SURFACE AND INTERFACE STRUCTURE OF DIBLOCK COPOLYMER BRUSHES

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ABSTRACT

The main objective of the work presented in this thesis is to understand the surface and interface structure and dynamics of diblock copolymer brushes (DCBs). DCBs are stimuli-responsive materials and the surface properties of a DCB can be changed from those characteristic of one polymer block to those characteristic of the other one by treating the DCB with a solvent selective for one of its blocks. For this purpose, polystyrene-block-polyacrylate or polyacrylate-block-polystyrene brushes were synthesized using the “grafting from” technique in combination with atom transfer radical polymerization (ATRP).

In the first part of this project the internal structure of DCBs after the synthesis and surface rearrangement were investigated using neutron reflectivity (NR) and grazing incidence small angle X-ray scattering (GISAXS). It was found that the internal brush structure depends strongly on the synthesis sequence of polymer blocks and the value of $\chi N$. For small values of $\chi N (\chi N \leq 11)$, a model of two layers with an interfacial region of finite width provides a good description of the data. The interface width is found to be larger for DCBs which have the polymer block with the lower surface energy synthesized next to the substrate. A three layer model must be used to describe the structure of DCBs of larger $\chi N$ values ($\chi N \geq 23$) and of sufficiently asymmetric composition. The necessity of including a third layer is consistent with the presence of a lateral ordering of some type in the center of the brush, as evidenced by correlation peaks in the GISAXS data. The
spacing of the in-plane ordering varies with the thickness of the poly(methyl acrylate) (PMA) block. After a DCB is treated with a selective solvent, Bragg rods appear in the GISAXS pattern. The appearance of Bragg rods indicates the formation of a new 2D structure which has a lateral spacing on the order of the total thickness of the brush. The Bragg rods disappear upon heating to 80 °C.

Roughness correlation between the interfaces of a DCB has been detected using longitudinal diffuse X-ray scattering and X-ray reflectivity. The amplitude of the fringes in the longitudinal diffuse scattering decreases with increasing thickness of the DCB, indicating that the interactions between substrate and brush surface decrease as the thickness of the DCB increases. Roughness correlation of the brush is observed after annealing the brush but, it is lost after the brush is swollen in the vapor of a nonselective solvent, dichloromethane.

A remarkable suppression of polymer film surface fluctuations by the tethering of one end of each chain in a densely grafted brush has been demonstrated experimentally using X-ray Photon Correlation Spectroscopy (XPCS), a direct measure of dynamics. Within the range of time and length scale investigated, 0.2 s to 1100 s, and 200 nm to 5 μm, no relaxation of the brush surface could be observed, even 170 °C above the bulk glass transition temperature of corresponding untethered chains, suggesting that the surface relaxation time is increased by at least three orders of magnitude as compared to a film of untethered chains of comparable thickness. The observation of the suppression of long wavelength fluctuations on the surface of a dry homopolymer brush is consistent with theoretical predictions.
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CHAPTER I

INTRODUCTION

Polymer brushes are formed by tethering an ensemble of polymer chains to a surface such that each chain has one end covalently bound to the surface and the tethering points are sufficiently close together that the chains must stretch appreciably away from the Gaussian coil configurations preferred in a melt of untethered chains. When polymer chains are tethered to a surface, two cases can be distinguished depending on the grafting density. In the first case, the distance between two anchored polymers is greater than the radius of gyration \( R_g \) of the unperturbed chain so that the segments of distinct polymer chains do not interact with each other. If there is a strong attractive force between the polymer chains and the surface, the polymer chains are flattened out to a “pancake-like” conformation. When there is a weak or repulsive interaction between the polymer chains and the surface, the polymer chains are attached to the surface through a short stem and form a typical random coil, yielding a “mushroom” conformation. A completely different picture can be obtained when the polymer chains are attached to the surface at high grafting densities. Dense grafting of polymer chains on an interface enforces a strong overlap among the coils, increases the segment-segment interactions and the corresponding interaction energy. In this case, polymer chains avoid each other to minimize segment-segment interactions by stretching away from the surface. Stretching
of polymer chains decreases the number of possible polymer conformations and hence the configurational entropy of the polymer chains. The deformation of tethered polymer chains reflects a balance between enthalpic interaction and elastic free energies.

Stretching lowers the interaction energy per chain, $F_{\text{int}}$, at the expense of a high elastic free energy, $F_{\text{el}}$. Stretching and retraction forces establish a new equilibrium at a higher energy level in which the chains are stretched perpendicular to the surface.\textsuperscript{2-3}

Alexander\textsuperscript{3} considered a flat, nonadsorbing surface to which monodisperse polymer chains are tethered. The polymer chains consist of $N$ statistical segments of diameter $a$. The average distance between the tethering points, $s$, is much smaller than the radius of gyration, $R_g$, of an untethered chain. The free energy per chain is given as

$$F = \nu \phi^2 s^2 \frac{d}{a^3} + \frac{d^2}{R_0}$$  \hspace{1cm} (1.1)$$

where $\nu$ is a dimensionless excluded volume parameter, $\phi$ is the monomer volume fraction within the layer, $R_0$ is the radius of an unperturbed coil and $d$ is the brush layer thickness. The first term in the right hand side of equation (1.1) represents the interaction energy between statistical segments and the second term reflects the elasticity of Gaussian chains. The equilibrium thickness, determined by the minimization of $F$ with respect to $d$, grows linearly with $N$, while the $R_g$ of untethered chain only grows as $N^{3/5}$ when the chain is in a good solvent. Linearity of equilibrium height of tethered chains with $N$ is maintained in theta and poor solvents, while in the melt equilibrium height is proportional to $N^{2/3}$. No matter whether in the presence of a good solvent, a theta solvent, a poor solvent, or in a melt state, the polymer chains in a tethered polymer brush exhibit deformed configurations. Alexander,\textsuperscript{3} in his simple scaling argument, assumed that the
segment density depth profile is step-like and all free chain ends are located at the same distance from the interface.

Semenov\(^4\) assumed that the free chain ends may be located at any distance from the interface for the case of polymer brushes in the melt. Theory incorporating this refinement was developed for brushes in solvent by Milner et al.\(^5\)\(^-\)\(^8\) and independently by Priamitsyn et al.\(^9\)\(^,\)\(^10\) The analytical self consistent field (SCF) calculations\(^5\)\(^-\)\(^10\) showed that the potential of a chain is a parabola. All the properties obtained from the more detailed parabolic brush description are consistent with the scaling analysis of Alexander.\(^3\) The equilibrium properties of homopolymer brushes in the melt or good solvent have been extensively studied and are reasonably well understood.

Polymer brushes are model systems for many practical polymer systems such as block copolymers and graft copolymers at fluid-fluid interfaces, and polymer micelles. They are also of interest due to their potential practical uses to control adhesion,\(^11\)\(^-\)\(^17\) lubrication,\(^18\)\(^-\)\(^20\) or wetting\(^21\)\(^,\)\(^22\) properties of surfaces, flocculation in colloidal dispersions,\(^23\)\(^,\)\(^24\) solvent flow through channels,\(^25\)\(^-\)\(^29\) and to create protein and cell-resistant biosurfaces.\(^30\)\(^-\)\(^33\) Polymer brushes are very attractive in surface modification since thin polymer films created by covalent attachment of polymer chains to a substrate have very strong resistance against various solvents and high temperature.

The covalent attachment of polymer chains onto a substrate can be achieved either using “grafting to”\(^34\) or “grafting from”\(^34\) approaches. Since the “grafting to” method yields low grafting densities and very thin polymer layers due to the required diffusion of long polymer chains, it will not be dealt with further. In the “grafting from” approach, initiators are immobilized onto the substrate and in-situ, surface-initiated polymerization
performed to create a tethered polymer layer. Immobilization of initiator molecules can be achieved using one of a couple different techniques. The most popular technique is to introduce a self-assembled monolayer (SAM), which has the initiating groups for the polymerization. Since the propagation of polymer chain only requires the diffusion of small monomer molecules, it is possible to obtain high grafting densities and thick polymer films.

Rühe and co-workers\textsuperscript{35} were first to synthesize polystyrene (PS) brushes from azo-initiators using the “grafting from” approach. They used conventional radical polymerization and achieved 2-3 μm thick PS brushes. The only disadvantage of their method is the high polydispersities, measure of the distribution of the molecular weights (PDI = M\textsubscript{w}/M\textsubscript{n} \approx 2), that are characteristics of conventional radical polymerization. Following Rühe’s work, Jordan et al.\textsuperscript{36-38} reported the cationic ring-opening polymerization of 2-ethyl-2-oxazoline and surface initiated anionic polymerization of styrene on gold substrates. Although surface initiated anionic and cationic polymerizations yield monodisperse chains, they were rarely 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. Later on, Fukuda\textsuperscript{39} and Hawker\textsuperscript{40} synthesized homopolymer brushes following the “grafting from” method, but using controlled radical polymerization (CRP) techniques. Fukuda et al.\textsuperscript{39a} synthesized poly(methyl methacrylate) (PMMA) brushes on silicon substrates by the combined use of Langmuir-Blodgett and atom transfer radical polymerization (ATRP) techniques. Hawker et al.\textsuperscript{40} synthesized PS brushes on silicon substrates using nitroxide mediated radical polymerization (NMRP). They showed that it
is possible to control the molecular weight and the thickness of the brush while
maintaining low polydispersities ($M_n = 51000$, PDI = 1.14).\textsuperscript{40} NMRP, in general, requires
a high polymerization temperature which may not be compatible with certain substrates,
such as polymer films. 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 attainable
with carbocationic\textsuperscript{36,37} and anionic\textsuperscript{38,41-43} polymerizations. Due to these advantages,
polymer brushes are synthesized using CRP techniques by a majority of groups currently
pursuing the study of polymer brush properties. 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 do not only help to
reduce the value of the polydispersity relative to the conventional radical polymerization,
but also open new doors to synthesize brushes with functional groups or to synthesize
block copolymer brushes.

The synthesis of diblock copolymer brushes (DCBs) becomes possible with the
introduction of CRP techniques. A DCB is a polymer brush that made up of chains, each
containing two polymer blocks chemically joined end-to-end with one of the polymer
blocks tethered to the substrate by the other end of one block. Husseman et al.\textsuperscript{40} reported
the synthesis of block copolymer brushes on silicate substrates using surface initiated
NMRP and ATRP. However, the copolymer brushes they synthesized were not diblock
copolymer brushes in a strict definition. The first block was PS and the second block was
a 1:1 random copolymer of PS/PMMA.
Zhao and Brittain\textsuperscript{44-47} reported the synthesis of PS-\textit{b}-poly(acrylate) tethered DCBs, in which first a homopolymer brush of PS was polymerized from a self assembled monolayer using a carbocationic polymerization and then the polyacrylate block was polymerized by the ATRP of MMA from the chloro-terminated PS chains. They investigated the properties of these DCBs using ellipsometry, attenuated total reflectance FTIR (ATR-FTIR), X-ray photoelectron spectroscopy (XPS), water contact angle measurements and atomic force microscopy (AFM). They found that the DCBs of PS-\textit{b}-PMMA (The first block listed is that next to the substrate, the second that polymerized second) exhibited reversible surface changes in response to solvent treatment. The advancing water contact angle increased from 75° (characteristics of PMMA) to 99° (characteristics of PS) after the brush was treated with cyclohexane. Cyclohexane is a good solvent for PS (M\textsubscript{n} \textasciitilde 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 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 reversible changes in the chemical composition at the polymer/air surface. XPS analysis confirmed the compositional changes after treatment with the selective and good solvents. Zhao et al.,\textsuperscript{45} using AFM, showed that the surface of PS-\textit{b}-PMMA is relatively smooth, with root-mean-square roughness of 0.8 nm (1\textmu m×1\textmu m) after dichloromethane treatment. When this brush was treated 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 were used and the composition of solvent was gradually changed from
dichloromethane to cyclohexane. These studies showed that the DCBs are stimuli-responsive materials and the 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. Zhao et al.\textsuperscript{45-47} suggested a mechanism for the surface rearrangement (also called “switching”) which is shown in Figure 1.1. When these diblock copolymer brushes were synthesized, they were 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.\textsuperscript{45-47} assumed that an “as-deposited” brush has a lamellar structure in which the layer next to substrate contains predominantly the first block synthesized and the layer next to air surface contains predominantly the second block synthesized. The interface between the domains rich in the two polymer blocks is assumed to be sharp. They explained the chemical composition changes at the surface determined by contact angle measurement, AFM and XPS by hypothesizing the collapse and aggregation of PMMA blocks to form a core to minimize unfavorable interactions with cyclohexane. They speculated that the PS chains form a layer around the PMMA core, resulting in an array of micelles with an ellipsoid shape after surface rearrangement. This state of the brush was denoted as the “switched” state.

DCBs garnered enormous interest after the seminal paper of Zhao et al.\textsuperscript{44-47} Sedjo et al.\textsuperscript{48} synthesized the same DCB of PS-\textit{b}-PMMA from a silicate substrate using reverse ATRP since this synthetic method is easier than the method used by Zhao and co-workers.\textsuperscript{44-47} They reported that the surface of such a PS-\textit{b}-PMMA brush reorganizes after selective solvent treatments. Baum and Brittain\textsuperscript{49} studied the synthesis of PS-\textit{b}-}
poly(N,N-dimethylacrylamide (PS-\textit{b}-PDMA) and PDMA-\textit{b}-PMMA DCBs from silicate substrates using the reversible addition fragmentation chain transfer (RAFT) technique. They found that these brushes displayed reversible surface properties upon treatment with block-selective solvents. In this study, they added free initiator to the reaction vessel to get better control of molecular weight and polydisperisty. Adding a free initiator not only improves the reaction control, but also untethered polymer chains grow from the free initiator when polymer chains grow from the immobilized self-assembled monolayer. It was of interest to determine if the polymer chains grown from the substrate and from free initiator had the same properties. Baum\textsuperscript{49} analyzed both the polymer chains formed in solution and the chains formed at the surface. To analyze the grafted chains, she cleaved the grafted chains from the surface. GPC analysis of the degrafted PS revealed $M_n = 11400$ g/mol and PDI = 1.14, values which were comparable to values of $M_n = 10600$ g/mol and PDI = 1.11 found for the free chains of PS in the same reaction. Similar results have been obtained when brushes have been synthesized using NMRP\textsuperscript{40} and ATRP.\textsuperscript{39a} Matyjaszewski et al.\textsuperscript{50} reported the synthesis of polystyrene-\textit{b}-poly(\textit{tert}-butyl acrylate) (PS-\textit{b}-PtBA) DCBs from SAMs by ATRP. They hydrolyzed the PtBA to yield poly(acrylic acid). After the hydrolysis, the advancing water contact angle significantly decreased from $86^\circ$ to $18^\circ$. They demonstrated that it is possible to tune the properties of the surface, such as hydrophilicity. Mathers et al.\textsuperscript{42} reported synthesis of polyisoprene-\textit{b}-poly(ethylene oxide) DCBs on silicon oxide surfaces by anionic polymerization using a surface bound 1,1-diphenylethylene monolayer. They reported that the surface rearrangement of these DCBs was incomplete. This was explained by proposing that the insufficient time was allowed for the polar groups attached to the polymer backbone to
reorganize. Following the publication of these papers, various groups\textsuperscript{51} reported the synthesis of DCBs by wide variety of monomers and their surface rearrangement using selective solvents and heating. These studies determined the efficiency of switching for various monomers,\textsuperscript{51e} block lengths,\textsuperscript{51e} and temperatures.\textsuperscript{51d} Recently, Beers and co-workers\textsuperscript{51e} investigated the influence of individual block length on the solvent response behavior of poly(n-butyl methacrylate)-\textit{b}-poly(2-(\textit{N},\textit{N}'-dimethylamino)ethyl methacrylate) DCBs using a block copolymer brush gradient layers. They found that the surface response properties can be suppressed by a second block containing longer chains and enhanced by using longer chains in the polymer block in which the chains are tethered to the substrate, which is in good agreement with the findings of Zhao et al.\textsuperscript{44-47}

There are three reports in the literature of the synthesis of triblock copolymer brushes. Boyes et al.\textsuperscript{52} studied the switching properties of polystyrene-\textit{b}-poly(methyl acrylate)-\textit{b}-polyethylene (PS-\textit{b}-PMA-\textit{b}-PS) and PMA-\textit{b}-PS-\textit{b}-PMA brushes synthesized by ATRP. They showed that triblock copolymer brushes also exhibited the same surface response to selective solvent treatment as diblock brushes do. Kim and co-workers\textsuperscript{53} investigated the effect of quenching methods on the reinitiation efficiency of the polymer blocks by synthesizing triblock polyacrylate brushes. Huang et al.\textsuperscript{54} reported the formation of PMMA-\textit{b}-PDAEMA-\textit{b}-PMMA and PMA-\textit{b}-PMMA-\textit{b}-PHEMA brushes and phase segregation of these materials upon exposure to a poor solvent for the outer block. They explained the changes on the surface in response to selective solvent treatment with the mechanism suggested by Zhao et al.\textsuperscript{45-47}

Balazs and coworkers\textsuperscript{55,56} have considered theoretically the structure of grafted diblock layers in both poor\textsuperscript{55} and selective solvents\textsuperscript{56} using 2D Self-Consistent-Field
(SCF) calculations and scaling arguments. They predicted a variety of ordered structures with descriptive designations such as “onion”, “garlic”, “dumbbell” and “flower-like” occurring for different values of block length of each block and the quality of the solvent. Gersappe et al.\textsuperscript{57} studied the internal density profile of block copolymers with changing connectivity using SCF and monte carlo simulations (MC). They showed that a lateral phase separation for an AB block copolymer brush formed well-defined domains of A and B, while random and alternating copolymer brushes do not show lateral phase separation. These studies\textsuperscript{55-57} considered only low grafting densities and compatible polymer blocks so that the exchange interaction parameter, $\chi_{AB}$, was approximately zero.

The structure of the densely grafted brush has also been considered theoretically by Ferreira and Leibler\textsuperscript{58} for symmetric AB copolymer. For a fixed quality of solvent there is a minimum value of $\chi_{AB}$ below which the demixing does not occur. As $\chi_{AB}$ increases, the interface between the A-rich and B-rich domains narrows and depletion in overall monomer density at the domain/domain interface becomes more enhanced. Heine and Wu\textsuperscript{59} point out that the interface between the A-rich and B-rich domains will be sharper when the brush is “dry” using numerical SCF and scaling arguments. They extend the work of Ferreira and Leibler to the case in which the end of the polymer block (B) next to the air surface is charged. Their SCF calculations suggest that for small $f_B$ it may be possible to switch the character of the “wet” brush surface using a switchable applied voltage. Pickett\textsuperscript{60}, using both scaling and numerical SCF calculations, has noted that for the case of a narrow interface that portion of a dry brush consisting of the A-rich domain constitutes a realization of an Alexander brush in which the chain ends are constrained to be only at the two interfaces, while the B-rich domain constitutes a
standard polymer brush. For a properly designed "taper" copolymer in which the local composition along each chain varies gradually from pure A to pure B, the interface becomes very broad and the "B" ends of the chains are forced to be at the outer surface. None of these predictions has been experimentally verified.

The theoretical and experimental published work on DCBs has mostly focused on the switching properties. Despite the switching ability of various diblock brushes in different solvents,\textsuperscript{44-49,51,52,54-56} the mechanism of the surface rearrangement is still a mystery since the internal structures of both the “as-deposited” and “switched” states are not known. None of the characterization techniques used in these studies can probe the surface and internal structure of DCBs in a complementary way. AFM and contact angle measurements only probe the outer surface of the DCBs and XPS provides information from the top 7-10 nm. To understand how surface rearrangement proceeds, one must probe the “as deposited” structure and the “switched” structure. There is only one experimental study that probes the structure of a dense DCB. Recently, Devaux et al.\textsuperscript{61} studied the swelling behavior of highly stretched PS chains grown on a silicon surface using neutron reflectivity. They also synthesized a poly(deuterated styrene)-\textit{b}-polystyrene DCB. They calculated the domain thicknesses, roughness and density profile by fitting the neutron reflectivity profile. The interface width between the domains is measured roughly as 6 nm. Since the aim of the work is not to resolve the internal structure, the authors did not really work hard to fit the data well. Since to switch one block type away from the surface involves disrupting the existing ordered structure, fluctuations at interfaces also play a key role in the rearrangement mechanism.
There are always fluctuations at the interface between A-rich and B-rich domains in a bulk ordered block copolymer and at the surface of soft matter. The details of both sorts of fluctuations will determine the manner in which the rearrangement occurs, just as thermal fluctuations in bulk block copolymer materials strongly impact the temperature needed to disorder a bulk lamellar diblock mesophase. If the “as-deposited” brush shown in Figure 1.1 is to rearrange in a way suggested by Zhao when exposed to solvent selective 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. The fluctuations at these two interfaces will be different because the red blocks are tethered at both ends, while the blue blocks are tethered at one. No experimental results have been published for the fluctuation behavior of either interface of a DCB either in the melt or in the solvent-swollen state. Purely elastic fluctuations of homopolymer brushes have been studied theoretically by Fredrickson et al., Xi and Milner and Solis and Pickett. All considered the Alexander model of a strongly stretched brush in which the free ends are assumed to be located at the free surface. Fredrickson et al. argued that long wavelength fluctuations should be suppressed on the brush surface, due to the cost of chain stretching required to create surface undulations. They also argued the short wavelength fluctuations should be suppressed due to the action of surface tension. Thus, there is a preferred wavelength on the order of the equilibrium height of the brush.

The first objective of this work is to understand the internal and surface structure of “as-deposited” and “switched” DCBs for solving the mechanism of surface rearrangement. A second objective is to determine the effect of tethering on the surface
fluctuations and surface dynamics of DCBs and homopolymer brushes. In this work, various X-ray and neutron scattering techniques are used to study the structure and the dynamics of interfaces of DCBs. These scattering techniques will be reviewed in the following chapters. The background, experimental procedures, results and discussions and the conclusions of the research will be presented in a separate chapter for each topic. The thesis is organized as follows.

In chapter II, the basic principles of specular and off-specular X-ray and neutron scattering measurements and theoretical models to explain scattering phenomena and off-specular scattering measurements are discussed. Chapter III deals with the internal structure of ultrathin DCBs as resolved in the direction normal to the surface. The experimentally obtained interface width values from neutron reflectivity will be compared to the interface width values obtained from theoretical calculations for untethered diblock copolymers. The internal structure of DCBs in the plane of the sample is investigated using grazing incidence small angle X-ray scattering (GISAXS) and the presence of in-plane liquid-like structures is shown for the first time for “as-deposited”, “dry” and “switched” brushes in Chapter IV. The elucidation of vertical roughness correlation between the interfaces of a diblock brush using specular and off-specular X-ray scattering is discussed in Chapter V. The effects of thickness, annealing and solvent vapor on the roughness correlation are studied and the implications of interface roughness correlation for surface fluctuations will be pointed out in Chapter 5. Relaxation of surface height-fluctuations on PS and PnBA homopolymer brushes will be investigated using a direct measure of dynamics, X-ray photon correlation spectroscopy. The results are compared to that of films of untethered chains in Chapter VI.
Figure 1.1. Cartoons of the structures of the “as-deposited” and “switched” states of a DCB as suggested for PS-\textit{b}-PMMA brushes by Zhao et al.\textsuperscript{45-47}
CHAPTER II

X-RAY AND NEUTRON SCATTERING FROM SOFT CONDENSED MATTER

2.1 Introduction

X-ray and neutron scattering techniques appropriate for the investigation of the surface and interfaces of soft-matter thin films have become available in the last two decades with the technological developments of surface diffractometers and synchrotron radiation facilities. These techniques can be non-destructive 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 hundreds of nanometers, depending on the incident angle and the energy of the incoming beam. Another advantage of the scattering techniques is that the surfaces and interfaces of liquids, polymers, organic multilayers, etc., can be investigated on an atomic length scale. Because of these advantages, the interest in and use of scattering techniques has surged. 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

The refractive index \( n \) characterizes the interaction of a material with the incident radiation. For both X-rays and neutrons, the refractive index has a magnitude slightly less than unity, and is given by

\[
n = 1 - \delta + i\beta
\]  
(2.1)

where \( \delta \) is the real part of the refractive index and is related to \( b/V \), the scattering length density (SLD) of the material, by

\[
\delta = \frac{\lambda^2}{2\pi} \left( \frac{b}{V} \right)
\]  
(2.2)

where \( \lambda \) is the wavelength of the incident radiation. \( \beta \) is the imaginary part of the refractive index and represents the absorption component, which can be calculated from a measured mass absorption coefficient, \( \mu \)

\[
\beta = \frac{\mu \lambda}{4\pi}.
\]  
(2.3)

\( \beta \) is generally of order \( 10^{-7} \) or \( 10^{-8} \) for X-rays interacting with polymeric materials. For neutron reflectivity (NR) measurements, \( \beta \) may be even smaller and may be neglected, except when a material in the sample contains Li, B, Cd, Sm or Gd. In X-ray reflectivity (XR) measurements, \( \beta \) becomes larger for materials containing elements with high atomic numbers, and for such elements cannot be ignored.

XR is sensitive to differences in electron density, \( \rho_e \), a quantity related to the atomic numbers \( Z_i \) of the constituent elements and mass density \( \rho \). In calculations and discussions of the sample structure, electron density is often replaced with the real part of
the refractive index, \( \delta \), or X-ray scattering length density (SLD), \((b/V)_x\), which are given by:

\[
\left( \frac{b}{V} \right)_x = r_0 \rho_e
\]  

(2.4)

\[
\rho_e = \frac{N_A \rho \sum b_i}{MW}, \quad b_i = Z_i
\]  

(2.5)

where \( b \) is total scattering length in the scattering volume \( V \), \( r_0 \) is the classical electron radius (2.82 \( \times \) 10\(^{-13} \) cm), \( N_A \) is Avogadro’s number, \( \rho \) is mass density, \( \sum b_i \) is the total scattering length in a structural unit and is given by the sum of the atomic numbers of the atoms in the structural unit and \( MW \) is the molecular weight of this structural unit. For polymer samples, the structural unit is usually taken as a repeat unit of the polymer.

NR detects the variation in the neutron SLD, \((b/V)_n\). While X-ray scattering length varies in a monotonic fashion through the periodic table, the neutron scattering lengths of the elements do not. The elements or isotopes which differ slightly in atomic number may have a large difference in neutron scattering lengths. In fact, neutron contrast can be obtained through selective deuteration due to the widely different scattering lengths of hydrogen \((b_H = -3.74 \times 10^{-15} \) m) and deuterium \((b_D = 6.67 \times 10^{-15} \) m). \((b/V)_n\) is calculated using the following formula:

\[
\left( \frac{b}{V} \right)_n = \sum \frac{b_i}{V_i} = \frac{\rho N_A}{MW} \sum b_i
\]  

(2.6)

where the summation should be carried out over a repeat unit of the polymer.
2.3 Specular Reflectivity

The first specific technique to be discussed is that of specular reflectivity, which is performed in a reflection geometry, as shown in Figure 2.1, which illustrate an interface separating air or vacuum, with refractive indice \( n_0 \), and condensed matter with refractive index \( n_1 \). When a beam of radiation illuminates the interface with an incidence angle \( \theta_0 \), some of the radiation is reflected and some is refracted. The ratio of the refractive indices determines the angle of refraction, \( \theta_1 \), by Snell’s law

\[
n_0 \cos \theta_0 = n_1 \cos \theta_1. \tag{2.7}
\]

The refractive index of air or vacuum, \( n_0 \), is 1 and \( n_1 \) is slightly less than 1 for soft-condensed matter. Thus, \( \theta_1 \) is smaller than \( \theta_0 \). Radiation is totally reflected back to the medium 0 and only an evanescent field penetrates into the medium 1 for incident angles smaller than the critical angle which is given by

\[
\theta_c \approx \sqrt{2\delta}. \tag{2.8}
\]

Reflectivity, \( R \), is defined as the ratio of reflected intensity to the incident intensity. \( R \) is equal to 1 for incidence angles smaller than the critical angle and it decreases rapidly with the perpendicular component of the incident wavevector, \( k_z \), for angles larger than the critical angle. In vacuum, the \( z \) component of the wavevector (normal to the surface) is given by

\[
k_{z,0} = 2\pi \sin \theta_0 / \lambda. \tag{2.9}
\]

Since the angle of incidence and the detection angle are equal in reflectivity measurements, there is only a \( z \) component of the wavevector. In a medium \( i \) with scattering length density \( (b/N)_i \), the \( z \) component is modified such that
Where $k_{c,i}$ is the critical value of $k_{z,i}$ below which total reflection occurs for layer $i$. The ratio of reflected beam amplitude to incident beam amplitude (or “reflection coefficient”) at an infinitely sharp interface separating two media, $i$ and $i+1$, is given by

$$r_{i,i+1} = \frac{k_{z,i} - k_{z,i+1}}{k_{z,i} + k_{z,i+1}}.$$  \hspace{2cm} (2.11)

The reflectivity, $R$, is then given by an expression derived by Fresnel:

$$R = \frac{I_r}{I_0} = r_{0,i}^* r_{i,0} = \left( \frac{k_{z,0} - k_{z,i}}{k_{z,0} + k_{z,i}} \right)^2 = \left( \frac{q_{z,0} - q_{z,i}}{q_{z,0} + q_{z,i}} \right)^2 = R_F (k_{z,0})$$ \hspace{2cm} (2.12)

where the asterisk denotes the complex conjugate and $q_{z,0} = 2k_{z,0}$ is the magnitude of the scattering vector characterizing the reflected beam. Fresnel reflectivity, $R_F$, is proportional to $k_{z,0}^{-4}$ at values of $k_{z,0} \gg k_{z,c}$ for an infinitely sharp interface. The presence of surface roughness or diffuse interfaces causes the scattering intensity to fall off more rapidly than $k^{-4}$.

When there is a uniform thin film with thickness $d$ deposited on a substrate, the radiation reflected from the film consists of both radiation reflected from the air/film surface and radiation reflected from the film/substrate interface. The overall reflection coefficient of the sample is given by

$$r = \frac{r_{0,1} + r_{1,2} \exp(2ik_{z,1}d)}{1 + r_{0,1} r_{1,2} \exp(2ik_{z,1}d)}$$ \hspace{2cm} (2.13)

where $r_{1,2}$ and $r_{0,1}$ are reflection coefficient between the substrate and the film and between the air and film, respectively. The exact reflectivity, $R$, which is calculated using equation (2.12), is simply
As a result of interference of the reflected beams from different interfaces, the reflectivity profile contains a series of maxima and minima. These oscillations are called “Kiessig fringes.” The thickness of the film, $d$, may be readily estimated from the spacing of two successive minima, $\Delta q_{z,1}$, in a fashion which is independent of the refractive index of the film

$$d = \frac{2\pi}{\Delta q_{z,1}} \propto \frac{2\pi}{\Delta q_{z,0}} \text{ for } q_{z,0} \gg q_{z,c}$$

(2.15)

where $q_{z,c}$ is the magnitude of the scattering vector at the critical angle.

Up to this point, our analysis of reflectivity has dealt with the reflectivity from infinitely sharp interfaces. The interfaces between the substrate and the film and between the consecutive polymer layers are not infinitely sharp. In the real world, each interface shows a gradient in the density in going from the air into the film. Reflectivity from a thin film which has a surface rms roughness, $\sigma$, can be expressed for $q_{z,0} \gg q_{z,c}$ as

$$R(q_{z,0}) \approx \frac{16\pi^2 \rho_0^2 (\Delta \rho^2)}{q_{z,0}^4} e^{-q_{z,0}^2 \sigma^2}$$

(2.16)

at large $q_{z,0}$, this expression is equal to

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

(2.17)

From equation 2.17, it is clear that the reflectivity profile is very sensitive to the value of $\sigma$. A reflectivity measurement will be more sensitive to the magnitude of the roughness at the higher values of $q_{z,0}$ since the reduction in the reflectivity is greater.
The electron density gradient, $\partial \rho_e(z)/\partial z$, is a delta function for a sharp interface.

We may conveniently and effectively approximately model the structure of a diffuse air/film interface by assuming the electron density of the interface to have an error function shape, with the width characterized by $\sigma$. In this case, $\rho_e(z)$ across the interface is given by

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

(2.18)

with $\rho_1$ is the electron density of the film. The error function is defined as

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

(2.19)

Information about the film thickness, characteristic spacing of periodic structures and approximate thickness of other key components of a film’s structure can be derived from the reflectivity data without detailed analysis. Further 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. The structure of the thin film cannot be obtained by directly inverting the reflectivity data, due to the loss of phase information.\(^{69-71}\) Instead, a candidate model is assumed for the film structure and the parameters of the model are varied using a non-linear regression until a simulated reflectivity curve for the film structure agrees well with the experimental data. There are three means of calculating reflectivity from model structure profiles.

In two of these methods, reflectivity from an arbitrarily complex electron density profile can be calculated from a discretized version of the electron density profile. The real structure is approximated as a stack of $N$ homogenous layers, each of thickness, $d_i$, and electron density, $\rho_{e,i}$. 

21
The first method may be referred to as the “Parratt formalism”. In the Parratt formalism, the reflection and transmission coefficients at each interface in the discretized structure are calculated recursively, starting with the substrate/layer interface. The reflection coefficient at that interface is given in equation (2.12). This result is used to solve the general recursive equation

\[
    r_{i-1,i} = \frac{r_{i-1,i} + r_{i,i+1} \exp(2id_i k_{z,i})}{1 + r_{i-1,i} r_{i,i+1} \exp(2id_i k_{z,i})}
\]

(2.20)

where \(d_i\) is the thickness of the \(i\)th layer and \(r_{i,i+1}'\) is calculated using equation (2.11). Overall sample reflectivity is obtained as the modulus squared of the air/top layer reflection coefficient. The Parratt formalism takes dynamical scattering effects into consideration and this becomes important for values of \(q_z\) close to \(q_{z,c}\).

The second method is so called “optical matrix formalism”. The optical characteristics of any single layer \(i\) are summarized in a matrix \(M_i\) which contains the coefficients of two simultaneous linear differential equations linking the amplitude of the electromagnetic field in the layer and its derivative. The equations may be solved analytically for any form of refractive index profile through the layer. Often, the profile within the layer is assumed to be constant, yielding

\[
    M_i = \begin{bmatrix} m_{11,i} & m_{12,i} \\ m_{21,i} & m_{22,i} \end{bmatrix} = \begin{bmatrix} \cos(k_{z,i}d_i) & \sin(k_{z,i}d_i)/k_{z,i} \\ -k_{z,i} \sin(k_{z,i}d_i) & \cos(k_{z,i}d_i) \end{bmatrix}.
\]

(2.21)

If this single layer is on a substrate characterized by \(k_{c,N+1}\), the reflectance (reflection coefficient) of the supported film is given by

\[
    r_i = \frac{k_{z,i} k_{z,N+1} m_{12} + m_{21} - ik_{z,N+1} m_{11} + ik_{z,i} m_{22}}{k_{z,i} k_{z,N+1} m_{12} - m_{21} + ik_{z,N+1} m_{11} + ik_{z,i} m_{22}}.
\]

(2.22)
The reflectance of a stack of uniform layers which form the discretized profile can be calculated by multiplying the transfer matrices of all N layers to form the transfer matrix of the total film, $M_T$

$$M_T = M_1 M_2 \ldots \ldots M_N$$ \hspace{1cm} (2.23)

and calculating $r$ as in equation (2.22) using the elements of $M_T$. Reflectivity is obtained by multiplying the reflectance with its complex conjugate. The optical matrix formalism also take the dynamical scattering effects into consideration.

The third method makes use of the “Born Approximation” in which the problem is simplified by assuming the scattered and reflected fields are always negligible in magnitude compared to the incident field. This approach is only acceptable for $q_z > 4q_{z,c}$ and for samples that have no large electron density gradients. The reflectivity averaged over the coherence of the beam is given by

$$R(q_z) = R_F(q_z) \left| \frac{1}{\rho_s} \int_0^\infty dq z e^{i q z} \frac{\partial \rho_z}{\partial z} \right|^2$$ \hspace{1cm} (2.24)

where $\rho_s$ is a reference electron density, for example that of the substrate. In this approach, the dynamical scattering effects are not considered, but contributions of various structural features to the reflectivity may be explicitly separated and studied.

2.4 Off-specular X-ray Scattering

The specularly reflected intensity from a perfectly smooth surface is generally lower than the theoretically calculated Fresnel reflectivity, $R_F$, due to the surface roughness. The missing intensity is diffusely scattered in off-specular directions, i.e. for exit angles $\theta_f \neq \theta_i$. Specular reflectivity is only sensitive to the laterally averaged
electron density profile $\rho_s(z)$ in the direction normal to the surface ($z$-direction). Analysis of the specular reflectivity gives the integral roughness of the surface averaged in the lateral direction ($x$ and $y$ directions) and the frequencies captured in the range of $q_z$ investigated. On the other hand, analysis of the off-specularly scattered intensity yields information about the lateral correlations and in-plane surface fluctuations. The electron density of a sample can be described by the function $\rho(x, y, z)$ in three dimensions. This function can be decomposed into two functions, the electron density of the nominal surface $\rho(z) = \langle \rho(x, y, z) \rangle_{(x, y)}$ and fluctuations $\delta \rho(x, y, z)$ away from laterally averaged value in the following manner:

$$\rho(x, y, z) = \rho(z) + \delta \rho(x, y, z)$$

(2.25)

The scattering from the full electron density profile, including the diffuse scattering from the fluctuations $\delta \rho(x, y, z)$, can be calculated by applying certain approximations such as the Born approximation\(^76\) (kinematical formulation) or, at a higher level of sophistication, the Distorted Wave Born Approximation (DWBA).

### 2.4.1 Born Approximation

The Born approximation\(^76\) is the simplest formulation for calculating the scattering for a single rough interface. It is valid in the so-called “weak scattering regime”, i.e., when the cross section for the scattered radiation is small, and hence multiple scattering effects may be neglected. The Born approximation\(^76\) takes only single scattering events into account. In this approximation, the scattering function $S(q)$ of a surface is given by
\[ S(q) = \frac{(\Delta \rho_e)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \int \int \exp\{q_z^2 C(X,Y)\} \times \exp\{-i(q_x X + q_y Y)\} dXdY \tag{2.26} \]

where \( \Delta \rho_e \) is the electron density contrast between the bulk values of the two materials next to the interface, \( \sigma \) is the rms roughness of the interface and \( C(X,Y) \) is the height-height correlation function, with \( X = x - x' \) and \( Y = y - y' \). Since the height-height correlation function goes to zero as \( X \) and \( Y \) go to infinity, the integral in equation (2.26) contains a delta-function component. The delta-function part can be separated from the rest by writing

\[ S(q) = S_{\text{spec}}(q) + S_{\text{diff}}(q), \tag{2.27} \]

where

\[ S_{\text{spec}}(q) = \frac{(\Delta \rho_e)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \delta(q_0) \tag{2.28} \]

and

\[ S_{\text{diff}}(q) = \frac{(\Delta \rho_e)^2}{q_z^2} \exp(-q_z^2 \sigma^2) \times \int \left[ \exp\{q_z^2 C(R)\} - 1 \right] \exp(-iq_z \cdot R) dR, \tag{2.29} \]

are the explicit expressions for the specular and diffuse parts respectively with the lateral vectors \( q_0 = (q_x, q_y) \) and \( R = (X^2 + Y^2)^{0.5} \). Equation (2.29) shows that \( S_{\text{diff}}(q) \) is proportional to \( (\Delta \rho_e)^2 \). The electron density contrast at the polymer/polymer interfaces is typically weak and these interfaces generally can not be studied readily by XR or off-specular x-ray scattering unless special techniques are used such as contrast variation. Derived equations (2.26) - (2.29) are not valid for \( \theta_i = \theta_c \) or \( \theta_f = \theta_c \) since in the Born approximation all multiple scattering events are neglected.
2.4.2 Distorted Wave Born Approximation (DWBA)

The DWBA provides a superior, but rather complicated treatment of diffuse scattering from surfaces in comparison to the Born approximation. 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 the DWBA, the scattering process is assumed to yield a small perturbation to the solution of equations for a smooth surface and the cross section is calculated in first-order perturbation theory. Detailed calculations have been done by Sinha et al. for a single surface and by Holy et al. for layer systems including the effect of vertical interface roughness correlations.

The expressions for the diffuse scattering cross section in DWBA are very similar to those obtained using the Born approximation. The most important difference is that the transmission functions for the incident radiation, \( t_i(\theta) \), and scattered radiation, \( t_f(\theta) \) are considered in the calculation of the scattering function. The functions \( t_i(\theta) \) and \( t_f(\theta) \) are given as

\[
\begin{align*}
t_i(\theta) &= \frac{2k_{i,z}}{k_{i,z} + k_{t,z,i}} \\
t_f(\theta) &= \frac{2k_{f,z}}{k_{f,z} + k_{t,z,f}}
\end{align*}
\]

where \( k_{i,z} = k \sin \theta_i \), \( k_{f,z} = k \sin \theta_f \), \( k_{t,z,i} = nk \sin \theta_{t,i} = k(n^2 - \cos^2 \theta_i)^{1/2} \), and

\[
k_{t,z,f} = nk \sin \theta_{t,f} = k(n^2 - \cos^2 \theta_f)^{1/2}.
\]

To account for refraction, the perpendicular wavevector transfer in the vacuum \( q_z = k_{f,z} + k_{i,z} \) has been replaced by that in the sample
medium, \( q_{z,f} = k_{z,f} + k_{z,i} \). The diffusely scattered X-ray intensity \( I_{\text{diff}} \) from a single surface is given by

\[
I_{\text{diff}} \sim |f_i(\theta_i)|^2 S(q) |f_j(\theta_f)|^2
\]  

(2.32)

with the scattering function \( S(q) \) given as

\[
S(q) = \frac{(\Delta \rho)^2}{q_{z,i}^2} \exp\left[-\left[(q_{z,i})^2 + (q_{z,f})^2 \right] / 2 \right] \times \int \left[ \exp \left[ i q_{z,i} R \right] C(R) \right] - 1 \exp(-iq_{z,i}R) dR
\]

(2.33)

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 \( t_i(\theta) \) and \( t_f(\theta) \) and are called the Yoneda\textsuperscript{79} peaks. When \( \theta_i, \theta_f \gg 3 \theta_c \), the factors \( |t_i(\theta)| \) and \( |t_f(\theta_f)| \) approach unity and \( q_{z,i} \) approaches \( q_z \) so that the DWBA result reduces to that from the Born approximation.

2.4.3 Types of Off-Specular Scattering Experiments

The geometry of a typical scattering experiment is shown in Figure 2.2. Detector position is specified by \( \theta_f \) for in-plane (x-z plane) scattering measurements. For out-of-plane scattering an additional angle, \( \psi \), between the plane of incidence and the plane of detection must be specified. The wavevector transfer, \( q_z \), is controlled by varying the incident and exit angles. The \( x, y \) and \( z \) components of the wavevector transfer are given by

\[
q_x = k (\cos \theta_f \cos \psi - \cos \theta_i)
\]

(2.34)

\[
q_y = k \cos \theta_i \sin \psi
\]

(2.35)
\[ q_z = k(\sin \theta_i + \sin \theta_f) \, . \] (2.36)

Four different types of off-specular scattering measurements can be done in grazing incidence geometry. Trajectories in reciprocal space for three of those scans and a specular reflectivity scan are shown in Figure 2.3. These scans will be explained briefly in the following paragraphs.

In a specular reflectivity measurement, \( \theta_i = \theta_f \) and \( \psi = 0 \), such that the resulting wavevector, \( q_z \), has only a z component with the form of \( q = (0, 0, 2k \sin \theta) \). When the detector position is always offset from the specular condition by a fixed angle \( \Delta 2\theta \), the scan is called a longitudinal diffuse scan. For the longitudinal scan \( q_z \) is varied while keeping \( q_z \), equal to some small fraction of \( q_z \). The longitudinal scan is also used to measure the diffuse scattering contribution close to the specular peak. The pure specular reflectivity can be approximated by subtracting the estimated diffuse scattering in the specular direction using an interpolation between two longitudinal scans, one measured with the detector offset in one direction and another with the detector offset to the other side of the specular condition. A longitudinal scan can give information about the vertical roughness correlations between the interfaces.

Transverse scans, which are very similar to “rocking curves”, are another way to perform off-specular scattering measurement. In a transverse diffuse scan, diffuse scattering is measured at various values of \( q_x \), keeping \( q_z \) constant. A rocking curve is performed by fixing the angle \( (2\theta) \) between incident and scattered directions and then varying the angle of incidence by rocking the sample. Therefore, \( q_z \) varies slightly and penetration depth varies. The resulting wavevector transfer \( q \) has both a vertical component \( q_z \) and a non-zero component \( q_x \). The data can be analyzed qualitatively by
comparing the shape of the scan with well-known transverse scan data from other systems such as untethered thin polymer films or quantitatively by fitting the data with an appropriate model. A transverse scan can give information about the characteristics of surface fluctuations and in-plane correlations.

When the off-specular scan is done by fixing the incident angle ($\theta_i$) and scanning through the detector angle ($2\theta$), it is called a “detector scan”. In a detector scan, $q_x$ increases slowly as $q_z$ increases away from the specular condition. A trajectory of a detector scan is shown in Figure 2.3. In this geometry, the accessible values of $q_x$ and $q_z$ are limited on one side of the trajectory, due to the sample horizon. A constant sample area is illuminated during the detector scan. A detector scan can show if a material has interface roughness correlations.

The last type of off-specular measurement is the so-called “$q_y$ scan”. The incident angle is constant and the detector is scanned out of the incidence plane in a $q_y$ scan. This scan probes a range of $q_y$ values for constant $q_z$ and penetration depth. It differs from the rocking curve in that $q_z$ is held absolutely constant and only the in-plane dimension is probed. The first three types of off-specular scattering measurement are often done with a beam which is much larger in the $y$ direction than in the $x$ direction, while a $q_y$ scan requires comparable resolution in both directions. If the incident angle is below the critical angle of the film and the penetration depth of the evanescent wave is less than the film thickness, the resulting scattering is related only to the film structure and scattering from the interface with the substrate does not interfere.
Figure 2.1. Schematic of a beam incident on an interface at an angle $\theta_0$ with respect to the interface, together with the reflected portion of the beam and the radiation refracted at an angle $\theta_1$.

Figure 2.2. Schematic of a scattering geometry. The wavevectors of the incident and scattered X-rays are $k_i$ and $k_f$, with the incidence and exit angles $\theta_i$ and $\theta_f$, respectively. The momentum transfer is defined by $q = k_f - k_i$. The so-called “specular scattering” corresponds to $\theta_i = \theta_f$. Otherwise, the scattering is called “off-specular scattering”. Detector is denoted with D.
Figure 2.3. Trajectories of scans in reciprocal space \((q_x, q_z)\). The region below the solid line is inaccessible for in-plane scattering (beam or detector below the sample). Dashed line shows transverse (rocking) scan, dashed-dotted line represents specular reflectivity scan, inclined dashed-dotted line is a longitudinal diffuse scan (reflectivity with offset \((\delta \theta)\) and dotted line shows a detector scan. (Adapted from reference 71)
3.1 Introduction

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 or the other of their blocks. This means they may be used as stimuli responsive materials in sensors, biomimetics or microfluidics. Zhao et al.\textsuperscript{45} showed for the first time, using contact angle measurements and atomic force microscopy (AFM), that the surface of a PS-\textit{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-\textit{b}-PMMA DCB (with the first block noted being that next to the substrate) was 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 good 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 changed after selective solvent treatment, forming a nanopattern at the surface.
After this seminal paper, the surface rearrangement of diblock\textsuperscript{42,46-49,51} and triblock\textsuperscript{52-54} copolymer brushes were studied by various authors using contact angle measurements, AFM, XPS, ATR-IR and ellipsometry. Most of these studies demonstrated that surface rearrangement could be observed with a variety of block combinations in various solvents, but none of them explained how the surface rearrangement occurs. Zhao and co-workers\textsuperscript{45} conjectured what the internal structures of the brush films might be in the as-deposited and “switched” states, but they did not confirm the internal structure since it could not be resolved with their techniques. 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 and switched states is the first step to understanding and controlling surface rearrangement. There have been self-consistent field (SCF) theoretical studies\textsuperscript{57} of what to expect for equilibrium “wet” brushes when it can be assumed that the composition varies only in the direction perpendicular to the substrate. There have also been 2D SCF\textsuperscript{55,56} and Monte Carlo\textsuperscript{57} simulations for wet brushes in which composition varies in the directions both parallel and perpendicular to the substrate. 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 interaction parameter (χ) between solvent and polymers, molecular weight or length (N) of the chains. Two studies\textsuperscript{58,59} have focused on brushes in the melt state. Heine and Wu\textsuperscript{59} point out that the interface between the A-rich and B-rich domains will be sharper when the brush is “dry”. In this chapter, we present first experimental results elucidating the internal structure of “as-deposited” ultrathin DCBs using NR.
XR and NR are very powerful techniques that characterize 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 ($\theta$) to yield a reflectivity curve. Information about the film thickness, microroughnesses at the substrate/film and air/film surface and electron density profile for XR, or neutron scattering length density (SLD) profile for NR, 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 XR and 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.

3.2 Experimental

DCBs containing deuterated polystyrene (dPS) blocks were synthesized for NR measurements. Since NR measurements require substrates at least 6 cm in one dimension, the polymerizations were performed in a dry box instead of a Schlenk flask. The polymerization procedure was therefore modified from that for typical synthesis of a PS-$b$-PMA$^{52}$ brush.
3.2.1 Materials

Deuterated styrene (d8-S, C/D/N Isotopes 98%, Cambridge Isotope Laboratories 98%) and methyl acrylate (MA, Aldrich 99%)\textsuperscript{80} were passed through a column of activated basic alumina and degassed with high purity nitrogen for 1 h prior to use. CuBr (Aldrich, 98%) was purified as described in the literature.\textsuperscript{81} \textit{N,N,N',N',N''-Pentamethyldiethylenetriamine} (PMDETA, Aldrich 99%), ethyl 2-bromoisobutyrate (E2Br-iB, Aldrich 98%) and anhydrous anisole (Aldrich) were used as received. Silicon ATR crystals (25x5x1 mm) were obtained from Harrick Scientific. Silicon wafers (100) doped with phosphorus having 500±50 μm thickness were purchased from Umicore Semiconductor Processing; wafers doped with boron were not used since boron absorbs neutrons. All other reagents were purchased from either Aldrich or Fisher Scientific and used as received.

3.2.2 Substrate Preparation

ATR crystals and silicon wafers (60 mmx35 mmx0.5 mm) were cleaned by treatment with a freshly prepared “piranha” solution\textsuperscript{82} (70/30, v/v, concentrated \( \text{H}_2\text{SO}_4/30\% \text{ aqueous H}_2\text{O}_2 \)) at 100 °C for 2 h and were then rinsed with distilled water and dried with a stream of compressed air.

3.2.3 General Procedure for Deposition of Surface Bound Initiator

A 100x50 mm\textsuperscript{2} crystallizing dish was placed in a dry box, and a freshly cleaned silicon wafer and ATR crystal were placed in the crystallizing dish. The (11-(2-bromo-2-ethyl)propionyloxy)undecyltrichlorosilane was utilized as a surface-bound initiator. Dry
toluene (30 mL) and a 25 vol.% solution of the trichlorosilane initiator in toluene (0.6 mL) were added to the dish via syringe and the dish was covered with a piece of glass carrying a Teflon gasket and heated at 60 °C for 4 h in a box filled with technical grade nitrogen. The silicon wafer and ATR crystal were then removed, sequentially washed with toluene, ethanol and methylene chloride, and then dried in a stream of compressed air.

3.2.4 Procedure for Surface ATRP from a Flat Silicon Substrate

CuBr, anisole (a good solvent for styrene, methyl acrylate, PS and PMA) and monomer were 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 were applied to the flask and it was left under a nitrogen atmosphere. PMDETA was added to the mixture via syringe and the solution stirred at reaction temperature until it became homogeneous (~ 5 min). Then the flask was sealed and transferred to the dry box along with the free initiator (E2Br-iB), ATR crystal, silicon wafer and a 100x50 mm² crystallizing dish. An initiator-modified ATR crystal and silicon wafer were placed in the crystallizing dish in the dry box. Polymerization solution was added to the crystallizing dish, followed by the addition of free initiator. The final concentrations were as follows: [d₈-S]₀ = 3.9 M, [anisole]₀ = 5 M, [PMDETA]₀ = 25 mM, [CuBr]₀ = 12 mM and [Br-iB]₀ = 5 mM or [MA]₀ = 3.7 M, [anisole]₀ = 6.1 M, [PMDETA]₀ = 30 mM, [CuBr]₀ = 15 mM and [Br-iB]₀ = 15 mM. The dish was covered with a piece of glass carrying a Teflon gasket on it to prevent evaporation of the solution. The polymerization proceeded at 90-100 °C for a period of time depending on the
thickness targeted, after which the ATR crystal and silicon wafer were removed. To remove untethered polymer chains, the ATR crystal and silicon wafer were placed in a Soxhlet extractor and extracted with tetrahydrofuran (THF) for 24 h followed by sonication in THF for 30 min.

3.2.5 Block Copolymerizations

To create a block copolymer brush, a second block was polymerized by ATRP in the same manner as the 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, the ATR crystal and silicon wafer were cleaned and extracted to remove any untethered polymer before proceeding to the next polymerization. Figure 3.1 shows an idealized diblock copolymer brush structure. It has been assumed by a majority of papers in the literature that an “as-deposited” diblock brush has a lamellar structure with a layer rich in the first block synthesized next to the substrate and a layer rich in the other block adjacent to the air surface. Most of the schematic drawings in brush papers have also shown a sharp interface between domains rich in different blocks.

Throughout this thesis, DCBs will be called with the corresponding thickness values of each block. For example, dPS14-PMA3 indicates that the diblock brush has a 14 nm thick dPS layer next to initiator layer and 3 nm thick PMA layer next to air surface.
3.2.6 Characterization Methods

ATR-FTIR spectra were recorded using a Nicolet System 730 spectrometer using a modified 4XF beam condenser (Harrick Scientific). Spectra were recorded at 2 cm\(^{-1}\) resolution, and 500 scans were collected. 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 μl drop were determined using the tilting stage method. 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.

Brush internal structure was characterized using NR and grazing incidence small angle X-ray scattering (GISAXS). 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. Such measurements provide information on nonlamellar structure internal to the brush, and particularly on lateral correlations in the plane of the brush. GISAXS experiments were carried out at the 8-ID-E beamline at the Advanced Photon Source using a monochromatic X-ray beam with a wavelength of 0.1675 nm. 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 1200×1200 pixel array, the scattered intensity was recorded at a fixed angle of incidence, \(\alpha_i\), of the X-ray beam onto the sample surface.
NR measurements were performed on the NG1 reflectometer at the National Institute of Standards and Technology (NIST) Center for Neutron Research using a wavelength of 4.75 Å. To maximize the intensity, the sizes of the collimating slits and detector slits were increased during the measurement as incident angle (θ) increased by keeping the relative resolution in q approximately constant (δq/q ≈ 0.02). Data were corrected for both the varying slit size and background. To reduce background scattering, all measurements were done with the sample in an aluminum sample chamber evacuated by a turbomolecular pump.

To obtain structure of thin films, a candidate model is assumed and the parameters of the model are varied using a non-linear regression until a simulated reflectivity curve calculated for the model structure using the Parratt formalism\textsuperscript{72} agrees sufficiently well with the experimental data. If enough is known about the film's composition and structure from its preparation or other techniques, this indirect analysis is very powerful, providing film thicknesses and interface widths with great precision. It is not a unique solution, but other reasonable models can be tried and excluded.

3.3 Results and Discussion

Scheme 3.1 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 was synthesized according to literature\textsuperscript{50}
precedent and used as a surface-bound initiator. Solution deposition of the initiator onto silicon substrate and ATRP of dPS and PMA on the surface was confirmed using ATR-FTIR, contact angle measurements and ellipsometry. Figure 3.2a shows the ATR-FTIR spectrum of surface immobilized trichlorosilane initiator, which is used to synthesize dPS14-PMA3 diblock brush, with three predominant peaks. The 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. The 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 in Figure 3.2b, indicates the formation of homopolymer brush of dPS14 from the immobilized initiator. The peaks are assigned for initiator layer is still present in Figure 3.2b, since the penetration depth of the IR beam (~0.5 \(\mu\)m) is much larger than the thickness of the brush layer. Figure 3.2c demonstrates the ATR-FTIR spectrum of dPS14-PMA3 brush after the PMA brush is synthesized from dPS-Br macroinitiator. This brush exhibited 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\(^{-1}\). Characteristic contact angles for all diblock brushes studied are shown in Table 3.1. The molecular weights of the free polymer chains and \(\chi_N\) values of the PMA-\(b\)-dPS and dPS-\(b\)-PMA samples are shown in Tables 3.2 and 3.3, respectively. The specific experimental ATRP conditions to synthesize homopolymer dPS and PMA and diblock copolymer brushes of dPS-\(b\)-PMA and PMA-\(b\)-dPS were given in the experimental section. PMDETA was 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.\(^{83}\) It has been shown that the low
concentration of initiator on flat surfaces causes an insufficient concentration of the
deactivator to provide control during the surface ATRP reactions. To overcome this
problem, free initiator (ethyl-2-bromoisobutyrate, E2BriB) was added to the reaction
solution. 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. synthesized DCBs of PS, PMMA and poly(dimethylacrylamide) from a surface
immobilized azo-initiator using RAFT. The addition of free initiator, 2,2'-
azoisisobutyronitrile (AIBN), was required to obtain a controlled polymerization. They
compared the molecular weight of free polymer chains with that of the tethered polymer
chains, by cleaving a homopolymer brush prepared on high surface area non-porous
silica. Their results indicated 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 determined that the initiator efficiency ranged from 0.15 to 0.19. Tsuji
and co-workers compared the molecular weights for degrafted and free PS synthesized
by RAFT and ATRP. They found that if the polymerization was performed without using
a free RAFT agent, the $M_n$ values of the grafted and free polymers increased with
increasing conversion at the early stages of polymerization, but leveled off at conversions
higher than 20%, while the PDI value was in the range 1.5-3.0. The addition of free
RAFT reagent to the system provided a linear increase of $M_n$ with conversion and PDI
values less than 1.4. The $M_n$ value of grafted polymer was very close to that of the free polymer and the PDI value of grafted polymer was always slightly larger than the PDI value of the free polymer. GPC analysis revealed that the graft polymers synthesized by RAFT gave a GPC curve with a prominent shoulder assigned to the recombined (dead) polymer. The GPC curve of the graft polymer synthesized by ATRP did not have any shoulder, suggesting that the recombination on the surface is insignificant in the ATRP system. Patten et al.\textsuperscript{84} synthesized PS from silica nanoparticles using ATRP. They gained information about the molecular weights and molecular weight distributions of the grafted polymer by etching the silica cores using HF (5%). The molecular weight of the grafted polymer increased linearly with increasing conversion and the PDI was around 1.2. They also compared the degrafted chains with the free chains polymerized from free initiator and they found that the $M_n$ for degrafted chains was 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. Hawker and co-workers\textsuperscript{40} performed NMRP of styrene on silica gel and they observed $M_n$ (free polymer) = 48000 g/mol, PDI=1.20 and $M_n$ (degrafted polymer) = 51000 g/mol, PDI= 1.14. The significance of these results is that the analysis of free polymer provides a reasonable estimate of the brush molecular weight and PDI. There has been only one report\textsuperscript{85} that has compared the molecular weight of degrafted PMMA brushes grown on a flat substrate. They used a large gold substrate and degrafted the chains by treatment with I$_2$. Since they did not use a free initiator, a comparison between free and degrafted polymer was not possible. They observed a linear dependence up to a film thickness of 33 nm and above that the dependence was non-linear. They also estimated the initiator efficiency as 0.1, which is reasonably close to the value obtained by Brittain et al.\textsuperscript{86}
According to these results, it is possible to make reasonable conclusions about the molecular weight and polydispersity of polymer brushes. First, 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. The latter is especially important for the calculation of the occupied area of single polymer brush chain and overall grafting density of the polymer brushes.

Another important question for our system is the reinitiation of the second block from the macroinitiator. Reinitiation of the second block depends strongly on the concentration of polymer chains corresponding to “living” chains. To initiate the block polymerization, the grafted polymer chains forming the first block must 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.\textsuperscript{87} reported that at high conversions, the rate of propagation ($k_p$) slows down considerably, 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 will induce loss of end groups. Conversion must not exceed 95% to avoid end-group loss. In our studies, the conversion was never allowed to exceed 70% in order to reduce the contribution of termination reactions. It is possible to estimate the reinitiation efficiency by doing a reinitiation experiment. In a reinitiation experiment, a monomer is polymerized from the SAM using the usual polymerization conditions. After the
polymerization is done, the thickness and molecular weight are measured. In the second step, 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. After the polymerization of the second monomer, the thickness of the second block and the molecular weight are measured again. The decrease in the growth of the second layer is associated with a decrease in the grafting density. Reinitiation experiments have been performed with PS and we found that 91% of the first polymer block reinitiated. Kim et al.\textsuperscript{53} found that the reinitiation efficiency depends on the quenching method to end the polymerization. They showed that for simple solvent rinsing between the polymerizations, 85-90% of the active chains were preserved during the quenching step. If a large excess of Cu(II)Br\textsubscript{2} (deactivator) is used to quench the polymerization, more than 95% of the active chains support growth of an additional block.

3.3.1 Structure of DCBs with PMA on the bottom

Figure 3.3 shows the neutron reflectivity as a function of scattering vector normal to surface, $q_z$, for all samples from the PMA-$b$-dPS series. The fits were obtained using a model of the brush structure consisting 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 were modeled by convolution with appropriate Gaussian functions as well. In other words, a purely lamellar structure model was used. The reflectivity curves have been measured up to the $q_z$ value of 0.24 to resolve the smaller scale details of the interface structure. For all these films, such a model captures all the features of the
reflectivity curves, 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.

However, it is also important to note the variations in $\chi N$ among the samples. The parameter $\chi N$ is key in characterizing the tendency of untethered block copolymer chains to microphase segregate in the bulk. For large values of $N$, block copolymer chains of near symmetric composition order in the bulk for values of $\chi N$ of order 10. The value above which ordering occurs is still larger for smaller values of $N$ for which fluctuations become important. The value of $(\chi N)_{ODT}$ also increases as one moves away from symmetric composition. Since the PS-\textit{b}-PMA has not been widely studied, there is no published value of $\chi$. For making rough comparisons to the behavior expected in the bulk we have thus estimated the value of $\chi$ from solubility parameter arguments. The exchange interaction parameter $\chi_{AB}$ is given as

$$\chi_{AB} = V_r \left( \delta_A - \delta_B \right)^2 / RT$$

(3.1)

where $\delta_i$ is the solubility parameter of species $i$, $V_r$ is the reference volume and $R$ is the universal gas constant. The value of the solubility parameter can be estimated using a group additivity calculation, as described by van Krevelen.\textsuperscript{88} Values calculated this way for PS and PMA are compared in Table 3.4 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 doing an estimate the value of $\chi_{PS-b-PMA}$ simply using equation 3.1 we take into account published values of $\chi_{PS-b-PMMA}$ and $\chi_{PS-b-PI}$, which should bound the value of $\chi_{PS-b-PMA}$. In a small-angle neutron scattering study\(^8\) of disordered dPS-b-PMMA the value of $\chi_{PS-b-PMMA}$ was determined as 0.041 at 298 K. The value of $\chi_{PS-b-PI}$ was measured by small-angle X-ray scattering as 0.14 at 298 K.\(^9\) Using a constant reference segment volume for all values of $\chi$, we can estimate ratios of the relative magnitudes of $\chi_{PS-b-PMA}$, $\chi_{PS-b-PMMA}$ and $\chi_{PS-b-PI}$.

$$\frac{\chi_{PS-b-PMA}}{\chi_{PS-b-PMMA}} = \frac{(\delta_{PS} - \delta_{PMA})^2}{(\delta_{PS} - \delta_{PMMA})^2} = 64$$  \hspace{1cm} (3.2)

$$\frac{\chi_{PS-b-PMA}}{\chi_{PS-b-PI}} = \frac{(\delta_{PS} - \delta_{PMA})^2}{(\delta_{PS} - \delta_{PI})^2} = 0.22$$  \hspace{1cm} (3.3)

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 equation (3.2) or (3.3).

Values of $\chi_N$ are included in Table 3.2 and 3.3. One sees that the value of $\chi_N$ for the thinnest sample is sufficiently low, suggesting that it is unlikely that untethered chains of this composition and length would microphase segregate in the bulk. In order to confirm the layered structure is the right model for the samples with low $\chi_N$ values, a model of a single layer of uniform SLD was used to try to fit the data. An acceptable fit could not be achieved with this model, even for the sample that has the lowest $\chi_N$ value. The separation of PMA and dPS segments observed for this sample is due to the effective fields acting on the chains as a result of the tethering and preference of dPS for the surface due to its lower surface energy. The SLD profile for sample PMA6-dPS5, shown
in Figure 3.4, has, in contrast, a well defined bottom and top layers. The value of $\chi N$ for this sample is markedly higher and the biasing is sufficient to yield well-defined microphase segregation and interface.

That the structure is indeed lamellar may be checked by using 2D GISAXS measurements, which are sensitive to variations in structure in the plane of the sample. The 2D GISAXS pattern for the PMA8-dPS2 sample shown in Figure 3.5a 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-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 0.3. The GISAXS data pattern shown in Figure 3.5b belongs to a thicker sample and shows scattering peaks to the left and right of the center. These indicate the presence of an in-plane liquid-like ordering which will be discussed further in the next chapter.

The stabilization of a lamellar structure is also favored by the presence of van der Waals interactions between the substrate and the polymeric layers, which serve to suppress fluctuations in the surface and in the interface between lamellar layers. The very smooth surfaces seen for the PMA-$b$-dPS samples are consistent with the presence of such a suppression of fluctuations, though further proof of the fluctuation suppression will be the subject of the 5th and 6th chapters. The root mean square roughness ($\sigma_{rms}$) at the air surface for this series varies from 0.3 to 0.6 nm. We have reported in a paper that the roughnesses at different interfaces of thin dPS-$b$-PMA diblock copolymer
brushes are correlated. The PMA-\textit{b}-dPS samples in this work exhibit the same conformal roughness behavior.

We may make additional observations on the structure of the brushes on the basis of details of the models. We have elaborated our model to the extent that we have considered explicitly both the SiO\textsubscript{x} on the substrate and the initiator layers. The thickness of the oxide layer was 1.2\( \pm \)0.2 nm, and the thickness of the initiator layer varied from 1.2 nm to 1.9 nm. The thickness of the initiator layer expected from a calculation based on the expected structure was 2.1 nm, whereas XR measurements done on a sample consisting of only an initiator layer on a substrate yielded 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, as long as the density of initiator sites is still large enough that it substantially exceeds the grafting density of the polymer chains. The only role of the initiator layer is to provide an initiation point for polymerization. In our case, it seems that many of the bromine atoms at the end of the initiator molecules have been consumed for the initiation step. The SLD value of the initiator layer is very close to zero, consistent with the near zero value of SLD for alkyl chains (e.g. \(-\text{CH}_2\text{-}\)).

The values of SLD observed in each of the polymer-rich layers yield valuable quantitative information about the brush structure. The SLD is shown in Figure 3.4 as a function of depth for the lamellar model of sample PMA6-dPS5. The upper bold line in Figure 3.4 marks the value of SLD calculated for pure dPS at a density characteristic of a
bulk melt (1.14 g/cm³) and the lower bold line represents the value of SLD calculated for pure, bulk PMA melt. The best fit model involves a value of SLD for the dPS-rich layer that is lower than the SLD for pure dPS. It also includes a value of SLD for the PMA-rich layer that is higher than the SLD value for pure PMA. There is substantial mixing of the two types of blocks in both layers.

For ready comparison with theoretical calculations, it is convenient to focus specifically on a measure of the width of the interface between the two layers. In order to calculate the interface width, the SLD profile was first converted to a profile of volume fraction of dPS or PMA. It is not possible to calculate volume fractions unambiguously for the whole SLD profile since, very close to the substrate, there is a mixing of the SLDs of three components: the initiator segments, the PMA segments and the dPS segments. In those locations, there are two independent variables and one equation to solve. The same problem exists near the air surface where the model SLD contains contributions from the air, the dPS segments and the PMA segments. The composition profile in the neighborhood of the interface between the two polymer layers in one model structure is shown in Figure 3.6. 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 convention. 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 interface width \( a_I \). In our SLD model, the width at the interface between PMA-rich and dPS-rich layers is expressed using an error function and the two parameters describing interface
width can be readily interchanged. The value of $a_l$ may be calculated by multiplying the rms roughness by a factor of $(2\pi)^{1/2}$. The interface width between the polymer domains varies from 2 to 3.3 nm for the PMA-$b$-dPS series. Even though the calculated interface width is not large if it is compared to the values obtained for untethered chains of PS-$b$-PMMA, when the total film thickness is taken into consideration, the interfacial region constitutes 25-30 % of the films.

3.3.2 Structure of DCBs with dPS on the bottom

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 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 surface with dPS segments. Figure 3.7 shows the specular NR curves for dPS5-PMA2, for which $\chi_N$ has a value of about 9.5 and dPS14-PMA3, for which $\chi_N = 20.5$. The data from both samples have been modeled using the same sort of two layer lamellar model used for the PMA-$b$-dPS brushes. 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 figure of merit, $\chi^2$ of less than 0.5. The SLD depth profile for dPS5-PMA2 is given in the inset of Figure 3.7. The final SLD profile does not exhibit two well-defined layers, and exhibits a large interface width, $\sigma_{\text{rms}}$, between the polymer layers. As with the thinnest PMA-$b$-dPS films, the thinnest dPS-$b$-PMA film contain 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. Although dPS5-PMA2 has a more symmetric composition than does PMA2-dPS4 and almost similar block lengths as PMA2-dPS4, the interface width in dPS5-PMA2 is twice as large (Table 3.5). 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-PMA2 has an interface width of 4.2 nm and 60% of the film is composed of polymer/polymer interface. The experimental interface widths are compared in Table 3.5 with estimates from the theory of Helfand and Wasserman in the narrow interface approximation limit.96

Of the 6 samples from the dPS-$b$-PMA series listed in Table 3.3, the last four samples could not be fit using a two layer model; instead a three-layer model had to be used. The NR curves for these samples and the corresponding fits using three-layer models are given in Figure 3.8. The calculated SLD profile for dPS14-PMA9 is shown in Figure 3.9. The thicknesses for the oxide and initiator layers are the same as used with samples for which the two-layer model worked. The SLD 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, 7 and 5 nm for the bottom, middle and top layers.

The GISAXS data set from each of these samples 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. One example is shown in Figure 3.5b. NR cannot resolve the lateral variations in SLD corresponding to this structure, but it is sensitive to variations with depth in the laterally averaged 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. It appears these do not extend through the entire thickness of the brush, but rather we conjecture that there is a laterally uniform layer at the air surface and at the substrate interface.

3.3.3 Comparison with Theory

These results may be compared with theoretical expectations for immiscible homopolymers and bulk ordered block copolymer materials and with self-consistent field theory (SCFT) calculations for a diblock brush. The width of an interface between immiscible homopolymers is, in general, smaller than that for a corresponding diblock copolymer, but the two values tend toward equality for sufficiently large value of $\chi_N$ ($\chi_N \geq 20$).\textsuperscript{97} Thus, the interface width value for the immiscible homopolymer pair is a lower bound for the interface width in the bulk diblock copolymer. The interface width between immiscible homopolymers of infinite molecular weight is given by\textsuperscript{98}

$$a_\infty = \frac{2b}{(6\chi)^{1/2}} \quad (3.4)$$

where $b$ is the average of the homopolymer statistical segment lengths and $\chi$ is the exchange interaction parameter between the homopolymers.

Using equation (3.4) with a value of statistical segment length, $b = 0.71$ nm, yields a value for $a_\infty$ 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 diblock copolymer interfaces, but also because interface fluctuations due to capillary waves have been ignored in the calculation. For untethered diblock copolymer chains, the effective interface width measured by NR
represents a convolution of the intrinsic width and a further broadening due to capillary fluctuations\(^{62, 99, 100}\) in the position of the nominal interface. A proper comparison must account for the capillary waves, if they are active. The mean-square displacement of the interface from its average position, \(\langle (\Delta z)^2 \rangle\), is given by

\[
\langle (\Delta z)^2 \rangle = k_BT \ln(\lambda_{\text{max}}/\lambda_{\text{min}}) / 2\pi\gamma_{\text{AB}}
\]  

(3.5)

where \(\lambda_{\text{min}}\) and \(\lambda_{\text{max}}\) are the minimum and maximum wavelengths of the fluctuations, and \(\gamma_{\text{AB}}\) is the interfacial tension between immiscible homopolymers. When relative differences between the segment lengths are small, the interfacial tension between immiscible homopolymers of PS and PMA is given by\(^{62}\)

\[
\gamma_{\text{AB}} = b \rho_0 k_BT (\chi/6)^{1/2}
\]  

(3.6)

where \(\rho_0\) is the number density of segments. Using the value of \(b = 0.71\) nm and a value of \(1/\rho_0 = 137\) Å\(^3\), 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 \(\lambda_{\text{max}}\) and \(\lambda_{\text{min}}\), we turn to the theoretical work of Frederickson and coworkers\(^{65}\) on surface fluctuations in grafted brushes. They argued that surface modes 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 \(\lambda_{\text{max}}\) 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 \(\lambda_{\text{min}}\) 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 of \( \langle 2\pi(\Delta z)^2 \rangle^{1/2} \). Thus the interface width ascribed to interface fluctuations is about 2 nm. The overall interface width, \( a_H \), is then given by

\[
a_H^2 = a_\infty^2 + a_{\text{fluc}}^2
\]  \hspace{1cm} (3.7)

The calculated widths, including fluctuations, are compared to the experimentally measured interface widths and presented in Table 3.5. The calculated interface widths vary from 2.4 nm to 2.8 nm and are in fair agreement with the experimental values for the PMA-\( b \)-dPS series. For the dPS-\( b \)-PMA series, the theoretical values of \( a_I \) are lower than the experimental values. 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. The discrepancy between the experimental and theoretical \( a_I \) values can be explained by the fact 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.

The width of an interface, \( a_H \), between the lamellar domains of a symmetric block copolymer for the case where the interface width is narrow compared to the domain size is calculated by Helfand\(^{101} \) and given by

\[
a_H = \frac{\pi}{2} \left( \frac{\beta_A \beta_B}{\alpha} \right)^{1/2} P_{1/2} \left( \frac{\beta_A^2 + \beta_B^2}{2\beta_A \beta_B} \right)
\]  \hspace{1cm} (3.8)
where \( \beta_A^2 = \rho_{0A} b_A^4 / 6 \), \( \alpha = \chi \rho_0 \) and \( P_{1/2} \) is a Legendre polynomial of order 0.5. Helfand and Wassermann theory is valid in the limit of high degree of polymerization (\( \chi N \geq 20 \)). Using equation (3.8) \( a_H \) is calculated to be 1.44 nm. This value is much smaller than the experimentally measured \( a_I \) values in this work. This is expected since Helfand and Wasserman theory does not consider the effect of molecular weights and interfacial fluctuations on the interfacial width. The effect of molecular weight on the interfacial properties is considered by Broseta et al. The analytic expression they obtained for the interfacial thickness is given by

\[
a_{H,M} = a_H \left[ 1 + \ln \left( \frac{1}{\chi N_A} + \frac{1}{\chi N_B} \right) \right]
\]

where \( a_H \) is the interfacial width defined in equation (3.8) and \( N \) is the chain length.

Inclusion of this effect into the calculations produces an increase in the interfacial width as shown in Table 3.5. The effect of interfacial fluctuations are calculated as described earlier and convoluted with the interface width value obtained from equation (3.9).

Addition of molecular weight and interfacial fluctuation effects broaden the theoretical interface width (\( a_H \)). The calculated interface widths vary from 2.5 nm to 2.7 nm and they are in good agreement with the experimental interface width values for PMA-\( b \)-dPS brushes. The experimental interface width values of dPS-\( b \)-PMA brushes are larger than the theoretical values. The discrepancy of the experimental and theoretical values can be explained with the fact that theoretical models do not take surface affinities of blocks into consideration.

SCFT calculations can explicitly account for these additional effects at the substrate and air interfaces at various levels of detail. Here we compare the
experimentally measured values to interfacial widths calculated with a SCFT,\textsuperscript{59} 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. From previous studies,\textsuperscript{53} it is known that about 85 - 90\% of the first blocks reinitiate, resulting in a brush that contains about 10\% homopolymer. The segment density depth profiles for PMA and dPS calculated using parameters characteristic of the PMA6-dPS5 sample are shown in Figure 3.10. The overall grafting density has been taken as 0.9 chains/nm\textsuperscript{2} and the grafting density of the diblock chains as 0.8 chains/nm\textsuperscript{2}. (i.e. only 8 of 9 chains of the first block synthesized are assumed to reinitiate.) A value of interfacial width for comparison with the experimental value may be derived from Figure 3.10 using Helfand’s convention.\textsuperscript{93}

Here there is a discrepancy between the calculation and the profiles derived from NR. First, the calculated interfacial width of 4 nm is larger than that seen for the corresponding sample in which the PMA block is tethered to the substrate (2.8±0.8 nm). That is, the calculation is insensitive to the order in which the blocks are synthesized. 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.

The interfacial width calculated from SCFT for dPS-\textit{b}-PMA brushes is in good agreement with the experimental interface widths measured by NR. The segment density depth profiles for dPS and PMA calculated using parameters characteristic of the dPS14-
PMA9 sample are shown in Figure 3.11. The grafting density of the diblock was taken to be 0.5 chains/nm² and that for the homopolymer was taken to be 0.1 chains/nm². The interface width for dPS14-PMA9 is calculated as approximately 4 nm using Helfand’s method in Figure 3.11. The SCFT calculations were performed assuming the dPS segments are favored at both interfaces. The shape of the dPS segment density profile within the dPS-rich layer is nonmonotonic due to non-ideal mixing. SCFT calculations are still in progress and we believe the SCFT results will be improved by adding differing affinities of the two blocks for the substrate and air interfaces.

The internal structure of thicker brushes (d ≥ 25 nm), which have large χN values, cannot be described in general by one dimensional models that account only for layering in the z-direction. Rather, a 3-D model of internal structure is required. Detailed 3-D modeling of the internal structure to capture the features observed in GISAXS data will be the subject of the next chapter.\textsuperscript{103}

3.4 Conclusion

Neutron reflectometry measurements have revealed for the first time details of the internal structure of dPS-b-PMA and PMA-b-dPS diblock copolymer brushes. For the brushes with PS 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 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 χN ~ 7-22, such as studied here, each layer in the lamellar structure contains a substantial volume fraction of
each block. Less mixing would be expected for brushes with larger values of \( \chi N \). Our results suggest that the structure of the DCBs is not similar to the structures of DCBs suggested by Zhao and co-workers.\textsuperscript{45-47} Figure 3.12 shows the cartoons that show the structure of the DCBs based on the neutron reflectivity results. 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 polymers for opposite interfaces and it was not considered by previous theories. For sufficiently thick brushes (\( d \geq 25 \text{ nm} \)), the internal structures in the as-deposited DCBs can no longer be represented with lamellar models, but rather in-plane structures must be considered.
Table 3.1. The advancing ($\theta_A$) and receding ($\theta_R$) water contact angles measured by tilting stage method.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Water contact angle(^a) 1(^{st}) layer</th>
<th>Water contact angle(^a) 2(^{nd}) layer</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>$\theta_A$ (deg) ± 3° $\theta_R$ (deg) ± 3°</td>
<td>$\theta_A$ (deg) ± 3° $\theta_R$ (deg) ± 3°</td>
</tr>
<tr>
<td>PMA2-dPS4</td>
<td>70  55</td>
<td>86  68</td>
</tr>
<tr>
<td>PMA6-dPS5</td>
<td>71  58</td>
<td>92  68</td>
</tr>
<tr>
<td>PMA7-dPS2</td>
<td>66  54</td>
<td>92  76</td>
</tr>
<tr>
<td>PMA8-dPS2</td>
<td>66  53</td>
<td>92  70</td>
</tr>
<tr>
<td>dPS5-PMA2</td>
<td>95  78</td>
<td>75  58</td>
</tr>
<tr>
<td>dPS14-PMA3</td>
<td>97  76</td>
<td>68  55</td>
</tr>
<tr>
<td>dPS15-PMA4</td>
<td>95  80</td>
<td>74  60</td>
</tr>
<tr>
<td>dPS15-PMA6</td>
<td>94  78</td>
<td>69  59</td>
</tr>
<tr>
<td>dPS11-PMA8</td>
<td>94  80</td>
<td>71  58</td>
</tr>
<tr>
<td>dPS14-PMA9</td>
<td>93  76</td>
<td>72  58</td>
</tr>
</tbody>
</table>
Table 3.2. Physical properties of samples for PMA-\textit{b}-dPS series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{n,PMA}^a$ (kg/mol)</th>
<th>$M_{n,dPS}$ (kg/mol)</th>
<th>$N_{PMA}$</th>
<th>$N_{dPS}$</th>
<th>$d_{PMA}^b$ (nm)</th>
<th>$d_{dPS}^b$ (nm)</th>
<th>$\chi N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA2-dPS4</td>
<td>1.8</td>
<td>5.7</td>
<td>21</td>
<td>51</td>
<td>2</td>
<td>4</td>
<td>7.2</td>
</tr>
<tr>
<td>PMA6-dPS5</td>
<td>4.8</td>
<td>5.7</td>
<td>55</td>
<td>51</td>
<td>6</td>
<td>5</td>
<td>10.6</td>
</tr>
<tr>
<td>PMA7-dPS2</td>
<td>4.8</td>
<td>3.2</td>
<td>55</td>
<td>29</td>
<td>7</td>
<td>2</td>
<td>8.4</td>
</tr>
<tr>
<td>PMA8-dPS2</td>
<td>6.6</td>
<td>3.2</td>
<td>76</td>
<td>29</td>
<td>8</td>
<td>2</td>
<td>10.5</td>
</tr>
</tbody>
</table>

$^a$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 (d) values are from NR.
Table 3.3. Physical properties of samples for dPS-$b$-PMA series.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_n,dPS^a$ (kg/mol)</th>
<th>$M_n,PMA^a$ (kg/mol)</th>
<th>$N_{dPS}$</th>
<th>$N_{PMA}$</th>
<th>$d_{dPS}$ (nm)$^b$</th>
<th>$d_{PMA}$ (nm)$^b$</th>
<th>$\chi N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPS5-PMA2</td>
<td>5.1</td>
<td>3.9</td>
<td>49</td>
<td>46</td>
<td>5</td>
<td>2</td>
<td>9.5</td>
</tr>
<tr>
<td>dPS14-PMA3</td>
<td>14.5</td>
<td>5.7</td>
<td>139</td>
<td>66</td>
<td>14</td>
<td>3</td>
<td>20.5</td>
</tr>
<tr>
<td>dPS15-PMA4</td>
<td>14.5</td>
<td>8.6</td>
<td>139</td>
<td>100</td>
<td>15</td>
<td>4</td>
<td>23.9</td>
</tr>
<tr>
<td>dPS15-PMA6</td>
<td>19.6</td>
<td>8.2</td>
<td>188</td>
<td>95</td>
<td>15</td>
<td>6</td>
<td>28.3</td>
</tr>
<tr>
<td>dPS11-PMA8</td>
<td>11.7</td>
<td>11.1</td>
<td>104</td>
<td>130</td>
<td>11</td>
<td>8</td>
<td>23.4</td>
</tr>
<tr>
<td>dPS14-PMA9</td>
<td>19.9</td>
<td>12.8</td>
<td>191</td>
<td>152</td>
<td>14</td>
<td>9</td>
<td>34.3</td>
</tr>
</tbody>
</table>

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

$^b$Thickness (d) values are from NR for the first two samples. The rest of the thickness values are from ellipsometry measurement.

$^c$Grafting density ($\sigma$) calculated using the following equation: $\sigma = \frac{N_A \rho d}{M_n}$. $M_n$ is the number average molecular weight, $N_A$ is the Avagadro’s number and $\rho$ is the bulk mass density for the material.
Table 3.4. Calculated\textsuperscript{a} and experimentally measured solubility parameters

<table>
<thead>
<tr>
<th>Monomer</th>
<th>Calc. $\delta$ (J/cm$^3^{1/2}$)</th>
<th>Exp. $\delta$ (J/cm$^3^{1/2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>methyl acrylate</td>
<td>19.9</td>
<td>19.9-21.3</td>
</tr>
<tr>
<td>styrene</td>
<td>19.1</td>
<td>17.4-19.0</td>
</tr>
<tr>
<td>methyl methacrylate</td>
<td>19.0</td>
<td>18.8-26.2</td>
</tr>
<tr>
<td>Isoprene</td>
<td>17.4</td>
<td>16.2-20.5</td>
</tr>
</tbody>
</table>

\textsuperscript{a}The method of Hoftyzer and van Krevelen is used to calculate the solubility parameter values. Solubility parameter values are taken from the published work of van Krevelen.\textsuperscript{88}
Table 3.5. The comparison of theoretical and experimental interface widths. $a_I$ is the experimental interface width obtained from neutron reflectivity measurements, $a_\infty$ is the theoretical interface width calculated using the theory of immiscible polymer blends, $a_{\text{fluc}}$ is the contribution of the interfacial fluctuations to the interface width, $a_H$ is the theoretical interface width calculated using the theory of diblock copolymers in the narrow interphase approximation and $a_{H,M}$ is the interface width calculated the diblock copolymer theory which includes the effect of finite molecular weight.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$a_{I,\text{exp1}}$ (nm)</th>
<th>$a_{I,\text{exp2}}$</th>
<th>$a_\infty$ (nm)</th>
<th>$(a_\infty^2 + a_{\text{fluc}}^2)^{1/2}$ (nm)</th>
<th>$a_H$ (nm)</th>
<th>$a_{H,M}$ (nm)</th>
<th>$(a_{H,M}^2 + a_{\text{fluc}}^2)^{1/2}$ (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMA2-dPS4</td>
<td>2.2±0.4</td>
<td>-</td>
<td>1.8</td>
<td>2.4</td>
<td>1.4</td>
<td>2.1</td>
<td>2.7</td>
</tr>
<tr>
<td>PMA6-dPS5</td>
<td>2.8±0.8</td>
<td>-</td>
<td>1.8</td>
<td>2.6</td>
<td>1.4</td>
<td>1.8</td>
<td>2.6</td>
</tr>
<tr>
<td>PMA7-dPS2</td>
<td>3.3±1</td>
<td>-</td>
<td>1.8</td>
<td>2.6</td>
<td>1.4</td>
<td>2.0</td>
<td>2.7</td>
</tr>
<tr>
<td>PMA8-dPS2</td>
<td>2.0±0.5</td>
<td>-</td>
<td>1.8</td>
<td>2.6</td>
<td>1.4</td>
<td>1.9</td>
<td>2.7</td>
</tr>
<tr>
<td>dPS5-PMA2</td>
<td>4.2±0.5</td>
<td>-</td>
<td>1.8</td>
<td>2.5</td>
<td>1.4</td>
<td>1.9</td>
<td>2.5</td>
</tr>
<tr>
<td>dPS14-PMA3</td>
<td>Na</td>
<td>-</td>
<td>1.8</td>
<td>2.7</td>
<td>1.4</td>
<td>1.7</td>
<td>2.7</td>
</tr>
<tr>
<td>dPS15-PMA4</td>
<td>Na</td>
<td>2.3</td>
<td>1.8</td>
<td>2.8</td>
<td>1.4</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>dPS15-PMA6</td>
<td>Na</td>
<td>1.0</td>
<td>1.8</td>
<td>2.8</td>
<td>1.4</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>dPS11-PMA8</td>
<td>4.9±1.4</td>
<td>5.4±2.5</td>
<td>1.8</td>
<td>2.8</td>
<td>1.4</td>
<td>1.6</td>
<td>2.7</td>
</tr>
<tr>
<td>dPS14-PMA9</td>
<td>5.5±2.8</td>
<td>4±0.8</td>
<td>1.8</td>
<td>2.8</td>
<td>1.4</td>
<td>1.6</td>
<td>2.7</td>
</tr>
</tbody>
</table>

*For the samples fitted by three layer model there are two polymer/polymer interfaces. $a_{I,\text{exp1}}$ stands for the interface between the bottom and middle polymer layer and $a_{I,\text{exp2}}$ stands for the interface between middle and top polymer layers.
Scheme 3.1. Synthesis scheme for dPS-\textit{b}-PMA DCB.

1\textsuperscript{st} step

\begin{align*}
\text{Cl}_3\text{Si-(CH}_2\text{)\textsubscript{11}O-C-C-Br} & \rightarrow \text{O-Si-(CH}_2\text{)\textsubscript{11}O-C-C-Br} \\
\end{align*}

Styrene, Anisole, CuBr/PMDETA, E2Br-iB, 100 °C

2\textsuperscript{nd} step

\begin{align*}
\text{O-Si-(CH}_2\text{)\textsubscript{11}O-C-C-Br} & \rightarrow \text{O-Si-(CH}_2\text{)\textsubscript{11}O-C-C-Br} \\
\end{align*}

3\textsuperscript{rd} step

\begin{align*}
\text{Methyl acrylate, Anisole, CuBR/PMDETA} & \rightarrow \text{O-Si-(CH}_2\text{)\textsubscript{11}O-C-C-Br} \\
\end{align*}

E2Br-iB, 90 °C
Figure 3.1. Idealized schematic of an ideal diblock copolymer brush with a very sharp interface between the two lamellar domains, each rich in a particular block.
Figure 3.2. ATR-FTIR spectra of (a) bromoisobutyrate initiator, (b) homopolymer dPS14 brush, and (c) diblock copolymer brush of dPS14-PMA3.
Figure 3.3. 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 series of PMA-\textit{b}-dPS brushes. Adjacent curves have been shifted vertically by two orders of magnitude for clarity.
Figure 3.4. The scattering length density as a function of depth for the PMA6-b-dPS5 sample. The text markings on the plot 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= 6.48x10^-6 Å^-2) and the lower bold line is that for bulk, pure PMA (b/V=1.26x10^-6 Å^-2).
Figure 3.5. GISAXS data for PMA8-dPS2 (a) and of a PMA14-PS20 (b) diblock copolymer brushes. Intensity is plotted as a function of $q_z$ and $q_y$ in false color.
Figure 3.6. The compositions of dPS (open circles) and PMA (filled circles), expressed as volume fractions, as a function of depth, in the region of the internal interface, for PMA6-b-dPS5 sample. The curves were derived from the SLD plot of Figure 3.4. A depth of zero corresponds to the beginning of the SiOₓ layer.
Figure 3.7. The neutron specular reflectivity (open symbols) and best fit model curves as a function of wavevector in the direction normal to the surface, $q_z$, for the two dPS-$b$-PMA brushes indicated, fit using a two-layer lamellar model. The lower curve has been shifted vertically by an order of magnitude for clarity. The inset shows the calculated SLD profile for dPS5-PMA2 as an example. The upper bold line represents the calculated SLD value expected for bulk, pure dPS and the lower bold line is that for bulk, pure PMA.
Figure 3.8. 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.
Figure 3.9. The SLD as a function of depth for the dPS14-PMA9 sample which has been fit using a three layer model. The bottom layer is 10 nm thick, the middle layer is 7 nm thick and the top layer is 5 nm thick. The upper bold line represents the calculated SLD value expected for bulk, pure dPS and the lower bold line is that for bulk, pure PMA.
Figure 3.10. Segment density of PMA (plusses) and dPS (crosses) as a function of depth for the PMA6-dPS5 brush calculated using SCF theory. Since not every PMA block reinitiates, the segment density of PMA from grafted homopolymer (stars) is shown as well. Grafting density for the diblock was taken to be 0.8 and that for the homopolymer 0.1.
Figure 3.11. Segment density of dPS (red plusses), PMA (green crosses) and dPS homopolymer (blue stars) as a function of depth for the dPS14-PMA9 brush calculated using SCF theory. Grafting density of the diblock was taken to be 0.5 chains/nm$^2$ and that for the homopolymer 0.1 chains/nm$^2$.

Figure 3.12. Cartoons of the structures of the “as-deposited” state of a DCB based on the Neutron reflectivity measurements.
CHAPTER IV

IN-PLANE ORDERING IN DIBLOCK COPOLYMER BRUSHES: A GISAXS STUDY

4.1 Introduction

The internal structure of DCBs in the direction normal to the surface has been investigated using NR, but this information alone is not sufficient to obtain the detailed internal structure of the diblock brushes. To resolve the internal structure of DCBs in detail, the structure in the plane of the sample (in \(x\) and \(y\)-directions) should be investigated as well as the structure normal to the plane of the sample. The presence of in-plane ordering with increasing value of \(\chi_N\) is shown in Chapter 3 for “as-deposited” dPS-\(b\)-PMA brushes. There is no theoretical or experimental work that predicts the presence of any kind of in-plane ordering in strongly stretched, “as-deposited” DCBs or DCBs that are heated above the \(T_{g,bulk}\) of constituent blocks.

Theoretical work has been reported for the internal structure of DCBs that are in contact with a solvent good for both polymer blocks,\(^58\) or a solvent selectively good for one of the polymer blocks.\(^55-57\) 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 using both scaling arguments and 2D SCF lattice calculations,\(^55,56\) and Monte Carlo simulations.\(^57\) The authors have suggested that the structures that emerge from 2D SCF calculations should have cylindrical geometry.\(^55,56\)
Zhao et al.\textsuperscript{45} showed that a regular nanopattern on the surface of the sample can be formed after switching the PS-\textit{b}-PMMA DCB by varying the composition of a solvent mixture from that of pure dichloromethane to that of pure cyclohexane slowly. The possibility of forming nanoscale patterns raises enormous interest to study the switching ability of diblock brushes.\textsuperscript{42,45-49,51,52,54} Zhao et al.\textsuperscript{45-47} tried to explain the formation of these nanostructures with shielding of solvophobic PMMA chains by swollen PS chains as suggested by Zhulina et al.\textsuperscript{55,56} Zhulina and co-workers\textsuperscript{55,56} studied the equilibrium structure of tethered DCBs, which have low grafting densities and compatible polymer blocks ($\chi_{AB} \approx 0$), in a selective solvent. Agreement between theoretical and experimental work suggests that the grafting densities of PS-\textit{b}-PMMA brushes studied by Zhao et al.\textsuperscript{45} may be low. In Zhao’s work,\textsuperscript{45} a PS layer was grown from the surface by living cationic polymerization. The terminal secondary benzyl chloride groups were used in the ATRP of methyl methacrylate (MMA) using CuBr/PMDETA complex. They did not evaluate the blocking efficiency. Under homogenous conditions, the blocking efficiency should be very low because benzyl halides are poor initiators for ATRP of MMA, especially without the halogen exchange.\textsuperscript{104}

None of the earlier experimental studies\textsuperscript{42,45-49,51,52,54} on the switching behavior of DCBs can solve the mechanism of surface rearrangement, since the techniques (contact angle measurements, AFM and XPS) they have used, are not sensitive to the internal structure both in the plane and normal to the plane of the DCBs. Additionally, there is no theoretical study that considers the equilibrium structure of strongly stretched DCB with incompatible polymer blocks in a selective solvent. In this chapter, the in-plane structures
of “as-deposited”, presumably molten, and switched DCBs are investigated using GISAXS.

GISAXS is a very powerful technique to investigate the structure of buried interfaces as well as the surface structure in the plane of the sample. GISAXS combines the interface sensitivity of reflectivity geometry with the sensitivity of small angle diffuse scattering to colloidal scale structures. It has recently become the major characterization technique for the investigation of internal structure of block copolymer thin films, porous thin films, and dewetted thin polymer films. GISAXS measurements provide information on nonlamellar structure internal to the brush, and particularly lateral correlations in the plane of the brush.

4.2 Experimental

4.2.1 Materials

Same materials that were described in section 3.2.1 were used in this study. Additionally, \( n \)-butyl acrylate (\( n \)-BA, Aldrich 99%) was passed through a column of activated basic alumina and degassed with high purity nitrogen for 1 h prior to use to synthesize diblock brushes with poly (\( n \)-butyl acrylate) (P\( n \)BA) blocks. Anhydrous acetone (Aldrich) was used as received.

4.2.2 Substrate Preparation

ATR crystals and silicon wafers (38 mm x 16 mm x 0.5 mm) were cleaned by treatment with a freshly prepared “piranha” solution (70/30, v/v, concentrated...
H$_2$SO$_4$/30% aqueous H$_2$O$_2$) at 90-100 °C for 2 h and were then rinsed with distilled water and dried with high purity nitrogen.

4.2.3 General Procedure for Deposition of Surface Bound Initiator

A freshly cleaned silicon wafer and ATR crystal were placed into a dried round-bottom flask. The flask was sealed using a septum and flushed with high purity nitrogen for 30 min. Dry toluene (15 mL) and a 25 vol. % solution of the trichlorosilane initiator in toluene (0.3 mL) were added to the flask via syringe and the flask was heated at 60 °C for 4 h under an atmosphere of nitrogen. The silicon wafer and ATR crystal were then removed, sequentially washed with toluene, ethanol and methylene chloride, and then dried in a stream of compressed air.

4.2.4 Procedure for Surface ATRP from a Flat Silicon Substrate

An initiator modified ATR crystal and silicon wafer were placed in a 100 ml Schlenk flask and sealed with a rubber septum. The flask was degassed and back-filled with nitrogen three times and left under a nitrogen atmosphere. CuBr, anisole and monomer were added to a separate 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 were applied to the flask and it was left under a nitrogen atmosphere. PMDETA was added to the mixture via syringe and the solution stirred at reaction temperature until it became homogeneous (~ 5 min). The solution was then transferred to the flask containing ATR crystal and silicon wafer via cannula, followed by the addition of free initiator (E2Br-iB). The polymerization proceeded at 90-100 °C for a
period of time depending on the thickness targeted, after which the ATR crystal and silicon wafer were removed. To remove untethered polymer chains, the ATR crystal and silicon wafer were placed in a Soxhlet extractor and extracted with tetrahydrofuran (THF) for 24 h followed by sonication in THF for 30 min. The final concentrations were as follows: \([S]_0 = 3.9 \text{ M}, [\text{anisole}]_0 = 5 \text{ M}, [\text{PMDETA}]_0 = 25 \text{ mM}, [\text{CuBr}]_0 = 12 \text{ mM} \quad \text{and} \quad [\text{Br-iB}]_0 = 5 \text{ mM}; [\text{MA}]_0 = 3.7 \text{ M}, [\text{anisole}]_0 = 6.1 \text{ M}, [\text{PMDETA}]_0 = 30 \text{ mM}, [\text{CuBr}]_0 = 15 \text{ mM} \quad \text{and} \quad [\text{Br-iB}]_0 = 15 \text{ mM}; \quad \text{or} \quad [\text{nBA}]_0 = 2.3 \text{ M}, [\text{anisole}]_0 = 6.1 \text{ M}, [\text{PMDETA}]_0 = 25 \text{ mM}, [\text{CuBr}]_0 = 12 \text{ mM} \quad \text{and} \quad [\text{Br-iB}]_0 = 10 \text{ mM}.

4.2.5 Block Copolymerizations

Preparation of diblock copolymer brushes was conducted in a manner similar to that for homopolymer brushes. The order of the blocks in the diblock brush was determined by the order of polymerization from the surface. For example, the PMA-\text{b-}\text{PnBA} brush was produced by first polymerizing the PMA block using methyl acrylate and then polymerizing the PnBA block using \text{n-butyl acrylate}. After each polymerization, the ATR crystal and silicon wafer were cleaned and extracted to remove any untethered polymer before proceeding to the next polymerization. Annealing of diblock brushes was performed at 180 °C for 12 hours in a high vacuum oven (2x10^{-6} \text{ torr}) and then samples were rapidly (~ 40 °C/min) quenched to room temperature.

4.2.6 Solvent Treatment of Diblock Copolymer Brushes

DCB surfaces were rearranged with different solvents to investigate the internal structure of switched samples. Samples were exposed to a solvent, which is good or theta
solvent for the polymer block synthesized next to the substrate and a poor solvent for the polymer block synthesized second. Various selective solvents were used for surface rearrangement of diblock copolymer brushes of various molecular compositions. Cyclohexane was used as a selective solvent to rearrange the surfaces of PS-\(b\)-PMA and PS-\(b\)-PnBA diblock brushes. Samples were exposed to cyclohexane at 60 °C for 150 min. Surfaces of PMA-\(b\)-PS and PnBA-\(b\)-PS diblock brushes were treated with acetone at 45 °C for 150 min. PMA-\(b\)-PnBA brush surfaces were rearranged by treating the brush with ethyl acetate at 60 °C for 150 min.

4.2.7 Characterization Methods

FTIR-ATR, contact angle and ellipsometry measurements were performed as described in section 3.2.6. In ellipsometry measurements, for the layer thickness calculations the refractive index of PnBA was taken as 1.466. Atomic force microscopy measurements were performed in tapping mode using a Veeco Dimension 3100 in a clean room with a silicon tip that has a spring constant of 40 N/m and resonant frequency of 170 kHz.

Brush internal structure was characterized using grazing incidence small angle X-ray scattering (GISAXS) in the plane of the sample. In GISAXS measurements, scattering intensities are collected at a fixed glancing incident angle, \(\alpha_i\), for a range of both \(q_z\) and \(q_y\) corresponding to ranges of exit angles \(\alpha_f\) and \(2\theta_f\) using a 2-dimensional detector as shown in Figure 4.1. \(\alpha_f\) is the exit angle with respect to the film surface and \(2\theta_f\) is the exit angle with respect to the plane of incidence. Such measurements provide information on the structure within the brush, particularly on lateral correlations in the
plane of the brush, which cannot be precisely described with a one-dimensional scattering length density profile in the $z$ direction. GISAXS experiments were carried out at the 8-ID-E beamline at the Advanced Photon Source using a monochromatic X-ray beam with a wavelength of 0.1675 nm. 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. The scattered intensity was recorded using a two-dimensional image plate detector with 150 μm pixel size and 1200×1200 pixel array or a MAR CCD with 78 μm pixel size and 2048×2048 pixel array.

4.3 Results and Discussion

Using NR, the internal structure of diblock copolymer brushes was found to vary with tethering sequence and the magnitude of $\chi N$. When the $\chi N$ value is smaller than 11, the diblock brush has a lamellar morphology for the values of volume fraction of one block varying from 0.3 to 0.7. As the $\chi N$ value gets larger, the diblock copolymer brushes adopt a lamellar or non-lamellar morphology depending on the volume fraction of one block and incompatibility between the blocks. Symmetric and asymmetric diblock brushes of various blocks and with varying thicknesses were synthesized by ATRP. Molecular weights, chain lengths (N), the volume fraction of one polymer block and the $\chi N$ values of the investigated brushes are given in Table 4.1. Figure 4.2 shows a 2D GISAXS image for an asymmetric, “as-deposited” PMA14-PS20 DCB at an incidence angle of 0.19°. The sample was measured at room temperature, a temperature at which untethered PS chains of molecular weight greater than ca. 1.6$k^{118}$ form a glass and
untethered PMA chains are liquid (T_{g,bulk} = 10 °C). The GISAXS data contain correlation peaks at 2\theta_f = \pm 0.86° (q_y = \pm 0.056 Å^{-1}) indicating that the structure within the diblock brush is not laterally uniform in the plane of the sample, i.e. there is some sort of in-plane ordering. The spacing of the in-plane ordering, \(d_{in}\), is calculated as 11.2 nm from the following equation:

\[
d_{in} = \frac{2\pi}{q_y}
\]  \tag{4.1}

where \(q_y\) is the value of in-plane wavevector at the maximum of the correlation peak. When these data were collected they represented the first time in-plane ordering had been observed for an as-deposited DCB.

The lateral correlation lengths of the in-plane structures were determined from the widths of the peaks, in the \(q_y\) direction, using the Debye-Scherrer relation

\[
\xi = \frac{2\pi}{\Delta q_y}
\]  \tag{4.2}

where \(\Delta q_y\) corresponds to the full width of the correlation peak at half maximum. Values of \(\xi\) calculated this way are compared to the spacing of the in-plane ordering in Table 4.2. Lateral correlation length, \(\xi\), varies from 17 to 20 nm for all the samples shown in Table 4.2. The position of the maximum of the correlation peak gives the domain-domain distance of the in-plane structure and this spacing varies from 10 to 14 nm. The fact that the values of \(\xi\) and domain size lie close to one another implies that the ordering is limited to correlation between nearest neighbors; there is no long-range ordering.

Diblock brushes in the “as-deposited” state are not necessarily in thermodynamic equilibrium since the structure vitrifies during the solvent removal if at least one block is
glassy at room temperature. Before the solvent is removed the swollen brush has some internal morphology. Due to the fact that the plasticized brush can equilibrate on time scales that may coincide with the time scale of the brush synthesis and workup, it is even possible that this morphology is an equilibrium one. 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 we do not know. In the case that the solvent is equally good for both blocks, the vitrified structure might closely resemble a shrunken version of the wet morphology. Equilibrium widths of interfaces between domains would be expected to be smaller after removal of solvent, but it is unlikely that in the short time available during the rapid solvent removal the segments of the two blocks could demix to sharpen the interface to its equilibrium dimension. Likewise, it is unlikely that microdomains 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. We expect that the collapse upon solvent removal has foremost altered microdomain sizes and microdomain spacings of the brush internal structure, not the symmetry of the structure (e.g. lamellar vs. cylinders in a matrix). Whether these structures are kinetically trapped or in thermodynamic equilibrium can be investigated by measuring the GISAXS patterns of diblock brushes at temperatures above the bulk T_g of both polymer blocks. Figure 4.3 shows the 2D GISAXS images at incidence angle of 0.19° for as-deposited PMA16-PS27 diblock brush at room temperature, after ~10 min. at 120 °C, after ~10 min. at 180 °C and after 12 h annealing at 180 °C. The sample was kept
in high vacuum (2x10^{-6} torr) at all times when heated above 80 °C. Measurements at elevated temperatures were performed after heating the sample to the target temperature in approximately 5 minutes and then staying at that temperature for at least 10 minutes to reach thermal equilibrium. There are correlation peaks in the GISAXS scattering pattern for the as-deposited diblock brush above T_g of both polymers, and the intensity of the peaks grows with time at high temperature, indicating that the equilibrium internal morphology at temperatures above the T_g’s of both blocks is, indeed, characterized by such lateral ordering. It seems likely then that the as-deposited” structure has the general character that the equilibrium structure at that temperature would have if the brush had sufficient mobility to reach equilibrium. Horizontal line scans from the GISAXS images in Figure 4.3 are taken at $\alpha_f = 0.17^\circ$ and plotted as a function of in-plane wavevector, $q_y$, in Figure 4.4. It is clear from these line scans that there are important changes in the character of in-plane ordering at temperatures above T_g of the polymer blocks. First of all, the intensity of the correlation peak for the diblock brush substantially increases as the measurement temperature increases. With annealing at 180 °C, the intensity of the brush increases to a value almost three times that of the as-deposited brush measured. This clearly shows that increasing the mobility of the polymer chains in the diblock brush allows the perfection of the in-plane ordering. Therefore, a diblock brush may have an in-plane ordering in its minimum free energy state, since enhanced mobility of polymer chains favors stronger in-plane ordering. The spacing of the in-plane ordering for as-deposited diblock brush increases from 12.9 nm to 13.8 nm as the temperature rises from room temperature to 180 °C and the lateral correlation length decreases simultaneously from 17.9 nm to 15.9 nm. After annealing, the spacing is still 13.8 nm, but the lateral
correlation length increases to 18.8 nm. Thus, annealing provides better ordered in-plane structures.

In-plane ordering is observed only for certain block combinations. GISAXS scattering patterns are compared for asymmetric diblock brushes of \(PnBA11-dPS29\) and \(dPS29-PMA11\) of the same thickness at incidence angle of 0.19° in Figure 4.5. The GISAXS scattering pattern for \(PnBA11-dPS29\) does not contain correlation peaks, whereas the pattern for \(dPS29-PMA11\) has correlation peaks at \(2\theta_f = \pm 0.6^\circ\) \((q_y = \pm 0.039 \text{ Å}^{-1})\). Asymmetric DCBs of \(PS-b-PMA\), \(PMA-b-PS\) and \(PMA-b-PnBA\) with large \(\chi_N\) have in-plane ordering, whereas DCBs of asymmetric \(PS-b-PnBA\) and \(PnBA-b-PS\) do not have any in-plane ordering. This shows the molecular composition of the diblock copolymer brushes is an important factor, which determines whether a DCB has an in-plane ordering or not. The most important difference between the diblock brushes that have in-plane ordering and the diblock brushes that do not have any lateral ordering is the interaction between the polymer blocks. The strength of the interaction between polymer blocks is characterized by the product of exchange interaction parameter, \(\chi_{AB}\), and chain length, \(N\), that determines if the untethered diblock copolymer microphase segregates in the bulk. The exchange interaction parameter, \(\chi_{AB}\), has not been measured experimentally for \(PS-b-PMA\), \(PS-b-PnBA\) and \(PMA-b-PnBA\). Equation (3.1) indicates that the value of \(\chi_{AB}\) is proportional to the square of the difference between the solubility parameters of A and B. As the difference between the solubility parameters of two polymer blocks increases, the blocks become more incompatible with each other and they will microphase segregate to minimize the energetically unfavorable contacts. Experimentally measured values of solubility parameters from van Krevelen\(^8\) for all the polymers
studied in this work are given in Table 4.3. For each polymer there is a range of experimental solubility parameter values. The average of these values is used in our estimations for the strength of interactions. The very small difference between the solubility parameters of styrene and \( n \)-butyl acrylate suggests that PS and \( \text{PnBA} \) are compatible polymer blocks. We propose that diblock copolymer brushes of PS-\( b \)-PnBA and PnBA-\( b \)-PS do not have in-plane ordering due to the very small interaction parameter between their polymer blocks.

Although increasing the value of \( \chi_{AB} \) favors microphase segregation, the value of \( \chi \) is not the only parameter that determines if a block copolymer microphase segregates. \( \chi \) represents the magnitude of enthalpic contributions and \( N \) reflects the magnitude of entropic contributions to the free energy of the system. Absence of in-plane liquid like structure in the PMA8-dPS2 brush (Figure 3.5) that has a \( \chi N \) value of 10.5 and the presence of in-plane ordering in the PMA14-PS20 diblock brush (\( \chi N = 34 \)) as shown in Figure 4.2, provides an example of the general observation that in-plane ordering is observed when the \( \chi N \) value of diblock brushes is large.

The experimental phase diagram is shown for PS-\( b \)-PMA and PMA-\( b \)-PS brushes in Figure 4.6. When the value of \( \chi \) or \( N \) is small enough, lamellar structure is observed for wide variety of block compositions. The lamellar ordering is observed due to the interface biasing fields. When \( \chi \) or \( N \) is larger, lamellar structure is expected to be favored only for symmetric blocks. The critical value of \( \chi N \) is roughly 23. Lamellar structure is observed for values of \( \chi N < 23 \) and in-plane ordering is observed for values of \( \chi N > 23 \). The experimental values of \( f_{PS} \) varied from 0.28 to 0.93. The border between
these structures resembles a line but additional data is required around the critical value of $\chi_N$, and for symmetric blocks with larger value of $\chi_N$ to extract the exact shape of the border.

The value of $\chi_N$ is as crucial for diblock copolymer brushes as for untethered block copolymers in bulk. As the blocks become longer and more incompatible with each other, microphase segregation that minimizes contact enthalpy is favored over mixing. The effect of the value of $\chi_N$ can be more clearly observed when the horizontal line scans are taken from the 2D GISAXS images and plotted for varying values of $\chi_N$. Figure 4.7 shows intensity as a function the in-plane wavevector, $q_y$, for three samples of dPS-$b$-PMA brushes which have $\chi_N$ values of 9.5, 23.4 and 45.2. The dPS5-PMA2 diblock brush that has a $\chi_N$ value of 9.5 does not have in-plane ordering as evidenced by the absence of correlation peaks. Brushes dPS11-PMA8 and dPS27-PMA11 with values of $\chi_N > 23$ have correlation peaks in the $q_y$ line scans and the intensity increases as the value of $\chi_N$ increases as shown in Figure 4.7. The increase in the intensity of the correlation peak with increasing $\chi_N$ is consistent with the contention that the boundaries of the in-plane structures become sharper as $\chi_N$ gets larger. Sharper interfaces give rise to stronger scattering.

For untethered diblock copolymers in bulk, the volume fraction of each component and the value of $\chi_N$ are both important in determining the minimum free energy of the system. Depending on the volume fraction, an untethered diblock copolymer can form different morphologies. As the volume fraction of one component increases from 0 to 0.5, in a canonical diblock system first spherical domains in a matrix,
then cylindrical domains in a matrix, then an ordered bicontinuous double diamond (OBDD) morphology and, finally, a lamellar structure is observed.\textsuperscript{119,120} When the volume fraction, $f$, of one block is 0.5, we may anticipate that the as-deposited symmetric diblock brush will tend to have lamellar morphology, i.e. the system has two layers lying parallel to the substrate and these layers are uniform in the plane of the sample. 2D GISAXS images are given for a symmetric ($f_{PS} = 0.49$) PMA10-PS9 and an asymmetric ($f_{PS} = 0.38$) dPS10-PMA9 diblock brushes in Figure 4.8. The symmetric brush does not have in-plane ordering, whereas the asymmetric brush has in-plane ordering with a spacing of 12.6 nm.

So far, we have seen that a DCB that has an asymmetric composition and a large value of $\chi N$ has in-plane ordering with a characteristic spacing on the order of 10-20 nm. It is of importance to elucidate what the physical origin of this spacing is and how it changes with molecular parameters. Asymmetric PS-$b$-PMA and PMA-$b$-PS diblock copolymer brushes were synthesized to determine the effect of block length on the spacing of the in-plane structures. Figure 4.9 illustrates how the peak for the lateral ordering for three diblock brushes varies as the thickness of PMA block is varied. It appears the spacing of the in-plane structure changes in a manner very closely tied to the thickness of the PMA block and it does not matter whether the PMA block is adjacent to the substrate or next to the air surface. The spacing of in-plane structure does not depend on the thickness of the PS block.

Whether the lateral ordering is intrinsic to the DCBs or can be due simply to the PMA block was readily checked by measuring GISAXS for a PMA homopolymer brush. The GISAXS pattern for a 16 nm thick PMA homopolymer brush in which the chains
have a molecular weight of 13k is shown in Figure 4.10. This PMA brush has a thickness and molecular weight similar to that of the PMA block in the diblock brush for which in-plane liquid-like structure is evidenced in Figure 4.2. The GISAXS pattern does not contain any correlation peak for the homopolymer PMA brush.

Hints as to the depth at which the in-plane structures lie in the brushes can be obtained by measuring GISAXS scattering patterns at various incident angles to verify that the in-plane structures lie at and around the polymer/polymer interface. The depth from which information is gathered about the sample varies with incident angle. For glancing incidence, the nominal penetration depth of the X-rays, $z_0$, may be taken as the depth at which the amplitude of the electric field falls to $1/e$ of its value at the surface. The value of $z_0$ is given by

$$z_0 = \frac{\lambda}{4\pi} \left[ \sqrt{\left(\alpha_i^2 - \alpha_c^2\right)^2 + 4\beta^2 + \alpha_c^2 - \alpha_i^2} \right]^{-1/2}$$

(4.3)

where $\alpha_i$ is the incidence angle of the incoming beam, $\alpha_c$ is the critical angle of the material and $\beta$ is the imaginary part of the refractive index. Measurements were made at incident angles of 0.14°, 0.16°, 0.19°, and 0.21°, corresponding to nominal penetration depths of 7, 10, 1850, and 2750 nm, respectively. These incident angles bracket the critical angles of PS and PMA, which are 0.16° and 0.19°, respectively. Figure 4.11 illustrates the portion of the structure through the brush that is probed for each incidence angle using the scattering length density profile obtained from NR for dPS14-PMA9. The correlation peaks seen for the four different penetration depths are shown in Figure 4.12.
in the form of plots of intensity as a function of $q_y$ (in-plane) at constant $q_z$. These are obtained by making horizontal cuts through the 2-D data. From the NR measurements we expect the in-plane structures to lie in the middle of the brush, not at the air surface or at the interface with the substrate. At an incidence angle of 0.14°, the scattering signal comes primarily from the vacuum/polymer surface and the top polymer layer. For this angle the correlation peaks are seen in the data, but are weak. As the angle increases to 0.16°, the x-rays penetrate more into the middle and bottom layers, the scattering volume increases by a factor of 0.4 and the intensity of the peaks increases by a factor of 0.4 suggesting that the intensity is stronger because there is more material to scatter in the enlarged scattering volume. The intensity increase is not due to new structure that is scattering in the volume that has been added by going to a higher incident angle. At incident angle of 0.19°, the beam is already penetrating all the way through the film so the intensity is almost same for the incident angles of 0.19° and 0.21°. This basic quantitative analysis suggests that more detailed data analysis is required to locate the position of the in-plane structures within the brush.

Whether the surface of a diblock copolymer brush rearranges upon exposure to a selective solvent depends on the chain length of each block, interaction parameter between polymer blocks, interaction parameter of selective solvent with each block, grafting density and the molecular weights of each block.\textsuperscript{42,45-49,51,55,56} It has been shown for certain chain length combinations, the diblock brushes rearrange more readily than for others.\textsuperscript{55,56} The 2D GISAXS scattering pattern at incidence angle of 0.19° for a PMA14-PS20 diblock brush after treatment with acetone is shown in Figure 4.13. The correlation peaks persist even after switching and the spacing and correlation length associated with
those also remain unchanged. This indicates that in-plane ordering is highly stable. The internal structure of the DCB layer is totally unaffected after switching. However, a new type of scattering feature, Bragg rods, appear. These contain intensity distributed over a broad range of $q_z$ and indicate the existence of a 2-D structure of some sort. The fact that the Bragg rods appear without the internal morphology changing suggests that the surface is primarily responsible for the Bragg rods. The intensity of the Bragg rod increases as the incident angle decreases suggests that this structure formed through rearrangement process must be at the air surface, not in the interior of the brush. The Bragg rods appear at values of $2\theta_f = \pm 0.3^\circ$ ($q_y = \pm 0.021$ Å$^{-1}$), corresponding to a spacing of about 30 nm, which is larger than the spacing associated with the correlation peaks (12 nm). The Bragg rods appear upon switching only for the brushes of asymmetric composition. The spacing of the Bragg rods is on the order of the total thickness of the brush. The Bragg rods are observed for PS-$b$-PMA and PMA-$b$-PS brushes, but not for PS-$b$-P$n$BA brushes. The absence of the Bragg rods in the GISAXS data of PS-$b$-P$n$BA brushes indicates that the surface rearrangement is not successful for the diblock brushes containing PS and P$n$BA blocks. This shows that the value of the interaction parameter between the two polymer blocks is as crucial in determining the brush morphology as is the interaction parameter of each block with the selective solvent. PS-$b$-PMA has a greater tendency to microphase segregate into domains than does the PS-$b$-P$n$BA.

Change in the surface morphology may be probed in a complementary fashion using AFM. An intermittent-contact mode AFM height images of the PMA14-PS20 brush in as-deposited state and after switched in acetone is shown in Figure 4.14. The AFM height of the brush shows a distinct surface morphology in the switched state. The
2D isotropic power spectral density spectrum obtained from this height image is shown in Figure 4.15. The PSD contains a shoulder associated with a spacing of 30 nm, which is consistent with the spacing evident in the Bragg rods (Figure 4.13).

The structure formed during the selective solvent treatment is frozen when the diblock brush is taken out of the solvent. Thus, the structure of the brush is not in equilibrium after switching. If the brush is treated with a good solvent for both polymer blocks, the contact angle of the surface reverts to that of the as-deposited brush and the Bragg rods disappear from the GISAXS pattern. These observations are consistent with the contention that the surface rearranges to the as-deposited state after exposure to solvent that is good for both blocks. Various groups have now demonstrated with different experiments that this surface rearrangement process is reversible, but it is still not clear how the surface switches with a selective solvent or how the surface rearranges back to the original state. To resolve the surface rearrangement mechanism clearly one needs to follow the rearrangement using a technique that gives detailed information on the surface and internal structure in-situ. Unfortunately, it is not possible to perform in-situ switching during the GISAXS measurement due to experimental problems caused by the presence of the liquid. Attempts were made to switch diblock brush surfaces using solvent vapor, but these were unsuccessful. This suggests that the solvent that partitions into the brush from a vapor is not enough to plasticize the brush sufficiently for rearrangement, or that the density of unfavorable polymer-solvent interactions is not high enough to drive the rearrangement next to vapor. While it has not been possible to follow with in situ GISAXS, the structure rearrangement next to solvent liquid, a rearrangement driven by elevated temperature is readily studied. If a PMA-b-PS brush is switched in
acetone, it is expected that the PS chains will aggregate to reduce interactions with acetone and the PMA chains will form a shell around the PS chains.\textsuperscript{55,56} If this brush is heated and polymer chains gain enough mobility, the PS blocks should cover the air surface due to their lower surface tension. After the diblock brush has been switched and the Bragg rods have been observed in the GISAXS data, the temperature is increased. In Figure 4.16 is a series of GISAXS patterns collected from sample PMA16-PS27 at various temperatures. The spacing obtained from the correlation peak is 13.8 nm and the spacing obtained from the Bragg rod is 29.1 nm at room temperature. Upon heating, the value $q_y^*$ at which the correlation peaks are observed does not change, while the position of the Bragg rod shifts to a smaller value of $q_y$ (Figure 4.14). To probe the structure at 41 °C, the sample temperature was raised to 41 °C and then the sample allowed to equilibrate for 10 minutes at that temperature. The same amount of time was allowed for equilibration at each subsequent temperature. The spacing obtained from the Bragg rod at 41 °C is 31 nm. After heating to 65 °C, the intensity of the Bragg rod decreases and the Bragg rod moves to smaller $q_y$ values. The spacing obtained from the Bragg rod at 65 °C is 40 nm. At 70 °C the spacing of the structure becomes 42 nm and the intensity of the Bragg rod decreases further. As the temperature increases, the spacing gets larger and the intensity of the Bragg rod decreases. The Bragg rod has disappeared completely at 80 °C. We propose that in order for this structure to disappear, the PS chains must become mobile below the bulk $T_g$ for a PS homopolymer of the same molecular weight, which is $\sim 96$ °C.\textsuperscript{118} The fact that the structure is substantially impacted at temperatures far below the bulk $T_g$ of PS is consistent with our earlier observation\textsuperscript{51d} that the PS block of 17k
(T_g,bulk = 90 °C)\textsuperscript{118} in semi-fluorinated diblock brushes are sufficiently mobile to rearrange at around 65 °C, which is approximately 30 degrees below the bulk T_g of 30k PS.\textsuperscript{118}

Two possible explanations for the enhanced mobility of PS chains below the T_g,bulk are the presence of residual solvent in the brush or a depression of the glass transition temperature from its value in bulk. It is also possible both effects contribute at the same time. It is obvious that acetone may be trapped in the brush during the surface rearrangement. The sample was dried after switching only by blowing technical grade nitrogen on it for approximately 20 seconds. This treatment leaves residual solvent in the brush, though at least some of this is probably removed when the sample is heated under high vacuum, since the boiling point of acetone is 56 °C under atmospheric conditions and much lower than that under vacuum. Although the boiling point of acetone is lowered under high vacuum, if the PS block is glassy at this temperature, it is not possible to get rid of all the acetone in the brush. In order to remove all the acetone from the brush, the PS chains must have some mobility.

The question of what happens to the T_g in supported thin films is very provocative in polymer community. There are various reports of contradictory results. It has become clear recently that the T_g of PS decreases as the film thickness decreases.\textsuperscript{121} There is also an agreement on the elevation of T_g of a film when the polymer film has attractive interactions with the underlying substrate, for example as in the case of PMMA chains on a silicon surface.\textsuperscript{122} Unfortunately, the literature data for brushes of grafted polymer chains is still ambiguous. Tsukruk et al.\textsuperscript{123} argue 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, based on direct measurement of heat dissipation and the thermoelastic response using AFM.
Prucker et al.,\textsuperscript{124} using optical waveguide spectroscopy, find that the $T_g$'s of free-radically polymerized PMMA polymer brushes decrease as the brush thickness decreases from 200 nm to 3 nm. Molecular dynamics of grafted layers of PDMS by Kremer et al.\textsuperscript{125} suggest that a lowering of $T_g$ should be expected in brushes of thickness less than 40 nm. Data from two other papers in the literature suggest that the value of $T_g$ for grafted polymer chains is higher than that in the bulk. Nealey and DePablo\textsuperscript{126} reported that the $T_g$ of a 45 nm thick film of PS in which a small fraction of the chains were end-tethered to the substrate increases approximately 25 °C, as detected using ellipsometry and a localized thermal probe technique. They measured thin films that contain mostly untethered chains, and the grafting density of those that were tethered was much lower than that in the present work. Fukuda and co-workers\textsuperscript{127} have reported that dense PMMA brushes (thickness $>50$ nm) synthesized by ATRP have $T_g$ values approximately 8 °C higher than the bulk value. They also showed that 15-25 nm thick densely grafted PMMA brushes exhibit a value of $T_g$ roughly 20 °C above that of bulk samples of PMMA of the same molecular weight. A final aspect of the diblock copolymer brushes that may contribute to their mobility at temperatures below the $T_g$ of corresponding untethered homopolymer chains is the fact that the PS chains are attached to PMA chains. The low $T_g$ value of PMA may reduce the overall $T_g$ of the diblock copolymer film below the $T_g$ of PS in bulk. It remains to determine the $T_g$ of untethered PS-$b$-PMA diblock copolymers corresponding to the brushes. Despite the fact that we have been unable to ascertain the precise cause of the mobility, it is clear that the PS block in these brushes is mobile below the $T_{g,\text{bulk}}$ of untethered chains of corresponding molecular weight.
The in-situ measurement gives hints about the mechanism of the disappearance of the Bragg rods from the GISAXS data. After surface rearrangement an energetically unfavorable structure is formed in the close proximity to the air surface. Other studies have already shown that the air surface shows the characteristic contact angle of the polymer block that “likes” the rearrangement solvent. This suggests that after switching the air surface of the diblock brush is covered mostly by PMA chains even though the surface energy of PMA is higher than that of PS. In this non-equilibrium state, the brush still maintains the internal ordering formed during the synthesis. The structure at the air surface could be formed by the fuzzy spheres or cylinders of PS chains shielded by PMA chains. The exact shape and structure can only be estimated by detailed fitting of the 2D data, which will be the subject of future work. We can still get valuable qualitative information from the in-situ measurement. When the temperature gets higher and the PS chains become mobile, they begin to move and try to disrupt the energetically unfavorable ordering of the brush at the air surface. The spacing of the domains becomes larger and the ordering at the surface completely disappear around 80 ºC and the PS chains cover the air surface due to their lower surface energy. Coverage of the air surface by PS chains was confirmed by measuring the water contact angle. The advancing water contact angle of 96° is characteristic of PS.

4.4 Conclusion

In summary, the presence of in-plane ordering in diblock copolymer brushes “as-deposited”, heated above the bulk T_g’s of the constituent blocks, or in a switched state, has been shown using GISAXS. To our knowledge, there is no theory predicting an in-
plane ordering for densely tethered diblock copolymer brushes of highly incompatible blocks. This in-plane ordering implies that the strictly lamellar structure of the brushes favored by the biasing influence of the interfaces is disrupted with an increase in the value of $\chi_N$. The spacing of the in-plane ordering in “as-deposited” brushes is correlated with the thickness of the PMA layer.

After switching, a new 2D structure is formed at the air surface of the brush as suggested by the increase in the intensity of the Bragg rod with decreasing incident angle. Thus, the early mechanism suggested by Zhao$^{45}$ following the theoretical work of Balazs$^{55,56}$ may not be exactly apply to this case. To solve the mechanism, the 2D GISAXS data will have to be modeled quantitatively.
Table 4.1. Physical characteristics of brush samples that are measured using GISAXS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>$M_{n_f}$</th>
<th>$M_{n_s}$</th>
<th>$N_f$</th>
<th>$N_s$</th>
<th>$f_f$ (nm)</th>
<th>$\chi_N$</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPS5-PMA2</td>
<td>5.1</td>
<td>3.9</td>
<td>49</td>
<td>46</td>
<td>0.52</td>
<td>9.5</td>
</tr>
<tr>
<td>dPS10-PMA9</td>
<td>11.5</td>
<td>14.6</td>
<td>103</td>
<td>170</td>
<td>0.38</td>
<td>27.3</td>
</tr>
<tr>
<td>dPS11-PMA8</td>
<td>11.5</td>
<td>11.1</td>
<td>103</td>
<td>130</td>
<td>0.44</td>
<td>23.3</td>
</tr>
<tr>
<td>dPS14-PMA9</td>
<td>19.9</td>
<td>12.8</td>
<td>191</td>
<td>152</td>
<td>0.56</td>
<td>34.3</td>
</tr>
<tr>
<td>dPS29-PMA11</td>
<td>31.6</td>
<td>14.6</td>
<td>282</td>
<td>170</td>
<td>0.62</td>
<td>45.2</td>
</tr>
<tr>
<td>PMA8-dPS2</td>
<td>6.6</td>
<td>3.2</td>
<td>76</td>
<td>29</td>
<td>0.28</td>
<td>10.5</td>
</tr>
<tr>
<td>PMA10-PS9</td>
<td>8.7</td>
<td>10</td>
<td>101</td>
<td>96</td>
<td>0.51</td>
<td>19.7</td>
</tr>
<tr>
<td>PMA14-PS20</td>
<td>7.9</td>
<td>21.1</td>
<td>92</td>
<td>203</td>
<td>0.31</td>
<td>29.5</td>
</tr>
<tr>
<td>PMA16-PS27</td>
<td>10.6</td>
<td>28.4</td>
<td>123</td>
<td>273</td>
<td>0.31</td>
<td>39.6</td>
</tr>
<tr>
<td>PMA16</td>
<td>13</td>
<td>-</td>
<td>-</td>
<td>-</td>
<td>1</td>
<td>-</td>
</tr>
<tr>
<td>PnBA11-dPS29</td>
<td>12.9</td>
<td>61.6</td>
<td>100</td>
<td>594</td>
<td>0.15</td>
<td>69.4</td>
</tr>
</tbody>
</table>

The sample names incorporate integers indicating the thickness of the first layer polymerized and the increase in thickness of the whole film when the second block was polymerized. These were measured using ellipsometry.

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.

Subscript “f” is used for the first block and subscript “s” is used for the second block.
Table 4.2. Lateral correlation length and spacing values for some of the DCBs measured at incidence angle of 0.19° and at room temperature.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Spacing (nm)</th>
<th>Lateral Correlation Length (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>dPS15-PMA4</td>
<td>11±0.6</td>
<td>18±2</td>
</tr>
<tr>
<td>dPS15-PMA6</td>
<td>11±0.7</td>
<td>16±0.8</td>
</tr>
<tr>
<td>dPS14-PMA9</td>
<td>11.1±0.3</td>
<td>16.2±0.5</td>
</tr>
<tr>
<td>dPS11-PMA8</td>
<td>14±0.5</td>
<td>15.8±0.5</td>
</tr>
<tr>
<td>PS27-PMA11</td>
<td>13±0.2</td>
<td>28.8±0.3</td>
</tr>
<tr>
<td>dPS29-PMA11</td>
<td>16±0.4</td>
<td>22.9±0.6</td>
</tr>
<tr>
<td>PMA12-dPS20</td>
<td>11.6±0.6</td>
<td>NA</td>
</tr>
<tr>
<td>PMA12-PS28</td>
<td>15.1±0.7</td>
<td>NA</td>
</tr>
<tr>
<td>PMA14-PS20</td>
<td>11.2±0.4</td>
<td>18.1±0.3</td>
</tr>
<tr>
<td>PMA14-dPS23</td>
<td>13.1±0.2</td>
<td>16.7±0.5</td>
</tr>
<tr>
<td>PMA16-PS27</td>
<td>13±0.4</td>
<td>17.4±0.1</td>
</tr>
<tr>
<td>PMA18-PnBA15</td>
<td>20±0.6</td>
<td>24.3±0.5</td>
</tr>
</tbody>
</table>

*aSpacing is calculated using equation (4.1).  
*bLateral correlation length is calculated using Debye-Scherrer formula (Equation 4.2). The width of the peak is taken as full width at half maximum value.

Table 4.3. Experimentally measured solubility parameters.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Exp. $\delta$ (J/cm$^3$)$^{1/2}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polystyrene</td>
<td>17.4-19.0 (J/cm$^3$)$^{1/2}$</td>
</tr>
<tr>
<td>Poly(methyl acrylate)</td>
<td>19.9-21.3 (J/cm$^3$)$^{1/2}$</td>
</tr>
<tr>
<td>Poly(n-butyl acrylate)</td>
<td>18.0-18.6 (J/cm$^3$)$^{1/2}$</td>
</tr>
</tbody>
</table>

*aExperimental solubility parameter values are taken from the published work of van Krevelen.84
Figure 4.1. The schematics of GISAXS measurement. $\alpha_i$ is the incident angle and $\alpha_f$ 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.
Figure 4.2. GISAXS scattering pattern is given for an asymmetric diblock copolymer brush of PMA14-PS20. The incident angle is $\alpha_i=0.19^\circ$. 
Figure 4.3. 2D GISAXS data for PMA16-PS27 measured at (a) room temperature, (b) after 10 min. at 120 °C, (c) after 10 min. at 180 °C and (d) after 12 h annealing at 180 °C. The incidence angle is 0.19°.
Figure 4.4. Horizontal line scans taken from the 2D GISAXS images of PMA16-PS27 in Figure 4.3 are shown as intensity as a function of in-plane wavevector at room temperature (black spheres), after 10 min. at 120 °C (red squares), after 10 min. at 180 °C (blue diamonds) and after 12 h at 180 °C in high vacuum (green triangles).
Figure 4.5. 2D GISAXS scattering patterns are plotted as a function of exit angles for asymmetric DCBs of (a) PnBA11-dPS29 and (b) dPS29-PMA11 at the incidence angle of 0.19°.
Figure 4.6. Experimental phase diagram for PS-$b$-PMA and PMA-$b$-PS brushes. Bold line shows the critical value of $\chi_N$ below which lamellar structure is observed for DCBs and above which in-plane ordering is observed. The value of $\chi_{N_c}$ is approximately 23.
Figure 4.7. Intensity as a function of in-plane wave vector, $q_y$, for dPS5-PMA2 with $\chi_N$ value of 9.5 (blue circles), dPS11-PMA8 with $\chi_N$ value of 23.5 (red circles) and dPS29-PMA11 with $\chi_N$ value of 45.2 (black circles) is plotted at incidence angle of 0.19°.
Figure 4.8. GISAXS scattering patterns for a PMA10-PS9 which have $f_{PS} = 0.49$ (left) and a dPS10-PMA9 which have $f_{dPS} = 0.38$ (right) diblock copolymer brushes at incidence angle of 0.19°.
Figure 4.9. Intensity as a function of in-plane wave vector, \( q_y \), is given for dPS11-PMA8 (blue diamonds), PS27-PMA11 (pink squares) and PMA18-PnBA15 (green triangles). Peak intensity is not normalized for measurement time.
Figure 4.10. 2D GISAXS scattering pattern measured at room temperature is given for a 16 nm thick homopolymer PMA brush at incidence angle of 0.19°. Molecular weight of the brush is 13 k.
Figure 4.11. The penetration depth of the X-ray beam at various incident angles are shown in a SLD profile obtained from neutron reflectivity for dPS14-PMA9.
Figure 4.12. $q_y$ linecuts from the GISAXS patterns measured at incidence angles of 0.14° (black circles), 0.16° (red circles), 0.19° (blue circles) and 0.21° (green circles) for a DCB of dPS14-PMA9 which has a three layer structure. At each incidence angle, the measurement time is 20 seconds.
Figure 4.13. GISAXS scattering pattern is given for an asymmetric diblock copolymer brush of PMA16-PS27 after switching in acetone at 45 °C for 150 min. The incident angle is $\alpha_i = 0.19^\circ$. The peak spacing for the liquid-like ordering is 13.2 nm and the spacing corresponding to the Bragg rod position is 29.3 nm.
Figure 4.14. Intermittent-contact mode AFM height images for a PMA14-PS20 diblock brush in as-deposited state (left) and after switched in acetone (right).
Figure 4.15. 2D isotropic power spectral density curve calculated from AFM intermittent-contact mode measurements on a PMA14-PS20 brush after switched in acetone.
Figure 4.16. GISAXS data from a PMA16-PS27 diblock brush taken at various temperatures after it has been treated with acetone at 45 °C (a), 41 °C (b), 65 °C (c), 70 °C (d), 75 °C (e) and at 80 °C (f). The sample was equilibrated for 10 min. at each temperature before performing the measurement.
CHAPTER V
INTERFACE ROUGHNESS CORRELATIONS IN DIBLOCK COPOLYMER
BRUSHES DETERMINED BY SPECULAR AND OFF-SPECULAR X-RAY
SCATTERING

5.1 Introduction

The degree to which the surface of a film replicates an underlying surface is very
important for a variety of applications such as coatings and biomimetics. The correlation
of interface morphology, or roughness, between two interfaces of a film, has been studied
for films of metallic multilayers, small molecules, langmuir-blodgett films, polymers spun-cast onto a substrate, and for free-standing films. For small molecule liquid films, the film surface follows that of a smooth substrate for thicknesses less than about 6 nm because van der Waals interactions with the substrate suppress thermally stimulated capillary waves on the surface. The observation of partial suppression of thermally stimulated waves on the surface of thin polystyrene films as thick as 50 nm raised the question of whether this peculiarity of polymer films is due to long-range interactions with the substrate or whether it is intrinsic to the viscoelastic character of polymer films. Shin et al. showed that even in the absence of a supporting substrate, the interfaces of a polystyrene film may have correlated structures if the film is thinner than twice the radius of gyration of the chains ($R_g$), due to confinement effects. For polystyrene films that vitrify rapidly upon the loss of solvent during spin-casting,
correlation of the surface with the substrate may be observed in "as-spun" films of 22 - 116 nm in thickness (2R_g≥18 nm) but this correlation is an artifact of the hydrodynamic flow that occurs upon spinning, and is lost when the films are annealed at a temperature above the glass transition temperature. Spun cast films of symmetric block copolymers\textsuperscript{143} show such metastable interface correlation over a smaller range of thicknesses than do films of homopolymer, and this has been attributed to the presence of ordered lamellar domains. Replication of the substrate roughness over all length scales is not possible because the surface roughness occurs on a much smaller length scale than the length associated with the microphase separation. That is, the free block copolymer thin film cannot be considered as a simple liquid, at least in the lateral direction, and this hinders replication of the roughness.

Polymer brushes are versatile monomolecular coatings that have properties very different from those of films of untethered polymer chains. In a brush, one end of each chain is tethered to the substrate and the density of this tethering is sufficiently high that the chains must stretch away from the surface.\textsuperscript{1} It is of interest to know if this tethering mediates interactions with the substrate such that the probability that the surface of a brush is correlated with the underlying substrate is enhanced. Certainly in the theoretical extreme of a strongly stretched brush the thickness of the brush is less than 2R_g and one could expect correlation based on the findings of Wang et al.\textsuperscript{147} DCBs, shown schematically in Figure 5.1, are the focus here because their surfaces can rearrange in response to a change in the environment, particularly changes in an adjacent solvent.\textsuperscript{44,51c} However, the diblock brush also represents a special case of enhanced confinement, since by its nature a strongly segregated diblock brush must contain, next to the substrate, a
brush layer that closely approximates an Alexander brush. That is, one end of each chain is tethered at a definite location on the substrate and the “free” end of that block is required to be at the interface between the bottom and top domains. This enhanced degree of confinement could make interface correlation possible for thicknesses larger than in the case of films of small molecules. Here we show that, indeed, the interfaces of DCBs can be correlated over a wide range of thicknesses, that the existence of the correlation is not an artifact of deposition history, and that weakening the segregation at the internal interface and roughening the air surface by swelling with a nonselective good solvent weakens the interface correlation.

5.2 Experimental

5.2.1 Sample Preparation

Deuterated polystyrene-\textit{b}-poly(methyl acrylate) (dPS-\textit{b}-PMA) and PMA-\textit{b}-dPS DCBs have been synthesized by atom transfer radical polymerization (ATRP) using synthetic techniques described in section 3.2. Briefly, a self-assembled monolayer (SAM) of 11-(2-bromo-2-methyl)propionyloxy)undecyltrichlorosilane initiator was deposited atop a silicon substrate. Polymerization of the first monomer, A, was initiated from the SAM to form the first block by ATRP. Then the polymerization was continued with a different monomer, B, to create the second block. High grafting density (~0.6 chains/nm$^2$) brushes were synthesized both with dPS as the A block and with PMA as the A block. Implicit in the vast majority of reports of diblock copolymer brush synthesis has been the presumption that the brush, as deposited, has a lamellar morphology, as
depicted in Figure 5.1, with a layer rich in A lying next to the substrate and a layer rich in B adjacent to the surface.

5.2.2 Specular X-Ray Reflectivity

The structure of the film in the direction perpendicular to the surface was probed using X-ray reflectometry (XR). The data are typically plotted, as shown in Figure 5.2, as some function of the ratio of specularly reflected intensity to incident intensity, $R$, as a function of the magnitude of the scattering vector component perpendicular to the surface, $q_z$, as illustrated in Figure 5.1. From regressing the data with a model of the film structure one may estimate values of the film thickness, integrated microroughnesses at the air/film and substrate interfaces, and parameters of the interfaces inside the film, if they exist and if sufficient electron density contrast is available. All X-ray measurements were performed at beamline 1-BM at the Advanced Photon Source (APS). The spectrometer used a double-crystal monochromator to choose a wavelength of 1.24 Å. The samples were mounted in a helium-filled sample chamber on a goniometer providing translations in $x$, $y$, and $z$ and rotation in $\theta$, and the scattered intensity collected with a NaI scintillation detector. The reciprocal space resolution $\delta q_z$ was 0.001 Å$^{-1}$.

5.2.3 Off-Specular X-ray Scattering

Details of the structure in the plane of the interface were obtained by collecting scattering data for scans in which the scattering vector $q$ had a component in the plane of the interface (i.e. $q_x \neq 0$) as is shown Figure 5.1, in what is known as an “off-specular scattering” experiment. Longitudinal diffuse scattering is one of the four different ways
to do off-specular scattering measurement. The longitudinal scans were performed by increasing the incident and detector angles in a coordinated manner, but with the incident angle offset by 0.07° from the specular condition. This is far enough away from the specular peak, which has a half-width of 0.03° at its base, so that the measured scattering is all diffuse scattering. These longitudinal scans contain information on the interface lateral structure. Transverse scans were collected as step scans for four different values of $q_z$, 0.15, 0.2, 0.3, and 0.35 Å$^{-1}$. The values of $q_x$ used for the scans were optimized for each sample to provide approximately a logarithmic spacing of data points. The intensity is plotted as a function of $q_x$ on a log-log scale. The data can be analyzed qualitatively by comparing the shape of the scan with well-known transverse scan data from other systems such as untethered thin polymer films or quantitatively by fitting the data with an appropriate model. Samples were translated perpendicular to the beam direction after each scan to minimize radiation damage to the sample. These data were measured with a resolution of $\delta q_x \approx 1 \times 10^{-4}$ Å$^{-1}$ at $q_z = 0.30$ Å$^{-1}$. The unattenuated beam had a flux of about $2 \times 10^{13}$ (photons/s cm$^2$).

5.3 Results and Discussion

When the reflectivity and longitudinal scans measured in He for an "as-deposited" dPS15-PMA6 DCB are plotted as in Figure 5.2, oscillations are observed in both scans and these oscillations are in phase with one another. Both types of oscillation result from interference of x-ray beams reflected from the air/film and film/substrate interfaces. That they are in phase indicates that the interfaces are correlated, despite the fact that the thickness of the film is 4.2 times $R_g$ of the corresponding diblock chain in its unperturbed
melt state. This correlation is observed even though bulk PMA \( (T_g = 10^\circ C)^{95} \) is molten at the temperature of the measurement \( (25^\circ C) \). The overall thickness of the film is 21 nm, with the dPS block layer having a (nominal) thickness of 15 nm (as measured by ellipsometry before polymerization of the second block). Thus interface correlation is observed here for a film thickness more than three times that for which correlation is observed for small molecule liquid films.\(^{134} \) Van der Waals interactions alone are insufficient to give correlation over such a long distance. The amplitude of the oscillations in the longitudinal diffuse scattering does get weaker with increasing PS-\( b-\)
PMA total brush thickness, but persists even to an overall thickness of 54 nm. The interactions between the surface and the substrate responsible for the correlation do then decrease in strength with increasing distance from the substrate.

The internal brush structure is found to change with the tethering sequence of blocks brings the question about the presence of interface roughness correlation for PMA-\( b-\)PS brushes (PMA is next to substrate). Figure 5.3 shows the reflectivity and longitudinal scans plotted for a PMA11-PS21 brush in which PMA block has nominal thickness of 11 nm and PS block has nominal thickness of 21 nm. Oscillations in the longitudinal scan are in phase with the Kiessig fringes in the reflectivity indicating that these brushes have conformal roughness as the PS-\( b-\)PMA brushes have. However, the correlation is weaker than that seen for the dPS15-PMA6 brush that is shown in Figure 5.2, since the overall thickness of PMA11-PS21 is larger than dPS15-PMA6 brush.

To test if the correlation is due to a kinetically trapped structure, the specular reflectivity and longitudinal diffuse scattering of the dPS15-PMA6 diblock brush were measured again after the brushes were annealed at 140 \( ^\circ C \) for 4 hours in a high vacuum
oven (2x10^{-6} torr) and then rapidly quenched (~40 °C /min) to room temperature. The oscillations in the reflectivity and longitudinal scans were still in phase, as shown in Figure 5.4, meaning that the interfaces were still correlated. The amplitude of the oscillations in the longitudinal diffuse scan is an indication of the strength of the roughness correlation. Once the brush is annealed above the glass transition temperature of both polymers, the roughness correlation would become less pronounced if it is not the result of an equilibrium aspect of the brush structure. In the case of spun-cast films of untethered chains, the interface/interface correlation observed just after spin-casting is lost upon annealing. The amplitudes of the oscillations in the longitudinal scan in Figure 5.4 are not weaker than the amplitudes of the oscillations of the longitudinal scan in Figure 5.2, indicating that the strength of the interface roughness correlation does not change with annealing.

It is important to know the length scale of the roughness correlation in the vertical and horizontal directions. The spacing of the oscillations in the longitudinal scan already defines the vertical roughness correlation length, which is the total film thickness in this case. Unfortunately, there is not enough electron density contrast between PMA and PS to detect the roughness correlation at the polymer/polymer interface with X-rays. For this reason, off-specular neutron scattering measurements were done on the diblock brushes with the selective deuteration of PS block to enhance the neutron scattering length density contrast between the polymer domains. Enhancing the neutron contrast between polymer blocks did not help to resolve the issue of whether the roughness of the middle interface is correlated with that of another interface or not, since the off-specular neutron scattering intensity was not appreciably above the background scattering. The flux of the
neutron beam of $\sim 1.3 \times 10^4$ n/(s cm$^2$) is very weak compared to the x-ray flux of about $2 \times 10^{13}$ photons/(s cm$^2$).

It has long been known for metallic multilayers that low frequency roughness in the substrate is replicated by each layer deposited. In contrast, high frequency roughness generally is uncorrelated. Buschbaum$^{139,140,143}$ have demonstrated for spun-cast PS films that the conformality between the bottom and the top of the polymer layer seen for larger length scales vanishes at decreasing in-plane length scales. Therefore, there is a smallest replicated in-plane length scale ($R_c$) above which the roughness of the substrate is replicated by the polymer film and below which it is not replicated, as it is illustrated in Figure 5.5. $R_c$ can be estimated by successively measuring off-specular scans with increasing value of in-plane wavevector, $q_x$ or $q_y$. There are three methods to estimate $R_c$ using off-specular scans. The first one is to perform longitudinal diffuse scans using a pencil detector at increasing values of offset detector angle until no oscillation is observed in the longitudinal diffuse scan. The second one is to perform a detector scan in which the sample is fixed at one angle of incidence and the detector position is varied around the specular peak. Detector scans are measured at increasing values of $q_y$ to detect the value of $q_y$ at which the fringes disappear. Buschbaum et al.$^{139,140,143}$ used this approach for spun-cast PS films and the authors calculated the value of $R_c$ as approximately 100 nm. The last method is to conduct a GISAXS measurement using a 2D detector and then take linecuts in the vertical direction to imitate a longitudinal diffuse scan. The trajectories through $q_x$-$q_z$ space for specular scans and different types of off-specular scans are shown in Figure 2.3.
A 2D GISAXS image for a PMA8-dPS2 brush is shown in Figure 5.6. The GISAXS data were measured at 181 °C, a temperature at which both polymers are molten in the bulk, untethered state. The incidence angle of 0.27°, which is above the critical angle of both polymers, ensures the penetration of x-rays all the way through to the substrate. The black vertical line in Figure 5.6 shows the trajectory in $\alpha_f$, $2\theta_f$ space that a specular reflectivity scan would take and the orange lines correspond approximately to the trajectories for three longitudinal diffuse scans with increasing values of $q_y$. The data from these longitudinal cuts from the GISAXS image along with the reflectivity cut are plotted as a function of $q_z$ with increasing values of $q_y$ in Figure 5.7. The oscillations in the longitudinal scan are in phase with fringes in the reflectivity. The amplitude of the oscillations in longitudinal scans decreases with increasing $q_y$. There is no oscillation in the longitudinal scan at $q_y = 0.0187$ Å$^{-1}$. $R_c$ can be taken to be equal to $2\pi/q_y$, where $q_y$ is the value of the largest in-plane wavevector at which oscillations are observed in a longitudinal scan. $R_c$ calculated in this way is 39 nm, and this represents an upper bound. For in-plane length scales greater than 39 nm, the substrate roughness is replicated by the brush/air surface. $R_c$ value may be even smaller than our estimation. The intensity of the longitudinal scans is so weak at higher values of $q_y$ that it is very difficult to differentiate the off-specular intensity from the background scattering at large values of $q_y$.

Swelling of the brush by a good solvent is found to strongly perturb the roughness correlation between the top and bottom interfaces. That is, a wet brush and a melt brush behave in a fundamentally different way. Samples were swollen for 8 hours in the vapor of dichloromethane, which is a good solvent for both the dPS and PMA blocks, and then the specular reflectivity and longitudinal diffuse scans were measured again. These are
shown in Figure 5.8. The amplitudes of the fringes in the reflectivity curve in Figure 5.8 are lower than those in Figure 5.2 and the overall level of the reflectivity is lower, both indicating that the brush gets rougher after swelling. There are no fringes in the longitudinal scan of the frequency seen in the reflectivity. The conformality in interface roughness has been lost. When the polymers are swollen with the solvent vapor the brush thicknesses increase. In the specific case shown, the film swelled 86%. The absorption of the solvent brings several changes to the brush. First, the concomitant increase in thickness necessitates that each individual chain stretch more. One anticipates that changing the chain stretching also changes the degree to which the brush surface will replicate an underlying surface. Secondly, incorporation of the solvent reduces the value of an effective interaction parameter between the blocks, making the internal interface less sharp, or eliminating it, and thus weakening the "layered" character of the brush. Thirdly, the interfacial tension of the brush surface is altered, which will influence the propensity for thermal stimulated surface waves. Finally, adding the solvent plasticizes the film, increasing mobility. We conjecture that the most important effects of the solvent swelling are the disruption of the definition of the layered structure and the decrease in interfacial tension. These should favor the roughening of the surface.

The surface of the polished silicon substrate is known to be smooth. Roughness correlation between the air/film and film/substrate interfaces implies that the air/film surface should be smooth for values larger than $R_c$. Thus, long-wavelength fluctuations have to be highly suppressed on top of a diblock copolymer brush surface. The surface fluctuation spectrum of polymer brushes was treated theoretically by Fredrickson et al. In their theory, the authors assumed that the chains are strongly stretched and all the
chain ends are located at the free surface of the brush as it was suggested by Alexander.\textsuperscript{3} Surface modes of wavelengths that are longer than the unperturbed radius of gyration of a tethered chain, $R_g$, require lateral displacements of chains over characteristic distances greatly exceeding $R_g$ to maintain a constant monomer density. To achieve these lateral displacements, the system has to pay an entropic penalty. However, surface modes with wavelengths shorter than $R_g$ require limited stretching of the chains in the lateral direction. Hence, the grafting constraint is irrelevant for short-wavelength modes, and the free energy cost is proportional to the additional interfacial area imposed by distortion. The competition between the elastic restoring force at long wavelengths and the surface tension penalty at shorter wavelengths leads to an energetically preferred wavelength of the order of equilibrium brush height for thermally excited surface modes on an incompressible brush. Later, Xi and Milner\textsuperscript{66} treated the same problem, but without the constraint that all free chain ends be artificially located at the top surface. They found that the energy for long-wavelength surface waves on a melt brush has the same form as found by Fredrickson et al.\textsuperscript{65} with a slightly different coefficient.

Experimentally, fluctuations on the DCB surface can be studied using “off-specular” X-ray scattering. When the exit angle differs from the incident angle, the scattering vector, $q$, contains an in-plane component, $q_x$, as shown in Figure 5.1. Thus, lateral structure correlations and in-plane fluctuations on the surface are probed. Data from transverse scans at $q_z = 0.2$ Å$^{-1}$ from several PS-\textit{b}-PMA brushes are shown in Figure 5.9. The Gaussian-like shape of the data at the lowest values of $q_x$ is dictated by the profile of the specular beam and just reflects the resolution function of the instrument. The Yoneda peaks\textsuperscript{79} at $q_x = 0.0034$ Å$^{-1}$ result from the enhancement in the electric field
(and thus the scattering intensity) at the surface when either the incident or exit angle is equal to the critical angle for the sample. Between the specular and Yoneda peaks is a region in which details of the surface structure manifest themselves. If the transverse scan is measured with the same instrument geometry (slit large in the $y$ direction) for a bulk liquid, the intensity decays with a slope of -1 in this region since the surface behavior of bulk liquid is dominated by capillary waves. When the transverse scan is measured from a thin liquid film on a solid substrate, thickness dependent surface behavior is observed due to van der Waals interactions between substrate and the thin liquid film. For a 9 nm thick film of cyclohexane, there is a kink in the transverse scan data which corresponds to a low wave vector cutoff, $q_{l,c}$. The scattering intensity just changes much more slowly than slope of -1 for values of $q_x < q_{l,c}$ and it decays with the power law of -1 for $q_x > q_{l,c}$. When the thickness of a cyclohexane hexane film increases to 22 nm, the scattered intensity decays with a power law exponent of -1 over the entire range of $q_x$ accessible and $q_{l,c}$ is hidden under the specular peak. The slowly changing intensity for $q_x < q_{l,c}$ indicates the suppression of surface fluctuations of wavelengths larger than $2\pi/q_{l,c}$.

Wang et al. studied, using off-specular scattering, the surface structure of PS films resulting, presumably, when the fluctuations formed in the surface of the polymer melt film during thermal annealing were "frozen" during thermal quenching. They argued that the data could not be satisfactorily interpreted using capillary wave calculations assuming attractive van der Waals substrate film interactions. An increase in the surface integral mean square roughness with film thickness was observed, but comparison of its form with the logarithmic increase expected from capillary wave theory was inconclusive. A thickness dependent lower wavevector cutoff, $q_{l,c}$, varied more slowly with thickness than
expected for capillary waves. Finally, 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 were interpreted using the capillary wave theory. These deviations from expectations were ascribed to strong confinement effects even for film thicknesses considerably larger than the \( R_g \) of one chain. Later work\(^{152-156}\) using diffuse X-ray scattering and X-ray photon correlation spectroscopy (XPCS) showed that when the surfaces of films of untethered PS chains are measured well above \( T_g \) the capillary wave model describes the data well. Thus, the difficulties with these early measurements of Wang et al.\(^{147}\) lie with the fact that the films are quenched from the melt state.

Scattering intensity is nearly constant in the region between the Yoneda and specular peaks for all the brushes for which data are shown in Figure 5.9. These data were measured for samples quenched to RT after annealing the brushes at 140 °C for 4 hours. There is no kink in the data corresponding to \( q_{l,c} \). This shape is typical for surfaces such as semiconductors or tightly cross-linked polymer films that have surface roughness characterized only by small in-plane length scales. Figure 5.9 suggests that the long wavelength fluctuations are highly suppressed on the surface of a diblock copolymer brush. The smallest in-plane length probed during these measurements at \( q_z = 0.20 \) Å\(^{-1}\) was 186 nm. The absence of \( q_{l,c} \) and nearly constant scattering intensity for all brushes in Figure 5.9 show that the \( q_{l,c} \) is larger than the highest \( q_z \) measured in the transverse scans. Thus, long-wavelength fluctuations with wavelengths larger than 186 nm are highly suppressed on the surface of PS-\( b \)-PMA diblock copolymer brushes.

The long-wavelength fluctuations are highly suppressed on the PMA-\( b \)-PS brushes as well as on the PS-\( b \)-PMA brushes. Transverse scans taken at \( q_z = 0.20 \) Å\(^{-1}\) for
PMA-\textit{b}-PS brushes of three different thickness are given in Figure 5.10. Transverse scans were performed at \( q_z \) values of 0.15, 0.20, 0.30 and 0.35 Å\(^{-1} \). Since the maximum value of \( q_x \) that can be reached increases somewhat with increasing value of \( q_z \) for which the transverse scan was run, the smallest in-plane length scales probed get smaller with increasing value of \( q_z \). For \( q_z = 0.35 \) Å\(^{-1} \), the smallest in-plane length scale measured is ca. 66 nm. Figure 5.11 shows transverse scans for \( q_z = 0.35 \) Å\(^{-1} \) for a series of PS-\textit{b}-PMA brushes of different thicknesses. Though there is a slight change in slope at higher values of \( q_x \) for some of the samples, nowhere is a slope of -1 seen. These small changes in slope do not correspond to a value of \( q_{l,c} \). Rather, it is most likely that they may be modeled using the model of a self-affine rough surface with an appropriate correlation length. Recently, Foster and co-workers\(^{157} \) demonstrated that the scattering from surfaces of PS brushes synthesized by conventional free radical polymerization can be well described by assuming the surfaces have self-affine roughness, suggesting that the surfaces of homopolymer brushes are solid-like on the length scales studied here. The transverse scans of diblock copolymer brushes are even flatter than the transverse scans for PS brushes synthesized by conventional free radical polymerization. It may be that the long wavelength fluctuations are even more suppressed for diblock copolymer brushes than the homopolymer brushes of PS. However, this needs to be investigated further by doing detailed modeling of the block copolymer brush data using the self-affine model.

5.4 Conclusion

In summary, X-ray scattering measurements have revealed for the first time that the air/brush and brush/substrate interfaces of diblock copolymer brushes can be
correlated over length scales to which the scattering measurements are sensitive. The correlation is found for film thicknesses much higher than those for which correlation is seen in small molecule liquids. This correlation is intrinsic to the structure of the dry brush, since it persists after annealing at a temperature above the glass transition temperatures of both polymers, proving that the correlation is not due to kinetic trapping of a morphology formed during the brush deposition. However, the correlation is disrupted when the brush is swollen with the vapor of a good, nonselective solvent for the two blocks. Roughness correlation implies that the long wavelength fluctuations on the surface of DCBs are highly suppressed. The suppression of surface fluctuations is confirmed using indirect evidence from transverse diffuse X-ray scattering, in qualitative agreement with the theory of Fredrickson et al.\textsuperscript{65} It remains to observe directly $q_{l,c}$ or the maximum in the static structure predicted by Fredrickson et al.,\textsuperscript{65} or to observe with a dynamics measurements directly the suppression of the surface fluctuations on the brush.
Figure 5.1. Schematic of a diblock copolymer brush with the incident and exit X-ray beams, corresponding scattering vector, \( q \), and components perpendicular to the surface, \( q_z \), and parallel to the surface and in the plane of incidence, \( q_x \). The wavevectors of the incident and scattered X-rays are \( k_i \) and \( k_f \), with the incidence and exit angles \( \theta_i \) and \( \theta_f \), respectively. Specular scattering corresponds to \( \theta_i = \theta_f \). Otherwise, the scattering is called “off-specular scattering”.

Figure 5.2. The specular reflectivity (open circles) and longitudinal diffuse scattering (solid circles) from a dPS-b-PMA diblock copolymer brush with total thickness of 21 nm, dPS layer thickness of 15 nm and PMA layer thickness of 6 nm. Multiplying the scattering intensities by $q_z^4$ emphasizes the fringes and normalizes for a trivial $q_z^{-4}$ dependence. The longitudinal scan intensity has been offset by an arbitrary amount for clarity.
Figure 5.3. The specular reflectivity (open circles) and longitudinal diffuse scattering (solid circles) from a PMA-\textit{b}-PS diblock copolymer brush with total thickness of 32 nm, PMA layer thickness of 11 nm and PS layer thickness of 21 nm. The longitudinal scan intensity has been offset by an arbitrary amount for clarity.
Figure 5.4. Comparison of the specular reflectivity and longitudinal scans from the same dPS-\textit{b}-PMA brush as in Figure 5.2 (thickness of 21 nm) after annealing at 140 °C for 4h reveals that the correlation persists.
Figure 5.5. Schematic drawing of two interfaces at a mean distance $d$, corresponding to the film thickness as obtained from reflectivity measurements (mean interface position marked with the dashed lines). The roughness spectrum of the lower interface is only transferred for in-plane length scales larger than $R_c$. The amplitude of roughness is greatly exaggerated for clarity. (Adapted from reference 135).
Figure 5.6. 2D GISAXS image is taken from a diblock brush sample of PMA8-dPS2 which has 8 nm thick PMA block and 2 nm thick PS block as determined by neutron reflectivity. The data were collected at 181 °C with an incidence angle of 0.27°. The vertical black line cut represents a reflectivity scan and the inclined orange lines show trajectories approximately equal to those for longitudinal scans at different $q_y$ values, $q_y$ increasing as the lines move farther away from reflectivity line cut.
Figure 5.7. Reflectivity (dark blue circles) and longitudinal linecuts taken from GISAXS image of PMA8-dPS2 brush at $q_y = 0.0014$ Å$^{-1}$ (red circles), $q_y = 0.0052$ Å$^{-1}$ (black circles), $q_y = 0.0107$ Å$^{-1}$ (brown circles), $q_y = 0.0161$ Å$^{-1}$ (green circles), and $q_y = 0.0187$ Å$^{-1}$ (blue circles). Incidence angle is 0.27° and the measurement temperature is 181 °C. For clarity the curves have been shifted vertically by an arbitrary amount.
Figure 5.8. Specular X-ray reflectivity and longitudinal diffuse scattering from a dPS-$b$-PMA brush (thickness of 21 nm before swelling) after swelling in CH$_2$Cl$_2$ vapor for 8 hours. The thickness change during the swelling is 86% to 39 nm.
Figure 5.9. Transverse diffuse scattering for DCBs of PS-b-PMA of varying thickness at $q_z$ value of 0.2 Å⁻¹ measured at room temperature. The total thickness values are shown for the corresponding data next to each curve. Curves have been shifted by an order of magnitude vertically for clarity.
Figure 5.10. Transverse diffuse scans taken at $q_z = 0.2 \, \text{Å}^{-1}$ for PMA-$b$-PS brushes with thicknesses ranging from 7 nm to 32 nm. Curves have been shifted vertically by an order of magnitude for clarity.
Figure 5.11. Transverse scan data for PS-$b$-PMA diblock copolymer brushes of the thicknesses shown at $q_z$ value of 0.35 Å$^{-1}$. Curves have been shifted vertically for clarity.
CHAPTER VI

SURFACE DYNAMICS OF MOLTEN HOMOPOLYMER BRUSHES BY X-RAY PHOTON CORRELATION SPECTROSCOPY

6.1 Introduction

Polymer brushes have recently gained enormous interest in the field of thin polymer films because they have better solvent, chemical and thermal stability than do films of corresponding untethered chains.\textsuperscript{1} Tethering to a substrate with a distance between tethering points that is smaller than the radius of gyration ($R_g$) of the unperturbed chain stretches the chains from their Gaussian conformations and alters the physical properties of films formed from the chains. The surface dynamics of polymer brushes are expected to differ from those of untethered films because the chains are confined in both the lateral and vertical directions. Fredrickson and co-workers\textsuperscript{65} argued that on the surface of a homopolymer brush modes of surface fluctuations that would be present on a semi-infinite sample of untethered chains are suppressed due to the entropic penalty chains must pay to stretch sufficiently to allow long wavelength fluctuations. The result is that surface fluctuations of a wavelength comparable to the brush thickness should predominate. Later Milner\textsuperscript{66} and Pickett\textsuperscript{67} reached conclusions similar to those of Fredrickson et al.\textsuperscript{65} The observation of correlation between the roughnesses of the top and bottom interfaces of a diblock copolymer brush has offered indirect evidence that this is
true, but it remains to demonstrate this directly with a measurement of surface dynamics.

There have been a few published experimental studies on the cooperative dynamics of “wet” homopolymer brushes in a solvent. Fytas and coworkers performed evanescent wave dynamic light scattering (DLS) measurements of polymer brush dynamics in good and theta solvents using polydisperse brushes ($M_w/M_n \approx 2$) synthesized by conventional free radical polymerization. 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. DLS is not a surface sensitive technique due to the large penetration depth (0.5 μm). Opaque polymer melts cannot be measured with DLS and the length scale measured is much larger than probed with X-ray techniques. Since X-ray photon correlation spectroscopy (XPCS) uses radiation of shorter wavelength and can address long time-scales, it has become a primary technique for the investigation of the dynamics of smectic liquid-crystal membranes, opaque magnetic colloidal systems, block copolymer vesicles, liquid surfaces and surfaces of spun-cast polymer films. XPCS has an intrinsic surface sensitivity due to the small penetration depth at incident angles lying below the critical angle of the polymer. Kim and co-workers demonstrated that the surface dynamics of spun-cast polymer films is wave-vector, thickness, viscosity, surface tension and molecular weight dependent, as is expected from a theory of overdamped capillary waves. They showed that the surface viscosity is thickness and wave-vector independent, which is in good agreement with the theory. Although the chemical synthesis of dense polymer brushes has now been widely studied, the dynamics of these brushes remain to be elucidated,
especially in the melt. Herein, we report first observations with XPCS of the surface
dynamics of molten, high density PS homopolymer brushes of well-defined molecular
weight, synthesized by the “grafting from” with ATRP. These clearly show that when the
chains are tethered, surface fluctuations are remarkably suppressed at length scales
exceeding the thickness of the brush, as anticipated by theory.65-67

6.2 Experimental

6.2.1 Sample Preparation

Polystyrene (PS) brushes of thickness 9, 26, 38, and 48 nm and poly(n-
butylacrylate) (PnBA) brushes of thickness 30 nm were synthesized by atom transfer
radical polymerization (ATRP) using synthetic techniques described in section 3.2.52
Briefly, a self assembled monolayer (SAM) of 11-((2-bromo-2-methyl)-propionyloxy)
undecyltrichlorosilane initiator was deposited on a silicon substrate that is cleaned using
piranha solution. Polymerization of the chosen monomer was initiated from the
immobilized SAM to form the homopolymer brush of high grafting density (typically
~0.6 chains/nm²) using ATRP. The thickness, calculated grafting densities, molecular
weights, distance between anchoring points (s) and radius of gyration (Rg) values for each
sample are shown in Table 6.1. The brushes were annealed in a high vacuum oven for 12
hours at 150 °C to remove excess solvent and then cooled at ~ 40 °C/min to room
temperature. Brush thicknesses were determined using X-ray reflectivity (XR). XPCS
data were collected with the samples at the temperature of interest.
6.2.2 Specular X-ray Reflectivity (XR)

Specular XR measurements were done prior to the XPCS measurements to

determine the thickness and interface roughness of each brush sample. XR was measured

using a spectrometer mounted on a 12 kW rotating anode X-ray generator (Rigaku, 12

kW RU200) with Cu Kα radiation (λ = 1.54 Å). The resolution in scattering vector, δqz,

was about 0.001 Å⁻¹. The background intensity was subtracted from the experimentally

measured specular intensity to obtain true specular reflectivity.

6.2.3 X-ray Photon Correlation Spectroscopy (XPCS)

The XPCS experiments were performed at beamline 8-ID-I at the Advanced

Photon Source (APS) using an X-ray beam energy of 7.5 keV. The experimental

graphometry is illustrated schematically in Figure 6.1. An X-ray incidence angle of αi=0.14°

(below the critical angles of both polymers, αc=0.17°) was used to ensure the penetration

depth was approximately 9 nm. Scattering from the film/substrate interface was

negligible and only fluctuations at the polymer/vacuum surface were probed for all

samples except a 9 nm thick PS brush. With X-rays it is possible to access values of the

in-plane wave vector up to 10⁻² nm⁻¹. A direct-illumination charge coupled device (CCD)

camera, located 3545 mm downstream of the sample, was used for recording the off-

specular diffuse scattering from the brush surface. Data were collected at two different

beam times, with the results being consistent. The beam dimensions were 20x20 μm²

with X-ray coherence lengths of 7 and 90 μm in the horizontal and vertical directions,

respectively. The typical flux was ~3x10⁹ photons/sec. Later measurements were run

using higher flux and a coherence that was improved by a factor of ~20. The x-ray
exposure time of any point on the sample was limited to 10 min to avoid well-known beam damage. Before and after the XPCS measurements, XR was measured to ensure that the beam damage at the measured spot was sufficiently small that the dynamics of the film surface were not altered. Under conditions of partial coherence, the scattering pattern exhibits random interferences, so called “speckles”, which vary in time as the surface modes experience random thermal fluctuations. Analysis of the normalized intensity-intensity time autocorrelation function, $g_2$, of such a speckle pattern yields the characteristic relaxation times of the sample. The intensity-intensity time autocorrelation function is given as

$$g_2(q,t) = \frac{<I(q,t')I(q,t'+t)>}{<I(q,t')>^2}$$  \hspace{1cm} (6.1)

where $I(q,t')$ is the scattering intensity at wavevector transfer $q$ at time $t'$. The angular brackets refer to averages over time $t'$ and $t$ denotes the delay time. Methods for determining $g_2$ are described in detail elsewhere.$^{177}$

6.3 Results and Discussion

That the fluctuations at the surface are remarkably suppressed is clear from the comparison in Figure 6.2 in which $g_2(\tau)$ ($q_|| = 5.3 \times 10^{-3}$ nm$^{-1}$) is plotted for the 26 nm thick film of tethered PS chains and for a roughly comparable film of untethered chains made by spin casting and annealing. The relaxation for the surface of the film of untethered chains is clearly observed and fitting with a single exponential form,

$$g_2 = 1+ \beta \exp (-2t/\tau)$$  \hspace{1cm} (6.2)
where $\beta$ is the speckle contrast, yields a relaxation time, $\tau$, of 32 sec. In contrast, the $g_2$ function for the brush indicates no relaxation within the experimental window. If the brush had a surface relaxation with a single exponential shape and a relaxation time of ca. 30,000 sec or smaller, 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. Data collected at much shorter times for two of the samples also demonstrated that there was no relaxation at times as short as tenths of a second. For untethered polymer films the relaxation time is determined by several factors including molecular weight and thickness. The molecular weight of the PS brush is smaller than the molecular weight of the untethered PS film, but it does not affect the observed behavior. Kim and co-workers\textsuperscript{151} already showed that the relaxation gets faster as the molecular weight decreases for untethered polymer films. Therefore, $\tau$ should be even shorter than 32 s for an untethered PS film which has the same molecular weight as PS brush have. This difference between the untethered PS film and the PS brush implies that the suppression of surface height fluctuations results from tethering of polymer chains to the substrate.

Experimental intensity normalized time autocorrelation functions for a value of the in-plane wave vector $q_{\text{ii}}$ of $3.4 \times 10^{-3}$ nm$^{-1}$ at 230 °C for 26, 38, and 48 nm thick PS brushes and for $3.1 \times 10^{-3}$ nm$^{-1}$ at 230 °C for 9 nm thick PS brush are shown in Figure 6.3. $g_2(q,t)$ is flat over the entire range of time delays for all brushes indicates that the fluctuations are suppressed for four different thickness. It should also be noted at this point that intensity normalized time autocorrelation functions measured at the first beam time showed thickness dependent behavior as shown in Figure 6.4. Apparent relaxations
seen in the previous data for 26 and 48 nm thick PS brushes (Figure 6.4) can be explained as resulting from the paste 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. Relaxations due to paste at relatively low temperature can be made to disappear by raising the temperature. This causes lower molecular weight additive materials to be volatilized away in the vacuum, leaving a material that is still viscoelastic, but with the relaxation times shift to higher times. Figure 6.5 demonstrates that 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 to 3000 seconds. Apparent relaxations with the 9 nm brush sample slowed as temperature increased in the first beam time. This was due to loss of volatiles from the paste. To overcome this problem in the second beam time, samples were heated at 230 °C to remove lower molecular weight additive materials and then the XPCS measurements were started.

Kim and co-workers\textsuperscript{151,152} measured the surface dynamics of untethered PS films at 150, 160 and 170 °C. Since the relaxation time gets faster with increasing temperature it is difficult to see the whole relaxation for films of untethered chains above 170 °C. PS brushes were measured at temperatures varying from 140 °C to 230 °C, which is the highest available temperature with this setup. Shown in Figure 6.6 is $g_2(q,t)$ as a function of delay time at $q_0=3\times10^{-3}$ nm$^{-1}$ for a 48 nm thick PS brush and for a 30 nm thick PnBA brush at various temperatures. No relaxation was seen for a brush at any temperature investigated. The highest temperature is of the order of 130°C above the glass transition temperature, $T_g$, of the untethered chains of the same molecular weight ($T_g \sim 100$ °C). For
a 30 nm thick PnBA brush no surface relaxation was seen for temperatures up to 170 °C above the $T_g$ of untethered chains (~ -50°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 6.7 presents $g_2(\tau)$ for five values of $q_{||}$ from the lowest to the highest measured with reasonable statistics, corresponding to a range of length scales from 620 nm to 3100 nm.

All of these observations are consistent with the theoretical predictions of Fredrickson et al.\textsuperscript{65} and Milner and coworkers\textsuperscript{66} for brushes of monodisperse tethered chains. They argued that long wavelength fluctuations would be suppressed due to the entropic penalty incurred to stretch chains sufficiently to create surface fluctuations with wavelengths much larger than the height of the brush. Short wavelength fluctuations are suppressed due to surface tension. They anticipated that the competition between the elastic restoring force at long wavelengths and the surface tension penalty at shorter wavelengths leads to an energetically preferred wavelength of the order of equilibrium brush height. Unfortunately, the scattering intensity falls off so quickly with in-plane wave vector $q_{||}$ that it is difficult to get to sufficient high $q_{||}$ values to see the dynamics that should be present for length scales comparable to the thickness of the brush.

An interesting question is whether the suppression of the surface fluctuations is due to this mechanism alone, or whether perhaps the brushes are not truly in a melt state. It is very unlikely that the suppression of fluctuations on the surface is due to changes in $T_g$ of the film as a whole induced by tethering. Changes seen in the structure of dry DCBs after annealing at 180°C suggest that segments in the interior of the brush are still quite
capable of rearrangement. Fukuda et al.\textsuperscript{123} used spectroscopic ellipsometry to investigate the difference between the $T_g$ of films of untethered poly(methyl methacrylate) chains and the $T_g$ of a PMMA brush with a high grafting density. At a thickness of 50 nm they found an elevation of $T_g$ of 8 °C, suggesting that in the brushes studied here, change in the $T_g$ of the film as a whole is not the issue. On the other hand, Nealey and DePablo\textsuperscript{122} using ellipsometry and a localized thermal probe technique, reported an increase of ca. 25°C in the $T_g$ of a 45 nm thick film of PS in which a small fraction of the chains were end-tethered to the substrate. That film contained mostly chains that were not covalently tethered, and the grafting density of those that were tethered was much lower than that in the present work, leaving open the possibility that films containing larger fractions of tethered chains could show even higher elevations of film $T_g$.

6.4 Conclusion

XPCS measurements have revealed clearly that the surface fluctuations of homopolymer brushes in the dry state are much slower than those of a corresponding film of untethered chains. For untethered PS films, while a relaxation of the surface height fluctuations has been observed in the (length and time scale) experimental window, no hint of a relaxation is observed for homopolymer brushes even 130 °C above the $T_g$ of the corresponding untethered PS chains in the bulk. For PnBA brushes this suppression has been followed to a temperature 170 °C above the $T_g$ of untethered chains. This suppression of surface dynamics is a result of tethering. Thus, tethering the polymer chains to a substrate indeed alters the dynamic at the surface. The observation of suppressed surface fluctuations is consistent with theoretical predictions.\textsuperscript{65-67}
Table 6.1. Physical properties of the polymer brushes measured using XPCS.

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness(^a) (nm) ±0.2</th>
<th>(M_n)(^b) (kg/mol)</th>
<th>(\sigma)(^c) (chains/nm(^2))</th>
<th>(s)(^d) (nm) ±0.03</th>
<th>(R_g) (nm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-9</td>
<td>9</td>
<td>10±0.5</td>
<td>0.6±0.03</td>
<td>1.4</td>
<td>2.8±0.1</td>
</tr>
<tr>
<td>PS-26</td>
<td>26</td>
<td>28±1.4</td>
<td>0.6±0.03</td>
<td>1.3</td>
<td>4.6±0.2</td>
</tr>
<tr>
<td>PS-38</td>
<td>38</td>
<td>34±1.7</td>
<td>0.6±0.04</td>
<td>1.3</td>
<td>5.3±0.2</td>
</tr>
<tr>
<td>PS-48</td>
<td>48</td>
<td>50±2.5</td>
<td>0.6±0.03</td>
<td>1.3</td>
<td>6.0±0.3</td>
</tr>
<tr>
<td>PnBA-30</td>
<td>30</td>
<td>25±1.3</td>
<td>0.8±0.04</td>
<td>1.1</td>
<td>3.6±0.2</td>
</tr>
</tbody>
</table>

\(^a\)Thickness (d) values are from XR.

\(^b\)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.

\(^c\)Grafting density (\(\sigma\)) calculated using the following equation: \(\sigma = \frac{N_A \rho d}{M_n}\). \(M_n\) is the number average molecular weight, \(N_A\) is the Avagadro’s number and \(\rho\) is the bulk mass density for the material.

\(^d\)\(s\) is the distance between the anchoring points.
Figure 6.1. Schematic of XPCS setup in reflection geometry. The wavevectors of the incident and scattered X-rays are $k_i$ and $k_f$, with the incidence and exit angles $\alpha_i$ and $\alpha_f$, respectively. (Adapted from Reference 149)
Figure 6.2. Intensity normalized time autocorrelation function vs. delay time at $q_u = 5.3 \times 10^{-3}$ nm$^{-1}$ for a 26 nm thick PS brush and 29 thick film of untethered PS chains ($M_u = 65k$) measured at 170 °C.
Figure 6.3. $g_2(\tau)$ for PS brushes at $q|| = 3.4 \times 10^{-3}$ nm$^{-1}$ for brushes of thickness 48 (empty triangles), 38 (filled circles) and 26 nm (empty squares) at 230 °C. $g_2(\tau)$ for the 9 nm (filled diamonds) thick PS brush was measured at $q|| = 3.1 \times 10^{-3}$ nm$^{-1}$. For the 26 and 47 nm brushes data were collected at much shorter times. Curves are vertically offset by an arbitrary amount for clarity.
Figure 6.4. Intensity normalized time autocorrelation functions ($g_2$) as a function of delay time at 230 °C for 9 nm (circles), 26 nm (squares) and 48 nm thick PS (triangles) brushes at $q_w = 1.1 \times 10^{-2}$ nm$^{-1}$, measured at first beam time. Curves are the best fits to the $g_2$ using a single exponential function. Curves have been shifted for clarity. Included here are data for times for which the paste under the sample contributes to relaxations.
Figure 6.5. Intensity normalized time autocorrelation functions ($g_2$) as a function of delay time at $q_0 = 2.9 \times 10^{-3}$ nm$^{-1}$ for a bare silicon wafer measured at room temperature with a paste (empty circles) and for a bare silicon wafer measured at 60 °C without using paste (filled circles). $g_2$ for a bare silicon wafer measured at 60 °C have been shifted vertically by an arbitrary amount.
Figure 6.6. Intensity normalized time autocorrelation function vs. delay time for (top) a 48 nm thick PS brush measured at 140, 190 and 230 °C at $q_v = 3 \times 10^{-3}$ nm$^{-1}$ and for (bottom) a 30 nm thick P$n$BA brush measured at 50, 100, 120 °C at $q_v = 3 \times 10^{-3}$ nm$^{-1}$. Curves have been shifted vertically for clarity.
Figure 6.7. Intensity normalized time autocorrelation function as a function of delay time at 190 °C for 38 nm thick PS brush at $q_\parallel = 2 \times 10^{-3}$ (filled diamonds), $3.9 \times 10^{-3}$ (empty squares), $5.4 \times 10^{-3}$ (filled triangles), $7.3 \times 10^{-3}$ (empty spheres), and $1 \times 10^{-2}$ nm$^{-1}$ (filled squares). Curves are offset by an arbitrary amount.
CHAPTER VII
CONCLUSION

The internal structure of ultrathin “as-deposited” DCBs of PS-\textit{b}\textsubscript{1}-PMA and PMA-\textit{b}\textsubscript{2}-PS has been resolved using NR and GISAXS. Internal brush structure depends strongly on the sequence in which the polymer blocks have been synthesized and the value of $\chi N$. For all samples studied, DCBs with $\chi N \leq 23$ adopt lamellar structures. The data from such structures are described well using models of two layers with an interfacial region of finite width. The interface widths are smaller for DCBs that have PMA blocks synthesized next to the substrate than for DCBs that have PS blocks synthesized next to the substrate. For dPS-\textit{b}\textsubscript{1}-PMA brushes that have values of $\chi N > 23$ and sufficiently asymmetric composition, a third layer must be included in the model to describe the NR data. The necessity of including a third layer is consistent with the presence of a lateral ordering of some type between the top and bottom layers of the brush. This in-plane ordering is peculiar to DCBs that have incompatible blocks. The spacing of the in-plane ordering changes in a manner very closely tied to the thickness of the PMA block. It remains to answer how the width of the interface between polymer domains changes with block composition and the quality of solvent as a future work. NR has been measured for dry PS-\textit{b}\textsubscript{1}-PMMA, PS-\textit{b}\textsubscript{1}-PnBA and all DCBs in vapor of good and poor solvents. The quantitative modeling of the NR data can show how the interface width changes with block composition and in various solvents. It is expected that the interface width would
be even broader for dry PS-\(b\)-PnBA than dry PS-\(b\)-PMMA and dry PS-\(b\)-PMA since the estimated interaction parameter is smaller for PS-\(b\)-PnBA than the estimated interaction parameters for PS-\(b\)-PMMA and PS-\(b\)-PMA. We also expect that the interface width is broader when the brush is “wet”.

After exposure of a DCB to a solvent selective for the block attached to the substrate (“switching”), new 2D structures are formed at the air surface of the brush. These structures disappear upon heating to 80 \(^\circ\)C, which suggests that the PS block must be mobile at 80 \(^\circ\)C to disrupt an energetically unfavorable structure. The qualitative information obtained from GISAXS data is only a small portion of what can be extracted about the internal structure. Once the 2D GISAXS data are fit with detailed models, it will be possible to resolve more of the internal structure of the DCBs. This structural information is crucial for determining the mechanism of surface rearrangement.

Roughness correlation between the substrate/polymer interface and air/polymer interface of DCBs has been detected using longitudinal diffuse X-ray scattering and specular X-ray reflectivity. Roughness correlation weakens with increasing thickness of the DCB, but persists up to total thickness of 54 nm. Correlation of the roughnesses of the top and bottom interfaces of the brush is observed after annealing the brush at a temperature above the glass transition temperatures of both blocks in the DCB. This correlation is lost after the brush is swollen in the vapor of a nonselective solvent, dichloromethane. The ability of to replicate the roughness of an underlying substrate could be essential for templating. This replication makes it possible to chemically modify a patterned surface with minimal alteration of the pattern shape with DCBs. Roughness correlation in DCBs implies that the fluctuations at the air surface are highly suppressed.
since the silicon substrate has a very smooth surface. Surface fluctuations of wavelength larger than 300 nm are found to be suppressed on a DCB surface using X-ray transverse diffuse scans. No relaxation of surface height fluctuations is observed in the experimental window of XPCS. This suppression of surface dynamics is a result of tethering.

It is of interest to determine how the domain/domain interface contributes to the roughness correlation. The presence or absence of roughness correlation at the domain/domain interface can only be determined using off specular neutron scattering which is currently limited with the weak neutron flux. It is not possible to differentiate the scattering of the brush from the background signal. With the new spallation neutron source it may be possible to do off-specular neutron reflectivity measurements in the near future.

Preliminary measurements demonstrated that the surface dynamics behavior of DCBs does not differ from that of homopolymer brushes. It remains to measure the surface height fluctuations at the domain/domain interface of DCBs. It is possible to selectively study the domain/domain interface by varying the incident angle if there is enough of electron density difference between the first and second blocks. To achieve sufficient electron density contrast, either fluorinated or brominated blocks should be synthesized. Suppression of surface fluctuations on the surface of molten brushes is predicted by Fredrickson and he argued that only fluctuations of wavelengths on the order of equilibrium thickness of the brush are present on the surface. Our studies showed that there are no surface fluctuations of wavelengths larger than 66 nm. To prove Fredrickson’s argument, either thicker brushes should be synthesized or measurements
that can probe higher values of the in-plane wavevectors should be done. Reaching larger values of the in-plane wavevectors is not possible at the moment using XPCS.
REFERENCES


(80) Commercial 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.


(82) Piranha 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.


