Tethering does not only change the surface dynamics of grafted chains but also the surface dynamics of 2.2k dPS chains spun cast on top of the grafted chains. The relaxation of surface height fluctuations of spun cast PS chains on a PS brush is dramatically slower compared to the same PS chains on a bare silicon surface. As the thickness of the brush layer (h_b) increases, relaxation time becomes larger. A model of a single layer of viscous fluid on a rigid substrate with a non-slip boundary condition does an excellent job of capturing the shapes of the data sets. Calculated

thicknesses from the model that are “effective” for the observed surface dynamics are found to be decreasing with increasing h_b . The structural model of bilayers obtained from NR consists of a bottom layer of one SLD, a top layer of a second SLD, and an interface between these two layers. The “top” layer thicknesses observed with NR found to be same within the uncertainties as the “effective” thicknesses from the single viscous layer analysis of the XPCS data.

When the grafting density of the brush is reduced, the surface dynamics of spun cast chains become very slow. NR results showed that this is due to increase in penetration depth and a decrease in “effective” layer thickness of the free chains on top.

Variation of the interface width with free chain molecular weight (M_n) is observed. Interface width is a decreasing function of M_n and decays exponentially with increase of M_n . Since brush chains with high grafting density are already stretched, even a significant increase in M_n of free chains is not enough to result in a dramatic decrease in the interface width.

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CHAPTER VII

APPENDIX

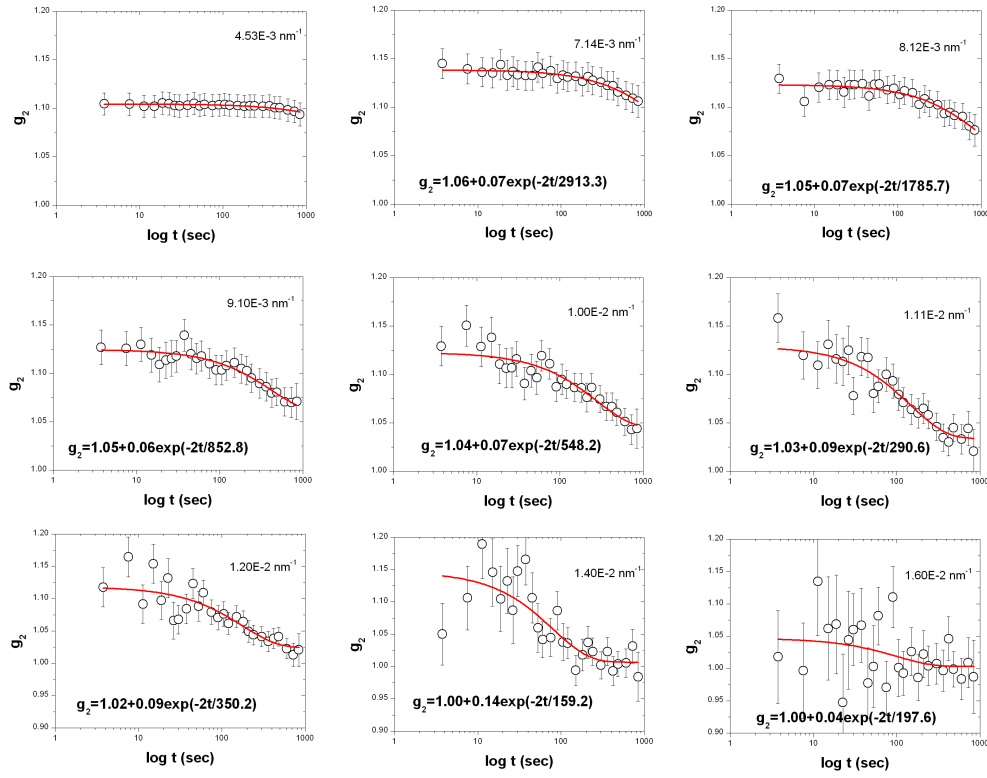


Figure 7.1: Autocorrelation functions (g_2) at different in-plane wave-vectors ($q_{||}$) for 45 nm untethered PS chains on 76 nm PS brushes with $\sigma = 0.6$ chains/nm² at 80°C.

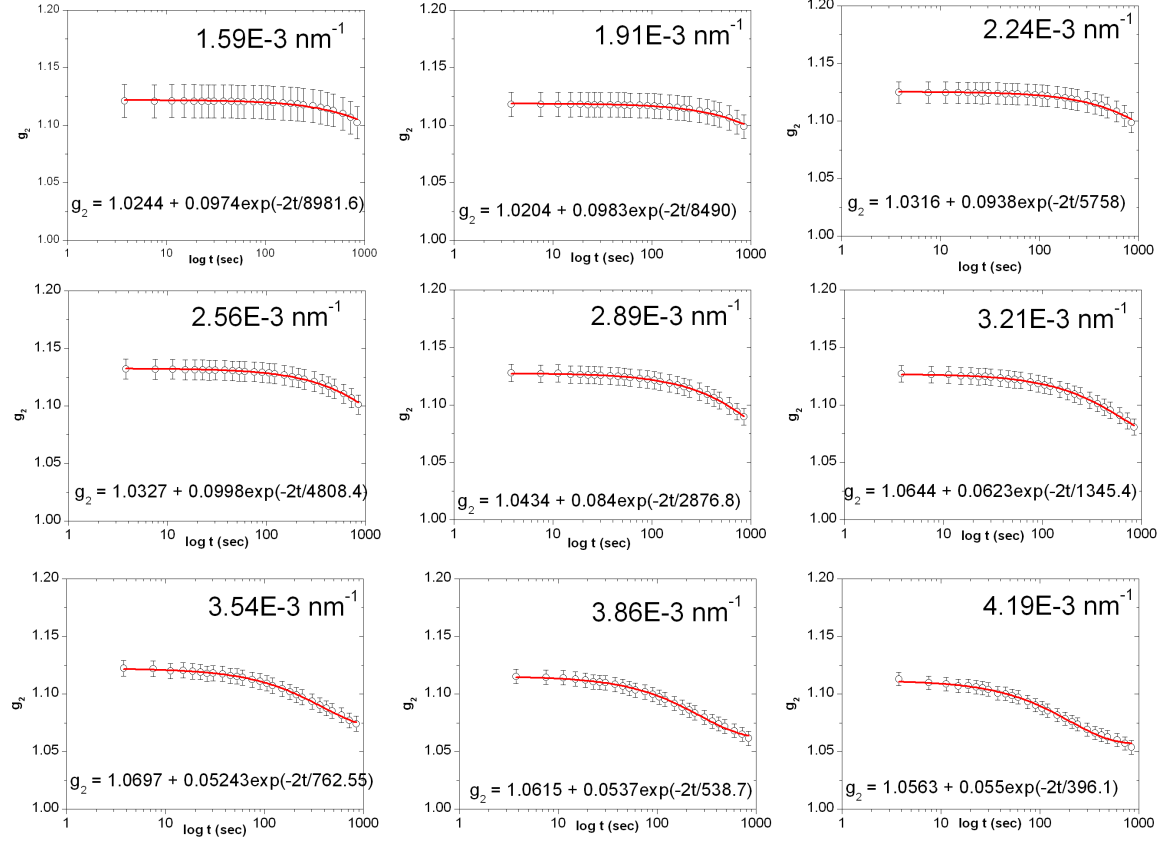


Figure 7.2: Autocorrelation functions (g_2) at different in-plane wave-vectors ($q_{\parallel}$) for 45 nm untethered PS chains on 76 nm PS brushes with $\sigma = 0.6$ chains/nm² at 100°C.

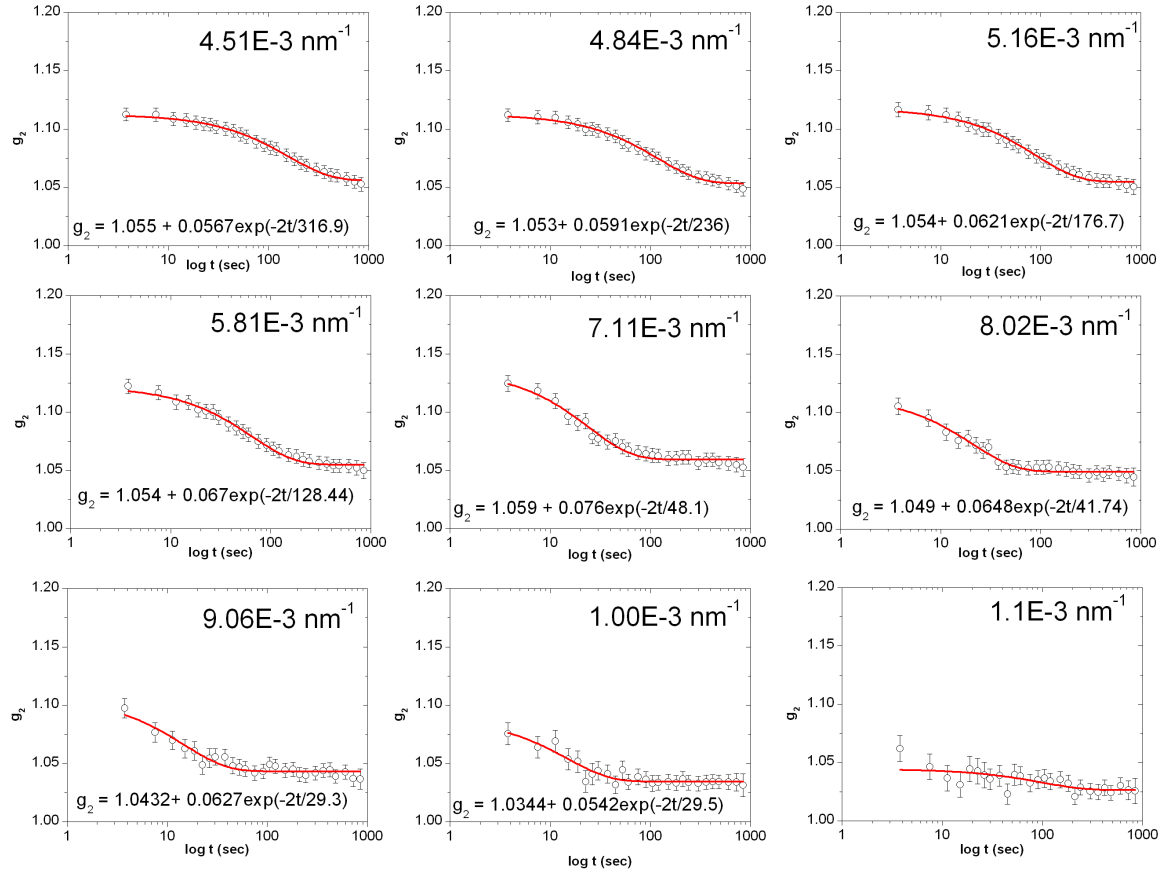


Figure 7.3: Autocorrelation functions (g_2) for 45 nm untethered PS chains on 76 nm PS brushes with $\sigma = 0.6$ chains/nm² at higher in-plane wave-vectors ($q_{||}$) at 100°C.

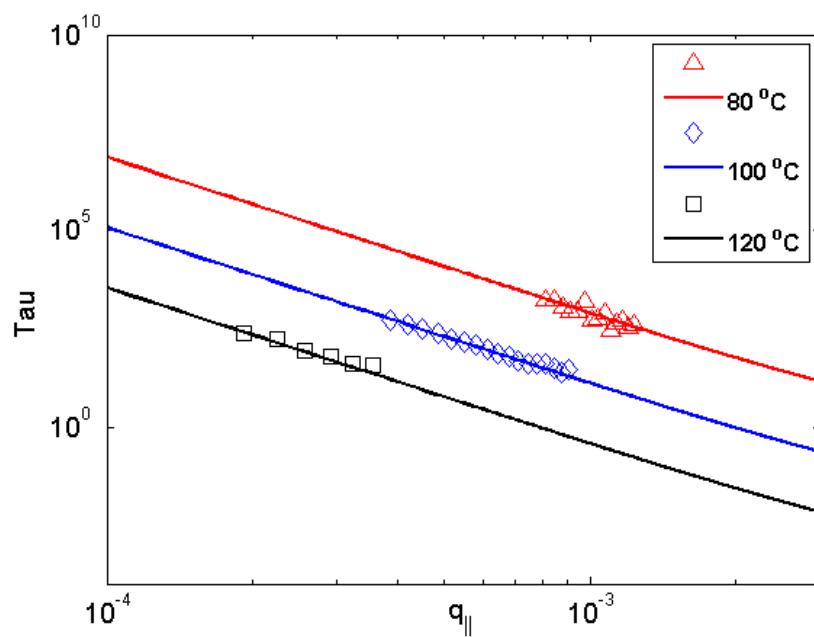


Figure 7.4: Time constants (τ) for 45 nm untethered PS chains on 76 nm brushes with $\sigma = 0.6$ chains/nm² at 80°C (triangle), 100°C (diamond), and 120°C (square). Lines represent least-squares fits based on Equation 5.1.

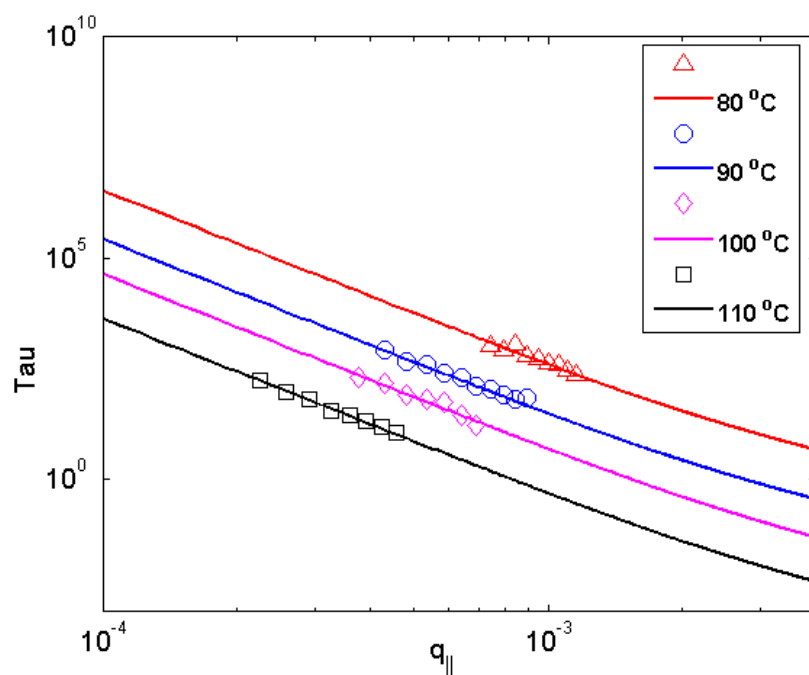


Figure 7.5: Time constants (τ) for 45 nm untethered PS chains on 44 nm brushes with $\sigma = 0.6$ chains/nm² at 80°C (triangle), 90°C (circle), 100°C (diamond) and 110°C (square). Lines represent least-squares fits based on Equation 5.1.

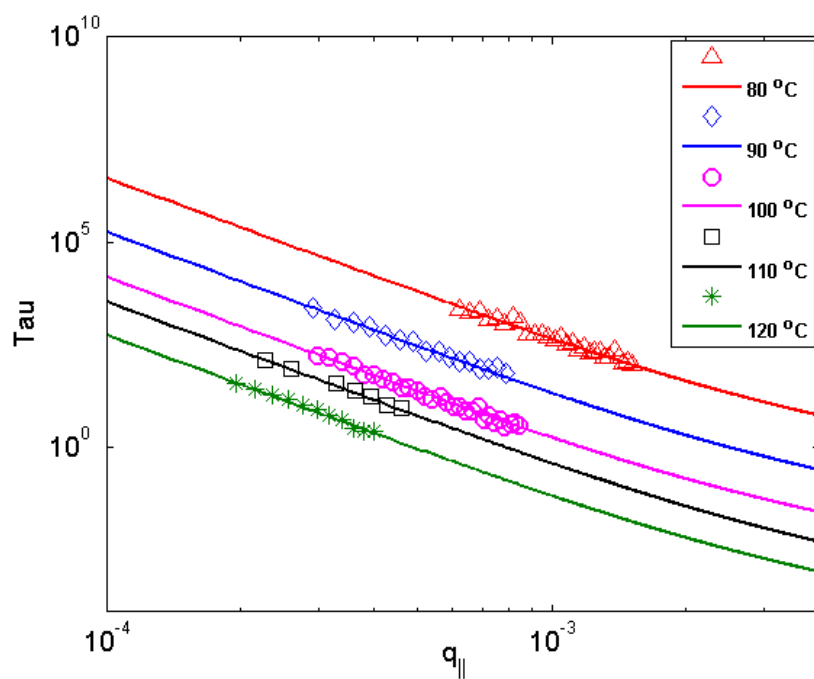


Figure 7.6: Time constants (τ) for 45 nm untethered PS chains on 21 nm brushes with $\sigma = 0.6$ chains/nm² at 80°C (triangle), 90°C (circle), 100°C (diamond), 110°C (square) and 120°C (star). Lines represent least-squares fits based on Equation 5.1.

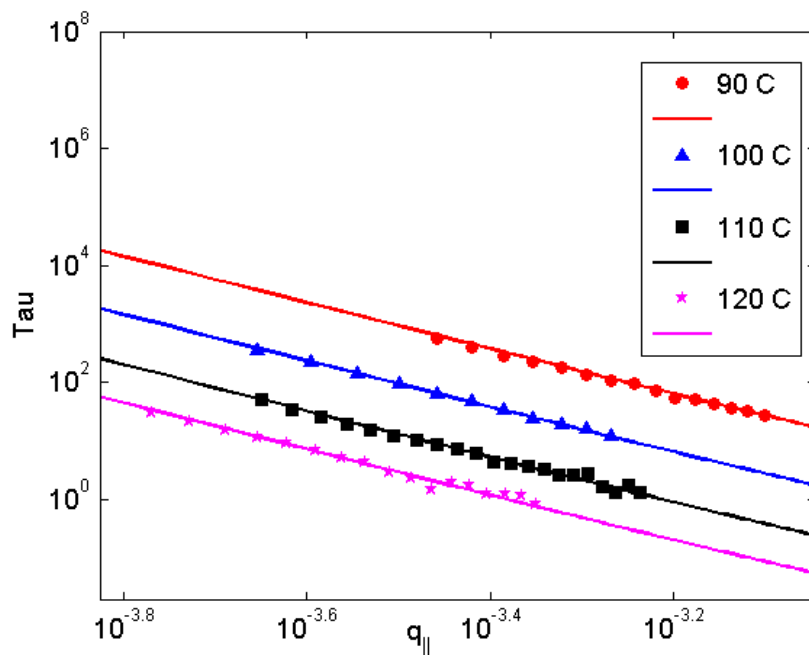


Figure 7.7: Time constants (τ) for 45 nm untethered PS chains on silicon wafer at 90°C (circle), 100°C (triangle), 110°C (square) and 120°C (star). Lines represent least-squares fits based on Equation 5.1.

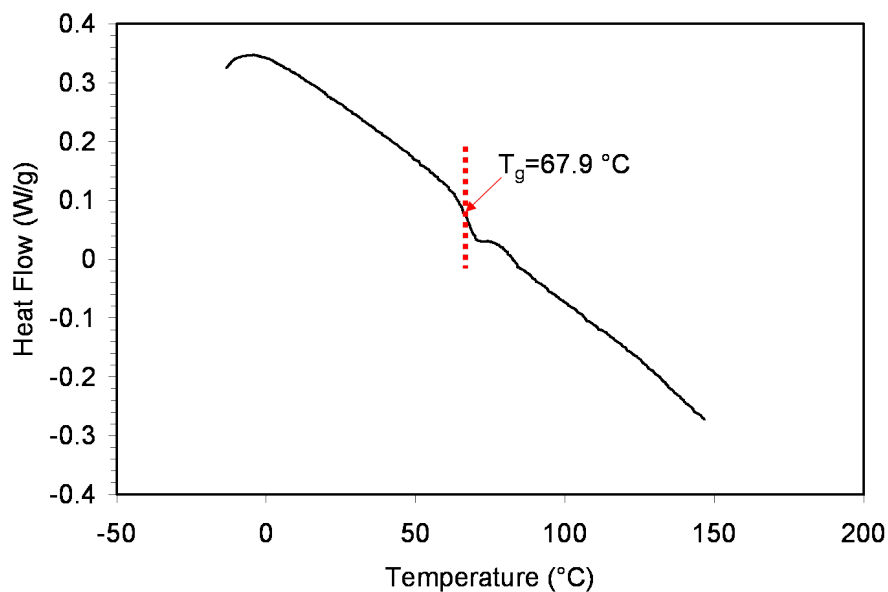


Figure 7.8: DSC curve of d-Polystyrene (dPS) with $M_n = 2200$ g/mole with a heating rate of 10°C/min.

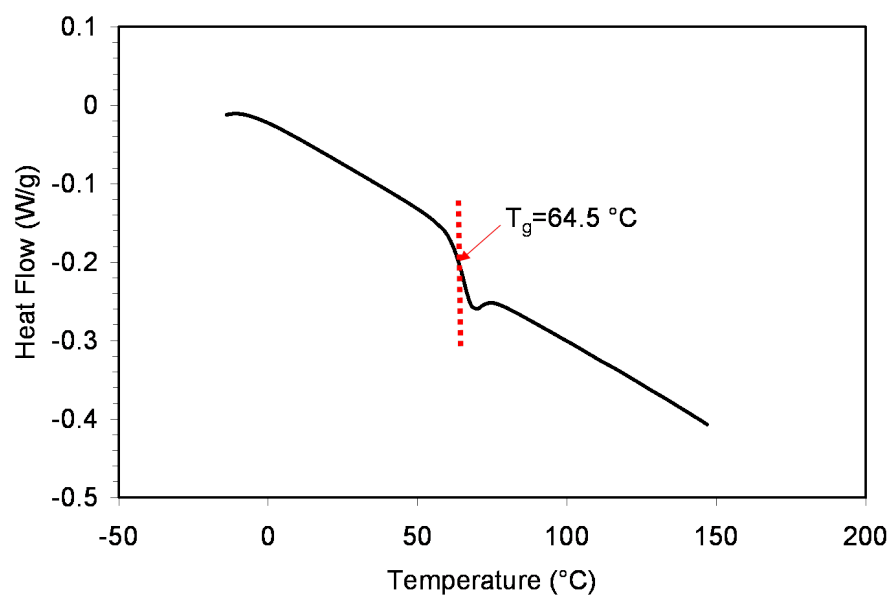


Figure 7.9: DSC curve of Polystyrene (PS) with $M_n = 2000$ g/mole with a heating rate of $10^\circ\text{C}/\text{min}$.