TETHERED POLYMER CHAINS ON SINGLE CRYSTAL SURFACES

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TETHERED POLYMER CHAINS ON SINGLE CRYSTAL SURFACES

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Dissertation

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ABSTRACT

Tethered polymer chains have drawn significant research attention over the last few decades because of their unique properties for various applications. The tethering density of the chains determines the state of the chains as well as the resulting properties, as shown by various theoretical and experimental work. Through the use of single crystals of crystalline-amorphous diblock copolymers, it is possible to study tethered polymer chains as the amorphous block is attached covalently to the crystal surface. This system provides the best control of tethering density and molecular weight as compared to previous methods. Previous work on PS-$b$-PEO and PS-$b$-PLLA found the reduced tethering density value for the transition into the interacting regime ($\tilde{\sigma}^*$) to be independent of molecular weight and solvent quality. Other factors that were not addressed were adsorption and chain stiffness. The role of chain adsorption using miscible polymers, namely PMMA-$b$-PLLA, and chain stiffness, with PEO-$b$-PCL where PEO is the amorphous block, has been determined. In order to determine the chain conformation and size of the PMMA adsorbed on the PLLA surface, Monte Carlo simulations were performed. Adsorption of the chain was found to increase $\tilde{\sigma}^*$, and the collapsed state in poor solvent led to a lower $\tilde{\sigma}^*$ when compared to the PS system. Also, the PEO tethers provided a unique opportunity to study the crystallizability of tethered polymer chains.
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CHAPTER I
INTRODUCTION

Tethered polymer chains, which consist of a monolayer of material, provide a unique opportunity to change the surface properties of a material without adding much mass. Properties such as adhesion, wettability, friction, and surface energy can be altered based on the chemical composition of the tethered chain as well as its physical state. This monolayer has minimal mass and allows the properties to be tailored for each application. These polymers, which are attached at one end to the surface or interface, have unique characteristics different from a free polymer film. The attachment of these chains inherently changes in the entropy of the system. In addition, the packing of these chains contributes to these property differences.

The physical state of the tethered polymer chains is defined by the tethering density ($\sigma$), or number of chains per unit area. At low tethering density, the chains adopt an unperturbed, mushroom conformation. At moderate tethering density, they begin to interact with neighboring chains which leads to slight conformational distortion due to an osmotic pressure increase. At much higher tethering density, they form polymer brushes. Polymer brushes exist at a tethering density where the chains are packed tightly enough that they begin to stretch perpendicularly to the substrate or interface greatly deforming their conformation. This state has highly different properties, such as good barrier to
diffusion and slower dynamics, from the others. At high tethering density, the substrate-tether interactions are irrelevant to the resultant properties; however, at low tethering densities this interaction can affect the conformation and the transition from one state to another. In order to obtain the desired properties for a given application, one should know a priori what state the tethered system is in at a given \( \sigma \). The goal of the research presented in this dissertation is to ascertain the transition in the low to moderate tethering density regime.

The physical state of tethered polymers and their transitions has been addressed in several theoretical and experimental studies. In theoretical treatments, the segment density is modeled as a function of the distance from the tether point for all regimes. It was found that the conformation of the chain, or chains, is dependent on intrachain, interchain, and chain-surface interactions. Scattering experiments have been used to verify these density calculations. According to scaling laws and mean-field calculations, the height of the layer is related linearly to the log of the tethering density at high values. The transitions are found by changes in the relationship as a function of tethering density. In most cases, the reduced tethering density (\( \tilde{\sigma} \)), or the number of tether points in the projected area of a single chain, is used to remove any chain-size effects. This allows for the comparison of varying systems.

To date, the most accurate analysis of the transitions from the non-interacting to the interacting regime and the transition from the interacting to the stretched brush regime was achieved utilizing crystalline-amorphous diblock copolymers. In this study, the crystalline block is crystallized in dilute solution to form a lamellar single crystal. Because the amorphous block is excluded from the crystalline lattice, it is tethered by the
covalent linkage to the top and bottom basal surfaces of the single crystal, forming a “sandwiched” structure. These copolymers, where polystyrene (PS) was the amorphous block, established the transitions through a change in the relationship between the lamellar crystal thickness ($d_{\text{CRYST}}$) and the crystallization temperature ($T_x$). A transition in the slope of $1/d_{\text{CRYST}}$ versus $T_x$ indicates the transition from the non-interacting to the interacting regime due to an increase in the surface free energy. The system was analyzed for different crystalline blocks, poly(ethylene oxide) (PEO) and poly(L-lactic acid) (PLLA), different solvent conditions, and a variety of molecular weights. It was found that the transition from the first regime into the second was consistent at $\tilde{\sigma}^* = 3.7$. While the results proved that the analysis of the system with the normalized reduced tethering density was consistent, the only tethered polymer that was investigated was PS. It should also be noted that the interactions between the PS and PEO or PLLA surface were unfavorable or repulsive. The next step is to determine the transition values in other systems, including those with attractive interactions where the conformation of the tethered chain at low $\sigma$ is altered.

Following a similar experimental procedure, this study evaluates the non-interacting-to-interacting transition in two other diblock copolymer systems. In the first, the transition of poly(methyl methacrylate) (PMMA) is elucidated using a PMMA-$b$-PLLA copolymer. Here, the interaction between the PMMA and the PLLA surface is attractive due to their miscibility in the melt state. The second tether is PEO. Poly(ε-caprolactone) (PCL) was used as the crystalline block (PEO-$b$-PCL). The PEO tether is more flexible than the PS and PMMA, which provides insight into any chain stiffness.
effects for the transition. In addition, PEO is known to be a semi-crystalline polymer. This provides an opportunity to analyze the crystallizability of semi-crystalline tethers.

Results show that the transition values for these two tethered chains, PMMA and PEO, are quite different from $\tilde{\sigma}^* = 3.7$ for PS in good and theta solvent. The PMMA system shows a much higher result at $\tilde{\sigma}^* = 7.5$. It is interesting to note that the chain characteristics of PMMA and PS are similar; therefore, the increase in $\tilde{\sigma}^*$ must be attributed to the attractive interactions, or altered chain conformation, on the PLLA crystal surface. The PEO tethers exhibit a $\tilde{\sigma}^* \approx 3.8$. The size of the chain is estimated by calculations for the theta state. This shows that the transition is the same as the PS sample for the theta state or lower in a poor solvent state. By comparing this set of samples, it appears that the chain dimension $R_g$ does not provide a complete picture of the underlying physics of tethered chain interactions.

Because the system is normalized by the projected area, $\pi R_g^2$, $\bar{\sigma}$ represents the number of chains needed in the area to create enough osmotic pressure for a transition to occur. In the PMMA study, the increase in $\tilde{\sigma}^*$ originates from a saturated layer of adsorbed segments below a layer of loops and tails. The higher transition value is representative of a predicted behavior from scaling theory. In the case of PEO, if the solvent is poor, the dimension of the chain formed a collapsed state where segment-segment interactions were maximized. Because there is little solvated volume within $R_g$ (segment density is high), the transition in poor solvent would be found to occur earlier than in good, or even theta, solvent, where the segment density in a unit volume is lower. These two studies provide evidence that knowledge of the conformation of the tethered chains is important for predicting $\tilde{\sigma}^*$. 

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The crystallization of PEO is heavily repressed by the tethering of a single layer onto the PCL crystal surface. In all cases, the PEO block molecular weight was smaller than the PCL molecular weight to ensure crystallization of the PCL block first. Electron diffraction and DSC show that the PEO tethers do not crystallize up to a $\sigma$ of $\sim$10.4. However, results have shown that if the PEO is crystallized first through epitaxial growth on a pre-made homopolymer PEO single crystal, then the PCL block does crystallize on the surface. In this case, $\sigma$ is much higher when the substrate is reversed (PEO $\sigma = 0.49$ nm$^{-2}$ and PCL $\sigma = 1.23$ nm$^{-2}$). The orientation of the PCL crystallites on the PEO surface was also analyzed. It appears there was a small tendency for the [110] and [T00] directions of the PCL to be parallel to the [120] or [T20] direction of the PEO due possibly to soft epitaxy from the fold surfaces of both crystals.
CHAPTER II

BACKGROUND

For several decades, the study of tethered polymer chains on surfaces and at interfaces has been at the forefront of polymer research. The simple modification of a surface by attaching a thin layer of polymer provides many technical advantages for changing the surface properties of a material. The physical or chemical attachment of one chain-end of a polymer results in varying properties for the tethered chain as well.\[1-3\]

It is this combination of physical properties due to chain conformations and chemical properties through the ability to tune the surface chemistry with selected monomeric systems that allows for the ubiquitous utilization of tethered polymers in applications such as adhesion,\[4,5\] wetting,\[6,7\] lubrication,\[8-10\] diffusion barriers,\[11,12\] preventing protein adsorption\[13-15\] or colloidal flocculation,\[16,17\] and responsive surfaces.\[18-21\]

There are many examples of tethered chains in common polymeric systems. These are illustrated in Figure 2.1. The first is the chemical attachment of the chain to a substrate, such as a silicon wafer. The second is the physical adsorption of diblock copolymers where one block adsorbs to the substrate forming the tethering point, while the other stretches into solution as the tethered chain. These are the more conventional tethers. Some other examples are single crystal surfaces of crystalline-amorphous diblock copolymers, the interface of a diblock micelle where the corona is the tether, or
the interface between microphase-separated diblocks in the melt. At extremely high tethering densities and high molecular weights, the tethered polymers are referred to as polymer brushes. It is also possible to create molecular brushes (Figure 2.1f). Here, the polymer backbone acts as the substrate and a high density of grafted side chains are the brushes.

![Figure 2.1 Schematic of tethered polymer systems.](image)

Tethered polymer systems are defined by a 2-dimensional concentration, or tethering density, $\sigma$. The number of tethering points in a given area ($S$) is the tethering density ($\sigma = 1/S$). $S$ is typically defined as the distance between tethering points, $r$, squared ($S = r^2$). The tethering density is an effective way to define an isolated system; however, if one wants to compare systems with different molecular weights or solvent conditions, $\sigma$ does not take into account any volumetric considerations for the size of the chain. In this case, a reduced tethering density, $\tilde{\sigma}$, is a better choice. $\tilde{\sigma}$ is defined as
\( \sigma \pi R_g^2 \) \cite{23}, the radius of gyration, \( R_g^2 \), accounts for the size of the chain, which is a function of molecular weight and solvent quality. By using \( \bar{\sigma} \) instead of \( \sigma \), it is possible to compare multiple systems. As a rule of thumb, \( \bar{\sigma} = 1 \) is when the chains begin to touch at the outermost radius. This does not, however, result in large enough tethering densities required to change the chain conformation.

Before any experimental work was done on the properties of tethered polymers, they were analyzed theoretically. The approach was to evaluate the conformation and monomer density of polymer brushes. One analysis was done using scaling laws.\cite{24,25} These studies assumed that the free chain-end was confined to a single plane at the outermost distance from the substrate which resulted in a step function for the monomer density. The next approach was to use self-consistent field theory (SCF) to analyze these conformations.\cite{3,26-28} The SCF model found a monomer density that followed a parabolic profile. Following these two base studies for polymer brushes, numerical treatments, as well as computer simulations, have been performed on tethered chains from low to high tethering densities. A full discussion of all theoretical and simulation work on tethered polymers follows.

2.1 Theoretical/Simulation Studies of Tethered Polymer Chains

There have been many attempts to model the tethered polymer system using a variety of numerical, analytical, and simulation approaches. In this section, a brief summary of all relevant studies with a focus on the more prevalent ones will be provided. In almost all of the studies, the main parameters of interest are monomer (segment)
density, height (thickness), and free chain-end location. Each of the three tethered regimes (non-interacting, interacting, and stretched brush) have been investigated individually; however, there has been little work on the transition from one regime to the next. The difficulty of this type of study lies in the complex changes in interaction as one goes from one regime to the next. The overview of these works will look at the assessment of tethered chains in the high, moderate, and low tethering density regimes.

2.1.1 High Tethering Density Regime (Polymer Brushes)

Early studies of tethered polymer chains addressed the highest tethering densities. Alexander,[24] with further elaboration by de Gennes[25] and Cantor,[29] used scaling law approximations to analyze the conformation of the polymers at tethering densities where the distance between tethering points are much smaller than the size of the chains, \( r \ll R_g \). At these tethering densities, the increased free energy of packing the large chains into a small volume results in a stretching of the chains perpendicular to the substrate. The stretching is an entropic contribution to the free energy of the system, which can be defined as:

\[
\begin{align*}
    f &= f_{sp} + f_{pp} + f_{el} \\
    &= f_{sp} + f_{pp} + f_{el}
\end{align*}
\] (2.1)

where \( f \) is the free energy, \( f_{sp} \) is the free energy associated with the substrate-polymer interactions, \( f_{pp} \) is the interchain interaction, and \( f_{el} \) is the elastic free energy of stretching. The substrate-polymer interaction is ignored in this scenario, and thus \( f_{sp} = 0 \). The polymer-polymer interaction can be modeled using the “Flory approximation.”[30] Using this assumption,
\[ f_{pp} \sim k_B T \nu N \varphi = \frac{k_B T \nu N^2 a^3 \sigma}{L} \]  \hspace{1cm} (2.2)

where
\[ \varphi = \frac{N a^3}{\nu^2 L} = N a^3 \sigma L \]  \hspace{1cm} (2.3)

and \( k_B \) is the Boltzmann constant, \( T \) is the temperature, \( \nu \) is the excluded volume parameter, \( N \) is the number of segments, \( \varphi \) is the segment concentration inside the layer, \( a \) is the size of the segment, and \( L \) is the layer thickness (height). The final term in equation 2.1 can be defined as:
\[ f_{el} = \frac{3}{2} kT \left( \frac{L^2}{R_0^2} + \frac{R_0^2}{L^2} \right) \]  \hspace{1cm} (2.4)

where \( R_0 \) is the unperturbed radius. For tethered chains in the stretched brush regime, \( L \gg R_0 \); therefore, \( R_0^2/L^2 \) is negligible. Combining equations 2.1, 2.2 and 2.4, the free energy of the polymer brush scales as:
\[ f \sim kT \left( \frac{\nu N^2 a^3 \sigma}{L} + \frac{L^2}{R_0^2} \right) \]  \hspace{1cm} (2.5)

where the prefactor, \( 3/2 \), was removed to simplify the scaling.

The next step is to derive the equilibrium thickness \( (L_{eq}) \) of the brushes by minimizing the free energy. Taking the derivative with respect to \( L \) and setting it equal to zero results in the following expression for \( L_{eq} \):
\[ L_{eq} \sim N^{\nu/3} a^{5/3} \sigma^{1/3} \]  \hspace{1cm} (2.6)

This relationship provides the dependence of the equilibrium brush thickness on molecular weight, \( N \), and tethering density, \( \sigma \), where \( \nu \) and \( a \) are constant. The thickness is proportional to \( N \), and it has a power law relation with \( \sigma \) \( (L_{eq} \sim \sigma^{1/3}) \). The major
assumptions of this theory are that the segment density (concentration), $\varphi$, is constant from $z = 0$ to $z = L$, where $z$ is the coordinate perpendicular to the substrate and that all chain-ends are confined to the layer, $z = L$. This results in a step-like function for $\varphi(z)$. All relevant dimensions and parameters for the theoretical treatment of polymer brushes can be found in Figure 2.2.

Self-consistent field (SCF) theory is another approach for analyzing the structure of polymer brushes. Here, two methods were adopted, analytical (aSCF)$^{[3,26,27,31-36]}$ and numerical (nSCF)$^{[28,37-41]}$. The SCF theory allows the chain-ends’ location and segment density to assume equilibrium conformations without being restricted by the assumptions imposed by the scaling theory. This allows the SCF theory to more closely model the real system.

![Figure 2.2 Schematic of the relevant parameters for analysis of polymer brushes.](image)

In the analytical solution, the main assumption is that the tethering density is large enough (in the polymer brush regime) that lateral inhomogeneities do not exist. This is implicit for all mean-field approaches. In addition, the free chain-end location is simply a function of the distance from the substrate, and back-folding of the chains is prohibited.
From these constraints, the chains were allowed to adopt their most probable conformation.

The tethered polymer system is constructed by assigning each monomer to a given coordinate. They are then allowed to fluctuate in the $z$-direction only because the density is high enough in the $xy$-plane that motion is highly restricted. The most probable conformation is a balance of stretching energy and Flory-like, excluded-volume interactions (interchain). Each chain has a maximum size similar to its end-to-end distance. Because the chain-end can be located within the layer, the segment density profile was much different. In the scaling law, all of the chain-ends are at the same distance from the substrate. As mentioned, this led to a step function for the profile with a constant value within the layer. In the SCF case, the inclusion of chain-ends created a variable segment density, especially near the surface. The analytical solution shows that the segment density profile, $\phi(z)$, now adopted a parabolic shape of the type $\phi(z) = \phi_{\text{substrate}} - cz^2$, where $c$ is a constant (see Figure 2.3). The density maintained a maximum at the substrate but decreased continuously to zero at the free surface. Although the profile has changed, the free energy calculation still led to the same scaling of thickness with tethering density, $L \sim \sigma^{1/3}$. This calculation gives a more reasonable prediction for the real system; however, the restriction of no back-folding is still unrealistic. The numerical solution of the SCF equations (nSCF) released this restriction.

The nSCF used numerical solution techniques to allow fluctuations of the system after it reached the most probable conformation. These fluctuations did not exclude back-folding of the chains. The equation for the conformation of the chain was discretized with a given grid spacing (corresponding to the Kuhn length), and an iterative
method was used to solve for the density and free energy. The results for the nSCF method are very similar to the aSCF results. The main differences are: 1) the location of the maximum monomer density is not at the substrate but at \( z^* \) and 2) the profile exhibits an extended tail at the layer surface. The \( \phi(z) \) profile for \( z > z^* \) is still approximately parabolic, as in Figure 2.3, and the free energy analysis still shows a scaling of \( L \sim \sigma^{1/3} \). A maximum was found at \( 0 < z \ll L \) with a depletion layer above the tethering point of the chain. The tail near \( z = L \) becomes negligible as \( \sigma \) increases.

Figure 2.3 illustrates the different \( \phi(z) \) profiles for the scaling theory (Alexander/de Gennes), analytical self-consistent field theory (aSCF), and numerical self-consistent field theory (nSCF). It is evident that each theoretical treatment of polymer brushes has different results. As one goes from scaling to the nSCF, the theoretical assumptions approach the real system. The scaling law exhibits a step-like profile with all of the chain-ends at the surface. The aSCF profile allows the chain-ends to be within the layer, and the profile becomes parabolic in shape with a maximum at the substrate. The nSCF also exhibits the parabolic shape for the segment density. Unlike the aSCF approach, the nSCF has a depletion layer with a maximum at \( 0 < z \ll L \). Experimental results, which will be presented in Section 2.3.1, verify the nSCF profile. Corrections to the aSCF theory by Kim and Matsen\textsuperscript{[42]} have included a depletion layer and extended tail as found in the nSCF theory.

Some new analyses of these constructions use other corrections to address issues such as the degree of stretching.\textsuperscript{[43, 44]} Netz and Shick\textsuperscript{[43]} introduced a new parameter, \( \beta_{st} \), to represent the degree of stretching. At low \( \beta_{st} \) values, the fluctuations near the substrate became increasingly important and led to deviations from the parabolic profile. As \( \beta_{st} \rightarrow \)
their mean-field theory agreed well with the aSCF results. In another approach, Manciu and Ruckstein\textsuperscript{[44]} addressed similar concerns; however, they modeled the system at high stretching to ultra-high stretching where a step-like profile appeared.

![Figure 2.3 Rough segment density profile sketches for the scaling theory, the aSCF theory, and the nSCF theory.](image)

Figure 2.3 Rough segment density profile sketches for the scaling theory, the aSCF theory, and the nSCF theory.

The presented theoretical approaches are only applicable at high tethering densities, or in the brush regime. The SCF equations became less reliable at tethering densities below the transition; therefore, new techniques needed to be developed to model systems in the interacting regime or in the non-interacting regime.

2.1.2 Intermediate Tethering Density Regime

The intermediate tethering density regime includes the interacting regime and transitions in and out of that state. This regime is also referred to the quasi-brush, pseudo-brush, crossover, or semi-dilute regime. The interacting regime consists of several different interactions, including intra-molecular, intermolecular (though not strong enough for high stretching), and substrate-polymer interactions. This creates a
more complex system to be modeled. Here, a single chain mean-field theory (SCMF) is used to determine the thermodynamic properties of the tethered polymer system.\[45-49\]

Little work has been done on the interacting regime, but the leading theoretical development is the SCMF theory. The SCMF theory has one major difference compared to the SCF theory discussed in the previous section. In the SCF theory, interactions between same chain and neighboring chain segments can not be distinguished. For SCMF, the equations explicitly account for \textit{intra}-chain interactions and \textit{inter}-chain interactions. The chain is constructed using the intra-chain interactions; while, the boundary conditions set the inter-chain interactions. This leads to significantly different results.

The central output of the SCMF theory is the probability distribution function of chain conformations. From this, all other conformational and thermodynamic quantities can be calculated, such as the height, density profile, osmotic pressure, and shape of the chain. The results for the segment density have shown similar results to the SCF model. A parabolic profile is found with increased flattening as the tethering density increases to a value where stretching is dominant. Because the SCMF model includes solvent molecule considerations, the flattening is an indication of increased osmotic pressure as well. The thickness and free energy of the layers were compared with the scaling predictions of Alexander/de Gennes and the SCF theory. It was found that the SCMF results do not follow the predicted scaling at the given tethering densities. From this, it can be concluded that the interaction (crossover) regime is broad compared with the non-interacting and brush regimes.
The validity of this theory was derived from comparison with experimental results by Kent et al. (see Ref 23, 45, and 47). An in-depth discussion of these results will be addressed in Section 2.3.2. For now, it is sufficient to say that the SCMF theory is an accurate means of analyzing the conformations and transitions of tethered polymer layers as their inter-chain interactions increase prior to the stretched state. The authors have also evaluated differences in solvent quality on the presented results.\[48\]

2.1.3 Low Tethering Density Regime

The final regime to discuss is the low tethering density regime. This can be defined as the regime where $\tilde{\sigma} << 1$, or far from interacting. Here, the relevant interactions are the intra-chain interactions as well as those with the substrate. In most cases, the interaction between the substrate and the chain is treated as neutral or repulsive. The chain, then, adopts a coil (mushroom) geometry in good solvent or a globule geometry in poor solvent. Because the chain conformation is not strongly affected by the substrate, the dimensions are similar to those of the unperturbed, untethered polymer. If, however, there is a strong attraction between the tether and substrate, the segments attempt to maximize the number of surface interactions. For this case, a new geometry is observed. The chain adopts a pancake-like conformation where the segment density is extremely high near the surface, and the chain dimensions are highly perturbed. For a visual representation of the three conformations, see Figure 2.4.

The density profiles of these various conformations were calculated by Adamuti-Trache et al.\[50\] using renormalization group theory. However, a transition from an
adsorbed state (pancake) to the brush state was predicted by Alexander[24] and further analyzed by Ligoure[51] and Ou-Yang and Gao[52] much earlier. In order to follow the style of the previous sections, these results will not be discussed in great detail. This section will focus on the evaluation of the segment density for individual molecules (low $\sigma$) in the adsorbed or desorbed state.

Figure 2.4 Single chain conformations with varying substrate and solvent interactions. (a) neutral or repulsive tether-substrate interactions in good solvent (b) neutral or repulsive tether-substrate interactions in poor solvent (c) attractive interactions in good solvent (d) attractive interactions poor solvent.

The renormalization group theory (RG) evaluated the tethered chains without idealized models and in the presence of fluctuation effects. The intermolecular interactions were irrelevant for this system. The only interactions considered are the intra-chain and substrate-chain. The results showed that the segment density is much higher near the surface with high substrate-chain interactions. There was a sharp, exponential-like decay in the density as $z$ is increased. This is representative of the “pancake” conformation. With highly repulsive interactions, a parabolic profile similar to the nSCF theory was found. The maximum was located around the $R_g$ of the chain,
which is indicative of the unperturbed dimensions despite tethering (Figure 2.4a and 2.4b). For interactions between these two extremes, the profiles exhibited behavior between the pancake and unperturbed states.

The RG theory did not take into account the transition from the pancake conformation to the brush state with changes in tethering density. This was briefly discussed by Alexander[24] and Ligoure.[51] The initial hypothesis was that the transition should be similar to a first-order phase transition; however, after analysis using the Guiselin model,[53] Ligoure found that what exists is a transition to a quasi-brush regime (similar to the interacting regime) that is not first order. These results matched well with the experimental results of Ou-Yang and Gao.[52]

The central goal of the research presented in this dissertation is to determine the transition from the non-interacting regime into the interacting regime. In this case, the conformation of the chains can be quite different as described by the RG theory. We have used materials with favorable substrate-chain interactions and unfavorable ones. The pancake or typical unperturbed conformations play a role in the location of this transition as compared among the different materials.

2.1.4 Simulations

The validity of these numerical approximations for the chain conformations at varying tethering densities can be supported by simulation results. The use of Monte Carlo (MC) and Molecular Dynamics (MD) methods has allowed researchers to model these tethered polymer systems. Two approaches can be taken and will be broken down
as such within this section. The first is to look at a collection of chains at a given
tethering density and given solvent conditions. The second is to simulate the
conformations of a single chain with variable interactions, i.e. solvent, substrate, and
monomer. Again, the main focus will be the segment density profile for these
simulations with minor discussions on transitions from one regime to the next. A
comparison of the simulations with the previously stated theories will also be provided.

2.1.4.1 Multiple Chain Simulations

Since the 1990’s, many attempts have been made to simulate tethered chain
systems using Monte Carlo\cite{54-58} and Molecular Dynamics\cite{59-63} techniques. Equipped
with the knowledge obtained from the theoretical methods, these researchers were able to
find the probable segment density profiles for these systems, including the relationship of
thickness, $L$, and $\sigma$, or $\Sigma$ (in this case a simple dimensionless quantity similar to $\tilde{\sigma}$).

Multiple chain simulations are an array of tethered chains with $N$ number of
segments (or monomers) per chain and a tethering density of $\sigma$ in a simulation box.
Typically, $N$ equals multiples of ten, sixteen, or fifty. The first segment is placed on the
impermeable substrate at $z = 0$. All successive segments are attached following a given
lattice or bond-distance. In both simulations, the interaction between the monomers is
representative of the solvent quality. For example, high attractive monomer interaction
represents poor solvent conditions. In some MD simulations, the solvent interactions
have been taken into account explicitly. In this case, the beads are subject to three
different potential contributions: the potential with connected beads (bead-spring model),
the potential with the surrounding solvent, and the potential due to non-connected beads. The difference between the two methodologies lies in the way to obtain equilibrium properties. For MC, an attempt is made to move chain segments from one position to another, and the change in energy is assessed to decide if the move is accepted. For MD, the classical equations of motion are solved numerically to allow relaxation to equilibrium. A more thorough summary of these techniques can be found in the book by Grest and Murat.\cite{64}

![Figure 2.5 Simulations of tethered polymer chains (a) using MC (b) using MD. The segment density profile ($\phi(z)$) as a function of distance ($z$) from the substrate. In (a), the symbols represent different tethering densities, $\sigma$, ($\blacktriangle = 0.12$, $\blacksquare = 0.08$, $\bullet = 0.04$) for $N = 99$, and the lines are parabolic fits.\cite{55} In (b), the sets of lines represent $N = 50$, 100, and 200, and each set represents different tethering densities ($\sigma = 0.03$, 0.07, 0.10).\cite{60}]

In all studies, the main results revolved around the $\phi(z)$ profile and changes therein. Although several different articles surrounding this topic have been published, the changes from one to another, typically in formalisms and treatment of the simulations, are minimal. The ever-present theme is that the $\phi(z)$ profile remains fairly consistent and comparable to the theoretical treatments. As one example, the results of Chakrabarti and Toral’s MC simulations\cite{55} exhibit the parabolic profile seen in the aSCF
theory (see Figure 2.5a). The MD simulations of Murat and Grest[60] also show the parabolic profile, though closer to the nSCF model (Figure 2.5b). Figure 2.5 also shows the change in profile with increasing tethering density. These results match well with those of the SCMF theory[47] which showed that the increased osmotic pressure at higher σ flattens the peak in the parabola.

Results for the scaling of the first moment of the chains, <z>, similar to L, and size perpendicular to the substrate, \( R_{g,z}^2 \), have shown that the grafting densities of these chains reached into the stretched brush regime. Lai and Binder[56] and Murat and Grest[59] have used the predicted scaling of \( L \sim N\sigma^{1/3} \) to obtain the onset of the stretched regime. Figure 2.6 shows their results. It can be seen that only at high values of \( N\sigma^{1/3} \) was the fitting to the lines met.

![Figure 2.6 Results for first moment, <z>, and z-component of the \( R_g^2 \), \( R_{g,z}^2 \), as a function of \( N\sigma^{1/3} \) (a) using MC simulations (b) using MD simulations. Upper curve in (a) is layer thickness while the bottom curve is \( R_{g,z}^2 \). Data along the y-axis in (b) is scaled by \( N\sigma^{1/3} \). Fitting to the lines represents the stretched brush regime, matching to scaling and SCF theories.[56,59]

In one set of simulations, Descas and coworkers[65-66] looked at the affect of adsorption on the state of each of the tethering regimes. Figure 2.7 is a schematic
illustration of their findings. Using MC simulations combined with scaling theory, they established the mushroom (DE in Figure 2.7) and brush (B in Figure 2.7) regimes for neutral or repulsive surfaces but found a slightly different set of states when adsorption is involved. It should be noted that their “brush” regime is representative of the interacting regime as discussed here, not the stretched brush regime defined as the “brush” regime in Section 2.1.1.

The system was modeled as a set of blobs, de Gennes blobs\(^{[25]}\) of size \(\xi\) for unadsorbed chains or tails, and adsorption blobs, or blobs made of adsorbed segments, of size \(\lambda\). de Gennes blobs are open circles in Figure 2.7; while, adsorption blobs are dark circles. In principle, \(\lambda < \xi\) except in the situation where the tethering density and adsorption are such that the surface is completely covered by adsorption blobs, then, \(\xi \approx \lambda\). Adsorption is achieved when \(\kappa > \kappa_c\), where \(\kappa\) is the dimensionless adsorption strength \((\varepsilon/\varepsilon_c - 1)\).

For attractive surfaces, \(\kappa > \kappa_c\) and low \(\sigma\), adsorption led to the pancake conformation (AE), as described by the RG theory. As the tethering density increased, there existed a second regime called the ASD regime. In this regime, individual chains begin experiencing interchain interactions, but the layer thickness does not change \((L \sim \lambda)\). The OSA (over-saturated adsorbed) state is the adsorbed semi-dilute state \((\xi \approx \lambda, L > \lambda)\). This transitional state occurred for finite length chains when the substrate was completely covered by segments, and loops and tails appear creating a slightly higher layer thickness. The final state is comparable to the “brush” state and is called the over-saturated brush state (OSB). The OSA and OSB states merge at high \(\kappa\). In the OSB
state, the layer thickness increases with $\sigma$. Finally, by comparing the chain dimensions with scaling laws, the authors were able to verify the existence of these states in MC simulations.

![Figure 2.7](image)

Figure 2.7 Schematic of the states of tethered polymer chains in desorbed ($\kappa < \kappa_c$) and adsorbed ($\kappa > \kappa_c$) states. The transitions in chain conformation ($\sigma^*$) are effected by $\kappa$. Single chain conformations (DE and AE) will be discussed in more detail later.\[66\]

The MC and MD methods and studies have shown that the predictions of the SCF and SCMF theories match well with the simulated data. More recent studies have been done on slightly different systems. Their results are beyond the scope of this dissertation; however, they will be mentioned briefly here. The first is a study on the effects of curved surfaces on the density profiles and predicted regimes or phases.\[67\] A second looks specifically at the entropic contributions in tethered systems.\[68\] Density functional theory has also been applied to tethered systems where the solvent was accounted for in the model.\[69\] These results match well with the simulations of Grest and Murat.\[60\] Finally, a third transition to a highly, or fully, stretched regime has been observed in good
solvent by Coluzza and Hansen\textsuperscript{[70]} using MC simulations, though the results are currently under debate.

2.1.4.2 Single Chain Simulations

Simulations of single chains are pertinent for studies of chain conformations at low tethering densities, or in the non-interacting regime. The RG theory shows that the chains form pancake conformations with high attraction to the substrate, but unperturbed coil conformations are formed with repulsive or neutral interactions. These conformations could likely play a key role in the transition into the interacting regime. It is, therefore, important to understand the segment densities, dimensions, and state transitions for the single chain with varying environmental constraints, such as solvent quality and interaction with the substrate.

The common approach for this type of study is to use MC simulations with varying chain lengths. As the chain length increases, the system approaches the pure thermodynamic state for transitions from coils to globules and desorbed to adsorbed ($N \rightarrow \infty$).\textsuperscript{[71]} Since a real polymer chain follows this same rule, simulating chains of very large $N$ is not necessary to investigate transitions of finite chains. In addition, chains with large $N$ take more computational time. Therefore, most simulations are carried out with $16 < N < 200$, which provides sufficient results for comparison to real chains.
A study of interest was done by Cosgrove and coworkers. They used MC simulations and SCF models to compare the segment densities of tethered chains in the adsorbed (pancake) and desorbed (coil) states. Figure 2.8 is a reproduction of their results for chains of $N = 50$ and $\sigma = 1.0$. The variable for distance from the substrate used here is the layer number, $z'$, which is representative of the number of lattice units. The dashed line represents the simulations. The solid line represents the SCF theory using a cubic lattice, and the dotted line represents the SCF theory using a hexagonal lattice. This SCF theory was applied for polymer adsorption, where the attractive
interaction can be varied, as developed by Scheutjens and Fleer.\[^{72,73}\] It can be seen that the simulations follow the SCF theory quite well. In the adsorbed case, $\varphi(z)$ is maximized near the substrate ($z' = 0$). For the desorbed case, the simulation results match well with the hexagonal lattice SCF results. These are also comparable to the nSCF results where there is a depletion layer near $z' = 0$ and a maximum at some distance $z > 0$ (or layer $z' > 0$).

Next, we can take a look at the dimensions of the chain both laterally, $R_{g,xy}^2$, and perpendicular to the substrate, $R_{g,z}^2$, as the interaction with the substrate, denoted here as $\varepsilon_s$, changes. Eisenriegler and coworkers\[^{71}\] first addressed this problem with chain dimensions after adsorption or in the presence of an impenetrable wall. The prevailing thought was that the chain can no longer maintain its three-dimensional random walk and is forced into assuming more of a two-dimensional conformation. In addition, if adsorption occurs, the number of monomers that interact with the substrate should be maximized, again affecting the size in two-dimensions. It was predicted, and further confirmed by MC simulations, that the scaling of the $R_g^2$ changes with the dimensionality of the chain. For three-dimensional chains in good solvent, the relationship $R_g^2 \propto N^{0.59}$ holds.\[^{74}\] In two dimensions, however, the relationship changes to $R_g^2 \propto N^{0.75}$. This was confirmed by measuring the $R_{g,xy}^2$ for highly adsorbed chains, and it is often used as the criterion for the onset of chain adsorption.\[^{75-76}\] In this case, $R_{g,z}^2$ was independent of $N$ due to the high adsorption energy.\[^{77}\] The dimensions for intermediate adsorption energies must be determined directly.
Additionally, a Langevin dynamics study by Shang and Geva\cite{78} determined the $R_g^2$ distributions for tethered and untethered chains in varying solvent conditions with either attractive or repulsive surface interactions. Their probability distributions indicated that a similar phenomenon occurs where the adsorbed chain dimensions have a larger dependence on $N$ for good solvent conditions. The results for poor solvent conditions are less convincing due to the measure of overall $R_g^2$. A much larger value was found for the adsorbed case. Here, the prevailing dimension is the $R_{g,xy}^2$, which becomes equal to $R_g^2$ for adsorption. In the case of repulsive surfaces, the chain dimensions for tethered and untethered chains were similar, as would be expected.

Lastly, let us address the issue of transitions from one state to another. As mentioned in the previous paragraph, one criterion for identifying an adsorbed chain is the change from $R_g^2 \propto N^{0.59}$ to $R_g^2 \propto N^{0.75}$. At varying monomer-substrate attraction energies, one can measure the simulation $R_g^2$ to obtain the value for adsorption.\cite{71,75-76} These studies dealt specifically with untethered chains; however, the transition value for tethered chains did not vary significantly.\cite{79-82} Some of these studies focused on traditional parameters for tethered chains, such as segment density, end-segment density, and number of adsorbed segments,\cite{79-80} while others focused on creating phase maps for a tethered chain.\cite{81-82} For the former studies, results indicated that the adsorbed chains formed pancake structures at a critical interaction value around $0.98 < \varepsilon_{sc} < 1.01$, depending on the method of analysis, and all tethered characteristics matched those of the previous studies. For the latter, phase maps for coil-to-globule (good-to-poor solvent conditions) and desorbed-to-adsorbed (monomer-substrate interaction) transitions were established. It should be noted again that these values are slightly dependent on $N$
because of the constraint that \( N \) is finite, and therefore, these transitions do not correspond to true thermodynamic values.

![Phase diagram of a tethered chain with length \( N = 64 \).](image)

Figure 2.9 Phase diagram of a tethered chain with length \( N = 64 \). For breakdown of the different states and their transitions, see the text. The DE and AE states are the same as Figure 2.7. \cite{81}

The relevant study focuses on the phase map of a flexible chain using the bond-fluctuation model. Luettmer-Strathmann and coworkers\cite{81} used a Wang-Landau algorithm\cite{83} to determine the chain conformations with varying interactions. To model the solvent conditions, the monomer-monomer interaction, \( \varepsilon_b \), was used to calculate the field variable, \( \beta_b \), where \( \beta_b = -\varepsilon_b/kT \). This value was varied where an increase in \( \beta_b \) is equivalent to a decrease in solvent quality. Monomer-substrate interaction, \( \varepsilon_s \), was utilized similarly with \( \beta_s \), which was varied to induce adsorption. As discussed in several previous works,\cite{84-87} there are five predicted states for the tethered chain. They are: a) desorbed-extended (DE), b) desorbed-compact (DC), c) adsorbed-extended (AE), d) adsorbed-compact (AC), and e) layered states (LS). In each, “extended” represents a coil conformation; while, “compact” represents a dense conformation. The layered states are intermediates between the DC and AC states; they consist of “layers” of monomers in the
z-plane until complete adsorption is achieved. Using MC simulations, the authors were able to obtain a phase diagram (see Figure 2.9) of each of these conformations as a function of the given field variables. An additional transition was found from the AE state to the AC state. Here, the adsorbed chain collapsed from the extended state to the compact state without desorbing.

In summary, the analytical and simulation results have provided a basis for the different regimes in tethered polymer systems, namely the non-interacting, interacting, and stretched brush regimes. They have successfully predicted the segment density profile for each of these regimes. In addition, the chain dimensions of the adsorbed state are significantly different than in the unadsorbed or untethered state, making the calculation of \( \bar{\sigma} \) in real systems more complicated. The analysis of transitions from one state to the next is difficult to obtain in simulations considering the diversity of system interactions with increasing tethering density. Experimental approaches have been made to determine the transition values and will be discussed in Section 2.3.

2.2 Experimental Methods of Preparing Tethered Polymer Chains

There are many ways to create tethered chains on a substrate or at an interface as briefly described in the introduction to Chapter II. The three main methods are physical adsorption, chemical attachment, and interfaces of diblock copolymers.\(^{[1]}\) This section will describe the various ways to exploit these methods to manufacture tethered chains with variable tethering densities. Within the physical interaction method, there is adsorption to a substrate or interface. The chemical attachment method utilizes either
preformed polymers or *in-situ* polymerization. Finally, diblock copolymers can include the interfaces in the melt, solution, or crystallized states; however, the study of tethers on flat surfaces is mainly restricted to the use of solution grown single crystals of crystalline-amorphous diblock copolymers. From a physics standpoint, the most appropriate way to study these polymers is to tether them to a solid substrate; however, some examples of adsorption to the surface of a liquid will be discussed.

The main goal of each of these methods is to have good control over the desired parameters to study the regime transitions. These parameters are mainly the tethering density and the molecular weight of the polymer. The exact tethering density and well-controlled molecular weights are both imperative to finding the proper $\sigma$ to define the system. In each section, a brief summary of the advantages and disadvantages of the presented method will be included.

2.2.1 Physical Interaction Methods

In the physical interaction methods, the polymer chains are always preformed. These can be either homopolymers or block copolymers.\[1\] In the case of homopolymers, a single end-group adsorbs to the substrate or interface; while, in the block copolymer case (either di- or triblock), a single block, or single chemical structure, adsorbs. The other block forms the tethered chain (see Figure 2.1b). In most cases, the adsorption of the end-group in the homopolymer tether leads to a chemical reaction. An in-depth discussion of the adsorption of diblock copolymers will be given here. There are two methods to physisorb diblock copolymers. One is using selective solvent where one
block attaches to the surface due to unfavorable solvent interactions. This is often used for creating a tethered polymer system on the liquid-air interface but also applies to adsorption to a solid substrate. The other, as mentioned earlier, is adsorption onto a substrate through attractive interactions of one block.

2.2.1.1 Adsorption onto a Solid Substrate

As an example of adsorption onto a solid interface, we will look specifically at the research of Parsonage and coworkers. In this study, a diblock copolymer of poly(2-vinyl pyridine) (PVP) and polystyrene (PS) was used for adsorption onto oxidized silicon and mica substrates. From a dilute solution of toluene (100 μg/mL), the PVP-PS was adsorbed onto the substrates after exposure for several days. The PVP formed the anchoring block due to insolubility in toluene; the PS block formed the tethered polymer. Using scintillation counting (the copolymer was labeled with tritium) and x-ray photon spectroscopy (XPS), the authors were able to determine the adsorbed amount. They found that there were no differences between the two substrates.

The authors compared σ with the ratio of the sizes of each block. It was found that with nearly symmetric blocks, the PVP, or anchoring block, played a larger role in determining the adsorbed amount. This implies that the anchoring energy dominated over the free energy of the tethered PS. However, for high asymmetric blocks, the molecular weight of the PS block dominated the adsorption. This occurs because the adsorption was not based on block-substrate attractive interactions and the solvation of the PS block led to better adsorption.
The advantages of using the physisorption of diblock copolymers are as follows. First, the use of pre-made polymeric material allows for good control over the molecular weight. Second, control over narrow polydispersity is also achieved. By having a well-defined molecular weight, it is easier to determine the size of the tethered chains to calculate $\tilde{\sigma}$. All theoretical treatments of tethered polymer systems assume a monodisperse sample. As discussed earlier, these parameters are important in defining the tethered system. Finally, the interactions of one block with the substrate are in dynamic equilibrium with the solution. Then, the study of the free energy driving force to form tethered layers and its balance with the free energy of the tethered layer itself is possible.

The disadvantages of this method include the inability to form high $\tilde{\sigma}$ layers. In this technique, $\tilde{\sigma}$ is increased by the addition of material to an already formed layer. The initially adsorbed polymers form a steric boundary through which the free polymers have difficulty adsorbing to the surface. Also, because the adsorption is in kinetic equilibrium, as discussed previously, the addition of more chains may lead to desorption of those originally adsorbed.

2.2.1.2 Adsorption onto a Fluid Surface

The second type of physisorption is onto a fluid-air interface. This is typically referred to as the Langmuir-Blodgett technique. A diblock copolymer is used (or a homopolymer with a large end-group) where one block has an affinity for the surface,
while the other has an affinity for the solvent. The surface block (or end-group) forms the anchoring point, and the solvated block forms the tether as shown in Figure 2.10.

![Figure 2.10 Schematic illustration of Langmuir monolayers of diblock copolymer for tethered chain studies.](image)

Kent and coworkers\[^{23}\] studied many systems of diblock copolymers adsorbed onto fluid surfaces. Typically, a diblock system of poly(dimethylsiloxane)-block-PS (PDMS-b-PS) was used in a variety of solvents. In this example, the PDMS formed the anchoring block at the solvent surface. The solvent quality for the PS block was changed to illustrate differences for good and poor solvents. This is possible due to the large difference in surface tension between the PDMS and PS. The PDMS block will preferentially adsorb to the surface for a wide variety of solvents.

Two methods of spreading can be used to form the monolayers on the fluid. One method is to deposit the dry grain onto the surface of the solvent. The second is to use dilute solution. In this case, chloroform was used because it is a good solvent for both blocks. To increase the surface density, either successive additions of the spreading solution were added or a movable barrier was used. In the trough where the monolayers were formed, a solid barrier was submerged. By moving the solid barrier, it was possible to increase or decrease the surface area available for the adsorbed monolayer. The adsorbed amount was measured using neutron reflectivity of deuterated copolymer
samples. As in the solid substrate example, the amount of adsorbed polymer as compared to block molecular weight, solvent quality, and specifically for this case, surface pressure was measured. This study was used to determine the transition values as a function of $\tilde{\sigma}$ and will be discussed in detail in Section 2.3.

The advantages and disadvantages of this method are similar to those for the solid substrate adsorption. The use of pre-made polymeric samples always has the advantage of control over molecular weight and molecular weight distribution. This method also has the advantage of providing more control over the tethering density through the use of the movable barrier; however, this technique may also disturb the adsorption equilibrium by desorbing material as the surface pressure increases.

The advantages and disadvantages presented in each section are general for methods with pre-made polymers. Chemical attachment methods also include the adsorption and reaction of pre-made homopolymers with reactive end-groups with an opportunity for slightly higher $\tilde{\sigma}$ due to smaller end-groups. Due to the disadvantage of low $\tilde{\sigma}$ in the physical interaction technique, additional methods have been developed for better control of the tethering density. One such method was developed from the chemical attachment of polymer chains.

2.2.2 Chemical Attachment Methods

Chemical attachment methods involve the chemical reaction between the tethered polymer chain and the substrate surface. The first technique, known as the “grafting-to” approach, involves the reaction of a functionalized end-group on a pre-made...
polymer with the substrate. The second is the immobilization of the initiator onto the surface to polymerize directly from the substrate. This is known as the “grafting-from” approach.\textsuperscript{[100-108]} Both of these methods lead to strongly bound tethered chains due to the chemical bond between the chain and the substrate, unlike the physical interaction method which is driven by secondary bonding, such as van der Waals’ or hydrogen bonding. A brief description of the “grafting-to” and “grafting-from” approaches will illustrate the advantages and disadvantages of each.

2.2.2.1 “Grafting-To” Methods

In the “grafting-to” method, homopolymers are synthesized using typical controlled polymerization techniques. The polymer is then capped with a reactive end-group, such as thiol for reaction with a gold surface,\textsuperscript{[95]} to chemically react with the given substrate. Typical reactions include -SH with gold and -OH or -SiX with the oxide layer on silicon. Solutions of the end-capped chains are exposed to the given substrate and allowed to react over time. As the exposure time increases, the tethering density increases, typically until the surface is completely covered. The reaction of a single atom per chain with the substrate means a large number of grafting sites are available. Some evidence suggests that grafting continues to occur after this point but at a much slower rate.\textsuperscript{[99]}

The advantages and disadvantages of the “grafting-to” method are similar to those for the physical interaction methods because of the use of pre-made polymers. The main advantages of using “grafting-to” over those methods are that the tethering energy is
much higher and that it creates a more robust system. Also, the surface area of coverage is much higher because of the reaction of a single end-group as compared to the spreading of an entire block. This inherently allows for higher tethering densities; however, at increasing molecular weights, the steric hindrance of the tethers prevents further grafting of additional chains by restricting the reactive end-group from diffusing to the substrate. This has been illustrated in the three grafting kinetics regimes in Ref. 99.

More recently, new methods have been developed to help alleviate some of the difficulties associated with the steric properties. One of these techniques is known as MAPA (mechanically assisted polymer assembly). In this technique, an elastomeric polymer film, PDMS, is used as the substrate. The elastomer is stretched to expose more surface area for grafting. The stretched PDMS is exposed to UV radiation and ozone to form a hydroxyl layer. This layer can then be introduced to a solution of polymer for the grafting-to reaction (or initiator for grafting-from). After the reaction is conducted, the stretching strain is released. Then, the surface area of the substrate greatly decreases (after the tethered layer has been formed) leading to higher $\sigma$. The relationship between the initial strain and $\sigma$ has been determined.

2.2.2.2 “Grafting-From” Methods

The “grafting-from” method has become the most widely used technique for creating tethered polymer systems, including polymer brush systems. This method consists of the immobilization of an initiator onto a substrate, such as gold or silicon. Then, the initiator-substrate is exposed to monomer under specific reaction conditions to
polymerize in-situ directly onto the substrate. Various polymerization methods such as radical,\textsuperscript{[100]} anionic,\textsuperscript{[101]} cationic,\textsuperscript{[102]} controlled radical (i.e. ini-fer-ter,\textsuperscript{[103]} TEMPO-mediated,\textsuperscript{[104]} and ATRP\textsuperscript{[105-106]}), ring opening metathesis (ROMP),\textsuperscript{[107]} group transfer (GTP),\textsuperscript{[108]} and others, have been utilized for this technique.

The in-situ polymerization of the tethered chains is the most effective way to address the problems with steric hindrance of the initially formed layer of pre-formed polymers. The polymerization of individual monomers does not introduce any steric barriers for high tethering density. At each initiation event, a tethered chain will be formed. It has been shown that this technique provides high molecular weight chains chemically grafted to the substrate. In fact, all controlled polymerization mechanisms are unaffected by the grafting of the initiator.

Another method to study the properties of tethered chains is by making a tethering gradient along a single surface.\textsuperscript{[111-113]} The fabrication of the gradient surface contains two main steps, grafting of the initiator followed by grafting of non-reactive filler. The gradient is created through diffusion or mechanical methods. A mixture of initiator and paraffin oil is heated at the edge of a silicon wafer to produce the diffusion-based gradient. The initiator evaporates, diffuses across the substrate, and reacts to become grafted.\textsuperscript{[111]} The ungrafted surface is then reacted with a long-chain hydrocarbon, typically \textit{n}-octyl trichlorosilane (OTS), to ensure that reactions only occur from the initiator. The mechanical gradient is made by dipping the initiator-grafted substrate into a solution containing the monomer, and it is slowly removed. The difference in exposure time results in a gradient of tethered polymer molecular weight and size.\textsuperscript{[113]}
The main advantage of the “grafting-from” technique, as described, is the ability to form polymer layers with high \( \sigma \). Also, it is possible to synthesize a wide variety of polymeric tethers restricted only by the ability to bond the initiator to the substrate. The lack of steric hindrance provides an opportunity to make tethered polymers with high molecular weights as well. Although \( \sigma \) is higher, the uniformity of the tethering density across the substrate can be questioned. It is highly dependent on the uniformity of both the grafting of initiator and the initiation and propagation of the chains. The additional disadvantages associated with this method derive from the characterization of the molecular weight and molecular weight distribution. Because of the increasing amount of material within the layer during polymerization, the molecular weight control decreases with reaction time. It can affect the reaction kinetics as well. Both of these factors lead to a larger polydispersity, making the calculation of \( \sigma \) less reliable. The determination of the molecular characteristics is done in one of two ways, either free initiator is included assuming the free and tethered reaction kinetics are the same or the initiator contains a cleavable bond to release the tethered polymers for characterization. Genzer\textsuperscript{114} has shown that the kinetics of free and tethered polymerizations do not necessarily match. In addition, the termination of the tethered chains is more likely to occur through combination.

2.2.3 Single Crystals of Diblock Copolymers

The final method of fabricating tethered polymer chains is a unique approach using diblock copolymers. The formation of solution-grown, lamellar single crystals
from crystalline-amorphous block copolymers results in the tethering of the amorphous block on the crystal surface (see Figure 2.1c). Because the thermodynamics of crystallization forbid the inclusion of the amorphous chains in the crystalline lattice, the junction between the blocks serves as the tethering point on both basal surfaces of the crystalline block single crystal, forming a “sandwich”-structure. Initial work on the solution crystallization of block copolymers, specifically poly(ethylene oxide)-block-PS (PEO-b-PS), was conducted by Lotz and coworkers.\textsuperscript{[115-116]} They proved that the crystallizable PEO could form single crystals; however, the “sandwich”-structure with amorphous blocks on both crystal surfaces was proven by Chen and coworkers much later.\textsuperscript{[117]} From this discovery, a novel approach to study the physics of tethered polymer chains was developed.\textsuperscript{[118-119]}

Crystallization of polymeric materials is most stable when the crystal adopts a lamellar structure. The thickness of the lamellae is determined by the degree of undercooling, $\Delta T$, where $\Delta T = T_d - T_x$ for solution-grown crystals.\textsuperscript{[120]} $T_d$ is the dissolution temperature, and $T_x$ is the isothermal crystallization temperature. For diblock crystals, this is the first step in controlling the tethering density of the amorphous blocks. By adjust the crystallization temperature, $T_x$, one can tune the number of folds per chain ($n$) in the crystal, thus changing the number of junction points, or tethering points, per surface area, $S$. The molecular weight of the crystalline block is also significant in tuning $n$. Using these two parameters, $T_x$ and $n$, it is possible to create a wide range of tethering densities. By changing the molecular weight of the amorphous block, $\bar{\sigma}$ can be tailored as well.
Single crystals of diblock copolymers provide a unique opportunity to create tethered polymer systems. Using well-established synthetic techniques for making diblock copolymers, see for example Ref. 121, specifically tailored polymers can be developed to address the previously stated issues. Controlled polymerization of each of the blocks ensures the tuning of the molecular weight for each block and provides a narrow polydispersity for each. This leads to a well-defined tether molecular weight and molecular weight distribution and an accurate knowledge of the number of folds. The stability of the isothermal $T_x$ combined with the molecular weight leads to good control over the thickness. By controlling the thickness, it is possible to control the tethering density accurately. All of these characteristics prove that the single crystal method has significant advantages for studying the physics of tethered chains over the other methods discussed. The glaring disadvantages for this type of tethered chain production are in the ability to choose the desired system. The diblock copolymers that can be used are limited to crystalline blocks and those that can be copolymerized or linked to the proposed crystalline block. In addition, the surface of a folded-chain crystal does not compare well with the traditional silicon and gold substrates. They are typically on the order of several microns in size, which can be limiting for applications. A complete list of the advantages and disadvantages of each of the presented methods can be found in Table 2.1.
Table 2.1 Listing of the advantages and disadvantages of common techniques for forming tethered polymer layers.

<table>
<thead>
<tr>
<th></th>
<th>Advantages</th>
<th>Disadvantages</th>
</tr>
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<tbody>
<tr>
<td><strong>Physical Adsorption</strong></td>
<td>+ control over molecular weight (MW) + low polydispersity + ability to determine tether free energy</td>
<td>- steric effects limit high tethering density - desorption from surface</td>
</tr>
<tr>
<td><strong>Solid Substrate</strong></td>
<td>+ strong surface interaction</td>
<td>- poor control of tethering density</td>
</tr>
<tr>
<td><strong>Fluid Surface</strong></td>
<td>+ adjustable tethering density</td>
<td>- easily desorbed</td>
</tr>
<tr>
<td><strong>Grafting-To</strong></td>
<td>+ same as PA for pre-made polymers + slightly higher tethering density than PA + robust films from covalent bonding</td>
<td>- steric effects limit high tethering density</td>
</tr>
<tr>
<td><strong>Grafting-From</strong></td>
<td>+ higher grafting densities + covalent linkage + not restricted by functionalization chemistry</td>
<td>- poor control of MW and polydispersity - poor tethering density uniformity</td>
</tr>
<tr>
<td><strong>Single Crystals</strong></td>
<td>+ good control of MW and polydispersity + good control of tethering density</td>
<td>- small system size - limited choice of polymers</td>
</tr>
</tbody>
</table>

2.3 Experimental Determination of Tethered Chain Regimes

The main objective of the research presented in this dissertation is to determine the transition $\bar{\sigma}$ value from the non-interacting to the interacting regime ($\bar{\sigma}^*$), specifically under varying tether-substrate interactions and tether characteristics. The importance of knowing this transition value lies in the resulting properties of tethered chains in each of these regimes. To know these values a priori will allow for the technological advance of tethered chain systems. These are especially important in the areas of responsive surfaces,[122] protein adsorption,[45] and fluid flow.[123] In each of these areas, the tethering density plays a major role in the material properties. Some research has already been conducted in determining the transition values for each of the
regimes, interacting and stretched brush. In addition, experimental studies have been conducted to verify the segment density profiles at low and high tethering densities.

2.3.1 Segment Density Profiles

The grafting of polymer chains onto various substrates has been possible for a few decades because of the physical and chemical attachment methods. Many research groups have utilized these techniques to attach polymer chains to both flat substrates and spherical particles to analyze the conformation of the chains at low and high $\sigma$. Neutron reflectivity and small angle neutron scattering (SANS) have been used to characterize the segment distribution. These experimental distributions were then compared with the theoretical predictions discussed in Section 2.1.

The study of tethered polymer chains at high $\sigma$ was done and compared with the SCF theory models, either the aSCF or the nSCF.$^{[124-128]}$ In many cases, curved surfaces of silica particles were used. These results provide a similar comparison; however, it should be noted that the conformation of the chains should be slightly altered when on a curved substrate as opposed to the flat substrate. In most cases, PS was used as the tethered chain, though others such as PDMS have also been studied. These chains were adsorbed by an end-group or chemically attached to the substrate. The results show that the predictions of the aSCF and nSCF theories are valid at high tethering densities.
Figure 2.11 Segment density profiles (φ(z)) for PS attached to a silicon substrate derived from neutron reflectivity measurements. The solvents used were $d$-cyclohexane (■ - 14.6°C, ○ - 21.4°C, * - 31.5°C, and △ - 53.4°C) and $d$-toluene (● - 21°C). The solvent quality of $d$-cyclohexane increases with higher temperatures.[124]

In particular, a study by Karim and coworkers[124] characterized the segment density of PS with a weight-average molecular weight ($M_w$) of 105,000 g/mol on a flat silicon substrate using neutron reflectivity. Their resultant $\phi(z)$ profiles can be seen in Figure 2.11. Each set of data represents the results at varying temperatures in $d$-cyclohexane and a single temperature for $d$-toluene. As the temperature increases, the $d$-cyclohexane becomes a better solvent for PS; the $d$-toluene is a good solvent. The value of $\tilde{\sigma}$ of this system is approximately 14.3. The results show that the prediction of the aSCF theory matches well with the data. Other published results also indicate that the aSCF prediction is the most accurate. This would indicate that there is a small amount of adsorbed material at the substrate. There is, however, some evidence that supports the nSCF prediction with a depletion layer near the surface.[128]

Studies were also done at lower $\sigma$ to determine the conformation both with and without adsorption of the tether.[129-131] In the first study by Cosgrove and coworkers[129]
the segment density of PEO attached to charged PS latex was determined. The charge on the surface of the PS particle induced adsorption of the PEO layers. Figure 2.12 shows the profiles as measured by SANS as a function of charge. The highly adsorbed chains (solid line, B) show profiles similar to those predicted by the RG of Adamuti-Trache and coworkers and SCF theory of Scheutjens and Fleer. The non-adsorbed chain (dotted line, A) shows the profile with a peak representative of the $R_g$ of the chains. The solid line, C, is of purely adsorbed chains without one end being grafted.

![Graph of segment density profiles](image)

Figure 2.12 Segment density profiles ($\phi(z)$) of PEO attached and adsorbed to PS latex spheres. (A) is the non-adsorbed case with low surface charge. (B) is the adsorbed case with high surface charge. (C) is the non-grafted, adsorbed case.[129]

A second study was done at low $\sigma$ using an alternate technique. Confocal microscopy on fluorescently labeled DNA was used to analyze the conformation directly without the fitting of scattered data.[130] Slices were taken at various $z$-values, and the fluorescence intensity over a pixilated area, $A$, was taken. The weighted segment distribution, $S(z)$, was determined from these results. The distance from the substrate was normalized by the $R_g$ of the molecule to create an $S(z)$ profile. These results showed a
parabolic-like profile with a peak around the $R_g$ of the DNA molecule. This experimental approach provides a unique way to study tethered chain conformations.

Each of these methods has shown that the predicted segment density for tethered polymer chains at varying $\sigma$ is accurate. If adsorption occurs, the chain adopts a pancake-like profile; while, for repulsive surfaces, a nearly unperturbed conformation is obtained. At high $\sigma$, the density profile is parabolic with a tail as one approaches the surface of the tethers. The next step is finding experimental evidence of transitions from one regime into the next. Although several approaches have been taken to address this concern, only recently has there been solid experimental evidence reported.

2.3.2 Transitions

The study of transitions from one regime to the next at specific $\tilde{\sigma}$ has taken a few different forms. In the initial works, comparison to the scaling law of $L \sim N\sigma^{1/3}$ was the most prominent way to verify the existence of polymer brushes. This technique was used mostly for the verification of this scaling law assuming the tethered chains were already in the brush state at moderate to high $\sigma$.\[^{52, 132}\] Several years later, work was done with systems of varying $\sigma$, using techniques such as neutron scattering or ellipsometry to determine $L$.\[^{23, 112}\] The transition to the brush regime was defined as the $\tilde{\sigma}$ value where the data fit with the scaling law. Other parameters, such as surface pressure ($\Pi$)\[^{133}\] or crystal thickness in diblock single crystals ($d_{\text{CRYST}}$)$[^{118-119}$, were used as well. Transitions in the relationship between these quantities and $\tilde{\sigma}$ were an indication of transitions from one regime to another.
The scaling relationship between $L$ and $\sigma$ is an easy way to determine the state of the tethers. The initial work by Auroy and coworkers\[132]\ verified the $L \sim \sigma^{1/3}$ relationship for PDMS attached to a silica surface. Using neutron reflectivity, they measured the layer thickness as a function of grafted amount. The results showed that in the $\sigma$-range tested, the slope of the log-log plot ($\log L$ vs. $\log \sigma$) was 0.33. This indicates that the range evaluated does not show any transition from the interaction regime to the brush regime. Because a singular system was measured, $\bar{\sigma}$ was not needed, and $\sigma$ is sufficient for analysis.

A second approach to finding the stretched brush regime was proposed by Kent\[23\]. Kent used the adsorption of a diblock copolymer, PDMS-$b$-PS, at the fluid-air interface of several solvents including ethyl benzoate and dioctyl phthalate. The tethering density was systematically adjusted using successive spreading of the copolymer and compression with a movable barrier. The thickness of the PS tethered layer, as measured by neutron reflectivity, was compared to the theoretical predictions of the SCMF results of Cariagnano and Szleifer\[47\]. The SCMF theory applies to chains in the interacting regime; therefore, data points that do not follow the predicted results are outside this regime.

Figures 2.13 and 2.14 show the results of Kent and the prediction of the SCMF theory at low and high tethering densities. Figure 2.13 shows the results for normalized thickness ($L/R_g$) as a function of $\bar{\sigma}$ at low values of $\bar{\sigma}$. The data appears to follow the predicted line (dashed) above a value of 2.5. This would indicate a transition from the non-interacting regime ($\bar{\sigma} < 2.5$) to the interacting regime ($\bar{\sigma} > 2.5$). This is the first experimental evidence of this transition. Figure 2.14 is the same relation at high $\bar{\sigma}$. It
can be seen that the data follows the prediction through the entire $\tilde{\sigma}$ range. This indicates that the PS tethers exist in the interacting regime up to a $\tilde{\sigma}$ value of 12. The transition to the brush regime ($\tilde{\sigma}^{**}$) was not reached. The reliability of the $\tilde{\sigma}$ values comes into question with these results. The techniques for increasing the surface layer density may lead to some dynamic desorption of the PDMS block; therefore, the location of the transition points may not be exact. These values do, however, provide sufficient estimates for further experimentation.

![Graph](image)

Figure 2.13 Relationship of normalized layer thickness ($L/R_g$) versus $\tilde{\sigma}$ for PDMS-$b$-PS layers at the fluid-air interface. The PS tether thickness was modeled using the SCMF theory (dashed line). Above $\tilde{\sigma} = 2.5$, the data follows the predicted line indicating that the PS tethers exist in the interacting regime.[47]

![Graph](image)

Figure 2.14 Relationship between $L/R_g$ and $\tilde{\sigma}$ over a larger range than Figure 2.12. Data follows the predicted SCMF relationship (solid line) up to $\tilde{\sigma} = 12$. This indicates that the PS tethers do not reach the brush regime prior to this value. Open symbols are in good solvent, while closed symbols are in theta solvent.[23]
A study by Wu and coworkers\cite{wu2003} using a new technique developed in their lab to create polymer tether gradients on a single substrate\cite{wu2004} focuses on the transition of poly(acrylamide) (PAAm) from the non-interacting regime to the brush regime. After the layer with a gradient tethering density was made, the authors measured the thickness of the tethers as a function of distance across the substrate using ellipsometry. The thickness was normalized by $R_g$, as is customary, and compared to the tethering density, which was a function of position on the substrate. The results can be seen in Figure 2.15. Below a certain threshold value, $L$ is independent of $\sigma$; however, at $\sigma = 0.065$ nm$^{-2}$, the $L \sim \sigma^{1/3}$ relationship can be seen. This is indicative of a transition into the brush regime. The $\tilde{\sigma}$ value for this $\sigma$ is estimated to be around 10, which is lower than the previous result of $\tilde{\sigma}^{**} > 12$. One interesting aspect of these results is that there does not appear to be a transition regime (interacting) as would be expected. Other results for contact angle measurements indicate that another transition may occur around $\tilde{\sigma} = 4.6$. The

Figure 2.15 Thickness of a gradient tethered polymer layer over a range of $\sigma$. $L/R_g$ is used as in the previous results. The transition from $L \sim \sigma^0$ to $L \sim \sigma^{1/3}$ occurs at $\tilde{\sigma} \sim 10$. This is an indication of the transition into the brush regime.\cite{wu2003}
accuracy of the calculation of $\sigma$ and the reliability of $\sigma$ come into question for this “grafting-from” approach of creating the gradient surface. For example, the polydispersity of the grafted chains is 1.7.

The final approach to elucidating the transition values for each regime was first introduced by Chen and coworkers\textsuperscript{118} and later expanded upon by Zheng and coworkers.\textsuperscript{119} In this approach, crystalline-amorphous diblock copolymers were used to find $\bar{\sigma}^*$ and $\bar{\sigma}^{**}$ for PS chains attached to different polymer single crystal surfaces. PS-$b$-PEO and PS-$b$-poly(L-lactic acid) (PLLA), where PEO and PLLA are the crystalline blocks, were used. The crystal thickness was used as a probe to determine the changes in interaction between the tethered PS chains.

The thickness, $d_{\text{CRYST}}$, of polymer single crystals is determined thermodynamically by the crystallization temperature, $T_x$. The relationship between $1/d_{\text{CRYST}}$ and $T_x$ is linear based on the theory by Hoffman and Lauritzen,\textsuperscript{120}

$$\frac{1}{d_{\text{CRYST}}} = \frac{\Delta h_d}{2\gamma_e} - \frac{\Delta h_d}{2\gamma_e T_d} T_x \quad (2.7)$$

where $\Delta h_d$ is the heat of dissolution and $\gamma_e$ is the surface free energy. Figure 2.16 shows two sets of data for PS-$b$-PEO (Fig. 2.15a) and PS-$b$-PEO (Fig. 2.15b). From equation 2.7, the slope of the fitted lines, $m$, is equal to $-\Delta h_d/(2\gamma_e T_d)$. In each system, $\Delta h_d$ and $T_d$ are constant; therefore, the transition in the slope, as seen in both figures, must be associated with the $\gamma_e$ term. According to the Hoffmann-Lauritzen theory of crystallization,\textsuperscript{120} the crystal thickness is thermodynamically-determined by the surface energy, $\gamma_e$. In the homopolymer case, $\gamma_e$ is defined by the fold-surface free energy, $\gamma_c$; however, in diblock copolymer single crystals, an additional term, $\gamma_t$, or the free energy
contribution from the tethered chains, must be considered. Simply put, $\gamma_c = \gamma_c + \gamma_t$. The change in $m$ is experimental evidence that the tethered chains begin to interact. The $\bar{\sigma}^*$ was calculated to be 3.7, as shown in the figures. This value was found to be independent of tether ($M^*_n$) and crystalline block molecular weight ($M^*_c$) and solvent quality.

Figure 2.16 $1/d_{\text{CRYST}}$ versus $T_x$ for (a) PS-b-PEO (b) PS-b-PLLA. Transitions in the slope, $m$, indicate a change in the surface free energy, $\gamma_c$. This change is attributed to the interaction of PS tethered chains.

Because the synthesis of these diblock copolymers is well-controlled, Zheng and coworkers\[119\] were able to make a series of copolymers to cover a large range of $\bar{\sigma}^*$. Using the same experimental method, $\bar{\sigma}^*$ was determined. The data analysis was slightly different for this case. No abrupt change was found in the second slope with increasing $\bar{\sigma}^*$. A new parameter, $\Gamma_{\text{PS}}$, which represents the reduced surface energy, was introduced:

$$\Gamma_{\text{PS}} = \frac{\gamma_c}{\gamma_c} - 1 = kT\bar{\sigma}^{\gamma/\gamma} \sigma^{\gamma/\gamma}$$

The right side of equation 2.8 represents the scaling law of Alexander. The minimization of the free energy, $f_{eq}$, for a single chain multiplied by $\sigma$ gives the free energy of the tethered chain system, $\Gamma_{\text{PS}} = f_{eq}\sigma$. Figure 2.17a shows the relationship of $\Gamma_{\text{PS}}$ with $\bar{\sigma}$. If
\(\sigma\) is taken to be an order parameter, then the transition at \(\sigma^* = 3.7\) is first-order like due to discontinuity. It is difficult to predict \(\sigma^{**}\) directly from this graph. A plot of \(\Gamma_{PS}\) versus a new parameter \(x\), where \(x = T\sigma^{2/3}\) and \(k\) and \(a\) are constant, gives the prediction of the scaling law for the brush regime. Figure 2.17b illustrates that when the data falls along the predicted line, the stretched brush regime is reached. This occurred at a \(\sigma^{**}\) of 14.3. This transition is second-order like because it is continuous.

![Graphs](image)

Figure 2.17 Illustration of both transitions in tethered polymers. (a) \(\Gamma_{PS}\) as a function of \(\sigma\) (b) \(\Gamma_{PS}\) versus the parameter \(x\) (\(x = T\sigma^{2/3}\)). The \(\sigma^*\) transition is first-order like at 3.7 in (a). The brush regime is reached at \(\sigma^{**} = 14.3\) where the data follows the Alexander scaling law (dashed line) in (b).[119]

The values of \(\sigma^*\) and \(\sigma^{**}\) for PS chains were determined with high reliability using the diblock copolymer single crystal method. The quality of control over \(M_n^a\), \(M_n^c\), and \(\sigma\) result in good reliability in the accuracy of these values. Unfortunately, these results are specific to PS with PEO and PLLA substrates. There exists a repulsive or neutral interaction between the tether and substrates. The main objective of the research presented in this dissertation is to determine the validity of \(\sigma^*\) for other polymer
systems taking into account other considerations such as tether-substrate attraction using the same experimental technique of Chen and Zheng.

2.4 Crystallization of Tethered Polymer Chains

The second objective is to study the ability of tethered chains of crystalline polymers to crystallize when attached to a substrate. This can be achieved by using crystalline-crystalline diblock copolymers, specifically PEO-\(b\)-poly(\(\varepsilon\)-caprolactone) (PCL). Some studies of the characteristic crystallization of tethered polymers in simulations and of crystalline-crystalline diblock copolymers single crystals have been performed previously and will be presented here.

The first consideration is the ability of chains to crystallize at extremely high tethering densities. If \(\tilde{\sigma}\) is extremely high, the chains will be tightly compressed such that they have no choice but to completely stretch away from the surface. This can be denoted as the highly, or fully, stretched regime.\(^{[70]}\) A study by He and coworkers\(^{[134]}\) indicates that this conformation is comparable to the crystallization of the tethered chains.

Using MD simulations, they have found that the structure factor and correlation function of these fully stretched chains is reminiscent of those for crystallized polymers. The authors use the parameter \(\Sigma = N_{\text{chain}}/l_{\text{box}}^2\) for the tethering density, where \(N_{\text{chain}}\) is the number of chains and \(l_{\text{box}}\) is the size of the simulation box. A value of \(\Sigma = 1\) represents a simulation box that is completely filled with chains. At \(\Sigma = 0.8\), the chains begin to exhibit crystallization within the core layer. The crystallization does not occur near the substrate or at the surface of the chains. As \(\Sigma\) is increased to 0.95, crystallization
proceeds from the core to the surface layer. This means that the broad transition from a “melt-like” brush layer to a “crystalline-like” brush layer occurs at $0.8 < \Sigma < 0.95$. The possibility of reaching this tethering density in a real system is unlikely due to steric issues in compressing the chains to this extent.

The next issue to address is the crystallizability of semi-crystalline chains when tethered to a substrate at low or moderate tethering densities. It is well-known that crystalline-amorphous diblock copolymers exhibit crystallites in nanophase-separated melts where the tethering density is assumed to be quite high.$^{[135-139]}$ The obvious questions are: in a single layer of tethered chains, what are the characteristics of crystallization? Is it possible for these chains to crystallize? If so, how does the crystallizability depend on $\tilde{\sigma}$? The easiest way to address these issues is to utilize the single crystals of diblock copolymers with two crystalline blocks.$^{[140-142]}$

The first study of these types of systems was done by Sun and coworkers$^{[140]}$ using a PEO-$b$-PCL copolymer with $M_n^{PEO} = 5k$ g/mol and a $M_n^{PCL} = 5k$ g/mol. Single crystals of PCL were grown in a dilute solution of $n$-hexanol. The resultant crystals had PEO chains tethered on each side. Figure 2.18a shows an atomic force microscopy (AFM) phase image of the collected crystals. It can be seen that the crystals exhibit a highly dislocated morphology and are stacked upon one another. Figure 2.18b shows the resultant electron diffraction (ED) pattern obtained using transmission electron microscopy (TEM). Two sets of diffractions appeared. The first set is the six spots associated with the set of (110) and (200) planes of the orthorhombic PCL crystal; the second set is the four spots associated with the (120) planes of the monoclinic PEO crystal. The PEO diffraction spots indicate that a single crystalline PEO layer has formed.
with an exact orientation. The orientation is 22 – 30° between the 𝐚-axes of the two crystals. It is peculiar that the electron diffraction would exhibit single crystal-like patterns from the presented morphologies. One would expect rings or arcs associated with each sets of planes indicating that no or some orientation is exhibited.

Figure 2.18 Characterization of PEO-𝑏-PCL crystals grown in 𝑛-hexanol. (a) AFM (b) TEM ED. (a) The truncated morphology indicates that the PCL block has crystallized first to form the single crystal substrate with PEO on the surface. (b) The outer spots represent the (110) and (200) diffractions of PCL. The inner spots are the (120) diffractions of PEO.\textsuperscript{140}

A second study was done by Yang and coworkers\textsuperscript{142} using PEO-𝑏-PLL A with $M_n^{PEO} = 5k$ g/mol and $M_n^{PLL A} = 5k$ g/mol. The approach for growing single crystals was quite different than the previous study. In this case, the single crystals were grown from a thin film of the diblock copolymer. The PLLA crystals were grown at a $T_x$ that was much higher than the melting temperature of PEO ($T_{m}^{PEO}$). Again, the PEO chains were tethered on the PLLA crystal surface. The system was quenched below $T_{m}^{PEO}$ to allow the PEO chains to crystallize. The resultant morphology can be seen in the TEM image of Figure 2.19a. The ED pattern for this crystal is shown in Figure 2.19b. The
morphism shows a dislocated, multi-layer crystal; however, there is no stacking of crystals. The ED spots for the pseudo-orthorhombic PLLA crystal should be single crystal-like because the dislocations should provide lattice matching (though some misalignment may occur resulting in arcs instead of spots). The (110) and (200) spots of the PLLA are located on the inside due to a smaller \( d \)-spacing than the arcs of the (120) planes of PEO. The PEO arcs indicate that the orientation on the PLLA crystal surface is not perfectly aligned like the PEO-\( b \)-PCL results. The arcs, as opposed to rings, do indicate that there is some preferential alignment. The authors explain this by soft epitaxy between the crystal lattice of the PEO with the lattice and folds of the PLLA. The angle between the \( a^* \)-axes of these crystals is approximately 21°.

![Figure 2.19 Characterization of a PEO-\( b \)-PLLA crystal grown from a thin film. (a) bright-field TEM (b) ED. The inner spots of the ED pattern represent the (110) and (200) diffractions of PLLA. The outer spots are the (120) diffractions of PEO.][142]

The results of these two studies are found at a high \( \tilde{\sigma} \) because the molecular weights of the two blocks are symmetrical. It is difficult to estimate the \( \tilde{\sigma} \) without accurate crystal thickness data. The crystallizability of PEO at lower \( \tilde{\sigma} \) is of interest. In addition, further verification of any preferential orientation on the surface of PCL is desired.
CHAPTER III
EXPERIMENTAL

Several polymeric samples and analytical techniques were utilized for the study of the $\sigma^*$ transition and the crystallizability of tethered chains. The procedure for growing single crystals of the diblock copolymers is fairly standard with a few minor adjustments based on the particular sample. In addition to experimental work, some computer simulations were performed to approximate chain size and conformation in the real system because of the limitations in the experimental techniques.

3.1 Polymer Samples

The diblock copolymers used in this study are poly(methyl methacrylate)-$b$-poly(L-lactic acid) (PMMA-$b$-PLLA) and poly(ethylene oxide)-$b$-poly($\varepsilon$-caprolactone) (PEO-$b$-PCL). Each polymer was supplied by collaborators of our research group. The PMMA-$b$-PLLA sample was synthesized by Dr. Joseph X. Zheng with the use of Prof. Roderic P. Quirk’s lab. The synthesis of this polymer followed the schematic shown in Figure 3.1. A brief discussion of the synthesis of PMMA-$b$-PLLA is given to supplement the schematic.
PMMA-OSiR₃ was synthesized by the anionic polymerization of methyl methacrylate (MMA) from a functional initiator 4-(t-butyldimethylsiloxy)butyl lithium. This initiator was reacted with diphenylethylene (DPE) in the first step. It was used to initiate the living anionic polymerization of methyl methacrylate monomer in the presence of LiCl in THF at -78°C. The polymerization was complete in nearly 2 hours and was then quenched with methanol (MeOH). After repeated precipitation in cold hexane, PMMA-OSiR₃ was obtained as a white solid with a narrow polydispersity. The molecular weight can be readily controlled by the monomer/initiator ratio.

After the PMMA-OSiR₃ was synthesized, a secondary step to prepare a macroinitiator for the polymerization of PLLA was needed. The hydroxyl functionalized PMMA was prepared by acidic hydrolysis of the silyl ether of PMMA-OSiR₃. In a solution with THF, an aqueous solution of 2N HCl was added. The mixture was stirred overnight at room temperature. The material was recovered by precipitation in MeOH and filtered with repeated MeOH washes to remove HCl completely. After drying overnight in a vacuum oven at 40°C, the macroinitiator PMMA-OH was obtained as a white solid.

The hydroxyl functionalized PMMA was freeze-dried over three cycles before it was taken into the dry box, dissolved in anhydrous toluene or benzene, and reacted with triethyl aluminum in a ratio of 1:1 or 2:1. Sometimes, heating at 80°C for 5 to 10 minutes was necessary to promote the dissolution and reaction. After stirring at room temperature overnight, L-lactide was added to the mixture. It was taken out of the dry box, degassed again, and placed in an oil bath at 65°C for predetermined times. Then, it was cooled and precipitated in MeOH to obtain the PMMA-\textit{b}-PLLA copolymer as a white solid.
The molecular weight of the PMMA sample was measured using gel permeation chromatography (GPC) with polystyrene standards. The overall molecular weight was also characterized in this way. The molecular weight of the PLLA block was determined from hydrogen nuclear magnetic resonance (\(^{1}\)H NMR). For this sample, PLLA is the crystalline block, and PMMA is the amorphous, tethered block.

![Synthetic scheme](image)

**Figure 3.1 Synthetic scheme for the preparation of PMMA-\(b\)-PLLA.**

The PEO-\(b\)-PCL samples were provided by Dr. Jun-ting Xu of Zhejiang University in China. A monomethoxy functionalized 5k g/mol PEO was purchased from Aldrich and used as the base. The PCL block was polymerized from the –OH end. For a detailed description, see Ref. 143. The molecular weights were determined by GPC (overall) and \(^{1}\)H NMR (PCL block). For this series of samples, both blocks are semi-
crystalline. PEO and PCL have a similar $T_m$. It has been shown that the block with the higher molecular weight crystallizes first.\textsuperscript{[144-147]} Both samples used in this study have higher molecular weights of the PCL; therefore, the PCL block will crystallize first to form the single crystalline substrate with PEO tethered to the surface. The characteristics of each of these samples can be found in Table 3.1. The PEO-$b$-PCL samples will be denoted as EOCL-11 and EOCL-31 for the 11.3k g/mol and 31.5k g/mol samples, respectively.

Table 3.1 Molecular characteristics of polymer samples

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n^{\text{tether}}$ (g/mol)</th>
<th>$M_n^{\text{cryst}}$ (g/mol)</th>
<th>$M_n^{\text{total}}$ (g/mol)</th>
<th>PDI</th>
<th>$w_c$\textsuperscript{1}</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-$b$-PLLA</td>
<td>7800</td>
<td>22 300</td>
<td>30 100</td>
<td>1.14</td>
<td>0.74</td>
</tr>
<tr>
<td>EOCL-11</td>
<td>5000</td>
<td>6300</td>
<td>11 300</td>
<td>1.12</td>
<td>0.56</td>
</tr>
<tr>
<td>EOCL-31</td>
<td>5000</td>
<td>26 500</td>
<td>31 500</td>
<td>1.16</td>
<td>0.84</td>
</tr>
</tbody>
</table>

\textsuperscript{1} $w_c$, weight fraction of crystalline block

3.2 Solution Growth of Diblock Single Crystals

The foundation of the tethered polymer physics study is the creation of the tethered system using diblock copolymer single crystals. These single crystals are obtained using dilute solution crystallization with the self-seeding technique. This technique provides a large population of single layer crystals of equal size. This large population of crystals provides a sufficient sample size for good experimental statistics. In addition, it gives ample opportunity to locate crystals for TEM and AFM experiments.
3.2.1 Self-Seeding Procedure

The self-seeding procedure was first introduced by Lotz as a way of growing uniformly-sized polymer single crystals. The basic outline of the procedure can be seen in Figure 3.2. First, the polymer and solvent are mixed at room temperature at dilute solution conditions, typically with a weight percent polymer of 0.005%. The solvent quality should be theta-to-poor for the polymer so that dissolution is only achieved upon increasing the temperature. Next, the sample is increased to the dissolution temperature \( T_d \). It is kept there for a predetermined amount of time, \( t_d \). It is then quenched to room temperature \( T_q \) overnight to allow the crystalline polymer to crystallize with the same thermal history. Then, the sample is placed in an oil bath at the self-seeding temperature, \( T_s \), for a time \( t_s \). At this temperature, about 99% of the crystals dissolve leaving only small nuclei to nucleate crystal growth. Finally, the sample is quenched to a set isothermal crystallization temperature, \( T_x \), in an oil bath until complete crystallization has occurred \( (t_x) \). The \( T_d \) and \( T_s \) are strongly sample dependent. The general \( t_d \) is 10 minutes, and the general \( t_s \) is 20 minutes. Samples are left at \( T_x \) for several days to ensure complete crystallization. Detailed descriptions are found in Sections 3.2.2 and 3.2.3.
3.2.2 PLLA Sample

A PMMA-\textit{b}-PLLA sample with molecular weights of 7.8k g/mol for the PMMA block and 22.3k g/mol for the PLLA block was mixed with amyl acetate at a concentration of 0.003 wt%. The sample was placed in an oil bath at a temperature of 130.0°C ± 0.1°C to dissolve the polymer sample. The sample was dissolved for 10 minutes and then quenched to room temperature in air overnight. After crystallization of the PLLA was verified by a white precipitate, the sample was placed in an oil bath at a $T_s$ of 110°C ± 0.1°C. The sample was self-seeded for 20 minutes and quenched in an oil bath with an isothermal $T_x$ with a precision of ± 0.2°C. The crystallization temperatures for the PLLA block ranged between 65°C and 90°C. The crystallization proceeded for 1 – 2 days to avoid degradation of the PLLA. The crystallization time was increased with increasing $T_x$ due to slower kinetics with a smaller undercooling ($\Delta T = T_d - T_x$).

3.2.3 PCL Samples

PEO-\textit{b}-PCL samples were used with similar conditions. All samples were mixed with \textit{n}-hexanol at a concentration of 0.003% and dissolved at 80°C ± 0.1°C. The sample was dissolved for 10 minutes and then slowly cooled to room temperature in the oil bath overnight. The slow cooling was necessary because the sample fell out of solution prior to crystallizing if it was directly quenched. The first sample with molecular weights of 5.0k g/mol for the PEO block and 26.5k g/mol was placed in an oil bath at a $T_s$ of 46°C ± 0.1°C. The second sample, with a PEO molecular weight of 5.0k g/mol and PCL
molecular weight of 6.3k g/mol, was self-seeded at a $T_s$ of 52°C ± 0.1°C. Both samples were self-seeded for 20 minutes and then quenched in an oil bath at an isothermal $T_x$ with a precision of ± 0.2°C. The crystallization temperatures ranged between 22°C and 45°C. The crystallization proceeded for 2 – 5 days with increased time at higher $T_x$.

3.2.4 Consecutive Growth of Homo- and Diblock Polymers

An additional crystallization technique proves helpful in studies of diblock copolymer single crystals. That is the lateral epitaxial growth of homopolymers and diblock copolymers.[117] Here, a single crystal is grown under certain conditions. Then, these crystals are used as the seeds for further growth of the opposite molecular architecture. Because the crystalline block and homopolymer are the same material, epitaxial growth occurs along the lateral surface of the original single crystal. This procedure can be repeated to form a nanostructure of changing height across the crystal surface (see Figure 3.3). The amorphous tethers form a patterned surface with a step-like profile at areas lacking the amorphous layer.

The epitaxial growth technique can be used to lower the nucleation barrier of the diblock copolymer for easier, more controlled crystallization, to verify the thickness of the crystalline layer, and to switch the crystallization kinetics of the crystalline-crystalline diblock copolymer. The procedure for utilizing this technique is quite simple. First, the inner-most crystal is grown using the self-seeding procedure. For this example, the homopolymer sample will be used as the seed. After the complete crystallization of the homopolymer crystals, a mixture of the diblock sample in the same solvent is dissolved at
This sample is then placed in the isothermal $T_d$ bath at the same temperature as the homopolymer seeds. The solution is allowed to come to thermal equilibrium for 10 minutes to prevent dissolution of the homopolymer seeds. Then, a few drops of the homopolymer solution are transferred into the diblock solution before the diblock crystals can grow. Finally, the crystalline block grows epitaxial on the seed at the same isothermal $T_x$. This procedure can also be conducted with the opposite structure where the diblock crystals are grown as the seeds and added to the dissolved homopolymer. Then, the homopolymer grows epitaxially on the diblock single crystal. The width of each “layer” is determined by the mass of material in the solution and the $T_s$.

![Figure 3.3 TEM image of alternating growth of homopolymer and diblock copolymer of PEO and PS-$b$-PEO to form the step-profile surface.][117]

**3.2.5 Collection of Single Crystal Mats**

A collection of single crystals is referred to as single crystal mats. These mats are important for measurements where a larger amount of material is needed, such as DSC.
The procedure for crystallizing the sample is similar to that as mentioned above. The solution was made with a higher concentration ~0.005% (0.5 mg sample/10 g n-hexanol for the PEO-b-PCL samples) in a large test tube. The solution was self-seeded at a slightly higher temperature and for a longer self-seeding time. Because of the larger amount of solution, the thermal equilibrium is only reached at longer times. After, the tube was placed in an isothermal crystallization bath for 7 days to allow complete crystallization. The crystals were collected using vacuum filtration with a Buchner funnel and aspirator. The filter paper had a mesh size of 4 μm; therefore, the crystal size needed to be greater than 5 – 10 μm to ensure collection. Typically, crystals are grown from larger concentration; however, due to difficulties in the PEO-b-PCL crystallization at higher concentrations, two test tubes of crystals grown simultaneously were collected on the same filter paper. After filtration, the crystals were washed with pure solvent and placed into a vacuum oven for 5 days to allow for complete removal of residual solvent.

3.3 Characterization of Single Crystals

Characterization of the single crystals includes the determination of morphology and thickness using atomic force microscopy (AFM), morphology and crystal structure using transmission electron microscopy (TEM) and electron diffraction (ED), and crystallization of the tethers by TEM ED and differential scanning calorimetry (DSC). The experimental procedures for each of these techniques required the collection of single crystals from solution prior to analysis, except for DSC experiments on the bulk samples.
3.3.1 Atomic Force Microscopy (AFM)

A few drops of single crystal solution were transferred onto glass cover slides, and the solvent was allowed to evaporate. They were then placed in a vacuum oven for several hours to ensure the complete removal of the solvent. A Digital Instruments Nanoscope IIIA AFM was used in the tapping mode to determine the overall thickness of the sandwiched single crystal. The tapping mode with a carefully chosen cantilever tip-to-sample force was best for limiting damage to the single crystal. The scanner was calibrated in both the lateral and vertical directions using the standard grid. The typical measurement conditions were a scan size of 20 μm x 20 μm at a scan rate of 1 Hz with operation and resonance frequencies around 300 kHz. The resolution of the captured image was 512 x 512.

3.3.2 Transmission Electron Microscopy (TEM)

A few drops of the crystal solution were deposited onto a carbon-coated copper TEM grid with a mesh size of 400 μm. A similar solvent removal technique to the AFM sample preparation was used. A Philips Tecnai 12 microscope was used to obtain bright field (BF) and electron diffraction (ED) images. The accelerating voltage was 120 kV. The ED spacing was calibrated with a TlCl sample with specific $d$-spacing values and several higher-order diffractions.
3.3.3 Differential Scanning Calorimetry

The thermal characteristics of the bulk and crystal mat samples were obtained using a Perkin-Elmer PYRIS Diamond DSC coupled with an Intracooler 2P apparatus. A typical sample weight was 1.0 mg for bulk samples and 0.3 mg for crystal mat samples. The difference in pan weights between the reference and sample was kept less than 0.005 mg. The heating and cooling rates were varied depending on the sample.

3.4 Monte Carlo (MC) Simulation of Chain Conformations

The conformation of the tethered PMMA polymers is important for determining the reduced tethering density; however, it is difficult to perform measurements in the single crystal tethered state. The easiest approach to analyzing the size and conformation of these chains is to use Monte Carlo (MC) simulations to model their behavior under the experimental conditions. From these simulations, it is possible to gather pertinent information such as the chain dimensions $R_{g,x,y}^2$ and $R_{g,z}^2$ for adsorbed chains. The following sections describe the basic set-up and procedure for performing the MC simulations.

The simulation procedures follow closely with those presented by Luettmers-Strathmann and coworkers in Ref. 81. The bond-fluctuation (BF) model\textsuperscript{[149]} was used for this study of tethered polymer chains where $N = 16, 32, \text{ and } 64$. In the BF model, monomers occupy single sites on a cubic lattice with lattice constant, $a_c = 1$. The bond
lengths are allowed to vary between $b = 2a_c$ and $\sqrt{10}a_c$. The tethered state is achieved by fixing the first monomer to a position just above the hard surface at $z = 0$.

Two important interactions are accounted for in this simulation. One is the monomer-surface interaction, $\varepsilon_s$. An amount of $\varepsilon_s$ is added to the energy of the system when a monomer bead is located at $z = 1$. The second is the interaction between monomer beads, $\varepsilon_b$. A contribution of $\varepsilon_b$ is added to the total energy when beads $i$ and $j$ are located at a distance, $r_{ij}^2$, where $4 \leq r_{ij}^2 \leq 10$. Distances less than $r_{ij}^2 = 4$ are prohibited by hard-core interactions, and distances larger than $r_{ij}^2 = 10$ represent non-interacting monomers. The range of attractive interactions (2 - $\sqrt{10}$) is larger than in Ref. 81 (2 - $\sqrt{6}$). The extended interaction range extends the range of conditions where the polymer is amorphous.$^{[150]}$ This allows us to model amorphous chains in a wide range solvent conditions. The total energy of the system is calculated by:

$$E(n_s, n_b) = n_s \varepsilon_s + n_b \varepsilon_b$$

(3.1)

where $n_s$ is the number of surface contacts and $n_b$ is the number of monomer-monomer contacts. A single state of the system is defined by the set $(n_s, n_b)$.

In these simulations, three types of elementary moves were performed. They are local moves, pivot moves, and cut-and-permute moves. Local moves are typical displacements of a monomer to a nearest neighbor lattice site. Pivot moves are of the chain section beyond the pivot site about the $z$-axis. In cut-and-permute moves, the chain is cut at a chosen segment, and the tethered portion is exchanged with the top portion, which is then tethered to the surface before recombining the free-end monomer with the tethered portion.
3.4.1 Wang-Landau Algorithm

The simulations for tethered chains begin with the determination of the density of states. Because many chain conformations have the same contact numbers, a state \((n_s, n_b)\) has degeneracy. The density of states (dos) is the number of conformations for a given state \((n_s, n_b)\); it is written as \(g(n_s, n_b)\). The density of states of the tethered chain is not known \textit{a priori} but is determined by an iterative Wang-Landau algorithm.\[83\] In the WL algorithm, an elementary move attempt from one state \((n_s, n_b)\) to another \((n'_s, n'_b)\) is accepted with probability:

\[
p[n_s, n_b] \rightarrow [n'_s, n'_b] = \min\left(\frac{g(n'_s, n'_b)}{g(n_s, n_b)}, 1\right)
\]

(3.2)

where \(g(n_s, n_b)\) is the current estimate for the dos.

In the original Wang-Landau algorithm, the simulation proceeds through a number of iteration levels. After a move attempt, the dos is updated within the current iteration level. In addition, the histogram of visits to each state, \(h(n_s, n_b)\), is updated. After the move attempt is made, the updates are as follows:

\[
\begin{aligned}
\text{if accepted:} & \quad \ln(g(n'_s, n'_b)) \rightarrow \ln(g(n'_s, n'_b)) + \ln(f_i) \\
h(n'_s, n'_b) & \rightarrow h(n'_s, n'_b) + 1 \\
\end{aligned}
\]

(3.3)

\[
\begin{aligned}
\text{if rejected:} & \quad \ln(g(n_s, n_b)) \rightarrow \ln(g(n_s, n_b)) + \ln(f_i) \\
h(n_s, n_b) & \rightarrow h(n_s, n_b) + 1 \\
\end{aligned}
\]

(3.4)

where \(f_i\) is the refinement factor and is greater than 1. An iteration is complete when the histogram meets a flatness criterion, meaning each state is visited roughly an equal number of times. Then, the histogram is set to zero; the refinement factor is reduced; and
the procedure is begun again at the next iteration level. In this work, we employed the shortened WL algorithm for chains of length $N = 16$ and modified (frequent update) algorithm\textsuperscript{[151]} for chains of length $N = 32$ and $N = 64$.

3.4.2 Umbrella Sampling

Umbrella sampling is an important technique for refining the density of states. In umbrella sampling, the same WL acceptance criterion is used in simulations starting from a good estimate of $g(n_s, n_b)$. The histogram updates are the same during the simulation, equations 3.3 and 3.4, but the dos is only updated at the end. This was applied in the current simulations of chains of $N > 16$. Umbrella sampling removes any bias in the dos due to modifications in the WL algorithm. The high maximum number of monomer-monomer contacts results in a much larger number of conformations and in a wide range of degeneracy values. Unfortunately, this can lead to the omission of some states during the already long simulation time. The umbrella sampling time is chosen to ensure that all states are visited many times.

3.4.3 Production Stage

The production simulations are used to analyze important parameters associated with each configuration of each $(n_s, n_b)$. These include density profiles ($\varphi(z)$ and $\rho(x,y)$) and chain dimensions. The positions of each monomer were stored as a set of Cartesian coordinates $x_i, y_i, \text{ and } z_i$ (or position vector, $r_i$). For the set of monomers, $R_{g,xy}^2, R_{g,z}^2$,
mean average squared end-to-end distance, $<R_e^2>$, and the mean average bond length, $<b_l^2>$, were calculated from,

$$R_{g,xy}^2 = \frac{1}{N^2} \sum_{i<j} [(x_i - x_j)^2 + (y_i - y_j)^2]$$  \hspace{1cm} (3.5)

$$R_{g,z}^2 = \frac{1}{N^2} \sum_{i<j} (z_i - z_j)^2$$ \hspace{1cm} (3.6)

$$\langle R_e^2 \rangle = \langle (\vec{r}_N - \vec{r})^2 \rangle$$ \hspace{1cm} (3.7)

$$\langle b_l^2 \rangle = \frac{1}{N-1} \sum_{i=1}^{N-1} \langle (\vec{r}_{i+1} - \vec{r}_i)^2 \rangle$$ \hspace{1cm} (3.8).

The overall radius of gyration is $R_g^2 = R_{g,xy}^2 + R_{g,z}^2$. Several sets of simulation data for each $N$ were combined to find weighted averages and the standard error of the parameters. The simulation values of $R_g^2$ were compared with the experimental PMMA free $R_g^2$ to evaluate possible values of $R_{g,xy}^2$ and $R_{g,z}^2$ for the experimental system.

3.4.4 Evaluation of Density of States

After the dos has been collected, the thermodynamics of the system can be calculated using the partition function,

$$Z = \sum_{n_s, n_b} g(n_s, n_b) e^{-\beta E(n_s, n_b)}$$ \hspace{1cm} (3.9)

where $\beta = 1/k_B T$. The energy of the system, $E(n_s, n_b)$, is defined above as the sum of the monomer-surface and monomer-monomer interactions. It is dependent on the number $(n_i)$ of each as well as the strength ($\varepsilon_i$). A simple way to evaluate the system is by using
field variables, $\beta_s$ and $\beta_b$, where $\beta_s = -\varepsilon_s \beta$ and $\beta_b = -\varepsilon_b \beta$. Then, the partition function becomes:

$$Z(\beta_s, \beta_b) = \sum_{n_s, n_b} g(n_s, n_b) e^{\beta_s n_s} e^{\beta_b n_b}$$ (3.10).

The probability for a state $(n_s, n_b)$ at given fields $\beta_s, \beta_b$ is

$$P(n_s, n_b; \beta_s, \beta_b) = \frac{1}{Z} g(n_s, n_b) e^{\beta_s n_s} e^{\beta_b n_b}$$ (3.11).

For any quantity, $Q(n_s, n_b)$, the average is calculated as:

$$\langle Q \rangle = \sum_{n_s, n_b} P(n_s, n_b; \beta_s, \beta_b) Q(n_s, n_b) = \frac{1}{Z} \sum_{n_s, n_b} g(n_s, n_b) e^{\beta_s n_s} e^{\beta_b n_b}$$ (3.12).

At high $\beta_s$, the monomers have a higher probability of interacting with the substrate. At high $\beta_b$, the monomers have a higher probability to interact with each other. This is similar to tuning the solvent quality. Increasing monomer-monomer interaction is synonymous with poorer solvent conditions. Thermodynamic parameters such as free energy, entropy, heat capacity, average number of contacts, and susceptibility are derived from this partition function. The free energy is defined as:

$$G(\beta_s, \beta_b) = -\ln(Z)$$ (3.13)

and the average number of contacts, $\langle n_s \rangle$ and $\langle n_b \rangle$, are the first derivative of the free energy with respect to the appropriate field variable:

$$\langle n_s \rangle = -\left( \frac{\partial G}{\partial \beta_s} \right)_{\beta_b}$$ (3.14)

$$\langle n_b \rangle = -\left( \frac{\partial G}{\partial \beta_b} \right)_{\beta_s}$$ (3.15).
The second derivatives define the susceptibilities, $\chi_{ij}$. The susceptibilities are determined from fluctuations in the number of surface and monomer contacts.

$$\chi_{ss} = -\left( \frac{\partial^2 G}{\partial \beta_s^2} \right)_{\beta_s} = \langle n_s^2 \rangle - \langle n_s \rangle^2$$  \hspace{1cm} (3.16)

$$\chi_{bb} = -\left( \frac{\partial^2 G}{\partial \beta_b^2} \right)_{\beta_s} = \langle n_b^2 \rangle - \langle n_b \rangle^2$$  \hspace{1cm} (3.17)

$$\chi_{sb} = -\left( \frac{\partial^2 G}{\partial \beta_s \partial \beta_b} \right) = \langle n_s n_b \rangle - \langle n_s \rangle \langle n_b \rangle$$  \hspace{1cm} (3.18)

$$\chi_{total} = \chi_{ss} + \chi_{bb} + 2\chi_{sb}$$  \hspace{1cm} (3.19).
CHAPTER IV
GROWTH AND CHARACTERIZATION OF SINGLE CRYSTALS

The growth of uniform single crystals from dilute solution is the critical step to determining the physics of tethered polymer systems using diblock copolymers. From the self-seeding technique, a large population of such crystals was grown. The determination of the crystal thickness was performed on a large sample of crystals to ensure accurate results. It is this crystal thickness that provides an indirect method for determining the regime in which the tethered amorphous chains exist.

4.1 Self-Seeding in Dilute Solution

The self-seeding procedure was utilized in the crystallization of all samples for this study. The result was a solution of precisely manufactured single crystals. The thickness and size of the crystals was highly uniform. The thickness was determined by the isothermal crystallization temperature; while, the size was determined by the self-seeding temperature. At slightly higher $T_s$ ($+0.5^\circ$C), the size of the crystals increased, and the population of crystals decreased. The higher $T_s$ dissolved more of the dendritic crystals providing a higher mass of crystallizable chains. This lead to fewer seeds (lower population). The subsequent growth on these seeds by the dissolved material resulted in
larger crystals. The determination of a $T_s$ with a balance between size and population was important for reproducible results. The self-seeding time, $t_s$, also played a role in the determination of crystal size and population though not as critical.

Each sample has a specific set of $T_s$ and $t_s$ to obtain the best results. The molecular weight of the crystalline block as well as the ratio between the amorphous and crystalline blocks can alter the $T_s$ slightly from sample to sample. For the PMMA-$b$-PLLA sample, self-seeding was found to be most effective at $T_s = 113^\circ$C. The PEO-$b$-PCL samples had different $T_s$’s for each. They were 52$^\circ$ and 46$^\circ$C for the EOCL-11 and EOCL-31, respectively. When homo-PEO was used for epitaxial growth, the $T_s$ was 42$^\circ$C. The best $t_s$ was found to be 20 minutes for all samples.

4.2 Morphology of Single Crystals

Figure 4.1 is a set of two AFM height images of the PMMA-$b$-PLLA (a) and PEO-$b$-PCL (b) crystals. The PLLA crystal is lozenge-shaped because of the orthorhombic crystal structure. It is bound by four (110) growth planes. The PCL crystal is a truncated lozenge shape. It too has an orthorhombic crystal structure. The truncated morphology is created by differences in planar growth rates.$^{[152]}$ The crystallization temperature dependence of the growth in the [200] direction is different than that for the [110] direction. Because the [200] direction is slower, the (200) growth faces appear to form the truncated morphology (four (110) faces and two (200) faces). As the $T_x$ is increased, the [200] growth rate becomes increasingly more important, resulting in “elongated” truncated crystals.
The PLLA crystal was grown in amyl acetate at $T_x = 68^\circ$C. It has two layers of PMMA tethered chains on either side of the crystal. The exclusion of these chains from the crystalline lattice leads to their tethering on the surface. They exist on both basal surfaces due to the thermodynamic probability of having a chain end (or junction point in this case) at either side of the crystal. The PCL crystal was grown in $n$-hexanol at $T_x = 30^\circ$C. This crystal has PEO tethered on either side. The crystal was grown from the EOCL-31 sample. All crystals of either copolymer show the same morphology at all $T_x$’s and are the same as the homopolymer of each crystalline block.

![AFM height images of single crystals. (a) PMMA-b-PLLA (b) PEO-b-PCL. PLLA has a lozenge-shape and is bound by four (110) planes. PCL has a truncated lozenge shape and is bound by four (110) planes and two (200) planes.](image)

4.3 Crystal Structure of Single Crystals

The crystal structure of each copolymer was verified using the electron diffraction (ED) technique of TEM. Figure 4.2 is the bright-field image of PMMA-b-PLLA and PEO-b-PCL with each ED pattern as the insert. Both bright-field images show the same morphology as those seen in the AFM images of Figure 4.1. The PLLA ED image
exhibits the \((hk0)\) pattern from the [001] zone expected for the pseudo-orthorhombic, \(\alpha\)-form structure for PLLA.\(^{[153]}\) This matches the pattern for a homopolymer sample from the [001] zone of the crystal. The PCL ED image also shows the orthorhombic structure expected for a PCL crystal.\(^{[154]}\) Again, the electron beam is parallel to the [001] zone of the crystal, resulting in the \((hk0)\) diffraction pattern. In all cases, the crystal chain direction is parallel to the lamellar normal.

Figure 4.2 Bright-field TEM images of single crystals (a) PMMA-\(b\)-PLLA (b) PEO-\(b\)-PCL. The insets of each figure are the ED patterns for the [001] zone of the crystal.

4.4 Thickness Determination

In order to study the physics of tethered chain molecules using diblock copolymer single crystals, the thickness of said crystals must be measured. Due to the use of self-seeding, all crystals grown from dilute solution are of a similar size and have a thermodynamically determined thickness associated with \(T_x(d_{\text{CRYST}} \propto 1/\Delta T)\). It is difficult to measure the crystal thickness in solution; therefore, all thicknesses were
measured in the dry state. The crystal thickness is formed in solution. The amorphous layer thickness varies between solvated and the dried state, but drying did not affect the crystal thickness. The probe for measuring the tether physics is the crystal thickness, so the dried state measurements are still accurate.

Figure 4.3 AFM height image of a PMMA-\textit{b}-PLLA crystal grown at 68°C. The profile of the crystal thickness is also included. $d_{\text{OVERALL}}$ is 13.6 nm.

The overall thickness ($d_{\text{OVERALL}}$) of the PMMA-\textit{b}-PLLA and PEO-\textit{b}-PCL crystals was measured using tapping mode AFM. Figure 4.3 is an example of the height image and profile of a PMMA-\textit{b}-PLLA crystal grown in amyl acetate at 68°C. The stepheight function was used to measure $d_{\text{OVERALL}}$. The profile was flattened according to the leveling of the substrate on either side of the crystal. The $d_{\text{OVERALL}}$ was measured in several directions along the crystal (crystal average) and from many different crystals on the glass substrate (sample average). In Figure 4.3, $d_{\text{OVERALL}}$ is 13.6 nm. For a sample at 68°C, the average $d_{\text{OVERALL}}$ was 13.6 ± 0.1 nm.
A similar procedure was utilized for the PCL crystals. Several crystals were measured to obtain the average and standard deviation for the sample set. For a crystal grown at 30°C, the average $d_{\text{OVERALL}}$ was 12.9 ± 0.2 nm.

4.4.1 Calculation of Crystal Thickness ($d_{\text{CRYST}}$)

The observable parameter that is needed to determine the interaction of the tethered chains is the crystal thickness, $d_{\text{CRYST}}$. It is known that the amorphous portions form a “sandwiched” structure with the crystalline block in between them.\[^{[117]}\] Obtaining this quantity experimentally is difficult; therefore, an analytical approach has been developed to determine the $d_{\text{CRYST}}$ from $d_{\text{OVERALL}}$.\[^{[119]}\]

The crystalline thickness is determined from the volume fraction of crystallizable material ($\nu_{\text{CRYST}}$):

$$d_{\text{CRYST}} = d_{\text{OVERALL}} \times \nu_{\text{CRYST}}$$ (4.1)
The $\nu_{\text{CRYST}}$ is determined by the molecular weights and crystalline or amorphous densities of the two components. The equation to calculate $\nu_{\text{CRYST}}$ is:

$$\nu_{\text{CRYST}} = \frac{M_n^c / \rho_c}{M_n^c / \rho_c + M_n^a / \rho_a}$$  \hspace{1cm} (4.2)$$

where $\rho_c$ is the crystalline density of the crystalline block and $\rho_a$ is the amorphous density of the amorphous block. For a lamellar single crystal, there is some fraction of the crystalline chain that is amorphous (folds). This should lead one to believe that the use of a weighted fraction of the crystalline and amorphous densities for the crystalline block should be used. It has been shown, however, that the weight percent crystallinity of the single crystals is near 95%, and the weighted average of the two densities is not far from the pure crystalline density.\cite{119} The error between the two values is around 1%. Hence, it is still appropriate to use the pure crystalline density for the calculation of $\nu_{\text{CRYST}}$.

Table 4.1 shows $M_n$, $\rho_i$, and $\nu_{\text{CRYST}}$ values for each sample.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_n^a$ (kg/mol)</th>
<th>$M_n^e$ (kg/mol)</th>
<th>$\rho_a$ (g/cm$^3$)</th>
<th>$\rho_c$ (g/cm$^3$)</th>
<th>$\nu_{\text{CRYST}}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA-$b$-PLLA</td>
<td>7.8</td>
<td>22.3</td>
<td>1.19 [155]</td>
<td>1.28 [119]</td>
<td>0.73</td>
</tr>
<tr>
<td>EOCL-11</td>
<td>5.0</td>
<td>6.3</td>
<td>1.12 [119]</td>
<td>1.14 [156]</td>
<td>0.55</td>
</tr>
<tr>
<td>EOCL-31</td>
<td>5.0</td>
<td>26.5</td>
<td>1.12</td>
<td>1.14</td>
<td>0.84</td>
</tr>
</tbody>
</table>

The value for $d_{\text{CRYST}}$ in the PMMA-$b$-PLLA sample grown at $T_x = 68^\circ C$ (Figure 4.3) was determined to be 9.9 nm, $d_{\text{CRYST}} = (13.6 \text{ nm})(0.73)$. The values at each crystallization temperature for the PMMA-$b$-PLLA sample were calculated using the same procedure. For the PEO-$b$-PCL sample (EOCL-31), $d_{\text{CRYST}}$ for the crystal grown at $T_x = 30^\circ C$ (Figure 4.4) was 10.8 nm ($d_{\text{CRYST}} = (12.9 \text{ nm})(0.84)$). For this sample, even
though the PEO is a crystallizable material, it is amorphous under these conditions. Further evidence of this will be shown in subsequent chapters. Therefore, the amorphous PEO density was used to calculate $\nu_{\text{CRYST}}$.

4.4.2 Determination of $d_{\text{CRYST}}$ Through Lateral Epitaxy

The verification of this analytical method is an important part of this research. There are a few methods for doing so, including x-ray diffraction of crystal mats and growth of homopolymer on the lateral surface of the diblock crystal, that are discussed by Zheng.\[157\] In all methods, it was found that $d_{\text{CRYST}}$ determined by the volume fraction method was as accurate as the experimental methods. For this research, it is assumed that this method still holds; however, one sample of lateral growth of homopolymer was conducted for additional verification. The following is a description of these results.

Diblock crystals can be used as a seed to further grow homopolymer on the lateral surface. The epitaxial growth is possible because of lattice matching. The thermodynamic metastable thickness of these two crystal types at the same $T_x$ is not the same due to the energetic contribution of the amorphous chains on the diblock sample. However, near the interface between the two crystal types, the homopolymer crystal has the same $d_{\text{CRYST}}$ as the block copolymer crystal. As the crystal grows away from the seed, the thermodynamic thickness is achieved. A measurement of the interface thickness provides an accurate determination of $d_{\text{CRYST}}$ for the diblock sample. Figure 4.5 is an AFM height image of the PMMA-$b$-PLLA diblock crystal (center) with homopolymer PLLA growth on the outside crystallized at 75°C. The PMMA-$b$-PLLA
crystal was grown at 75°C using the self-seeding method. A homo-PLLA solution was made, and the polymer was dissolved at $T_d$. The homo-PLLA solution was quenched to 75°C. A few drops of the diblock single crystal solution were added to the homo-PLLA solution to act as seeds for growth. The morphologies of the two types of crystal are identical. The profile of this system can also be found in the figure. The value of $d_{CRYST}$ determined by this method is 10.60 nm which is commensurate to the calculated value of 10.58 nm. Thus, the analytical method was sufficient for determining $d_{CRYST}$ of the diblock sample.

Figure 4.5 PMMA-$b$-PLLA crystal with epitaxial growth of homo-PLLA on the outside. (a) AFM height image, (b) profile, and (c) close-up of interface between the two sections. The thickness at the interface between the two types of crystals (c) is similar to that calculated by the analytical method.
CHAPTER V
DETERMINATION OF THE ONSET OF THE INTERACTION REGIME

The transition from the non-interacting regime into the interacting regime ($\sigma^*$) is an important benchmark in tethered polymer properties. At this transition, the substrate is completely covered by the polymer chains, and the compression of these chains leads to a slight conformational change. This transition can be indirectly detected by the relationship between the crystallization temperature ($T_x$) and crystal thickness ($d_{\text{CRYST}}$) for these diblock copolymer systems. The thickness of the crystal is partially determined by the fold surface energy of the crystal. The addition of tethered chains influences this surface energy in such a way that enables the researcher to define the $\sigma^*$ for the experimental system as shown by Chen\textsuperscript{[118]} and Zheng.\textsuperscript{[119]} This analysis was performed on both the PMMA-$b$-PLLA and PEO-$b$-PCL samples.

5.1 Crystallization Theory

In the self-seeding procedure, crystallization occurs on the pre-existing seed made during the self-seeding step. The growth of the single crystal is determined by the creation of a new surface on this seed. This procedure is a secondary nucleation. The "nucleation" is the deposition of the dissolved polymer chain onto the crystal’s smooth
lateral surface. When this occurs, four new surfaces are created. These surfaces are the two \( ab \) surfaces and two \( bd \) surfaces as illustrated in Figure 5.1. The new \( ad \) surface has the same energetic contribution as the surface on which the chain deposited; therefore, there is no additional energy associated with this surface. The free energy of this nucleation with the dimensions \( a, b, \) and \( d \) can be expressed as: \([120]\)

\[
\Delta G_i = -abd\Delta g_f + 2ab\gamma + 2bd\gamma_c
\]

(5.1)

where \( \Delta G_i \) is the total free energy, \( \Delta g_f \) is the volumetric free energy gain, \( \gamma \) is the lateral surface free energy per area, and \( \gamma_c \) is the fold surface free energy per area. The first term is the free energy associated with the volume increase. This is always thermodynamically favorable and, thus, has a negative sign. The other two terms are associated with the free energy gain by creating new surface. The surface free energies destabilize the new crystal.

Figure 5.1 Schematic illustration of nucleation of a crystallizable segment onto a crystal seed.
In order for the crystal to grow into the single crystal form, a critical size of the new nucleus must be reached. At this critical size, crystal growth continues spontaneously. The crystal size can be determined by maximizing \( \Delta G_i \) with respect to the dimensions. In the case of polymeric crystals, \( b \) is constant and can be denoted as \( b_o \).

Then, differentiation of \( \Delta G_i \) with both \( a \) and \( d \) is performed,

\[
\frac{\partial \Delta G_i}{\partial a} = -b_o d \Delta g_f + 2b_o \gamma \quad (5.2)
\]

\[
\frac{\partial \Delta G_i}{\partial d} = -ab_o \Delta g_f + 2b_o \gamma_c \quad (5.3).
\]

Both of these terms are set equal to zero to find the maximum in \( \Delta G_i \), and the critical dimensions for \( a \) and \( d \) are:

\[
a^* = \frac{2\gamma}{\Delta g_f}, \quad d^* = \frac{2\gamma_c}{\Delta g_f} \quad (5.4, 5.5).
\]

The free energy change with volume can be expressed as the enthalpy change, assuming that the entropy of fusion does not change much with temperature:

\[
\Delta g_f = \Delta h_f - T \Delta s_f \quad (5.6)
\]

where \( \Delta h_f \) is the enthalpy of fusion at the dissolution temperature and \( \Delta s_f \) is the entropy of fusion. Then, \( \Delta s_f \) can be rewritten such that \( \Delta g_f \) is only a function of \( T \) and \( \Delta h_f \):

\[
\Delta g_f = \Delta h_f - T_d \Delta s_f = 0 \quad (5.7)
\]

\[
\Delta s_f = \frac{\Delta h_f}{T_d} \quad (5.8)
\]

\[
\Delta g_f = \Delta h_f - T_s \frac{\Delta h_f}{T_d} = \Delta h_f (T_d - T_s) = \frac{\Delta h_f \Delta T}{T_d} \quad (5.9)
\]
where $T_x$ is the crystallization temperature. From this derivation, it is possible to define $d_{\text{CRYST}}$, which is the same as $d$ described above, as:

$$d_{\text{CRYST}} = \frac{2\gamma_c T_d}{\Delta h_f \Delta T} \tag{5.10}.$$  

This equation can be rearranged to obtain the form used by Chen and Zheng:\[1^{118-119}\]

$$\frac{1}{d_{\text{CRYST}}} = \frac{\Delta h_f}{2\gamma_c} - \frac{\Delta h_f}{2\gamma_c T_d} T_x \tag{5.11}.$$  

5.1.1 Crystallization of Diblock Copolymers

The results of this derivation are modified for diblock copolymer single crystals. For the diblock crystals, the addition of large, amorphous chains on the top and bottom surfaces provides an additional energetic term that needs to be considered. The first approach to diblock single crystals was a theoretical discussion by DiMarzio and coworkers.\[1^{158}\] They addressed this system assuming a sandwich-like structure, which has since been verified (see Ref. 117), under thermodynamic equilibrium conditions.

A crystal of this form was assumed to be in an equilibrium state due to the competition between crystallization and chain compression on the surface. In typical single crystalline homopolymers, the equilibrium conformation is the extended chain crystal; however, in the diblock copolymer system, the amorphous chains would exhibit a highly stretched conformation if the crystal was in the extended chain form. This extreme stretching decreases the number of conformations for the amorphous chains and increases the overall free energy. Hence, the folded-chain conformation for the single
crystal is the thermodynamic equilibrium state. This conformation allows for the balance of the enthalpic contribution of crystallization and entropic contribution of the amorphous tethers to balance. The final state of the system (number of folds) is ultimately determined by the molecular weight of both blocks and the solvent quality.

The major goal of this study was to determine the equilibrium thickness (fold number) for the crystalline layer. DiMarzio’s model was based on the molecular weight of each block \((N_c, N_a)\) and the amount of solvent in the amorphous layer \((v_o)\). The three major parameters were the amorphous layer thickness \((l_a)\), the crystalline layer thickness \((l_c, \text{ where } l_c \text{ is synonymous with } d_{\text{CRYST}})\), and the distance between tethering points \((r)\).

The densities of each layer can be defined using these parameters as:

\[
\rho_i = \frac{N_i}{l_i r^2} \quad \text{for } i = c \text{ or } a
\]  

\((5.12)\).

Figure 5.2 is a schematic of the model system.

![Figure 5.2 Schematic of the DiMarzio model for solution grown diblock single crystals.](image)

The free energy of the layered system is comprised of three parts: the amorphous layer free energy \((E_a)\), the crystalline layer free energy \((E_c)\), and the interfacial free energy \((E_s)\). The defining equations for each of these contributions are:
where $H_a$ is the enthalpy of the amorphous layer, $S_a$ is the entropy of the amorphous layer, $\Delta H$ is the bulk free energy per monomer, and $\gamma_s$ is an energetic term that “accounts for all ignored and unsolved parts,” as stated by the authors. The amorphous part was treated following Flory’s theory. After deriving the definitions of $H_a$ and $S_a$ and minimizing the free energy of the total system with respect to $r$, DiMarzio and coworkers found the governing equations for $l_c$ and $l_a$. They are:

\[
\begin{align*}
l_c &= \frac{N_c \rho_c^{2/3} (\gamma_s + \gamma_c \rho_c)^{1/3}}{\rho_c (3k_B T)^{1/3} N_a^{1/3}} \\
l_a &= \frac{N_a^{2/3} (\gamma_s + \gamma_c \rho_c)^{1/3}}{(3k_B T \rho_a)^{1/3}}
\end{align*}
\]

It is now known that these equations are slightly inaccurate based on the scaling theory for polymer brushes of Alexander. These governing equations have been recalculated by Zheng by releasing the constant density constraint and utilizing the scaling theory free energy definition.

In DiMarzio’s model, the free energy of the amorphous layer was analyzed using the Flory theory for $H_a$ and $S_a$. Zheng used Alexander’s scaling approach to model the amorphous layer:

\[
E_a \sim k_B T \left( \frac{12 \rho_a a^3}{l_a r^2} + \frac{l_a^2}{N_a a^2} \right)
\]
with DiMarzio’s variables and where $v$ is the excluded volume and $a$ is the segment size.

The free energies of the crystalline layer and interfacial layer remain the same. The overall free energy minimum can be derived, and the equilibrium layer thicknesses are:

\[
I_a \sim \left( \frac{v(\gamma_c \rho_c + \gamma_s)}{k_a T} \right)^{1/5} N_a^{4/5}
\]

(5.19)

\[
I_c \sim \left( \frac{\gamma_c \rho_c + \gamma_s}{k_a T} \right)^{3/5} N_a^{-3/5} N_c v^{-2/5} \rho_c^{-1}
\]

(5.20).

For simplicity, the prefactors and segment size have been excluded. If this model is compared to the DiMarzio model, it can be seen that the amorphous layer thickness depends more strongly on the amorphous chain molecular weight ($I_a \sim N_a^{4/5}$ versus $I_a \sim N_a^{2/3}$), but both are between the good solvent conditions ($I_a \sim N_a^{3/5}$) and the stretched brush case ($I_a \sim N_a$). In addition, by replacing the constant density assumption of DiMarzio’s model with the variable definition derived from Zheng’s model, the scaling of both models agrees well.

The analysis of the diblock copolymer single crystal system indicates that the inclusion of the amorphous block on the basal surface of the single crystal will affect the thermodynamics of crystallization. The resultant crystal thickness is affected by the crowding of the amorphous chains on the surface. The molecular mechanism for creating the tethered surface is based on the addition of crystallizing chains onto the lateral growth surface. The amorphous chains are, thus, added nearly one at a time. This varies from the grafting-to and grafting-from techniques where the individual tethering is created simultaneously. The uniqueness of this mechanism combined with the indirect measurement through crystal thickness that provides evidence of the transition into the
interacting regime of tethered polymers. From equation 5.11, the slope of the relationship between $1/d_\text{CRYST}$ and $T_x$ is proportional to $1/\gamma_e$. Prior to the tethered chain interaction, $\gamma_e = \gamma_c$; however, the interaction of the tethered chains alters this relationship to $\gamma_e = \gamma_c + \gamma_t$. This new free energy term is similar to the $\gamma_s$ term in the DiMarzio model. This proves that the crystal thickness has a different dependence on $T_x$ after this transition.

5.2 Non-interacting Regime

The non-interacting regime exists when the tethered chains on the basal surface of the crystal are far enough apart that they do not affect the crystallization in a significant way. In this case, the plot of $1/d_\text{CRYST}$ versus $T_x$ follows a single slope that is similar to one obtained from the homopolymer in the same solution conditions. Figure 5.3 is a plot of the homopolymer PLLA $d_\text{CRYST}$ as replotted from Zheng.\textsuperscript{[157]} The data exhibits the single slope, $m$, that is equal to $-\Delta h_d/(2\gamma_e T_d)$. Figure 5.4 is a comparison of the diblock copolymer PMMA-\textit{b}-PLLA at low $T_x$ (low $\tilde{\sigma}$) with the homo-PLLA data. The $d_\text{CRYST}$ of the PLLA block was determined using the calculated method discussed in Chapter IV. It can be seen that the slope of the diblock data is nearly identical to that of the homopolymer, $m_{\text{homo}} = -0.0010 ^\circ\text{C}^{-1}$ and $m_{\text{diblock}} = -0.0011 ^\circ\text{C}^{-1}$, as calculated by the least mean squares fit trendline function in Excel. This is evidence that the PMMA tethers do not influence the PLLA crystallization and are thus in the non-interacting regime. In other words, $\gamma_e = \gamma_c$, or the surface energy associated with the fold-surface of the crystal.
Figure 5.3 $1/d_{\text{CRYST}}$ versus $T_x$ for a homopolymer PLLA in amyl acetate. The slope, $m$, is representative of PLLA in amyl acetate.

Figure 5.4 $1/d_{\text{CRYST}}$ versus $T_x$ for homo-PLLA and PMMA-b-PLLA at low $T_x$ (low $\tilde{\sigma}$). The slope of the two sets of data is nearly identical. This indicates that the PMMA is in the non-interacting regime.

These results are similar to those reported by Chen$^{118}$ and Zheng.$^{119}$ The low $T_x$ region, or low $\tilde{\sigma}$ region, is shown to be in the non-interacting regime. For their case, the PS tethers do not have an attractive interaction with the PLLA surface. Because of this,
they can be assumed to maintain their typical solution dimensions. For amyl acetate, the PS is in a good solvent. In the PMMA-b-PLLA system, the PMMA tether is attracted to the PLLA surface as determined by their miscibility in the bulk melt state.\cite{159} Thus, the conformation of the PMMA is much different than PS. Amyl acetate is a moderately good solvent for the PMMA (theta temperature is \(58^\circ\text{C}\)).\cite{155} The PMMA will, however, still adopt the pancake conformation. It is difficult to prove these conformations experimentally due to the small size and the measurement of the diblock single crystal thickness in the dry state.

The same non-interacting regime can be found for the EOCL-31 sample grown in \(n\)-hexanol. At low \(T_x\), in this case between \(29^\circ\text{C}\) and \(36^\circ\text{C}\), the slope exhibits a singular value. This slope is attributed to the PEO chains existing in the non-interacting regime. For the PEO chains at low tethering density, their interactions with the PCL substrate are repulsive because they are immiscible in the melt,\cite{146} similar to the PS-b-PEO and PS-b-PLLA systems in Ref. 118 and 119. Because they have repulsive interactions, the conformation of the PEO should be similar to the untethered state in \(n\)-hexanol.

5.3 Transition into Interacting Regime

As the crystallization temperature is increased in these systems (PMMA-b-PLLA and EOCL-31), a transition in the slope of \(1/d_{\text{CRYST}}\) versus \(T_x\) appears. Figures 5.5 and 5.6 show the results for PMMA-b-PLLA and EOCL-31, respectively. In both figures, it can be seen that the initial slope, associated with the non-interacting regime, transitions to a lower value above the critical temperature, \(T_c\). At this point, the \(\gamma_c\) becomes dependent
on both the free energy of the fold-surface as well as the interaction between the tethered chains ($\gamma_e = \gamma_c + \gamma_t$). This additional term in $\gamma_e$ leads to a smaller $m$-value because $m \propto 1/\gamma_e$ according to equation 5.11. The transition in the slope is, therefore, the transition into the interacting regime.

![Graph](image1.png)

Figure 5.5 Plot of $1/d_{CRYST}$ versus $T_x$ for PMMA-b-PLLA. A transition in the slope, $m$, indicates the transition from the non-interacting to the interacting regime for the PMMA tethers.

![Graph](image2.png)

Figure 5.6 Plot of $1/d_{CRYST}$ versus $T_x$ for EOCL-31. A transition in the slope, $m$, indicates the transition from the non-interacting to the interacting regime for the PEO tethers.
It becomes apparent that the $\gamma_s$ introduced by DiMarzio and coworkers\cite{158} is similar to the contribution from the tethered chains, $\gamma_t$, as determined by the slope change. This additional surface free energy term is ill-defined outside of being a contribution from the interaction of the tethers. It can be compared to the osmotic pressure of compressing the chains. As $\sigma$ increases, the chains are confined to a smaller volume and begin interpenetrating to accommodate. At the transition, the sudden increase in free energy derives from the increase in pressure among the confined chains. Here, the chains can no longer be compressed laterally and begin to relax perpendicularly to the surface. This transition defines the interacting regime even though the “touching” of adjacent chains may occur at a much lower tethering density.

In addition to changes in thickness, the axial ratio of the truncated PCL crystal also increases with crystallization temperature. By measuring the axial ratio of the resultant crystals, it is possible to confirm that crystallization took place in solution and not during drying of the solvent. Figure 5.7 shows the relationship between the axial ratio and $T_x$. The axial ratio is measure as the length of the $b$-axis (center of crystal to corner of two (110) planes) over the length of the $a$-axis (center of crystal to the (200) growth face). From the figure, one can see that the axial ratio increases. This indicates that the growth in the [200] direction is more dependent on $T_x$ than the growth in the [110] direction, meaning that the rate of (200) growth becomes significantly slower than the (110) growth. Thus, the (200) growth face becomes “elongated” resulting in higher values of the axial ratio. Because the axial ratio increases over the $T_x$ range, the crystallization of the PCL in solution was confirmed.
Figure 5.7 Axial ratio as a function of $T_x$ for PEO-$b$-PCL crystals. The axial ratio is determined by the length of the $b$-axis over the length of the $a$-axis.

PEO is a crystallizable polymer; therefore, any crystalline domains in the tethered layers may affect the interaction transition or lead to inaccurate calculations of $d_{\text{CRYST}}$. Before calculating $\tilde{\sigma}^*$, it is necessary to verify that the PEO chains are not crystallized. Three methods were used to determine the state of the PEO layers on the PCL single crystal. First, the $d_{\text{OVERALL}}$ was used to calculate the layer thickness of the PEO using the equation $d_{\text{OVERALL}} = d_{\text{CRYST}} + 2d_{\text{AMORPH}}$. Using the sample in Section 4.4.1, $d_{\text{OVERALL}} = 12.9$ nm as determined by AFM, and according to the $v_{\text{CRYST}}$ calculation, $d_{\text{CRYST}} = 10.8$ nm. The thickness of each PEO layer, $d_{\text{AMORPH}}$, was 1.05 nm. From this film thickness, it is difficult to grow PEO crystals. In addition, a crystal with a thickness of 1.05 nm, assuming that they have a flat-on orientation with the chain axis parallel to the layer normal, is highly unstable. It is possible to grow edge-on crystals with the chain axis perpendicular to the layer normal; however, one would still expect the resultant thickness to be larger than 1.05 nm after crystallization. Even at the highest crystallization
temperature of 43°C, the $d_{\text{AMORPH}}$ was still only 1.20 nm. It can be concluded that the layer thickness was not sufficient to result in crystallization of the PEO chains.

The second method was to use TEM ED to detect any diffraction spots from the PEO crystals. Figure 5.8 is the ED pattern of EOCL-31 grown at 43°C in $n$-hexanol. In this image, the characteristic diffractions for the orthorhombic PCL single crystal can be seen. They are characterized mainly by the intense spots representing the (110) planes and (200) planes (as labeled in the figure). There are no characteristic (120) diffractions associated with the crystallization of PEO (monoclinic unit cell). These diffractions would be found inside the six main PCL diffractions due to the larger $d$-spacing (smaller reciprocal lattice spacing) of the (120) planes. In fact, no additional diffractions were observed that may indicate the edge-on conformation as opposed to the flat-on conformation. Because of the small volume of PEO on either side of the crystal, there may not be enough mass to provide diffraction spots for the PEO. Also, nucleation in the thin layer of PEO may not occur at room temperature (quench temperature of the samples).

Figure 5.8 TEM ED pattern of EOCL-31 grown in $n$-hexanol at 43°C. The pattern exhibits only the characteristic diffraction spots of the orthorhombic PCL. It does not show the (120) diffractions associated with the monoclinic unit cell of PEO crystals.
Finally, differential scanning calorimetry (DSC) can be used to observe the crystallization temperature of the PEO block. Figure 5.9 is the cooling scan of bulk EOCL-31 at 10°C/min. The exothermic peak at 33°C is associated with the crystallization of the majority component, in this case PCL. A second exothermic, crystallization peak can be seen around -7°C. This peak is the crystallization of the minority component, PEO. The typical crystallization temperature for PEO is in the range of 20 – 30°C for heterogeneous nucleation. For homogeneous nucleation, the temperature is between -10°C and 0°C with a slight dependence on molecular weight. The value here is most likely lower due to the confinement from the PCL block. Because the crystallization in the bulk is suppressed by the block copolymer composition, as seen in other studies of PEO-b-PCL, it is safe to assume that in a tethered single layer on the surface of the PCL crystal, the crystallization temperature should also be below room temperature. The samples analyzed here were only quenched to room temperature after crystallization of the PCL block; therefore, the layer of PEO should be in the amorphous state as proven by these three methods.

Figure 5.9 DSC thermogram of the cooling of EOCL-31 at 10°C/min. Crystallization peaks of the PCL (33°C) and the PEO (-7°C) were observed.
5.4 Reduced Tethering Density Determination

Now that the transitions have been observed in the $1/d_{\text{CRYST}}$ versus $T_x$ graphs, $\sigma^*$ values can be calculated based on the crystal thickness. The calculation for the tethering density, $\sigma$, was approached in two different ways. Each is based around the number of folds ($n$) in the crystalline layer and the area occupied by a single crystallized chain. The first approach is defined by Zheng and coworkers\textsuperscript{[119]} as:

$$\sigma = \frac{N_A \rho d_{\text{CRYST}}}{2M_n}$$  \hspace{1cm} (5.21)

where $N_A$ is Avagadro’s number. The second approach is a calculation based on the stem length and fold number in a single chain. The formula for this analysis is:

$$\sigma = \frac{ud_{\text{CRYST}}}{2cNA_s}$$  \hspace{1cm} (5.22)

where $u$ is the number of turns in the stem helix, $c$ is the length of the $c$-axis in the unit cell, and $A_s$ is the stem area. These two calculations gave identical results. Then, $\sigma^*$ was calculated from $\sigma^* = \sigma \pi R_g^2$.

Prior to calculating $\sigma^*$, the radius of gyration for the PMMA and PEO must be determined. Prof. Chi Wu’s group from the Chinese University in Hong Kong performed light scattering experiments to analyze the hydrodynamic radius ($R_h$) of a similar PMMA molecule (homo-PMMA with $M_n = 7.9k$ g/mol) from the translational diffusion coefficients ($D$) in amyl acetate. $R_h$ values were used because of the small size of the polymer ($7.8k$ g/mol, $N = 78$). The relationship between $R_h$ and $R_g$ is $R_g = 1.5R_h$.\textsuperscript{[161]} The $R_h$ of PMMA was determined to be 2.3 nm; $R_g$ is then 3.4 nm. The $R_h$ was also evaluated
at varying temperatures within the applicable range used in the PLLA crystallization to ensure that the collapse transition did not occur. The results showed that the $R_h$ did not change between 57.2°C and 75.3°C, indicating that the solvent quality remained “good” for all $d_{\text{CRYST}}$ data points.

The $R_g$ for PEO in $n$-hexanol was estimated by the size of PEO in the theta state. The theta temperature for the PEO in $n$-hexanol was around 30°C as determined by light scattering; therefore, the solvent was near the theta point for PEO in the studied temperature range (25 – 45°C). Exact values for the PEO $R_g$ were not obtained. From Rubinstein and Colby,[162] the following equation and data was used to estimate the $R_g$ in the theta state:

$$R_g^2 = \frac{N_b b}{6}$$ (5.22)

where $b$ is the segment length (1.1 nm) and $N_b$ is the number of segments (36.5, $M_b = 137$ g/mol). From this, the $R_g$ for 5k PEO in the theta state was determined to be 2.6 nm. This is only an estimate of the size. Because of this, the approach is taken that the size of the chain may be smaller, and further discussions will consider this possibility. Using the AFM data and these calculations, it was then possible to analyze $\tilde{\sigma}$ for the PMMA-$b$-PLLA and EOCL-31 systems.

The range of $\tilde{\sigma}$ for both block copolymer systems has been calculated. For the PMMA-$b$-PLLA system, the $d_{\text{CRYST}}$ range between 66°C and 86°C was 9.5 – 11.0 nm. This leads to $\sigma = 0.165 – 0.189$ nm$^{-2}$. $R_g$ as determined from free PMMA in amyl acetate is 3.4 nm, and the $\tilde{\sigma}$ range is 6.0 – 6.9. The $d_{\text{CRYST}}$ range for the PEO-$b$-PCL system was 10.3 – 12.8 nm from 29°C – 44°C. The resultant $\sigma$ was 0.150 – 0.186 nm$^{-1}$. Using
an $R_g \sim 2.6$ nm, the $\tilde{\sigma}$ range is around 3.2 – 4.0. $\tilde{\sigma}^*$ values were determined at the $T_c$ for the PMMA and PEO transition into the interacting regime. The PMMA transition at $T_c = 75^\circ C$ was at $\tilde{\sigma}^* = 6.8$. The PEO transition at $T_c = 36^\circ C$ was $\tilde{\sigma}^* \sim 3.8$. It should be noted that the transition for PEO occurred at 36°C, which is near the theta point. Final conformation of the $\tilde{\sigma}^*$ can only be achieved with exact $R_g$ values. The value for PMMA deviates from $\tilde{\sigma}^* = 3.7$ found for PS, but the PEO transition is the same for the theta solvent or lower in poor solvent.

As was discussed previously, the interaction between the PMMA tether and the PLLA surface was attractive due to their miscibility in the melt. This attraction changed the conformation of the PMMA chains on the surface. These chains assumed a pancake-like profile instead of the typical unperturbed conformation found for the repulsive or neutral interaction case. The calculation of $\tilde{\sigma}^*$ was, therefore, inaccurate. The projected area of the pancake chain is much different than that of the unperturbed case. The size of the diblock single crystal system is quite small, making it difficult to determine the size of the pancake PMMA chains experimentally. In order to accurately determine $\tilde{\sigma}^*$, Monte Carlo simulations of a tethered chain with different solvent and substrate interactions were used to evaluate the experimental change in $R_g$ for the adsorbed, pancake conformation.
CHAPTER VI
SINGLE CHAIN CONFORMATION FROM MC SIMULATIONS

Knowledge of the conformation of the chain is important for calculating an accurate projected area for the reduced tethering density, $\tilde{\sigma}$. A tethered chain near a non-attractive surface (such as the PS for Zheng and coworkers\cite{119}) has the same dimensions as a free chain. Assuming a spherical shape of the Gaussian chain, the projected area is circular, hence the use of $\pi R_g^2$ in determining $\tilde{\sigma}$. In the adsorbed case, the chain exhibits a pancake conformation. The spherical chain collapses onto the surface forming a disc-shaped, nearly two-dimensional object. The third dimension, perpendicular to the surface, is negligible in length and irrelevant for the projected area calculation. The lateral dimension, or radius of the disc, is important. This radius is different than the $R_g^2$ of the free chain in solution because the chain is now mostly confined to two-dimensions. The dimensions are defined as $R_{g,xy}^2$ for the lateral dimension and $R_{g,z}^2$ for the perpendicular dimension. The projected area would now be defined as $\pi R_{g,xy}^2$.

In the PMMA-$b$-PLLA system, the PMMA adsorbs onto the surface of the PLLA crystal. It adopts the pancake conformation; therefore, the analysis of $R_{g,xy}^2$ is critical to finding $\tilde{\sigma}^*$. Unfortunately, the size of the chains and size of the crystal are too small to
analyze the PMMA $R_{g,xy}^2$ experimentally. A secondary approach is to utilize computer
simulations to model a tethered chain and compare the results to the real system.

Monte Carlo simulations were used to study the chain conformations with varying
interactions. Both the monomer-substrate (adsorption/desorption) and monomer-
monomer (expanded/collapsed) interactions were varied to evaluate the entire
conformation range. By changing the monomer-monomer interactions, the solvent
quality was effectively varied. Because the simulations were performed in Prof.
Luettmer-Strathmann’s lab, the procedure is nearly identical to that of Ref. 81 with some
differences discussed in Section 3.4. Chains of $N = 16, 32, \text{ and } 64$ were characterized to
determine self-consistency within the simulations. The $N = 32$ model is most similar to
the real PMMA in terms of number of segments (not number of monomers). These
results were compared directly to the free PMMA chain dimensions as determined by
light scattering to extrapolate the pancake dimensions.

6.1 Density of States Results

The Monte Carlo simulations following the Wang-Landau algorithm of the bond
fluctuation model were performed to collect the density of states data. The interaction
range ($2 - \sqrt{10}$) was chosen to maintain amorphous characteristics much like the
experimental PMMA. When the interaction range is limited to $2 - \sqrt{6}$, as in Ref. 81, the
chain can form an ordered, close-packed crystalline state, which is undesirable here.
Simulations were performed on chains of length $N = 16, 32, \text{ and } 64$. A typical result can
be seen in Figure 6.1. Figure 6.1 is the natural log of $g(n_s, n_b)$ ($\ln g$) versus $n_s$ and $n_b$ for a
chain of $N = 32$. The graph shows that the maximum number of bead-bead (monomer-monomer) contacts decreases as the number of bead-surface contacts increases. This is because the chain conformation cannot maximize both contacts simultaneously. The density of states represents the number of configurations available for a given state. Therefore, at lower $n_s$ and $n_b$ values, $g(n_s, n_b)$ is highest. At a given $n_s$ value, $\ln g$ increases with decreasing $n_b$ until a maximum is reached, after which $\ln g$ decreases. The slope of the curve at a given $n_s$ is related to the field variable $\beta_b$. A slope with a high positive value indicates that larger interaction values or lower temperatures are necessary to reach the state.

![Graph showing density of states](image)

Figure 6.1 Density of states diagram for a chain of length $N = 32$.

6.2 Determination of the Phase Diagram

After the density of states was collected from the simulations, the next step was to evaluate the probabilities of finding these states at varying conditions. Using the field variables $\beta_s$ and $\beta_b$, where $\beta_i = -\epsilon_i/k_B T$, the state of the tethered chain under these
conditions was found. At high $\beta_s$ values, the beads have a strong attraction to the surface. At high $\beta_b$ values, the beads have a strong attraction to each other, similar to poor solvent conditions. Near a transition from expanded to compact states or from desorbed to adsorbed states, there are maximum in the susceptibilities. The susceptibilities, $\chi_s$ and $\chi_b$, can be evaluated over the range of $\beta_s$ and $\beta_b$ to find the transitional values from the expanded to collapsed state for $\beta_b$ and the desorbed to adsorbed state for $\beta_s$. In addition, it is important to estimate the thermodynamic transitions in the limit of infinite chain length. These correspond to theta conditions for $\beta_b$ and the adsorption transition for $\beta_s$.

The main parameters used to determine the phase diagram of the tethered chain were the average number of contacts, $\langle n_s \rangle$ or $\langle n_b \rangle$, and the susceptibilities, $\chi_s$ or $\chi_b$. The average number of contacts is calculated from equation 3.12. The susceptibilities are evaluated from the fluctuations in the contact numbers. Figure 6.2 is a plot of $\langle n_s \rangle$ and $\chi_s$ as a function of $\beta_s$ for a chain of length $N = 32$ where $\beta_b = 0$, i.e. where there is no attractive bead-bead interaction (good solvent). The average number of surface contacts, $\langle n_s \rangle$, is represented by the dotted line, and the susceptibility, $\chi_s$, is represented by the solid line. Both have been normalized by $N$ and the line thickness accounts for error estimation. According to this graph, $\langle n_s \rangle$ exhibits a transition around $\beta_s = 1.0$ where the number of surface contacts increases dramatically. $\chi_s$ shows this transition as a peak, as would be expected because $\chi_s$ is the derivative of $\langle n_s \rangle$ and the second derivative of $G$. This transition represents the adsorption transition. At lower $\beta_s$ values, the state of the tethered chain is desorbed, like in the PS case.[118-119] At higher $\beta_s$ values, the chain is
adsorbed, like in the PMMA case. A similar transition was found for $<n_b>$ and $\chi_b$ as a function of $\beta_b$ for the collapse transition.

![Figure 6.2](image)

Figure 6.2 Average number of surface contacts ($<n_s>$, dotted line) and susceptibility ($\chi_s$, solid line) normalized by $N$ as a function of $\beta_s$ when $\beta_b = 0$. The sharp transition in $<n_s>$ and the peak in $\chi_s$ correspond to the adsorption transition of the tethered chain.

The graph in Figure 6.2 provides a two-dimensional representation of the adsorption transition at a given $\beta_b$ value. It is convenient to develop a three-dimensional representation of all states as a function of $\beta_s$ and $\beta_b$ (see also Figure 2.9). Figure 6.3 is a phase map or landscape for the $N = 32$ tethered chain studied here. Each regime is labeled as follows: desorbed expanded (DE), desorbed compact (DC), adsorbed expanded (AE), and adsorbed compact (AC). An additional set of states can be found at high $\beta_b$ and median $\beta_s$; these are the layered states (LS). The collapsed chain forms a set of layers with the bottom layer adsorbed on the substrate. The expanded states found at lower $\beta_b$ are in good solvent conditions; while, the compact states are found at higher $\beta_b$ corresponding to poor solvent conditions. The bright areas indicate the transitions from one state to another. The third dimension is the overall susceptibility ($\chi_{total}$, see equation 3.19) where brighter areas indicate large values of the susceptibility. The distinct lines
were created by finding the maximum in $\chi_{\text{total}}$. Figure 6.4 is an example of some of the conformations for the chain in each of the different phases described in the phase map. These conformations were taken directly from the simulation data. Each bead is assigned a Cartesian coordinate set, making the visualization of the conformations possible.

Figure 6.3 Phase map (landscape) of an $N = 32$ chain over the range of all $\beta_b$ and $\beta_s$ values. The five states: LS, AC, AE, DE, and DC can be seen. Transitions from one state to the next are indicated by the brighter streaks.

Figure 6.4 Examples of the chain conformations in each of the different phases.
In this phase diagram, there are several types of transitions. The first can be found as the white horizontal line at low $\beta_b$ values. This is the coil-globule transition with decreasing solvent quality. The value of this transition shown in the diagram is specific for the $N = 32$ case. For the desorbed conditions (DE to DC), it occurs around $\beta_b = 0.6$. The thermodynamic limit of this value, $\beta_\theta$, will be discussed in the next section.

The pair of horizontal lines for large values of $\beta_s$ represent the transition from extended to compact configurations for adsorbed chains. The first transition at $\beta_b = 0.55$ is a disordered semi-compact phase. The second transition is an ordered compact phase. Both are for the adsorbed case; however, the AC phase is found above $\beta_b = 1.2$. The horizontal lines found from the maximum $\chi_{\text{total}}$ are not shown to intersect with the collapse transition line. In actuality, they are merged with the slope associated with the $\chi_{\text{total}}$ peak for collapse, so the transition lines do intersect.

The second important transition is the adsorption transition. This is the vertical line located below the horizontal line for low $\beta_b$ values. The adsorption of an $N = 32$ chain in good solvent (DE to AE) occurs around $\beta_s = 1.2$. The thermodynamic transition for adsorption, $\beta_a$, will be discussed in the following section. For the compact conformation, the transition has several intermediates, the layered states, between the desorbed and adsorbed state. The line at low $\beta_s$ and high $\beta_b$ can be viewed as the initial transition for the adsorption (DC to LS). The initial adsorption from the DC state to the first LS state occurs around $\beta_s = 0$. This illustrates that the compact chain conformation (globule) adsorbs to the substrate as soon as an attractive potential is introduced. It is
probably due to the close proximity of the globule to the surface when the bead-bead contacts are high.

From this phase map, it is possible to choose the proper $\beta_s$ and $\beta_b$ values to analyze states of interest. We determined chain dimensions ($R^2_g$, $R^2_{g,xy}$, and $R^2_{g,z}$) for different chain lengths and use these to estimate the collapse and adsorption transitions in the thermodynamic limit. In addition, evaluations of the bead (segment) density as a function of the distance from the substrate ($\varphi(z')$) were made to compare with previous theoretical work.

6.3 Analysis of Chain Conformation

The conformations in each state were analyzed to determine the chain dimensions and segment distribution. According to equations 3.5 and 3.6, the given dimensions, $R^2_g$, $R^2_{g,xy}$, and $R^2_{g,z}$, for each conformation were calculated. Figures 6.5 and 6.6 show the changes in the chain dimensions as a function of $\beta_s$ and $\beta_b$, respectively, for a chain of length $N = 32$. The dramatic change in the set of $R^2_g$ values is an indication of the transition from one state to another. For Figure 6.5, it is the adsorption transition from the DE to the AE state ($\beta_b = 0$), which leads to a large increase in $R^2_{g,xy}$ and decrease in $R^2_{g,z}$ as the chain flattens out on the surface. At high adsorption, $R^2_{g,z}$ is negligible, and $R^2_{g,xy}$ is equal to $R^2_g$. For Figure 6.6, the transition is the coil-globule transition from DE to DC ($\beta_s = 0$) as seen in the decrease of all chain dimensions. Note that $R^2_{g,xy}$ is equal to
the sum of the $x$ and $y$ contributions to the $R_g^2$ measurement and is therefore larger than $R_{g,z}^2$ in both scenarios. The fact that $R_{g,xy}^2$ is not exactly equal to $2R_{g,z}^2$ indicates that the conformation is not perfectly spherical. The $\beta_s$ and $\beta_b$ transition values as determined from the location of the largest changes in the graphs match well with those found for the susceptibility curves.

Figure 6.5 $R_g^2$, $R_{g,xy}^2$, and $R_{g,z}^2$ as a function of $\beta_s$. The change in size indicates the adsorption transition for the DE to AE states.

Figure 6.6 $R_g^2$, $R_{g,xy}^2$, and $R_{g,z}^2$ as a function of $\beta_b$. The change in size indicates the collapse, or coil-to-globule, transition for the DE to DC states.

The next step is to analyze the thermodynamic limits for the transitions into the collapsed state ($\beta_0$) and the adsorbed state ($\beta_a$). The method utilized by Eisenriegler et
al.\cite{71} and Descas et al.\cite{79} was followed to find these values. Here, the ratio of

\[ \frac{R_{g,z}^2}{R_{g,xy}^2} \]

as a function of \( \beta_s \) should be independent of \( N \) to give the \( \beta_a \) transition. The

ratio of \( \frac{R_g^2}{N} \) as a function of \( \beta_0 \) provides the \( \beta_0 \) value. This transition occurs at a similar

\( \beta_0 \) value independent of \( N \); however, the transition becomes sharper as \( N \) increases. The

crossing of these normalized \( R_g^2 \) curves indicates the value of \( \beta_0 \). Figure 6.7 is the graph

of \( \frac{R_{g,z}^2}{R_{g,xy}^2} \) versus \( \beta_s \). The transition point where the curves of \( N = 16, 32, \) and 64 cross

each other is \( \beta_a = 0.98 \), which agrees with the value found by Descas and coworkers.\cite{79}

The point provided in the figure represents the error in calculating the \( R_g^2 \)'s using a set of

simulation results. Figure 6.8 is the graph of \( \frac{R_g^2}{N} \) versus \( \beta_b \). The \( \beta_0 \) transition point, or

solvent theta point, is 0.29. The error is estimated by the line thickness. These

transitions are the thermodynamic values for the adsorption and collapse transitions in

this study. All analysis of chain conformations in either good or poor solvent conditions

or before or after adsorption will be made far from these thermodynamic results.

Figure 6.7 Plot of \( \frac{R_{g,z}^2}{R_{g,xy}^2} \) versus \( \beta_s \). The thermodynamic adsorption point, \( \beta_a = 0.98 \),
is where the curves of \( N = 16, 32, \) and 64 cross. The error is estimated by the line thickness.
The final validation step is to compare the profiles of the MC simulation chains with the previous theoretical work to verify that the chains exhibit the predicted behavior. In the adsorbed case, it is expected that the majority of the beads are near the substrate. In the desorbed case, the beads are expected to be distributed throughout the layer with a maximum around the \( R_g^2 \). Figure 6.9 is a plot of the bead density (\( \varphi(z') \)) as a function of the layer number, \( z' \), at various \( \beta_s \) values for a chain of \( N = 32 \) with \( \beta_b = 0 \) (good solvent). The profile is calculated by evaluating the probability of finding a bead located some distance from the tethering point, \( z' \). It is clear that below \( \beta_a = 0.98 \) the chain exhibits the parabolic-like profile associated with the neutral or repulsive example in RG and SCF theories.\(^{31, 50}\) Above \( \beta_a = 0.98 \), the profile collapses down to show a majority of beads located in the few layers closest to the substrate (\( z' = 0 \)). Again, these results are in agreement with the RG theory and previous MC studies of this type.\(^{54}\)
Figure 6.9 Bead density profile ($\varphi(z')$) of a single tethered chain with repulsive or neutral ($\beta_s < 0.98$) and attractive ($\beta_s > 0.98$) interactions with the substrate. Chain adopts a parabolic-like profile in the repulsive case and a pancake conformation in the attractive case.

6.4 Comparison of Simulation and Experimental Systems

The main objective of this simulation analysis is to obtain an estimate of the chain size for the adsorbed case in the PMMA experimental system. In order to achieve this, model parameters corresponding to the physical system must be determined and the reliability of the simulation data as a model for the real system must be confirmed. Then, the comparison of the experimental PMMA system and the MC simulation of a single chain can be performed to determine a new $\tilde{\sigma}$ for the adsorbed conformation.

In this work, we use the Kuhn length ($l_k$) and number of Kuhn segments ($N_k$) to relate the model to the physical polymer. The conformations of a freely-jointed chain of Kuhn segments are entirely determined by the length and number of the segments. The
effect of the individual monomers on the overall conformation is included in the value of $l_k$; thus, $N_k$ is the significant quantity for comparison, not $N$.

Values of the Kuhn segment length, $l_k$, for the model system was calculated from the good solvent approach as well as the Gaussian approach. First, the mean average squared end-to-end distance, $<R_e^2>$, and the mean average bond length, $<b_l^2>$, were determined from the simulation data with equations 3.7 and 3.8, respectively. These values were taken from the theta condition, $\beta_b = 0.29$ and $\beta_s = 0$, and in good solvent conditions, $\beta_b = 0$ and $\beta_s = 0$. Note that both were in the desorbed state ($\beta_s < 0.98$).

From these values, the end-to-end distance, $R_e$, and the bond length, $b_o$, were determined by taking the square root of $<R_e^2>$ and $<b_l^2>$, respectively. The final pertinent parameter for the calculation of $l_k$ was the extended chain length, $L_e$. This value is defined as $L_e = (N - 1)b_o$. The next step was to calculate the good solvent $l_k$ and the Gaussian $l_k$ to compare for all values of $N$. Equations 6.3 and 6.4 are the good solvent and Gaussian formulas, respectively:

$$l_k = \frac{R_e^{1/(1-\nu_F)}}{L_e^{\nu_F/(1-\nu_F)}} \quad \text{(good)} \quad (6.3)$$

$$l_k = \frac{R_e^2}{L_e} \quad \text{(Gaussian)} \quad (6.4)$$

where $\nu_F$ is the Flory exponent for good solvent ($\nu_F = 0.59$). Table 6.1 shows the results for $R_e$, $b_o$, $L_e$, $l_k$, and $N_k$ for chains of length $N = 16$, $32$, and $64$ for both the good solvent and Gaussian analysis.

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Table 6.1 Tethered chain characteristics from MC simulations

<table>
<thead>
<tr>
<th>$N$</th>
<th></th>
<th>$R_e$</th>
<th>$b_o$</th>
<th>$L_e$</th>
<th>$l_k$</th>
<th>$N_k$</th>
</tr>
</thead>
<tbody>
<tr>
<td>16</td>
<td>good</td>
<td>14.9</td>
<td>2.8</td>
<td>41.3</td>
<td>3.5</td>
<td>12</td>
</tr>
<tr>
<td></td>
<td>Gaussian</td>
<td>12.6</td>
<td>2.7</td>
<td>40.7</td>
<td>3.9</td>
<td>10</td>
</tr>
<tr>
<td>32</td>
<td>good</td>
<td>23.5</td>
<td>2.8</td>
<td>85.5</td>
<td>3.7</td>
<td>22</td>
</tr>
<tr>
<td></td>
<td>Gaussian</td>
<td>18.4</td>
<td>2.7</td>
<td>84.0</td>
<td>4.0</td>
<td>20</td>
</tr>
<tr>
<td>64</td>
<td>good</td>
<td>36.5</td>
<td>2.8</td>
<td>173.8</td>
<td>3.9</td>
<td>43</td>
</tr>
<tr>
<td></td>
<td>Gaussian</td>
<td>26.0</td>
<td>2.7</td>
<td>170.5</td>
<td>4.0</td>
<td>43</td>
</tr>
</tbody>
</table>

Figure 6.10 shows the relationship of $l_k$ with $1/(N-1)$. The Kuhn length should approach a single value for both the good solvent and Gaussian coil evaluations as $N$ approaches $\infty$, or for $1/(N-1) \rightarrow 0$. It can be seen that this criterion is met for the simulation results. This confirms the field values for good solvent ($\beta_b = 0$ and $\beta_s = 0$) and theta solvent ($\beta_b = 0.29$ and $\beta_s = 0$).

Now that the reliability of the comparison has been confirmed, the $N = 32$ ($N_k = 21$) chain dimensions are used to determine the PMMA 7.8k g/mol ($N_k = 17$) dimensions based on the similar number of Kuhn segments. The value of $R_g^2$ of the PMMA polymer
measured by light scattering is experimental evidence of the size of the chain in good solvent. This value was compared with the $R_g^2$ value for the $N = 32$ chain in good solvent from the simulation. It is well-known that the free chain $R_g^2$ is identical to that of the tethered chain without adsorption onto the surface. The $R_g^2$ value from the MC simulation at $\beta_b = 0$ and $\beta_s = 0$ ($R_{g,DE}^2$), which is the good solvent, non-adsorbed state (DE), was 78.3. The ratio of $R_{g,DE}^2 / R_{g,free}^2$, where $R_{g,free}^2$ is the light scattering value for the PMMA, is 6.77. This ratio was compared with the ratio of the simulation and experimental adsorbed case. The adsorbed PMMA $R_g^2$ value is unknown; therefore, the equation

$$R_{g,ads}^2 = \frac{R_{g,free}^2 \cdot R_{g,AE}^2}{R_{g,DE}^2}$$  (6.5)

was used to calculate the experimental value. Because amyl acetate is a good solvent for the PMMA, the adsorbed expanded state (AE) is used for the adsorbed $R_g^2$. We obtain the value $R_{g,ads}^2 = 13.0$ nm$^2$ for an adsorbed chain ($\beta_s = 1.3$), and $R_g = 3.6$ nm. This value is larger than the free $R_g$. Figure 6.11 shows the change in $R_{g,ads}$ with $\beta_s$. It can be seen that in nearly all cases, the value is higher than the free PMMA with an apparent leveling off around 4.5 nm. Using $R_{g,ads}^2 = 13.0$ nm$^2$ ($R_g = 3.6$ nm), the new $\tilde{\sigma}$ was determined to be 7.5, a value larger than the original 6.7 and the PS value of 3.7. Figure 6.11 indicates that this holds true for a range of adsorption interactions. It should be noted that the overall $R_g^2$ was used for the calculation; $R_g^2$ is the sum of $R_{g,xy}^2$ and $R_{g,z}^2$. For the calculation of the projected area, one might argue that the $R_{g,xy}^2$ is more accurate;
however, this value is nearly an order of magnitude greater than \( R_{g,z}^2 \), thus dominating the value of \( R_g^2 \) (\( R_g^2 \approx R_{g,xy}^2 \)). Hence, \( R_g^2 \) is sufficient for evaluating the projected area and \( \tilde{\sigma} \).

Figure 6.11 \( R_{g,\text{ads}} \) of PMMA as a function of \( \beta_s \). All values are larger than \( R_{g,\text{free}} \) as measured by light scattering.
CHAPTER VII

ANALYSIS OF THE TRANSITION INTO THE INTERACTING REGIME

Including the previous results of Chen\textsuperscript{[118]} and Zheng,\textsuperscript{[119]} there are now three systems of diblock copolymer single crystals with amorphous tethered chains. Each of these systems was found to have a non-interacting-to-interacting transition over the studied crystallization temperature range. In each case, the value of $\bar{\sigma}^*$ was slightly different.

7.1 Comparison of Systems

As was discussed in Chapter V, the transition value for the adsorbed PMMA chains ($\bar{\sigma}^* = 7.5$) was larger than the value found for PS ($\bar{\sigma}^* = 3.7$). Also, the PEO transition value ($\bar{\sigma}^* \leq 3.8$) was equal to or smaller than the PS transition value. For the study of Chen and coworkers,\textsuperscript{[118]} the transition value was found to be independent of the molecular weight of the PS and the solvent quality, in both good and theta solvents. The differences seen in this research must derive from unique chain conformations in adsorption and collapse in poor solvent. By definition, the $R_g$ value enters the calculation of $\bar{\sigma}^*$, however, $R_g$ does not describe all aspects of chain conformation that are important in this problem. For the adsorbed case, the chain has adopted a quasi-2D
conformation when it forms a pancake on the surface. The volumetric considerations for this conformation are different than in the “spherical” case of the unadsorbed, 3D coil. Also, the interaction of the chain with the surface affects the conformational changes associated with inter-chain interaction and subsequent interaction transition. For the PEO case, if it is in the theta state, then the results support that the transition of $\tilde{\sigma} = 3.8$ for repulsive interactions is consistent for PS and PEO. If the solvent is poor, a complete collapse of the PEO chain occurs. Unlike in good or theta solvent conditions, the $R_g$ in this case is representative of a solid sphere size.

Table 7.1 Comparison of three tethered chain systems

<table>
<thead>
<tr>
<th>Tether</th>
<th>$\tilde{\sigma}$</th>
<th>$R_g$ (nm)</th>
<th>$l_k$ (nm) $^{[163]}$</th>
<th>$N_k$</th>
<th>$\sigma^*$ (nm$^{-2}$)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS – good</td>
<td>3.7</td>
<td>3.7</td>
<td>1.46</td>
<td>16</td>
<td>0.087</td>
</tr>
<tr>
<td>PS – theta</td>
<td>3.8</td>
<td>1.8</td>
<td>1.46</td>
<td>9</td>
<td>0.385</td>
</tr>
<tr>
<td>PMMA</td>
<td>7.5</td>
<td>3.6$^a$</td>
<td>1.32</td>
<td>17</td>
<td>0.183</td>
</tr>
<tr>
<td>PEO</td>
<td>$\sim$ 3.8</td>
<td>$\sim$ 2.6</td>
<td>0.80</td>
<td>57</td>
<td>0.178</td>
</tr>
</tbody>
</table>

$^a$ $R_g$ value calculated from MC simulations

Table 7.1 presents the relevant data for these three systems including $\tilde{\sigma}$, $R_g$, $l_k$, number of Kuhn segments, $N_k$, and $\sigma^*$. It is evident that the systems have some similarities and differences. For example, the size ($R_g$), stiffness ($l_k$), and number of segments for the PS in good solvent and for PMMA are nearly identical. It should be noted that the $R_g$ value listed in the table is the calculated one from the MC simulations (see Chapter VI). The free PMMA value of 3.4 nm is still similar to the value of 3.7 nm for the PS chain. Comparisons can also be made with other PS chains used in the previous study; however, the sample represented in Table 7.1 has the smallest number of
parameters that are different between the PS and PMMA systems. The only apparent difference, in fact, is that the PMMA sample is adsorbed onto the PLLA surface.

The dimension of the PEO chain is comparable to the PS in theta solvent but much smaller compared to those of PS in good solvent and PMMA. In addition to smaller chain dimension, the PEO has a larger number of segments because the $l_k$ is much smaller than in the previous two cases. The interaction between the PEO and PCL single crystal surface is neutral; therefore, it is more similar to the PS. In poor solvent conditions, the segment density in the volume of a single chain $(4/3\pi R_g^3)$ is much higher, especially with the 3-fold number of segments.

7.2 Influence of Adsorption

From Table 7.1, the PMMA $\tilde{\sigma}^*$ has a higher value than the PS transition value. The physical meaning of $\tilde{\sigma}^*$ is the number of tethering points in the area of a single chain, or the number of chains in the volume of a single chain. First, both values are above $\tilde{\sigma} = 1$, which corresponds to the point where neighboring chains begin to overlap at their exterior. This implies that the overlapping of chains depends on their ability to pack within the volume occupied by the single chain segments and solvent molecules $(4/3\pi R_g^3)$. At the transition point, $\tilde{\sigma}^*$, the lateral compression of chains experiences an increase in osmotic pressure resulting in the additional free energy of the surface ($\gamma_c = \gamma_c + \gamma_t$). The adsorption of the PMMA chain influences the transition value in two ways. For the adsorbed case, the conformation of the chain is confined to nearly two dimensions, instead of three as in the desorbed case. The number of contacts with the
surface increases beyond one (tethered point), and the conformation becomes expanded in the adsorption plane as shown in Chapter VI. This new conformation may facilitate the packing of chains in such a way that it increases $\bar{\sigma}^*$. The second consideration is the additional energy of adsorption. For the desorbed case, the free energy of the tether consists of the entropy of the chain and the enthalpy of interaction with solvent molecules and/or neighboring chains. In the adsorbed case, the entropy of the chain is decreased to maximize the enthalpy of interaction with the surface. The additional enthalpy created by contact may hinder conformational changes that result in losing surface contacts. The entropy of the chain would decrease as the tethering density was increased; however, the enthalpy of interaction could be maintained through rearrangement of the tethered chain and better packing within the layer volume. Thus, the transition into the interacting regime may be found at a higher value. In addition, changes in conformation may once again render the $R_g^2$ value an inaccurate normalization factor.

A final consideration for this diblock single crystal method is the availability of adsorption sites. As mentioned previously, the tethered chains are added to the crystal basal surface nearly one at a time as the crystallizing chain adsorbs to the lateral crystal surface. A situation arises where the currently tethered chains are adsorbed to the surface in complete coverage, therefore, not allowing the adsorption of a newly added chain. Figure 7.1 is a schematic illustration of this point. The crystal is in black with the already tethered chains in blue. The red chain is the crystallizing block, and the green chain is the newly added tether. The new amorphous chain adopts its desorbed conformation in solution (Fig. 7.1a). If adsorption occurs, the chain forms the pancake conformation once
added to the new surface (Fig. 7.1b). If the density is high enough, once the single
crystal has been formed, some fraction of the PMMA chains have the adsorbed
conformation; while, the other fraction has the desorbed conformation (Fig. 7.1c). This
effectively creates a non-uniform tethering density where the chains do not interact
exclusively with the nearest neighbor chains. The adsorbed chains interact with each
other, and the desorbed chains interact with each other. The true $\tilde{\sigma}^\ast$ would be a fraction
of the observed value corresponding to the fraction of chains adsorbed on the surface. It
is assumed that the adsorbed chains would still be the driving force for transition because
they are slightly larger in size ($R^2_{g,ads} > R^2_{g,free}$).

Figure 7.1 Schematic drawing of the creation of the tethered polymer system in diblock
single crystals. (a) Creation of new crystalline surface and addition of a single tethered
chain. (b) Adsorbed tether case. (c) Total coverage of adsorbed species leading to a
fraction of tethers being desorbed as they are added.

The saturated surface layer is similar to the over-saturated adsorbed (OSA) and
over-saturated brush (OSB) states described by Descas and coworkers\cite{65-66} and discussed
in Section 2.1.4.1. Although, from a thermodynamic standpoint, saturation may not
occur in this way because of a balance between the loss of entropy in completely
adsorbed chains and the enthalpy gain of interaction with the substrate; therefore, a more
appropriate picture is of a fraction of each chain completely covering the surface with the
unadsorbed fraction forming a layer above the adsorbed one, as shown for the OSB state in Figure 2.7. In fact, a comparison of the system described here, both experimental and computational, with the state diagram in Figure 2.7 could provide insight into the reason for the larger $\tilde{\sigma}^*$ in the PMMA case.

As mentioned in the Descas model\cite{66} in Section 2.1.4.1, the chains are made up of de Gennes blobs and adsorption blobs. The adsorption blobs contain $g$ monomers, and $\lambda \sim g^\nu (\nu = 0.59)$; the de Gennes blobs consist of a number of adsorption blobs, $\xi \sim g_{\Gamma}^{\nu_2}$, where $g_{\Gamma}$ is the number of adsorption blobs, $g_{\Gamma} = N/g$, and $\nu_2$ is the 2D Flory exponent ($\nu_2 = 0.75$). Figure 7.2 is a schematic illustration of this system.

The Descas phase diagram is derived as follows. The self-avoiding walk of a chain of adsorption blobs has a size of $R||$, or in our notation $R_{g,xy}$. The tethering density, $\sigma$, is $n/A$ or the number of chains per area. The first transition is $\sigma_{a^*}^*$ where the chains begin to overlap (AE to ASD transition). This occurs at:

$$\sigma_{a^*}^* = \frac{1}{R_{||}^2} \quad (7.1)$$
where $R_{\parallel 0}^2$ is the size of an isolated chain. The second transition occurs at surface saturation, when the surface blobs are tightly packed in the area of a de Gennes blob:

$$R_{\parallel}^2 = g_r \lambda^2 = \frac{N \lambda^2}{g}$$

(7.2)

and therefore,

$$\sigma_{b*} = \frac{1}{(g_r \lambda^2)}$$

(7.3).

At $\sigma_{b*}$, the thickness of the layer increases from $\lambda$. This transition is representative of the interacting transition as mentioned by the authors. Much larger values of the covering density are required to reach the scaling regime, $L \sim \sigma^{1/3}$. Thus, $\sigma_{b*}$ is synonymous with $\bar{\sigma}^*$. Data obtained from the MC simulations in Chapter VI have been used to estimate transition values $\sigma^*$, $\sigma_a^*$, and $\sigma_{b*}$ and obtain an approximate replica (Figure 7.3) for finite chains of a particular model of Figure 2.7. The lines representing $\sigma^*$ and $\sigma_a^*$ are determined from equation 7.1 with $R_{\parallel 0}^2 = R_{g,xy}^2$. To obtain $\sigma_{b*}$, we estimate the adsorption blob area from $\lambda^2 = R_{g,xy}^2 + 1$ and the number of blobs from $g_r \approx 0.5Nn_s$.

Because the authors used scaling laws and our results are based on data for finite chains of a particular model, quantitative differences arise; however, the qualitative features are similar. The adsorption transition corresponding to $k_c$ in Figure 2.7 is at $\beta_s = 1.0$. Qualitatively, Figure 7.3 is identical to Figure 2.7 except that we cannot identify the crossover region, OSA, with these tools.
Simulations of the single chain under the influence of a tensile force acting on the last bead (free end) supports the formation of the ASD state. These simulations are meant to imitate the compression of a chain during crowding. They show that the desorption of adsorbed blobs does not occur easily, indicating that the compression of the chains as tethering density increases will only force said chains into the ASD state. Thus, the $\sigma_b^*$ transition occurs while the original fraction of chains creating the ASD state is still adsorbed.

7.3 MC Simulation of Single Chain Under Tension

Simulations of tethered chains under tension are achieved by including a third field variable associated with applying a tension on the last bead of the chain. This tension acts like a spring attached to a rod extending from the tethering point in the $z$-direction. The “spring” attached from the “rod” to the last bead creates a force to pull it toward the point directly above the tethering point. This field variable is written as $\beta_T$, \begin{equation}
\end{equation}
and $\beta_T = -\varepsilon_T/k_B T$ where $\varepsilon_T$ represents the force. The first step is to determine the density of states over a new three-dimensional space:

$$g(n_s, n_b, r) = p(r; n_s, n_b) g(n_s, n_b)$$ (7.1)

where $r$ is the lateral distance of the last bead. The histograms found for this dos can be used to determine the probability distribution for the location of the last bead, $r$. Now, for given field variables, $\beta_s$, $\beta_b$, and $\beta_T$, the probability of finding that state is given by:

$$P(n_s, n_b, r; \beta_s, \beta_b, \beta_T) = \frac{g(n_s, n_b, r) e^{-\beta_s n_s} e^{-\beta_b n_b} e^{-\beta_T r}}{\sum_{n_s, n_b, r} g(n_s, n_b, r) e^{-\beta_s n_s} e^{-\beta_b n_b} e^{-\beta_T r}}$$ (7.2).

Figure 7.4 shows the probability distribution of finding the last bead a distance $r$ from the tethering point at varying interaction conditions (good solvent, adsorbed, theta solvent, and poor solvent) for a chain of length $N = 32$. As expected, the probability is high close to the tethering point ($r = 0$) when the chain is collapsed ($\beta_b = 1$, $\beta_s = 0$) and furtherst from the tethering point after adsorption ($\beta_b = 0$, $\beta_s = 1.3$). These probabilities are used in equation 7.1 to create the dos for tension evaluation.

Figure 7.4 Probability distributions of finding the last bead a distance $r$ from the tethering point for conditions ($\beta_b:\beta_s$) – (0:0), (0:1.3), (0.3:0), and (1:0).
The analysis of chain configurations was done following the same procedure as previously described. The aim of this set of simulations was to determine the conformational changes of the single chain under tension assuming that this is an appropriate approximation of the force induced by increasing the tethering density in the experimental system. It was found that at moderate $\beta_T$ values, the state of the chain ($n_s$, $n_b$) remained nearly constant (constant $<n_s>$) with only a change in chain size. At slightly higher $\beta_T$ values, only a single bead-surface contact was lost. This indicates that the adsorption interaction energy is sufficient to maintain contact with the surface as the chain is compressed with increasing tethering density.

Figure 7.5 shows some representative chain conformations from the AE and ASD states where the ASD state is represented by similar states ($n_s$, $n_b$) but under tension. These tension conformations support the idea that a semi-dilute layer of adsorption blobs is found on the surface at increased $\sigma$. These results suggest that $\sigma_b^*$ in the theoretical treatment, or $\tilde{\sigma}^*$ for experimental adsorbed chains, should be higher than those for unadsorbed chains (see Figures 7.3 and 2.7). Hence, the value expected for the PMMA experimental case should be larger than PS and PEO. In order to compare the values in a normalized fashion, Figure 7.6 represents $\tilde{\sigma}_b^* = (\sigma_b^*)(R_g^2, xy)$ as a function of the surface interaction field $\beta_s$ for adsorbed chains in good solvent ($\beta_s > \beta_a, \beta_b = 0$). It shows that a two-fold increase in $\tilde{\sigma}^*$ is expected for moderately adsorbed chains ($\beta_s = 1.4$), which is similar to the value of 1.3 used to calculate the change in $R_g$. This assessment makes the transition of PMMA comparable to that of PS in good or theta solvent.
Figure 7.5 Representative chain conformations for AE and ASD states (AE under tension). Simulations prove that $<n_s>$ remains relatively unchanged under tension.

Figure 7.6 $\tilde{\sigma}_b$ as a function of $\beta_s$ for adsorbed chains in good solvent ($\beta_s > \beta_a, \beta_b = 0$). This plot illustrates the predicted difference in $\sigma^*$ for the experimental system when adsorption is expected.

7.4 Segment Density

The last comparison is between the PEO sample and the PS in good and theta solvent. The mechanism for the difference between these two cases lies in the chain conformations, $R_g$, and the number of segments, $N_k$. The size of the PEO chain is $\sim 2.6$
nm; whereas, the PS size is 3.7 nm in good solvent and 1.8 nm in theta solvent. The $N_k$ values of each are 57, 16, and 9, respectively. Again, this discussion is moot if the estimate of the PEO size is accurate; however, a brief discussion should be provided given the possibility of poor solvent conditions with a smaller $R_g$. If the PEO chain is in a poor solvent, the conformation of the segments is in the highly compact state. The segment density for each of these systems can be calculated in the volume of a single chain. Using $4/3\pi R_g^3$, the segment densities for PS are 0.08 segments/nm$^3$ for the good solvent and 0.37 seg/nm$^3$ for the theta solvent. On the other hand, the PEO segment density is 1.28 seg/nm$^3$ (0.77 seg/nm$^3$ under theta conditions). This clearly indicates the highly compact nature of the PEO.

In the previous study by Chen,$^{[118]}$ $\bar{\sigma}^*$ was found to be independent of solvent quality (good or theta) for PS. This was expected from the use of $\bar{\sigma}$ where the chain dimensions are accounted for in $R_g^2$. Looking at Table 7.1, it is clear that the size is much smaller for the theta state, 3.7 nm in good solvent and 1.8 nm in theta solvent, and thus, the resulting $\sigma^*$ for the smaller chain is much bigger, 0.385 nm$^{-2}$ (theta) versus 0.087 nm$^{-2}$ (good). This is also supported by the PEO system under theta conditions. For these systems, the state of the chain is such that some space within the chain dimensions is not occupied by segments, but by solvent molecules as shown in Figure 7.7. The theta condition is the ideal case when the polymer segments have no preferential interaction with the solvent or polymer segments. It thus adopts a true Gaussian conformation, but it is still capable of accommodating other chains as the tethering density is increased.

The story is quite different for the collapsed PEO tethers. By being in a poor solvent, the chain is collapsed to maximize the number of segment-segment interactions.
As these chains are brought closer together with increasing $\sigma$, they are unable to accommodate other chains within the volume of a single chain. It should, therefore, be expected that $\tilde{\sigma}^*$ is smaller for chains in poor solvent and approaches a value of 1 in the limit of perfectly hard spheres. Although the size of the chain is accounted for in $\sigma$, the density of segments within $R_g^2$ is not. In the collapsed state, the density is much higher than in the good or theta solvent cases; therefore, the number of chains (tethering points) that can be found in the projected area of a single chain should be compromised ($\leq 3.8$). It should also be noted that the shape of the PEO tether should be more spherical due to the larger number of segments. The chains for PS are most likely more elliptical in nature at low $N_k$. Due to their asymmetry, ellipses also allow for easier packing as the tethering density increases which may result in a slightly higher $\tilde{\sigma}^*$.

Figure 7.7 Schematic drawings of the conformation of a tethered chain in good, theta, and poor solvents. The segment density within a unit volume (dotted line) is different from one state to the next with a dramatic change from theta to poor solvent.

This chapter has identified the differences found for the adsorbed PMMA and collapsed PEO $\tilde{\sigma}^*$ when compared to the previous studies of PS. Explanations have been given for the origins of these differences. An ASD state exists for the PMMA chains before the interacting transition, resulting in a higher $\tilde{\sigma}^*$ value, and the collapsed
nature of the PEO chain prevents overlapping of neighboring chains, resulting in a lower $\bar{\sigma}^*$. It is difficult to verify these explanations in the small experimental space of diblock single crystals. With the help of MC simulations, supporting evidence has been given for the validity of the proposed origin of varying $\bar{\sigma}^*$ values.
CHAPTER VIII
CRYSTALLIZATION OF TETHERED CHAINS

The PEO-\textit{b}-PCL copolymer provides the unique opportunity to study the crystallization and crystallizability of tethered polymer systems. Because the tethered block, in this case PEO, is crystallizable, it is possible to determine whether the constraint of one of the chain ends has an affect on crystallization. Other parameters to consider when analyzing this system are tethering density, crystallization temperature, crystal orientation, and chain orientation. Several methods were used to characterize these crystals. They include electron diffraction of the single crystals of PEO-\textit{b}-PCL and differential scanning calorimetry of single crystal mats. Finally, it is possible to induce PEO crystallization prior to PCL crystallization to form a PEO substrate with PCL tethers by reducing the PEO nucleation barrier.

8.1 Electron Diffraction of PEO-\textit{b}-PCL Single Crystals

The main technique for determining the presence of a crystalline layer on the PCL single crystal was electron diffraction (ED) from TEM. The diffraction of both the PCL crystal along with characteristic diffractions from PEO crystals indicates that the PEO
ethers have crystallized. The location and \( d \)-spacing of these diffractions provides information about the crystal and chain orientation with respect to the PCL surface.

Previous work done by Sun and coworkers\(^{[140]}\) approached this problem of crystallization of tethered chains on single crystal surfaces using PEO-\( b \)-PCL copolymers with molecular weights of 5k g/mol of each component. Their results indicated that the PEO tether crystallized on the surface of the PCL crystal (as evidenced by the PCL morphology) with a single crystal diffraction pattern oriented with the \( a \)-axes between the two crystals at an angle of 22 – 30\(^{\circ}\) (see Figure 2.18). The results of this study are troublesome because of several reasons. First, the morphology indicates an aggregation of single crystals with several screw dislocations (Figure 2.18a). These crystals should not give a pure single crystal diffraction pattern for the PCL, but instead, rings with the appropriate (110) and (200) \( d \)-spacing (Figure 2.18b). Second, because of the screw dislocations, the PEO layers are not necessarily monolayers. The PEO on one surface could interact with PEO on an above surface, thus disturbing the nucleation and crystallization of the tethered layer. Finally, one would not expect that the PEO layer would develop a single crystal diffraction pattern. Rather, a ringed pattern with no preferential orientation or arcs showing some preferential orientation would be a more likely result since the layer has no implicit reason for forming one single crystal. The observation to build on, however, is the fact that the PEO (120) reflections are found inside the PCL (110) reflections because the \( d \)-spacing of PEO (120) is larger (smaller spacing in reciprocal space) than the PCL (110), 0.463 nm and 0.414 nm, respectively.

Initial results of the EOCL-31 copolymer indicate that the PEO 5k g/mol tethers did not crystallize on the surface of the PCL single crystal, as was discussed in Section
5.3 and shown in Figure 5.8. The $T_x$ for this sample was 43°C, and the sample was collected for TEM/ED analysis at room temperature. According to the study by Sun et al.\cite{140}, the PEO crystallization occurred at 25°C when the sample was removed from the solvent. It should be noted that the tethering density for the EOCL-31 sample is much lower ($\sigma = 0.186$ nm$^{-2}$) than is expected for the sample with 5k g/mol PCL because the large difference in molecular weight indicates that the number of folds for EOCL-31 is much higher. From this comparison, it appears that the low tethering density of PEO on the PCL surface for the EOCL-31 copolymer inhibits the crystallization of PEO at room temperature. Further analysis is needed to determine the crystallization properties of PEO tethers.

8.2 PEO Crystallization as a Function of Temperature

One factor that may prevent the crystallization of PEO on the PCL single crystal surface is the ability of the PEO to nucleate. From AFM analysis, the thickness of the dry PEO layer is $1.2 \pm 0.2$ nm with a slight dependence on the crystallization temperature. Because this layer is thin, the nucleation of PEO crystals is hindered; therefore, the nucleation temperature should be decreased. In order to confirm that the crystallization of tethered PEO chains is dependent on tethering density, crystals grown at the same crystallization temperature (same tethering density) were quenched to different temperatures.
In the previous studies, the crystallization of PEO was achieved at room temperature by removing the crystals from the crystallization solution. It should be noted that the evaporation process can also induce crystallization. Looking at Figure 5.8, there is no observable diffraction associated with PEO crystallization. This sample was prepared by removing the crystals from the solution at room temperature and evaporating the solvent in vacuum. Even after an extended period of time, the crystallization of PEO did not occur. The temperature dependence of crystallization was tested by quenching the dry crystals in liquid nitrogen for 10 minutes. Figure 8.1 shows the TEM ED of one of the crystals. It was observed that even after quenching to a much lower temperature, the nucleation and subsequent crystallization of PEO did not occur as evidenced by the lack of PEO diffraction.

8.3 PEO Crystallization as a Function of Tethering Density

The nucleation temperature of PEO on the surface of PCL does not appear to be the limiting factor in its crystallization behavior. In each case, the PEO crystallization is
suppressed possibly by the layer thickness or by the tethering density. The next
parameter to address is the tethering density or reduced tethering density. The role of
proximity to other chains is critical in nucleation and growth of the crystalline PEO
phase.

The initial approach to addressing the role tethering density plays in supporting
crystallization of the PEO tethers is determining the crystallizability in different regimes.
The first difference occurs between the non-interacting regime and the interacting regime.
This was achieved using the EOCL-31 sample. At crystallization temperatures below
36°C, the PEO tethers are in the non-interacting regime as determined by Figure 5.6.
Above this value, they have reached the interacting regime. According to Figure 5.8, the
crystals grown at 43°C did not exhibit PEO crystallization from TEM ED experiments.
This crystallization temperature puts the PEO tethers in the interacting regime with $\sigma =
0.186 \text{ nm}^{-2}$ and $\bar{\sigma} \sim 3.9$. It was expected that crystals grown below this temperature
would not have crystallization of PEO on the surface due to larger interchain distances.
This was confirmed by TEM ED experiments of crystals grown at lower $T_x$. No crystals
were found to have PEO crystallization.

The limit of PCL crystallization was reached at 43°C for the EOCL-31 sample.
Above this temperature, the PCL crystals begin to dissolve in the $n$-hexanol solution. A
sample with a higher volume fraction of PEO is needed to further confirm any tethering
density dependence. For this purpose, EOCL-11 was used with an $M_n^{PCL}$ of 6.3k g/mol
and an $M_n^{PEO}$ of 5.0k g/mol. This composition is similar to those studied by Sun et al.\[140\]
This sample was crystallized using the same self-seeding technique. The DSC heating
and cooling curves shown in Figure 8.2 indicate that the melting and crystallization of
these two blocks in the melt is similar; therefore, it should be expected that the PEO
tether crystallization should occur around 25°C. Figure 8.3 is a TEM bright field image
and ED pattern of a crystal grown at 23°C in $n$-hexanol. Close examination of the
diffraction pattern again indicates that no PEO tether crystallization has occurred on the
crystal surface. The tethering density and reduced tethering density for this sample are
0.487 nm$^{-2}$ and approximately 10.4, respectively, as measured by AFM thickness results.
These values are much higher than those found for the EOCL-31 system. ED images of
multilayer and aggregate PEO-$b$-PCL crystals confirm the lack of PEO crystallization on
the surface of the PCL. Also, quenching of this sample to liquid nitrogen in the dry state
did not produce any PEO crystallization. It should be noted that the thickness of this
PEO layer was 3.0 nm.

![DSC Thermal Diagram](image)

Figure 8.2 DSC thermal diagram of EOCL-11 bulk sample. Heating and cooling were
done at 3°C/min. The crystallization of both components occurred around 35°C; while
the melting peaks were separated by a few degrees ($T_{m}^{\text{PEO}} = 48°C$ and $T_{m}^{\text{PCL}} = 55°C$).
8.4 DSC Analysis of Crystal Mats

Finally, the lack of PEO diffractions may be due to equipment limitations. The mass of PEO layers (and crystals) may be insufficient to observe diffraction patterns in the TEM ED results. As was mentioned in Chapter V, the apparent PEO layer thickness is less than 2.0 nm for the EOCL-31 copolymer. A second experimental approach to determining the PEO crystallization is to use DSC of crystal mats. The crystal mats provided a larger amount of material under the same conditions.

The mats were collected using a vacuum filtration method after crystallizing the PCL block at a temperature above the transition point of the interacting regime ($T_x = 38^\circ$C). Approximately 0.3 mg of material was collected. If the PEO has crystallized, an exothermic peak for the crystal melting should be observed in the DSC heating curve. Figure 8.4 shows that only the peak for PCL melting is detected. The heating rate was $2^\circ$C/min. Because the melting temperatures are higher than that found for the PEO in the...
bulk state, the shoulder and secondary peak are most probably from recrystallization of the material due to the slow heating rate. This supports the electron diffraction evidence that the PEO does not crystallize at room temperature.

Figure 8.4 DSC heating curve for PEO-\textit{b}-PCL crystal mats of EOCL-31. The heating rate was $2^\circ$C/min. No melting peak for PEO is observed.

Figure 8.5 is a thermal diagram for a heating scan at $10^\circ$C/min after quenching a new set of mats to $-20^\circ$C in the DSC directly after filtration. There is still no indication of PEO crystallization, providing further proof that PEO tether crystallization must be dependent on tethering density. The sample was then quenched to $-20^\circ$C again after complete melting of the PCL single crystal mats. Figure 8.6 shows the DSC thermal diagram for both cooling and subsequent heating. The crystallization peak for PEO at a temperature of $-10^\circ$C is seen in the cooling curve. After quenching the melted PEO-\textit{b}-PCL crystals, the PEO melting peak can be seen at $38^\circ$C. It should be noted that the layer thickness of the PEO tethers on the PCL single crystal is still quite small. The thickness, therefore, may still be a key factor in determining crystallizability along with tethering density.
Figure 8.5 DSC heating curve for PEO-\(b\)-PCL crystal mats of EOCL-31 after quenching to -20°C in the dry state. No melting peak for PEO is observed. The heating rate was 10°C/min.

Figure 8.6 DSC curves for PEO-\(b\)-PCL crystal mats of EOCL-31 after melting of the PCL single crystals and quenching to -20°C. The crystallization (-10°C) and melting peaks (38°C) for PEO are observed. The heating and cooling rates were 10°C/min.

8.5 Verification of Possible PEO Crystallization

All of the previously mentioned studies have shown that tethered PEO crystallization does not occur on the surface of PCL crystals at tethering densities well
within the interacting regime. The \textit{n}-hexanol solvent used for the diblock crystallization is a theta-to-poor solvent for the PEO chains. The influence of solvent should be taken into account since it was apparent that the dry state crystallization could not be induced with decreased temperature. The crystallizability of PEO in \textit{n}-hexanol was tested in two ways. The first was homo-PEO crystallization; while, the second was quenching the diblock solution to lower temperatures prior to PCL crystallization to enable the PEO to crystallize simultaneously. The second approach was done using the EOCL-11 sample given that the crystallization of the two components in this diblock sample is closest according to the DSC in Figure 8.2.

![Figure 8.7 Homo-PEO 5k g/mol single crystal grown at 30\(^{\circ}\)C in \textit{n}-hexanol. (a) TEM bright field (b) ED.](image)

Homopolymer PEO with a molecular weight of 5k g/mol was used to confirm the crystallizability of PEO in \textit{n}-hexanol. The sample was dissolved at 80\(^{\circ}\)C, and the self-seeding procedure, with \(T_s = 42^{\circ}\)C, was used. After dissolution and quenching, a white precipitate was found in the solution, indicating the formation of dendritic and aggregate crystals. The sample was seeded and crystallized at \(T_x = 30^{\circ}\)C. Figure 8.7 shows the TEM bright field image and ED pattern of the resultant PEO crystals. The square-shaped morphology indicates that the PEO single crystal has formed. The ED pattern exhibits

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the monoclinic diffraction pattern with the (120), (110), and (020) diffractions. Both of these results confirm the crystallization of homo-PEO in \( n \)-hexanol. The next step is to determine whether the diblock PEO can also crystallize.

The second method was to use the EOCL-11 sample to promote simultaneous crystallization of both blocks using a much larger undercooling in solution. The diblock copolymer was dissolved in \( n \)-hexanol at \( T_d = 80^\circ C \). The sample was then slowly cooled to -5\(^\circ C\) in an ice water bath with sodium chloride to depress the freezing temperature. This temperature was well above the freezing temperature of \( n \)-hexanol, \( T_f = -30^\circ C \).

Figure 8.8 is the resulting electron diffraction pattern from the aggregate, dendritic crystals. The PCL diffraction arcs were observed because they crystallized first, forming lamellar crystals. Two diffraction rings appeared that are not associated with the PCL orthorhombic unit cell. The \( d \) -spacing of these two rings are 4.60 Å (inner) and 3.82 Å (outer). The (120) diffraction of PEO is the most intense and found at a \( d \) -spacing of 4.63 Å. Taking into account small errors in calculating the \( d \) -spacing from the ED pattern, it was concluded that the innermost ring is associated with the (120) diffraction of completely unoriented PEO crystals. At first glance, it appears that the second ring is associated with the (200) diffraction of the PCL; however, after careful analysis, the second ring was assigned to the overlapping diffractions of the (112), (032), (\( \bar{1} \)32), (212), (\( \bar{1} \)24), (204), and (004), all with a \( d \) -spacing of 3.9 Å. The appearance of these diffractions indicates that the chain direction for the PEO crystals is perpendicular to the electron beam and most probably perpendicular to the PCL crystal surface normal as well. Because of the aggregate crystal structure, no true orientational analysis can be conducted.
Additional arcs can be seen around the (110) spots of the PCL, which is an indication of the aggregate crystals with various orientations. Also, spots at \( d \)-spacings larger than the PEO (120) diffraction ring are the (100) and (010) spots of PCL. They are typically extinct when the crystal is exactly parallel with the electron beam. The appearance of these spots simply indicates that the orientation of the PCL crystals in the beam was not perfect. These results prove that there exists the possibility of crystallizing the PEO block; however, when confined to a single layer on the PCL single crystal, crystallization does not occur as evidenced by the previous results.

![Figure 8.8 ED pattern from the EOCL-11 sample after slow cooling to -5°C in \( n \)-hexanol. The two additional rings indicate that the PEO block has also crystallized under these conditions.](image)

### 8.6 Switching Crystallization Kinetics

A unique opportunity arises in the study of the solution crystallization of crystalline-crystalline diblock copolymers. Typically, the dominant crystallization behavior is determined by the block length, where the larger block crystallizes first, or the
melting temperature, where the block with the higher $T_m$ crystallizes first due to larger undercooling at $T_x$. The PEO and PCL have similar $T_m$’s, therefore the larger block crystallizes first as demonstrated by all of the previous studies.\cite{140, 144-147} On the other hand, if the nucleation barrier of the smaller block (PEO) can be decreased, it is possible to crystallize it first, thus switching the crystallization kinetics.

The easiest way to accomplish this is to use a homopolymer PEO seed to induce the crystallization of the PEO in the diblock copolymer. It has been shown in various instances within this dissertation that it is possible to utilize seeds of one species (homo or diblock) to induce crystallization in the opposite species. The interesting facet of this approach is that the homo-PEO seed is nucleating the crystallization of the non-crystallizing moiety of the diblock copolymer under these solution conditions.

The 5k g/mol homo-PEO sample was used to grow square-shaped single crystals in $n$-hexanol at 26°C (as seen in Figure 8.7). Then, a solution of dissolved diblock EOCL-11 was placed in the same oil bath at 26°C. After 10 minutes, a small amount of the homo-PEO single crystals were added to the EOCL-11 solution to act as seeds for the crystallization of the PEO block. After a few days, a sample was taken and analyzed by TEM for both morphology and crystal structure. Figure 8.9 is an example of the crystals observed.

The square-shaped habit of the crystal indicates that the PEO block of EOCL-11 has crystallized on the homo-PEO seed. The darker section is indicative of a thicker layer on the lateral surface of the homo-PEO single crystal (central, lighter section). The PCL block is now the tethered layer on both fold-surfaces of the PEO single crystal. The next step was to use electron diffraction to analyze the existence of a central layer PEO
crystal (block sandwiched structure) as well as determine any crystallization in the PCL layers.

Figure 8.9 TEM image of homo-PEO/EOCL-11 crystal. The square shape indicates that the PEO crystal is the middle layer with PCL on either surface. The center is the homo-PEO; while, the outer, thicker layer is the EOCL-11 crystal section.

Figure 8.10 is a set of ED patterns collected from the four sectors of the PEO crystal. Figure 8.10a is from the top (angled to the right) sector. Figure 8.10b is from the lower right hand sector. Figures 8.10c and 8.10d are the subsequent sectors following around the crystal in a clockwise direction. In each of the ED patterns, the four (120) spots of the PEO monoclinic unit cell were observed. Because these spots were taken from the thicker section, this is further evidence that the PEO block crystallized on the lateral surface of the homo-PEO single crystal to form the center of the sandwich structure. Additional diffraction arcs were observed as well. These diffraction arcs are representative of PCL crystallization in the two tethered layers. The four arcs immediately outside the (120) spots of the PEO are at a $d$-spacing of 4.17 Å. The $d$-spacing for the (110) planes in the orthorhombic PCL crystal is 4.18 Å. The final two arcs are at a $d$-spacing of 3.73 Å. The $d$-spacing for the (200) planes in PCL is 3.75 Å.
These $d$-spacings confirm the crystallization of PCL on the PEO crystal surface with the $c$-axis of the PCL crystallites being parallel to that of the PEO and the surface normal. The appearance of diffraction arcs indicates that the PCL layer does not form a single crystalline structure, but consists of several small crystallite domains. These crystals are also on either side of the PEO single crystal due to the sandwiched structure.

The question arises: why does the PCL crystallize on the PEO surface when the PEO does not crystallize on the PCL surface at the same conditions? The simple answer to this question is the difference in tethering densities for these two states; however, the layer thickness is not completely discounted. When the PCL is crystallized first at 25°C, the PEO tethered layer has a tethering density of approximately 0.487 nm$^2$. However, in the opposite case, where PCL is the tethered layer, $\sigma = 1.23$ nm$^2$ as measured in AFM.

The thickness of the middle PEO crystalline layer, $d_{\text{CRYST}} = 16.5$ nm and $d_{\text{PCL}} = 10.0$ nm, was determined using the same volume fraction calculation as the previous results. The difference between amorphous PCL and crystalline PCL densities does not change the volume fraction significantly, 0.42 PEO with crystalline PCL and 0.41 with amorphous PCL. The tethering density was determined using 100% crystalline PCL because it is difficult to determine the exact crystalline fraction. This thickness was also confirmed with homo-PEO on the outside of the layered crystal as described in Section 4.4.2.

Because the tethering density was quite large, it is possible that the PCL chains crystallize almost simultaneously with the PEO. The area occupied by a single, crystalline PCL chain was 1.7 nm$^2$ (with a thickness of 10.5 nm). The area occupied by a single, crystalline PEO chain was 0.81 nm$^2$ (with a thickness of 16.5 nm). With some variability and error in measurements, this indicates that the area occupied by the PCL is...
nearly twice that of the PEO. The PCL cannot be 100% crystalline in this case. Only a small fraction can be crystalline to accommodate the volume change. The layer thickness must be a combination of the crystal thickness and the amorphous layer contributions. This makes it difficult to know exactly the reduced tethering densities because the crystallization of the PCL will facilitate the packing of these tethered chains. Determination of $\sigma$ for crystallization is difficult without measurements at lower values where no crystallization can occur.

In fact, the large tethering density value ($\sigma = 1.23 \text{ nm}^{-2}$) may also be a result of the influence of the crystallization of the PCL chains. The thermodynamically metastable lamellar crystals are each affected by the tethering of one block to the other. The solution grown PEO single crystals adopt the lowest free energy state considering the free energy of the fold surface and tethered PCL chains. The equilibrium conformation of polymer crystals is the extended chain crystal; however, due to the large amorphous chain entropy, this cannot be the case for diblock copolymer single crystals. When the crystallization of the PCL occurs, the crystallites also wish to be at the lowest free energy. The competition between the metastable thicknesses of the PEO and PCL blocks may compromise the PEO thickness. This would lead to a change in the tethering density after PCL crystallization as well. Hence, the most accurate assessment of $\tilde{\sigma}$ for crystallization must occur prior to crystallization in the PCL.

The likely difference in chain size, and therefore $\tilde{\sigma}$, between 5k PEO and 6.3k PCL is a major contributing factor to the crystallization of the PCL. As the single crystal forms, the size of the solvated chains on either surface, in both the PCL and PEO scenarios, influences the final crystal thickness. Because the environmental conditions
were kept constant (solvent and $T_x$), the appearance of PCL crystals must be attributed to the higher mass density on the crystal surfaces. This observation implies that the crystallizability of the tethered chain is dependent on $\sigma$. The relationship of $\sigma$ to the tethered chain regime in which crystallization occurs is unknown; however, it is assumed that it is much larger than the transition into the interacting regime as confirmed by the PEO study in Section 8.3 and the extremely large value for the PCL tethers, though slightly skewed due to the phase change as described in the previous paragraphs.

Figure 8.10 TEM ED patterns taken from the four sectors of the PEO/EOCL-11 crystal shown in Figure 8.8. (a) upper right (b) lower right (c) lower left (d) upper left.

The final attribute of this system to be analyzed was the orientation of the PCL tethers. From the ED patterns in Figure 8.10, the arcs indicate that the PCL crystallites have some orientational order. They are not single crystalline, as observed by the previously reported studies,$^{[140, 142]}$ because there are arcs not diffraction spots, showing a lack of perfect alignment of the planes within the electron beam. The second conclusion that was made is that the chain orientation, or the $c$-axis, of the PCL crystals is parallel to
the electron beam, as well as the PEO surface normal. This was concluded from the
diffractions associated with the [001] zone of the PCL crystallites.

There appears to also be some crystallite orientation on the crystal surface itself.
The (110) diffraction arcs of the PCL are nearly aligned with the (120) diffraction spots of the PEO. This gave some indication that the [110] direction of the PCL crystallites is parallel to the [120] direction of the PEO single crystal. In other words, though the $c$-axis is oriented parallel to the electron beam, the $ab$-plane is only partially oriented in the plane perpendicular to the beam. After many crystals were analyzed, this observation cannot be concluded to be absolutely true, but appeared to be a prominent feature. The origin of such orientation is unknown. Because the fold planes of the PEO and PCL are the (120) and (110) planes, respectively, there may be some soft epitaxy that occurs between the fold surfaces of each to create the orientational order.
CHAPTER IX
SUMMARY

The transition for the crossover from the non-interacting to the interacting regimes of tethered PMMA and PEO polymer chains was determined utilizing amorphous-crystalline diblock copolymers. These were PMMA-\textit{b}-PLLA and PEO-\textit{b}-PCL. In this study, the crystalline block, PLLA or PCL, was crystallized in dilute solution to form a lamellar single crystal, and the amorphous block was tethered to the top and bottom basal surfaces of the single crystal, forming a “sandwiched” structure. These copolymers exhibited a transition in the relationship between the lamellar crystal thickness ($d_{\text{CRYST}}$) and the crystallization temperature ($T_x$). This slope transition indicates the transition from the non-interacting to the interacting regime due to an increase in the surface free energy. The results show that the transition values for these two tethered chains, PMMA and PEO, are quite different from the previous study of PS.

The interaction between the PMMA and the PLLA surface is attractive due to their miscibility in the melt state. Because the Kuhn lengths ($l_k$) of PMMA and PS are similar, the transition value ($\tilde{\sigma}^*$) for PMMA was indicative of the influence of adsorption. In addition, the conformation of the PMMA chains was significant for the determination of $\tilde{\sigma}^*$. The single crystal system is too small to study the conformation
utilizing typical experimental methods; therefore, the size of the adsorbed chain was
determined with the help of MC simulations of a single tethered chain.

In these simulations, relevant chain parameters such as $R_g^2$, $R_{g,z}^2$, and $R_{g,xy}^2$ under
varying field conditions, $\beta_b$ and $\beta_s$. $\beta_b$ was a variation in bead-bead interactions, and $\beta_s$
was a variation in surface-bead interactions. The phase map for the single chain
including adsorption and collapse transitions was determined. By comparing the
experimental free $R_g^2$ with $R_g^2$ in the good solvent, desorbed condition in the simulation,
it was possible to estimate the adsorbed $R_g^2$ for the PMMA on the PLLA surface. The
adsorbed simulation value was calculated and converted to the real system length scale.
The PMMA transition value was found to be much higher than the PS results with $\tilde{\sigma}^*$
equal to 7.5.

The second tether was PEO on the surface of PCL single crystals. The PEO
tethers exhibited a $\tilde{\sigma}^*$ that was estimated to be equal to or lower than the PS sample.
For the PEO tethers, $\tilde{\sigma}^* \sim 3.8$. The interaction between the PEO tether and the PCL
substrate was repulsive; therefore, the conformation of these chains was similar to that of
the PS studies. The chains in this case, however, were in a theta-to-poor solvent. The
suppression of PEO crystallization was proven to by ED and DSC experiments with the
lack of PEO crystal diffraction and melting, respectively.

The results show that the chain dimension $R_g$ does normalize the systems for
comparison; however, the conformation of the chain is important for the physics of the
interacting transition. In the PMMA study, it was shown that a layer of adsorbed blobs
forms below a layer of desorbed chains. Following the prediction of Descas, an increase
in $\tilde{\sigma}^*$ is expected for adsorption conditions. In comparing the experimental and
simulated chains, the two-fold difference between PS and PMMA was achieved around \( \beta_s = 1.4 \).

The PEO \( R_g \) was calculated for theta solvent conditions. It was shown that for theta conditions, the transition value is equal to that of PS. However, if the chain formed a collapsed state and maximized intra-chain interactions (poor solvent), this conformation forms an effective hard core sphere (smaller \( R_g \)). Because of this, \( \tilde{\sigma}^* \) would be lower than the good solvent and theta solvent cases for PS. This indicates that the unoccupied volume within the PS chains was able to accommodate additional chains as the tethering density increased. On the contrary, the collapsed PEO chains would not, resulting in a lower \( \tilde{\sigma}^* \) value.

The crystallization of a single layer of tethered PEO was shown to be suppressed in the PEO-\( b \)-PCL copolymer single crystals. Electron diffraction and DSC experiments showed that the PEO tethers do not crystallize up to a \( \tilde{\sigma} \) of \(~10.4\ (\sigma = 0.487\ nm^{-2})\) even after quenching in liquid nitrogen in the dry state. However, if PEO was crystallized first through epitaxial growth on a homo-PEO single crystal, the PCL block does crystallize on the surface at room temperature. In this case, \( \sigma \) for the PCL was \( 1.27\ nm^{-2} \). Broad diffraction arcs indicate that moderately-oriented crystallites were formed on the PEO surface. The PCL crystallites formed with their \( c \)-axis parallel to the PEO chain direction (lamellar normal) and were occasionally found to be oriented with their [110] direction parallel to the [120] direction of the PEO single crystal, possibly through soft epitaxy of the folds between each crystalline block.
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