SINGLE CRYSTAL ENGINEERING
OF AMORPHOUS-CRYSTALLINE BLOCK COPOLYMERS
CRystALLIZATION, MORPHOLOGY AND APPLICATIONS

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Dissertation

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ABSTRACT

Single crystals of poly(ethylene oxide)-b-polystyrene (PEO-b-PS) diblock copolymers with different molecular weights and compositions were grown in dilute solution, and were utilized as ideal models for studying: (1) crystallization in nano-confined environments; (2) fabrication of uniform polymer brushes of varying tethering density; (3) modification of chemical and physical conditions for crystal growth. These studies have been referred to as “Single Crystal Engineering”.

The glass transition temperature of the PS layer in the single crystal of a PEO-b-PS copolymer ($M_n^{PS} = 17k$ g/mol, $M_n^{PEO} = 11k$ g/mol) is higher than the melting temperature of PEO layer. Therefore, the melting and crystallization behavior of this single PEO nano-layer confined between two PS glassy walls can be studied. Results show that the crystal orientation of the confined PEO nano-layer depends on the recrystallization temperatures.

After crystallization of PEO blocks, PS blocks are tethered to the basal surfaces of the crystal. The PS brushes generated from single crystals are uniform, because of the precision of the molecular weight and tethering density. The tethering density of PS brushes is manipulated by changing crystallization temperatures. It has been found that
the PS brushes start overcrowding when the reduced tethering density of PS brushes is 3.7 ± 0.1, independent of solvent.

During crystallization of PEO blocks in solution, the PS chains can chemically and physically affect the crystal growth front of PEO lamellae. The single crystals of a series of PEO-b-PS diblock copolymers were used as nucleation sites for the crystal growth of a homo-PEO fraction in solution. In the copolymers, $M_{n}^{\text{PEO}}$ is similar, and the $M_{n}^{\text{PS}}$ ranges from 4.6k to 17k g/mol. The results indicate that increasing the $M_{n}^{\text{PS}}$ leads to a higher reduced tethering density of the PS blocks on both the basal surfaces of the single crystals. The repulsion generated among the tethered PS blocks caused the PS blocks located near and at the edges to advance along the [120] direction.

Novel channel-wire arrays on a submicrometer length scale having chemical and geometric recognitions have been fabricated via alternating crystal growth of PEO-b-PS and homo-PEO. The spacing between arrays can be controlled down to 50 nm.
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CHAPTER I

INTRODUCTION

Polymer crystallization has been a long discussed fundamental research topic in the past half century. It is described as a thermodynamic first-order transition that is a nucleation controlled process. The nucleation barrier determines the crystallization kinetics. However, a specific trajectory of one macromolecule among many others during crystallization may encompass multiple steps. Crystallization begins with the adsorption of a part of one macromolecule and ends with the incorporation of that macromolecule into a crystal lattice in a chain-folded fashion. Whether or not crystallization can go forward and how fast it can take place relies on several selection processes on different length and time scales. These selection processes must be sequential and cooperative. The overall effect of these selection processes on free energies (both enthalpic and entropic origins) construct the nucleation barrier. One of these selection processes is based on the local environment (both physical and chemical) provided for polymer crystallization. Due to different physical and/or chemical environments, polymer crystallization could be enhanced, such as crystallization from the preordered state rather than the isotropic state, or hampered, such as crystallization under
the “self-poisoning,” in amorphous-crystalline polymer blends, or under nano-confinements.

Phase transitions of polymers that take place within confined geometries on the nanometer length scale may exhibit different transition behaviors from those in the bulk. These transitions are an important area of research. One approach utilized to construct nano-confined environments involves the use of diblock copolymers as templates. Below the order-disorder transition temperature of diblock copolymers (in UCST systems), phase morphologies such as lamellae, cylinders, spheres, gyroids, and hexagonally perforated layers can form. In order to study crystal structure and orientation evolutions within the nano-confined environments, single domains of phase morphologies need to be generated. In other words, macroscopic orientation of the phase morphologies needs to be obtained by utilizing a mechanical shear technique. It is important to note that morphological defects such as edge and screw dislocations do form. For example, in the case of poly(ethylene oxide)-b-polystyrene (PEO-b-PS) lamellar morphology studied by our group, the “communication” occurring between neighboring PEO layers always affects the PEO crystallization behavior in this confined environment. An ideal case of constructing a confined single lamella environment would be to obtain one PEO nano-layer sandwiched by two PS nano-glassy walls. Traditional methods, such as spin casting, cannot make such confinement geometry for one single PEO nano-film.

In the past decade, it has been recognized that polymer brushes are key to enabling a wide range of potential surface applications related to bio- and nanotechnologies. Several approaches on how to tether chains to substrates have been proposed through physical adsorption or chemical grafting of chains onto substrates via
``grafting to” or “grafting from” strategies. Both approaches lack the precise control of uniform chain distribution (tethering density) and/or uniform chain length of the tethered polymers. Based on the reduced tethering density, there are three regimes for polymer brushes: non-interaction regime, crossover regime, and highly stretched regime. So far, most theoretical treatments of tethered chains on flat solid substrates have been focused on the description of the non-interacting regime or the strongly stretched regime. It has been found that the transition between these two regimes is rather broad allowing a crossover regime to exist; however, the location of the boundaries between each of these two regimes is not quantitatively known. In experiments, the reported transitions between polymer brush regimes are quite contradictory. The very reason for the contradiction is because the uniformity of polymer brushes (chain length and distribution) cannot be precisely controlled by the traditional methods of making polymer brushes.

Single crystal lamellae of amorphous-crystalline block copolymers can be formed in dilute solution at low degrees of undercooling. The thickness of the lamella is on a nanometer scale, and the sizes of other two dimensions are much larger (as large as a millimeter). Therefore, growing single crystals in dilute solution is an approach to construct nano-films. More interestingly, this type of thin film consists of three layers, one crystalline layer sandwiched by two amorphous layers, because the amorphous blocks in amorphous-crystalline block copolymers are excluded from the crystal lattice and located on the lamellar crystal basal surfaces after the crystallization of the crystalline block. Each layer has a thickness of several nanometers.

In this research, we use single crystals of amorphous-crystalline block copolymers to form thin film templates and to generate polymer brushes to investigate some
fundamental issues, including the crystallization of a confined nano-film, different polymer brush regimes, and effect of local chemical and physical environment on the crystal growth. We also develop a new approach to construct a channel-wire array with chemical and geometric recognition, which has application potentials in nanotechnology. We coin a term, “Single Crystal Engineering”, to describe the applications of single crystals of block copolymers for both fundamental research and application study.

Crystalline PEO blocks form lamellar crystals, while amorphous PS chains are tethered on the PEO crystal basal surface and uniformly distributed, macroscopically, due to the chain-folded nature of the PEO crystal. The PEO-b-PS was synthesized with a very narrow molecular weight distribution before the polymer brushes are formed; therefore, the tethered PS chains have very uniform length. The PS tethering density can be adjusted by the composition of block copolymer and crystallization conditions, such as crystallization temperatures and solvents. Then, the transitions between each polymer brush regime can be observed experimentally. It thus provides a great chance to study the polymer brushes in both theoretical calculation and experimental observation.

During crystal growth process in dilute solution, tethered amorphous chains are dangling in solution. These dangling chains, especially those located near or at the edges of PEO crystals, can affect the crystal growth fronts. This provides us an opportunity to study the effect of local chemical or physical environments on the crystal growth.

After crystallization of crystalline blocks and solvent evaporation, the amorphous blocks solidify on the surfaces of the crystal lamellae. By careful molecular design of amorphous-crystalline block copolymers (polyethylene oxide-b-polystyrene, or PEO-b-PS, in the current research), the glass transition temperature of amorphous layer ($T_g^a$) is
controlled to be higher than the melting temperature of crystalline layer \( T_m^c \). Then, the melting and crystallization of the single crystalline nano-layer is confined by two glassy walls. The confinement effect on the crystallization of the nano-film in this unique geometry can be studied.

Chapter II gives a historical review on the aspects which relate to the current study: (1) General morphological aspects of polymer crystals, especially the lamellar crystal morphology; (2) Crystal structure of linear PEO and PEO-\( b \)-PS block copolymers and morphology of PEO lamellar single crystals in melt or dilute solution; (3) Phase transition of molecules in the confined environment; (4) Traditional methods to construct nano-confined space and thin films; (5) Crystallization and crystal orientation of PEO in the confined space constructed by microphase separated block copolymers; (6) Polymer brushes, polymer brush regimes and theoretical studies.

Chapter III gives the detailed experimental methods involved in this study, including differential scanning calorimeter (DSC), transition electron microscopy (TEM), electron diffraction (ED), atomic force microscopy (AFM), etc. The detailed procedures of self-seeding for single crystal growth are also described.

Chapter IV focuses on the characterization of the single crystals of PEO-\( b \)-PS grown in dilute solution. The single crystals of the copolymers are proved to be a three-layer structure with PEO layer in the middle sandwiched by two PS layers. The melting point of the PEO layer is measured by DSC scan on the single crystal mats. The thickness of the PS layer and PEO layer was calculated though the crystallinity and overall crystal thickness which is measured by AFM.
Chapter V focuses on the crystallization of a single PEO nano-layer confined by two PS glassy walls. A three-layer-structure thin film with the PEO nano-layer in the middle sandwiched by two PS layers is constructed by growing single crystals of PEO-\textit{b}-PS copolymer in dilute solution. The melting temperature of the PEO layer is lower than the glass transition temperature of PS layer. Therefore, the melting and crystallization of PEO is studied in this unique confinement environment. The crystallization kinetics of the PEO nano-layer is much slower than that of PEO in the bulk copolymer sample. After the PEO layer is melted, the crystal orientation of the recrystallized PEO changes with the recrystallization temperatures.

In Chapter VI, the thickness of the PEO crystal in the copolymer single crystal as a function of crystallization temperature is studied. From this the tethering density of PS chains is obtained. It was found that the tethering density increases with crystallization temperature. There is a transition at a reduced tethering density equal to 3.8, which is reflected by the slope change in the plot of PEO crystal thickness versus crystallization temperature. This transition is defined as the onset of chain overcrowding, and this transition point is solvent independent since the reduced tethering density is used as the characteristic parameter instead of tethering density.

Chapter VII focuses on the effect of the local chemical and physical environment from PS chains on the crystallization behavior of PEO. At the same crystallization condition, the tethering density of PS brushes is dependent on the PS chain length. The repulsion generated among these tethered PS blocks leads the PS blocks located near and at the edges to advance along the [120] direction of PEO crystals. When the crowdedness of PS chains is high enough, this local environment only accepts the PEO-\textit{b}-PS molecules
and rejects the homo-PEO molecules for the further growth. Furthermore, novel channel-
wire arrays having chemical and geometrical recognitions could be fabricated via
alternating crystal growths of PEO-\(b\)-PS and homo-PEO. These channel-wire arrays
provided robustly controlled array spacing down to 50 nm.

In Chapter VIII, a summary of the research highlights is addressed.
CHAPTER II

HISTORICAL BACKGROUND

2.1 Morphology of polymer crystals

2.1.1 Introduction

Polymer crystals have three-dimensional long-range order, and the crystallization of polymers is thermodynamically defined as a first-order transition. The driving force of polymer crystallization is the difference of free energies between the crystalline state and the amorphous phase in the undercooled melt. This driving force can be understood from the perspective of enthalpy and entropy: The attraction of the molecular segments and their incorporation into a crystal lattice, a favorable enthalpic change, is opposed by a loss of entropy resulting from crystallization. Although extended chain crystals represent the ultimate equilibrium crystal, the kinetics of polymer crystallization usually lead to chain-folded crystals in a thermodynamically metastable state.

It is the long-chain nature of crystalline polymers that leads to the crystallization behavior and morphological aspects which are different from traditional “small
molecule” solids, and some of those features are unique to polymers.¹ Polymer crystals have been studied for a long time. The early x-ray diffraction studies on fibers of naturally occurring polymers date back to the 1920s and the early 1930s. The x-ray diffraction patterns of bulk crystallized polymers are usually broad and diffuse, and the density of the specimens were in between those of the crystal and the amorphous melt. The heat of fusion is generally low, and the melting peaks are often broad. All these structural and thermodynamic properties indicate that the polymers consist of either crystals with a large degree of imperfection, or an intimate mixture of microscopic crystalline and amorphous phases.

Polymers, even chemically uniform homopolymers, are never fully crystalline, so they are characterized by the concept of crystallinity, a ratio between the crystalline volume (weight) and the overall volume (weight). No single local barrier can account for why these polymers do not crystallize further. It is rather a range of essentially kinetic factors that hinder the full incorporation of the polymers into the crystals. The root of these factors lie in the long-chain nature of polymers, which is reflected by the fact that the ratio of crystal size to polymer molecular size (typically 0.1-10 μm in length) is much smaller than that for small molecules.²

2.1.2 Fringed-micelle model and polymer spherulites

Crystals in bulk polymers were initially described as fringed micelles as shown in Figure 2.1.³⁴ Based on this model, the bulk polymer was thought to consist of crystals on the order of several hundred angstroms in size embedded in an amorphous matrix.
This model was quite successful for explaining the bulk macroscopic properties of polymers.

![Fringed micelle model of a partly crystalline polymer](image)

**Figure 2.1 Fringed micelle model of a partly crystalline polymer**

In the middle of the 1940s, it was found that the synthetic polymer crystallized in the melt and formed ordered aggregates in which the constituent crystalline units are arrayed in a spherical fashion, thus it was called a spherulite.\(^5\) Such spherical aggregates were also observed in some viscous and impure non-polymeric materials.\(^6\)\(^{10}\) It is difficult to explain the molecular structure and crystal orientation of polymer spherulites on the basis of the fringed-micelle model.

The structure of the spherulites is composed of radiating fibrils based on polarized light microscopy (PLM), so the original nucleus must develop a fibrillar habit. Furthermore, the fibrils must proliferate and therefore must “branch” in order to fill the space to develop a uniform density structure. It was proven that lamellar crystals are the
basic building blocks of spherulites in melt-crystallized PE.\textsuperscript{11,12} The polymer spherulite structure with chain folded lamellae is schematically shown in Figure 2.2. The lamellae in polymer spherulites are generally twisted, which is reflected in different spectacular ways such as the periodic banding in PLM or the development of a concentric ring pattern made of C shaped lamellar edges on the spherulite surface.\textsuperscript{13-15} Although the lamellar twisting in spherulites is well understood, the origin of twisted lamellae in spherulites has been a challenge in the field of polymer morphology. The rhythmic supply of material during the growth of spherulites is one explanation for lamellar twisting as voiced by Kyu.\textsuperscript{13} Surface stress induced by congestion at the fold surface is another explanation as proposed by Keith.\textsuperscript{14} Lotz and Cheng critically analyzed different explanations for lamellar twisting, and provided a unified explanation for the formation of non-planar (both twisted and scrolled) lamellar crystals based on structural disparities and the resulting unbalance of surface stress after a detailed study on the different natures and structures of polymer crystal fold surfaces.\textsuperscript{15}

![Figure 2.2 Schematic view of polymer spherulite with folded-chain lamellae.\textsuperscript{14}](image)
2.1.3 Folded-chain lamellar crystals

The first observation of lamellar single crystals was in polyethylene (PE) grown in dilute solutions.\textsuperscript{16-18} But the chain-folding concept came up as early as 1938, when Strokes suggested the chain-folding concept to account for the molecular orientation in solution-cast thin films of the polymer gutta percha [trans-1,4-poly(2-methyl-butadiene)] which occurs in nature.\textsuperscript{19} But this suggestion was not followed up and did not receive attention until Keller revived the concept, and established the occurrence of chain folding in his landmark paper on microscopic solution-grown crystals of polyethylene.\textsuperscript{17} As Keller proposed, a single polymer chain needs to thread many times through the same lamellar crystal, which it does by folding on the crystal surface as shown in Figure 2.3.\textsuperscript{2} This is the modern view of “chain-folded” polymer crystallization.

![Figure 2.3 A drawing of idealized folded-chain crystal lamella. The lines on the surface of the crystal delineate four sectors of eth fold domains. The arrows in each sector indicate the orientation of the fold planes.](image)

The lamellar crystals exhibited large lateral dimensions (from micrometer to millimeter) and a small thickness of around ~5 ~ 20 nm. The thickness of the lamellae was dependent on the crystallization conditions. Keller and O’Conner\textsuperscript{20} first reported the thickness of a lamellar polymer crystal. They found that the lamellar thickness was related to the crystallization temperature. More precisely, the thickness of the lamellae
was inversely proportional to the degree of undercooling instead of the crystallization temperature. The simple and common method to grow lamellar single crystals is in a dilute solution or in a thin film melt, but it was also observed in the bulk melt.  

Folded-chain single crystals of many crystallizable synthetic polymers at low undercoolings exhibit well defined lateral growth shapes (facetted crystals) which reflect the symmetry of the unit cell of the polymers, although there are some exceptions like polyacrylonitrile and polychlorotrifluoroethylene (which will be discussed later in subsection 2.1.3.3). These crystals are bounded laterally by smooth low-index growth faces. For example, the orthorhombic polyethylene (PE) crystals grown in dilute solution such as in xylene, develop lozenge shaped crystals bound by \{110\} faces as shown in Figure 2.4, or develop truncated lozenge shape crystals bound by \{110\} faces and short \{100\} faces as shown in the Figure 2.5. With increasing interaction between PE and solvent or increasing crystallization temperatures, the PE crystal shapes gradually evolve to become elongated crystals with curved “100” faces, such as in hexyl acetate (shown in Figure 2.5c). In the case of solution grown polyoxymethylene crystals, the single crystals exhibit a hexagonal shape bound laterally with by \{10 \overline{1} 0\} faces as shown in Figure 2.6. Poly(4-methylpenten-1) grown in solution has a square shaped single crystal reflecting its tetragonal unit cell as shown in Figure 2.7. The crystals are bound by \{100\} faces.
Figure 2.4 Solution grown polyethylene crystals with lozenge shape (a) Electron micrograph; (b) Schematic representation of the type of crystal shown in (a) with the lateral growth faces and sector boundaries.\textsuperscript{31}

Figure 2.5 Solution grown polyethylene crystals with truncated lozenge shape (a) Electron micrograph; (b) Schematic representation of the type of crystal shown in (a) with the lateral growth faces and sector boundaries; (c) Electron micrograph of solution grown polyethylene crystals with curved “100” faces.\textsuperscript{36}
Figure 2.6  Solution grown polyoxymethylene crystals with hexagonal shape  (a) Electron micrograph; (b) Schematic representation of the type of crystal shown in (a) with the lateral growth faces and sector boundaries

Figure 2.7  Poly(4-methylpentene-1) single crystal  (a) Phase contrast optical micrograph of crystal grown at 90 °C from 0.1% solution in an equivolume mixture of xylene and amyl acetate (b) Electron micrograph of one corner of a crystal shown in (a), (c) Schematic representation of the type of crystal shown in (a) and (b) with the lateral growth faces and sector boundaries
2.1.3.1 Sectorization in lamellar crystals

For folded-chain crystals, the lateral growth of the lamellar crystals occurs by the folding of chain molecules along the sides of the lamellae. The manner of growth inherently results in subdivisions of the crystals into distinct sectors (The sectors in folded-chain crystals are also termed “fold domains” as originally coined by Geil and Reneker\(^{40}\) which are distinguished from one another by the chain folding direction. In each sector, the chains are folded along the plane (fold plane) parallel to the particular lateral crystal face that subtends the sector. Nevertheless, the sectors in the same single crystal are crystallographically identical.

It can often be noted that cleavage occurs between the planes along the fold plane in the constituent sectors in the folded-chain crystal, since there is only van der Waals interactions between fold planes within the constituent sector (in the real case, this may not be completely true). In other words, the fold planes in each sector are cleavage planes.\(^ {41-43} \) On the other hand, within the fold plane and other non-fold planes, there is additional bonding between the planes due to the folds on the top and bottom surfaces of the lamellar crystals. This was illustrated in the case of PE crystals\(^ {42} \) as shown in Figures 2.8a and 2.8b and poly(4-methylpentene-1)\(^ {44} \) as shown in Figure 2.8c. The experiments were designed to observe with electron microscopy cracks in single crystals after deformation. The cracks parallel to the crystal faces (also parallel to the fold planes) are evident, while the cracks which intersect the fold planes are transversed by thin fibrils. These thin fibrils are attributed to the “pulling out’ and unzipping of the folded polymer chains during deformation. Cheng\(^ {45,46} \) applied this method to study the chain folding
direction of syndiotactic polypropylene (s-PP) folded-chain single crystals, and the results showed the chains do not simply fold along the a- or b- axis, instead they fold along the (110) plane or a combination of the a- and b- axis.

![Figure 2.8](image)

**Figure 2.8** Experimental observation of cleavage planes in single crystals (a) Electron micrograph showing a crack parallel to {110} fold planes in a portion of PE crystal.42 (b) Electron micrograph showing a crack which traverses the {110} fold planes with fibrils in a portion of PE crystals.42 (c) Region near an edge of a four-sectored lamella of poly(4-methylpentene-1)44

2.1.3.2 Non-planar lamellae

Depicting lamellar crystals as being flat, and depicting the fold stems in the lamellae as being normal to the fold surface, oversimplifies the features of the folded-
chain crystals. In reality, single layer folded-chain crystals are often not planar, for example, PE crystals adopt hollow pyramidal shapes. This was proven by transmission electron microscopy/electron diffraction and optical microscopy experiments on PE lamellar single crystals. A theoretical calculation on a polyethylene single crystal with a thickness of 12 nm assuming a perfect lattice orientation normal to a highly collimated beam of 80 kV electrons indicates that only the reflections corresponding to spacings greater than 0.25 nm can be obtained with appreciable intensity. This includes only two reflections of the polyethylene unit cell. But in actuality, as many as 7 orders of reflections have been obtained in the electron diffraction of polyethylene single crystals. It is obvious that some \{hk0\} planes within the crystal are tilted with respect to the incident electron beam. Dark field micrographs also indicate a difference in the average orientation of the reflecting planes and thus the molecules in different sectors. Bassett, et al directly observed the shape of the polyethylene single crystal suspended in solvent using an optical microscope in dark field mode, and they proposed a model of this hollow pyramidal shape as shown in Figure 2.9. If viewed along the pyramid axis, the crystals would exhibit a lozenge or truncated lozenge shape profile. The stems of the molecules throughout the crystal are oriented parallel to the pyramid axis (also the c-axis of the crystal), therefore the stems are inclined toward the fold surface (the sloping faces of the pyramids). The magnitude of the inclination of the sloping pyramid faces relative to the stems may be different from sector to sector.

The hollow pyramid character of the polyethylene single crystals has been attributed to the regular staggering between the levels of the folds in successive fold planes in each sector, while the occurrence of fold staggering is attributed to the
bulkiness of the chain folds. The idea is that the apposition of folds leveling one and another makes the folds too crowded on the fold surface, and that staggered chain folds can minimize the steric interactions between neighboring folds. The extent of the staggering still needs to satisfy the crystallographic registry in the interior of the crystals.\textsuperscript{31,33-36} It was also reported that the in-plane and inter-plane fold staggering can occur in the \{110\} fold sectors, whereas only inter-plane staggering occurs in the \{100\} sectors.\textsuperscript{35,36}

![Figure 2.9](image)

**Figure 2.9** Schematic representations of non planar PE crystals in which the fold surfaces of the sectors which are bounded by \{110\} growth faces are taken to be \{312\} (a) Four-sectored pyramidal crystal bounded by \{110\}. The lines drawn within the sectors represent the trace of the inter-section of the surface of the pyramid with a plane normal to the pyramid axis. (b) Six-sectored hollow pyramidal crystal of PE bounded laterally with \{110\} (longer) and \{100\} (shorter) lateral growth faces. The lines drawn within the sectors represent the trace of the intersection of the surface of the pyramid with a plane normal to the pyramid axis.\textsuperscript{35}

Non-planar pyramid crystals can be a morphological consequence of chain folding, which leads to chain staggering due to the bulkiness of the chain folding. Nevertheless, the bulkiness of the chain folding is not only associated with chain staggering contributing to the departure from planarity of the chain folded crystals.
Distortion of the unit cell in each sector can also be attributed to the bulkiness of the chain folding in each constituent sector.\textsuperscript{37, 48, 49} The unit cell of poly(4-methyl penten-1) is tetragonal (a = b ≠ c, where c is parallel to the axis of the chains).\textsuperscript{2, 39} The projection of the chain packing along c axis for a four-sectored crystal is shown in Figure 2.10.\textsuperscript{37} The crystals are bound by \{100\} faces, and the chains in each sector are folded along the \{200\} planes which are parallel to the \{100\} faces. The fold planes are identified as thick lines in Figure 2.10, and referred to as \{200\}_f planes, which are distinguished from the orthogonal set of \{200\}_nf planes (non-fold planes with thin lines in Figure 2.10). In an ideal crystallographic case, the \{200\}_f planes are identical to the \{200\}_nf planes. The distance between the \{200\}_f planes should be the same as the distance between the \{200\}_nf planes. But the experimental measurement shows there is \textasciitilde 1\% difference between the \{200\}_f planes and the \{200\}_nf planes in each sectors.\textsuperscript{37} This disparity in spacing has been attributed to the bulkiness of the chain folding. This phenomena was also observed in six sectored poly(oxymethylene) crystals. The spacing difference between $d_{\{10\}_f}$ and $d_{\{10\}_nf}$ is \textasciitilde 0.3\%. Keller also reported there is a disparity in spacing between the \{110\}_f and \{110\}_nf planes in certain truncated lozenge polyethylene crystals.\textsuperscript{48} These phenomena are attributed to the unit cell distortion which result from the bulkiness of the chain folds. As Bassett reported first, this unit cell distortion can also lead to the departure of planarity in poly (4-methylpentene-1) single crystals.\textsuperscript{50} But this non-planarity from the unit cell distortion is extremely small, and it can not be resolved by an optical microscope. Instead, dark field electron micrographs were used to reveal the non-planar feature.\textsuperscript{50}
Khoury summarized the origins of the non-planar character of the monolayer polymer crystals as follows: the departure from planarity in polymer crystals is attributed to the bulkiness of the chain folds. This bulkiness in the chain folds may result either in regular staggering of the chain folds, or in the slight buckling associated with a distortion of unit cell in the constituent sectors of the crystals. Each consequence of the bulkiness of the chain folds or the combination of the two can lead the non-planarity of the monolayer single crystal.

2.1.3.3 Irregular shaped lamellar crystals

Under suitable crystallization conditions (for example dilute solution at low undercooling), regular shaped monolayer lamellar crystals, which reflect the symmetry of their unit cells, can be formed for some polymers like polyethylene. But in some cases such as polyarylonitrile shown in Figure 2.11, polychloroethylene shown in Figure...
and polyvinylchloride,\textsuperscript{51} these polymer lamellar crystals from solution are not bound laterally by smooth growth faces. Instead, the crystals are rounded in character without crystallographically distinguishable microfaceting. This irregularly shaped crystal (irregular lateral habit) is attributed to configurational irregularities in the polymer chains. These configurational irregularities influence the packing of the molecule stems in the crystals side by side and/or the manner in which the molecules fold.\textsuperscript{1}

![Figure 2.11 Electron micrograph of polyacrylonitrile lamellar crystals.\textsuperscript{24}](image1)

![Figure 2.12 Single crystal of polychlorotrifuoroethylene of a grown from a 0.1\% solution in a low-molecular-weight polychlorotrifuoroethylene oil at 110°C. (a) Electro micrograph; (b) Select-area electron diffraction pattern obtained from the regime outlined in (a).\textsuperscript{30}](image2)
Solvent can also play a key role in the lateral habit of the lamellar crystals. As shown in the Figure 2.13, isotactic polystyrene can grow simple and regular hexagonal crystals in a good solvent, whereas it grows somewhat rounded crystals with a finely serrated periphery in poor solvent.\textsuperscript{52, 53}

![Figure 2.13 Single crystal of isotactic polystyrene grown in different solvent (a) Electron micrograph of a single crystal grown at 190°C from solution in atactic polystyrene;\textsuperscript{52} (b) Electron micrograph of a single crystal grown at 100°C from solution in trimethylbenzene for about 2000 hr.\textsuperscript{1}]

The origin of the irregular lateral growth in polymer folded-chain crystals may thus differ from polymer to polymer. Different factors including polymer chain configuration, polymer chain length, polymer-solvent interaction and solvent viscosity may play a role in forming the irregular lateral habits of single crystals.

2.1.3.4 Multilayered crystal and screw dislocation

In order to grow monolayer single crystals in dilute solution, low undercooling is normally utilized. Nevertheless, multilayered crystals consisting of several superimposed
folded-chain crystals of equal thicknesses are frequently observed along with monolayer crystals. High undercoolings favors the formation of multilayered crystals. The formation of additional chain folded layers on the basal layer in the multilayered crystal usually originates from screw dislocations which are located near the center of the basal layers. The Burger vector of these screw dislocation is parallel to the stems of the folded chains and is equal to the fold period. The overgrowth of layers evolve upon the fold surfaces of the basal layer either as spiraling ramps (growth from a single or several vicinal screw dislocations having the same hand) or as successive “closed” terraces (growth from a pair of vicinal screw dislocations of opposite hand). These patterns of developing additional chain folded layers in polymer crystals through screw dislocations are similar to the crystals of some nonpolymeric materials. Consecutive terraces in multilayered crystals of a given polymer can either be in crystallographic registry on some crystals, or be irregularly or regularly rotated relative to one another in other crystals of the same polymer. In some crystals, splaying between layers is observed, but not in others. Keller and Mitsuhashi illustrated a so-called four-leaf type crystal from solutions of relative low-molecular weight polyethylene in xylene. The electron micrograph is shown in Figure 2.14. Observed with a phase-contrast optical microscope from an edge-on perspective while suspended in liquid, the four-leaf type crystals showed that they consisted of two stacks of overlapping terraces which splay outwards from a common center, which look like two shallow cones in contact at the their apices. This special feature is schematically described in Figure 2.15.
2.1.3.5 Dendritic crystals

At sufficiently high undercoolings, dendritic crystals can form in dilute solution along with the “multilayered” crystals forming at the high undercoolings conditions described above. Khoury summarized some of the key characteristics of the dendritic polyethylene crystal: (1) The periphery of the constituent lamellae in the dendritic crystal are microfaceted; (2) The nucleation of new fold planes at the periphery of the lamellae occurs preferentially at the protruding corners; (3) During the development of the microfaceted basal lamella, screw-dislocation-like defects are generated intermittently. These defects at the reentrant corners act as sources to develop additional chain-folded crystals in a spiral fashion. One example of a dendritic polyethylene crystal is shown in
the Figure 2.16. Khoury drew a sketch to represent the development of a multi-sectored dendritic lamella of polyethylene as shown in Figure 2.17.

Figure 2.16  PE dendritic crystals  (a) Electron micrograph of a portion of a dendritic crystal of PE. Arrows B point to microfaceted periphery of the basal lamella. The formation upon the basal lamella of additional terraces which developed through the agency of screw dislocations can also be seen.  (b) A view at higher magnification of the region outlined in (a). Arrows C and D point to microfaceting at the sides of some of the larger terraces which developed upon the basal lamella.55
2.1.3.6 Features on fold surfaces of folded-chain crystals

The density measurement of the single crystal mats of polyethylene grown from solution\textsuperscript{59-65} showed only 75 – 90% crystallinity. In other words, the crystals contain an appreciable amount of disorder which is corresponds to the presence of the amorphous...
content. It is generally accepted that this amorphous part in single crystals predominantly located in the fold surfaces. Folded-chain single crystals can be described as a sandwich structure with a crystalline core whose density is close to unit cell density and two disordered surface region containing chain folds which have a lower average density than the core. Nevertheless, how chains fold on fold surfaces of the crystals has been a considerable debate and controversy.

In the crystallization kinetic theories of chain-folded crystals, there are two processes underlying the apposition of the successive planes (strips, ribbons) of folded molecules along the sides of the developing lamella. One is the initiation of the strips, which is induced by the formation of a two-dimensional surface nucleus at the periphery of the lamella; and the other is the propagation of the strips along the sides of the lamella.

If a fold length is constant, chain ends are incorporated in the crystals, and the chain ends of the neighboring chains in each stem are coordinately juxtaposed as shown in Figure 2.3, then the fold surface could reach minimum disorder and surface roughness at the fold surface. This is the idealized model of a chain-folded crystal, and the essential characteristics of this model are the smooth fold surface and adjacent reentry of the chain folding. In real chain folded crystals, various possibilities have been invoked to account for the incidence of disorder at fold surfaces of polyethylene crystals, which include: (1) exclusion of the chain ends from crystal lattice leading to cilia dangling from the fold surfaces of a lamella; (2) fluctuation of the fold period about a mean average value; (3) loose loops and (4) non adjacent reentry.
Keller pointed out that the possibility of chain end juxtaposition in a crystal lattice is very low.\textsuperscript{16} Usually there is more than one chain portion capable of folding along to the propagating strip (Figure 2.18a). Some of the chains will do the folding while the others will be left dangling as a cilium (Figure 2.18b). In a more complicated case, one chain has not competed its deposition in the developing strip before a new fresh chain starts to deposit a portion along the strip (Figure 2.18c). If the cilium is long enough, the dangling chain portion can reenter and fold further downfield along the same strip from which it was initially included (Figure 18d). This non adjacent reentry was referred as intra-strip nonadjacent reentry.\textsuperscript{1} Keller and Priest\textsuperscript{71} as well as Banks and Krimm\textsuperscript{72} reported that cilia occur at the fold surface of the solution-grown polyethylene crystals. Keller and Priest\textsuperscript{71} also reported that 90\% of the chain ends occur at fold surfaces of crystals.

Long dangling cilia can reenter the same developing strip through intra-strip nonadjacent reentry as described above, but they can also dangle out of the strip (Figure 2.18e) or fold outwards and initiate a new folding strip (Figure 2.18f), or participate in a strip passing-by (Figure 2.18g).\textsuperscript{59, 70} The reentry of chain folding shown in Figure 2.18 (f, g) was referred as inter-strip non-adjacent reentry.

Lauritzen and Passaglia’s theory predicted the existence of the disorder at the fold surface as shown in Figure 2.18(h, i).\textsuperscript{69} This is from sharp adjacent reentry with fold length fluctuation and loose folds with intra-strip adjacent reentry. But this prediction with irregular folding cannot be reconciled with the hollow pyramid crystal by regular stem staggering. Flory\textsuperscript{73} proposed a random nonadjacent reentry model of the chain
folded crystals as shown in Figure 2.19. Etching experiments\textsuperscript{74-76} indicated that the adjacent reentry folding is predominant. The fluctuation of the folding layer is \( \sim 2 \) nm.

Figure 2.18  Illustration of some different ways in which folding and the incidence of ciliation can occur at the periphery of chain-folded lamellae. \textsuperscript{59}
Wittmann and Lotz\textsuperscript{77} invented a polymer decoration method by depositing vaporized low molecular weight polyethylene on surfaces of crystals to study the chain fold orientation of the crystals. As shown in Figure 2.20a, the vaporized polyethylene (or polypropylene, or poly(vinylidene fluoride)) formed tiny elongated rods (roughly 50-100 nm long and 10 nm wide), and these rods are well aligned along different directions within different sectors of polyethylene single crystal lamellae. Wittmann and Lotz also proved these elongated rods are made of extended chain crystals from vaporized low-molecular-weight polyethylene. This technique has been applied to study the chain folding orientation of other polymer systems.\textsuperscript{78, 79} The key message of this technique is that the chain folding information is enhanced and reflected by the orientation of the crystal orientation of the vaporized material, which is induced by fold surfaces of crystal lamellae. The ordered orientation of the PE crystal rods indicate that chain fold surfaces,
from PE single crystals from solution for example, need to have certain orientational regularity (schematically shown in the Figure 2.20b) to induce the orientation of the decorating low molecular weight PE crystals.

Figure 2.20  PE crystal decorated by vaporized PE (a) Decorated single crystal of PE fraction ($M_w \approx 20,000$, PDI=1.1) grown in dilute solution (c=0.1%) of a mixture of tetrachloroethylene and p-xylene; (b) Schematic representation of the structure of the substrate crystals, of the orientation of the decorating lamellae, and of their relative crystallographic orientations for paraffin (left) and PE (right) substrate crystals.77
2.1.3.7 Lamellar crystals of copolymers

As mentioned above, 90% of polyethylene chain ends are located on the fold surface of the crystal lamellae.\textsuperscript{71} When the polymer chain ends are attached with an amorphous long segments (for a specific case, an atactic polystyrene (PS) chain was coupled to a poly(ethylene oxide) (PEO) chain to form a PEO-\textit{b}-PS diblock copolymer), the big chain ends (non crystallizable atactic polystyrene) must be excluded from the crystal lattice onto the polymer chain fold surface.\textsuperscript{80, 81} Two schematic fold models were proposed by the authors as shown in the Figures 2.21a and 2.21b. It is clear that the fold length in these two models is at a ratio of 1 to 2. The second model (in Figure 2.21b) may have some difficulty to reconcile the equal possibility of PS chains being locating on either folding surface of the PEO crystal lamellae. One half of the folding length and uneven fold surface energy would lead to PEO crystal instability, thus the bilayered model is the most plausible hypothesis.\textsuperscript{82} Nevertheless, the PEO-\textit{b}-PS block copolymer exemplifies chain folding in the crystal lamellae, and single crystals of the block copolymers exhibit regular polygonal lateral habits which are similar in shape to PEO homopolymer single crystals, and the unit cell of the block copolymer is also consistent with that of PEO homopolymer.\textsuperscript{83} It was also reported that a fractionation process may occur during the crystallization in solution where only the portion of copolymers with a certain composition can crystallize from solution at certain crystallization conditions like crystallization temperatures.\textsuperscript{81, 82}

Unlike the case of block copolymers discussed above,\textsuperscript{80, 81} random copolymers do not inherit the crystallization habit of the parent homopolymer. Branched
polyethylene\textsuperscript{84,85} has a larger $b$ and $c$ in the unit cell than linear polyethylene does, and the lateral habit of the crystal is also different as shown in the Figure 2.22.

Figure 2.21  Edge-on cross-sectional models of crystals of PEO-$b$-PS diblock copolymer showing the chain-folded character of PEO crystalline core of the crystals and the occurrence of the amorphous portion of the chain at the surfaces of the crystals.  (a) monolayer crystal,  (b) bilayer crystals.  \textsuperscript{80,81}

Figure 2.22  Crystals of a random ethylene-propylene copolymer  (a) Electron micrograph; (b) ED pattern of crystal A shown in (a) \textsuperscript{84}
2.1.3.8 Lath shaped lamellar crystals

Another lateral habit of the single crystal is that of lath-shaped chain-folded crystals, which are observed in some polymers like isotactic polypropylene\textsuperscript{86-88} and poly-L-glutamate.\textsuperscript{89} As shown in Figure 2.23, each lath-shaped crystal consists of only one fold domain. The chains are folded along the planes parallel to the long lateral axis of the lamella. This phenomena was also observed in a set of liquid crystalline polyesters.\textsuperscript{89-91}

![Figure 2.23 Illustration of a lath-shaped lamella in which the chains are depicted as being folded only long planes parallel to the long axis OY of the lathy.\textsuperscript{1}](image)

2.1.4 Extended chain crystals

In the past decade, a number of crystalline polymers have been found to grow lamellar single crystals from solution and the melt, and some are elongated while others are polygonal.\textsuperscript{2,92-96} Polymer single crystals are true crystals by any definition, they
show three dimensional long range order. Extended chain crystals with an absolute minimum free energy represent the ultimate equilibrium crystal, but the kinetic pathway of crystallization in solutions or melt usually leads to thermodynamically metastable folded-chain crystals (as described above). The extended-chain crystals are normally formed under high pressure or shearing conditions, or by a successive polymerization method. Figure 2.24 shows a polyethylene extended chain crystal grown in the melt under elevated pressure. The chains were proven to be parallel to the normal of the lamellar basal surface, and the thickness of the lamellae is close to the chain length of the extended chain conformation. The melting temperature of the extended-chain crystals is much higher than the regular folded-chain crystals.

![Electron micrograph of extended chain lamella of PE grown isothermally at 4.8 kb pressure and 220°C from melt for 20 hours.](image)

Figure 2.24 Electron micrograph of extended chain lamella of PE grown isothermally at 4.8 kb pressure and 220°C from melt for 20 hours.
2.2 Crystal structure of poly(ethylene oxide)

There are two crystal forms for linear PEO crystals. One is a helical crystal form (monoclinic),\textsuperscript{112,113} and the other is a planar-zigzag crystal form (triclinic).\textsuperscript{114} PEO forms the monoclinic form at normal crystallization conditions, while the planar-zigzag form can only develop under strong deformation.

The unit cell for the PEO crystals is shown in Figure 2.25,\textsuperscript{112} with unit cell parameters, $a = 0.805$ nm, $b = 1.304$ nm, $c = 1.948$ nm, and $\beta = 125.4^\circ$. The space group is assigned to be $P2_1/a-C_{2h}$\textsuperscript{5} based on the systematic absences of the $h0l$ at $h = \text{odd}$ and $0k0$ at $k = \text{odd}$. There are four helical molecules with the $c$-axis nearly perpendicular to the (10$\bar{4}$) plane in one unit cell. The helix has a $3*7/2$ conformation (Figure 2.25a\textsuperscript{112}), and is distorted from a $D_7$ point group (Figure 2.25b\textsuperscript{112}) due to the flexibility of the PEO molecular chain and the intermolecular interactions in the crystals. The helical chain conformation is close to a gauche-trans-trans sequence of bond rotations, with the gauche conformation between the two CH$_2$ groups.

The two-dimensional wide angle x-ray diffraction (WAXD) fiber pattern with c-axis uniaxially oriented PEO and reflection indices is shown in Figure 2.26a.\textsuperscript{112} This fiber x-ray diffraction pattern can be constructed by rotating the reciprocal lattice along the c-axis with parameters of $a^* = 1/(a \sin \beta) = 1.524$ nm$^{-1}$, $b^* = 1/b = 0.767$ nm$^{-1}$, and $c^* = 1/(c \sin \beta) = 0.630$ nm$^{-1}$, and $\beta = 180^\circ - \beta = 54.6^\circ$, as shown in Figure 2.26b. The (120) reflections (the strongest reflections) having $d$-spacings of 0.463 nm and are on the equator. Different sets of reflections almost superimpose in the fiber diffraction pattern:
The (132), (032), (112), and (212) reflections (d-spacing of ~ 0.380 nm) tilt ~ 67° away from meridian (the c-axis); The (204), (004), and (124) reflections (~ 0.390 nm) tilt ~ 36° away from the c-axis. (224); The (024) (~ 0.335 nm) reflections tilt ~ 46.5° away from the c-axis; The (108) and (308) reflections (~ 0.228 nm) tilt ~ 20° away from the c-axis; and the (328) and (128) reflections (~ 0.215 nm) tilt ~ 27.8° away from the c-axis. The tilting angles from the c-axis for different reflections are listed in Table 2.1.

Figure 2.25 (a) Unit cell of monoclinic PEO in the c-axis projection, and R and L stand for right- and left-hand helixes. (b) Molecular model of PEO with the helical symmetry D7, and (c) molecular structure of PEO. The figures give the internal rotation angles.
Figure 2.26  (a) 2D-WAXD fiber pattern of PEO crystals with the usual helical modification. (b) constructed by rotating the reciprocal lattice along the c-axis, and therefore, it is a c-axis (or \([00l]\)-) uniaxial pattern.\textsuperscript{112}

Table 2.1. Angles to c-axis and \(d\)-spacings of deflections in PEO 2-D fiber pattern

<table>
<thead>
<tr>
<th>Reflections</th>
<th>(d)-spacing nm</th>
<th>Angles with the c-axis (°)</th>
</tr>
</thead>
<tbody>
<tr>
<td>120</td>
<td>0.4625</td>
<td>90.0</td>
</tr>
<tr>
<td>032</td>
<td>0.3813</td>
<td>67.0</td>
</tr>
<tr>
<td></td>
<td>0.3786</td>
<td>67.1</td>
</tr>
<tr>
<td>112</td>
<td>0.3857</td>
<td>66.7</td>
</tr>
<tr>
<td></td>
<td>0.3775</td>
<td>67.2</td>
</tr>
<tr>
<td></td>
<td>0.3852</td>
<td>37.7</td>
</tr>
<tr>
<td>004</td>
<td>0.3970</td>
<td>35.4</td>
</tr>
<tr>
<td></td>
<td>0.3900</td>
<td>36.8</td>
</tr>
<tr>
<td></td>
<td>0.3391</td>
<td>47.1</td>
</tr>
<tr>
<td>024</td>
<td>0.3316</td>
<td>45.9</td>
</tr>
<tr>
<td>124</td>
<td>0.2543</td>
<td>58.5</td>
</tr>
<tr>
<td></td>
<td>0.2480</td>
<td>59.4</td>
</tr>
<tr>
<td>044</td>
<td>0.2519</td>
<td>58.8</td>
</tr>
<tr>
<td></td>
<td>0.2488</td>
<td>59.3</td>
</tr>
<tr>
<td></td>
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<td>21.9</td>
</tr>
<tr>
<td></td>
<td>0.2134</td>
<td>28.8</td>
</tr>
<tr>
<td></td>
<td>0.2174</td>
<td>26.8</td>
</tr>
</tbody>
</table>
PEO folded-chain single crystals can be grown in solution or melt.\textsuperscript{78, 83, 115, 116}

Figure 2.27 shows the typical morphology of chain folded single crystals from melt (Figure 27a\textsuperscript{116}) and dilute solution (Figure 2.27b). This lateral habit of low molecular weight PEO single crystals involves two (100) and four (140) growth faces. Depending on the crystallization temperature ($T_c$), the pair of (140) and ($\bar{1}40$) facets are often rounded, giving rise to two (010) prism faces. However, the PEO single crystals from dilute solution are often square shaped, laterally bounded with (120) faces, sometimes the b-axis is truncated with (010) faces or even rounded as shown in Figure 27b.\textsuperscript{83} The electron diffraction (ED) pattern of the lamella single crystal of PEO grown from dilute solution or melt is the same as shown in the Figure 2.28a,\textsuperscript{117} which indicates that the crystals grown from solution or melt have the same crystal structure. From the ED pattern in Figure 2.28a, it can be concluded that the c-axis of the PEO chain is parallel to the crystal lamella normal. Therefore the basal plane of the lamellae or the chain fold surface is the (104$\bar{5}$) plane, or very much close to it as shown in Figure 2.28b.

![Figure 2.27 PEO single crystal morphology](image)

(a) Electron micrograph of crystals grown from thin film melt;\textsuperscript{116} (b) Electron micrograph of crystals grown in dilute solution. H3 is a twin crystal with (100) twin plane, H4 is a untwinned single crystal.\textsuperscript{83}
However, in some PEO single crystals grown in solution, the chains tilt from the fold surface as evidenced by the ED pattern shown in Figure 2.29a. These crystals are called oblique crystals in literature. There is only one pair of the (120) reflections for those ED patterns. The ED pattern of the “oblique” structure was interpreted as the $c$-axis of the PEO chains is inclined to the basal plane of the lamellae, with the tilting being around the (120) plane normal (the [421] direction). The ED patterns as shown in Figures 2.28a and 2.29a could be mutually converted one to the other by a rotation of $25^\circ \sim 28^\circ$. 

Figure 2.28 PEO vertical single crystal (a) Electron diffraction pattern (either solution-grown or melt-grown); (b) Schematic drawing of vertical single crystal.

Figure 2.29 PEO oblique single crystals (a) Typical electron diffraction patterns (b) Schematic drawing of oblique single lamellar crystal.
The vaporized polyethylene decoration method\textsuperscript{77} was applied to study the chain fold direction in PEO single crystals grown from dilute solution as shown in the Figure 2.30.\textsuperscript{78} The results show the chain-folding direction is parallel to the (120) planes for solution-grown PEO single crystals. In the crystallization from dilute solution, the relative growth rates of the different faces are completely different from the case for melt-grown single crystals. The single crystals are laterally bounded by (120) faces, and the fast growth is along the [100] and [010] planes.\textsuperscript{78} PEO-\textit{b}-PS copolymers and other PEO block copolymers can also form chain folded single crystals from dilute solution with the same crystal structure as the PEO homopolymer. The amorphous block is excluded from the PEO crystal lattice after crystallization.\textsuperscript{80, 81, 118, 119}

\begin{figure}[h]
\centering
\includegraphics[width=0.5\textwidth]{image230.png}
\caption{TEM micrograph of PEO single lamellar crystal after PE decoration.\textsuperscript{78}}
\end{figure}

2.3 Nucleation in crystallization and the self-seeding technique

The free energy change for crystallization can be expressed by equation 2.1.

\[ \Delta G = \Delta G_c + \sum A \gamma \]  \hspace{1cm} (2.1)
Where, \( \Delta G_c = \Delta H - T\Delta S \) is the bulk free energy change for crystallization, \( A \) is the surface area, and \( \gamma \) is the specific surface free energy. Since the second term in the equation 2.1 is always positive, the nucleation process can be schematically presented as in Figure 2.31. The maximum of \( \Delta G \) corresponds to the critical nucleus size. Before this point, the nuclei are subcritical nuclei or embryos, and the free energy increases as the size of the embryos increase. Nuclei with a negative \( \Delta G \) are called stable nuclei or small crystals. Since there is a positive free energy change during the nucleation process, a certain degree of undercooling is needed before crystallization occurs. The \( \Delta G_m \) (free energy change at the critical nuclei size) is called the free energy barrier of crystallization.

![Figure 2.31](image)

Figure 2.31 Schematic representation of the change in free energy \( DG \) as a function of size illustrating the nucleation process

The initial process leading from the isotropic state to a growing crystal is called primary nucleation. Primary nucleation is also called homogenous nucleation if there are
no preformed nuclei or foreign surfaces involved. A foreign surface can frequently reduce the nucleus size needed for crystal growth since the creation of the interface between polymer crystal and foreign surface may be less hindered than the creation of the corresponding free polymer crystal surface in the polymer melt or solution. The resulting enhanced nucleation is called heterogeneous nucleation. One special heterogeneous nucleation is called self-nucleation (self-seeding), which describes the nucleation caused by crystals (crystallization seeds) which are chemically identical to the crystallizing materials. This self-nucleation has been applied in polymer crystallization in the melt and solution.  

80, 81, 120-124 Self-nucleation can enhance the crystallization rate and result in similar crystal sizes, especially in dilute solution. To some extent, the self-nucleation process can control the final crystal size by controlling the population of the seeds through the self-seeding temperature (the temperature to melt or dissolve the original crystal).

2.4 Phase transitions in confined environments

Phase transitions such as the glass transition, the liquid crystal transition and crystallization in confined environments have been of great scientific interest and the subject of intensive investigation during the past decades, since the phase transition behavior of the material in confined conditions is quite different from their bulk counter parts. The confinements could be force fields, limited domain size (say submicrometer or smaller), interfacial interactions or some combination of these.
Gong\textsuperscript{125} reported that the packing of colloid particles in a confined geometry can be ordered by applying a strong enough electric field as shown in the Figure 2.32, because the electric field induces the repulsive dipole-dipole interaction, while the colloid particles are randomly arranged without electric field.

![Electric field induces ordered arrangement of colloid particles](image)

Figure 2.32 Electric field induces ordered arrangement of colloid particles (A) Experimental schematic of the colloid particles between slides. A electric field is applied; (B) Different phases achieved by varying the electric field strength. (a) 3.1V/\mu m, (b) 2.0V/\mu m, (c) 0.6V/\mu m, (d) 0.3V/\mu m; (C) Small-angle scattering patterns observed by varying the field strength. (a) 3.1V/\mu m, (b) 2.0V/\mu m, (c) 0.6V/\mu m, (d) 0 V/\mu m\textsuperscript{125}
The orientation of microphase-separated block copolymers (micro-phase separation of block copolymer will be discussed in Subsection 2.6) is affected by the surface properties of substrates as predicted by theoretical calculation and observed through experimentation.\textsuperscript{126,127} Figure 2.33 shows the microphase-separated lamellae morphology of polystyrene-b-poly(methyl methacrylate) (PS-\textit{b}-PMMA). The orientation of the lamellae is affected by the properties of the substrate. In the vicinity of the air-film interface, the PS and PMMA lamellae are perpendicular to the film normal, while in the vicinity of the film-substrate interface which is modified by random PS-co-PMMA polymer brushes, the PS and PMMA lamellae are parallel to the film normal.

![Diagram of lamellar orientation in PS-\textit{b}-PMMA diblock copolymer thin film](image)

Figure 2.33 Lamellar orientation in PS-\textit{b}-PMMA diblock copolymer thin film (a) Illustration of the environment thin film; (b) Schematic view of the lamellar orientation of PS-\textit{b}-PMMA diblock copolymer thin film in the environment shown in (a).\textsuperscript{126,127}
Surface properties and domain size can also affect the liquid crystal phase transition and molecular orientation.\textsuperscript{128,129} Figure 2.34\textsuperscript{129} shows how the surface properties of the mica affect the orientation of 4’-n-octyl-4-cyanobiphenyl (8CB, a small liquid crystalline molecule) in a confined space. 8CB molecules are put into a sub-micrometer space between two mica films. 8CB molecules are parallel to mica surfaces if the mica film surfaces are not modified. When the mica surface is modified by dihexadecyldimethyl ammonium (DHDAA), the 8CB molecules are perpendicular to the mica film surfaces.

![Graph](image)

Figure 2.34  Effect of mica surface property on 8CB molecular orientation  (a) Oscillatory force between clean, untreated mica surface across nematic 8CB at 35°C; (b) Schematic picture of the planarly oriented 8CB between plates; (c) Force between two DHDAA-covered surfaces separated by 8CB in nematic phase (circle) and smectic phase (square); (d) Schematic drawing of the interdigitated structure of 8CB and the adsorbed DHDAA layer on mica surface.\textsuperscript{129}
Grünewald et al demonstrated that the chloride salt of dye confined in between two slides cannot crystallize when the space between the slides is smaller than 100 nm, even though the concentration is three order of magnitude higher than the saturation concentration. The morphology of the polymer crystal can also be affected by the thickness of the film as shown in the Figure 2.35. A main chain nonracemic chiral polyester named PET (R*-9) by the authors was found to be have different crystal morphologies (flat crystal lamellae or double twist helical crystal) whose formation is affected by the thickness of the melt from which the crystals were grown from. The flat crystal was formed in very thin melt films, while helical crystals were formed in thick melt films. These are two examples about the confinement effect on the crystallization behavior of molecules. The crystallization kinetics and crystal orientation in confined environments are also different from the corresponding materials in bulk state.

Figure 2.35  Electron micrographs of helical and flat crystals of a nonracemic chiral polyester crystallized at 145°C for 24 hours from melt. (a) helical crystal morphology from thick film. (b) flat crystal morphology from thin film.79
Some people studied the glass transition of thin films, either free standing or on substrates,\textsuperscript{139-141} and the glass transition of molecules confined in the porous matrix.\textsuperscript{142-145} Different reports seemed to show opposite trends with respect to the glass transition temperature ($T_g$) change as a function of thickness or domain size. A theoretical calculation\textsuperscript{146} claimed that the $T_g$ of thin film increases with decreasing film thickness if there is an attractive interaction between film and the substrate, in other cases, the $T_g$ of the film decreases with decreasing film thickness. This claim was echoed by the experimentalists.\textsuperscript{141, 142}

2.5 Construction of nano-confined environments

Different methods have been used to construct confinement which includes: (1) external force fields; (2) physical boundaries setup to limit domain size, especially on the nanometer size scale; (3) interfacial interaction; or some combination of these.\textsuperscript{79, 125-146} In most cases, the nanometer scale is always involved in the confinement effect on phase transitions of molecules. Therefore, how to build up the nano confined geometries is the key to study the phase transitions of materials in confined environments, and how to precisely control the nano-domain sizes to ensure that every molecule is under an identical confined condition is more difficult. Yet, it is essential to obtain precise and reproducible results. The methods to build up nano-confined environments can be summarized as the following: (1) Using porous or layered inorganic materials like using clays as a matrix with the molecules to be studied filling the layers or pores; (2) Applying
microphase-separation of immiscible block copolymers; (3) manipulating the thickness of thin films down to the nanometer size by spin-casting or other techniques.

2.5.1 Using porous or layered inorganic materials as templates

Porous glass, silicate gels, molecular sieves, zeolite, ceramics or layered clays are often used as matrices to provide nano-confined environments. Figure 2.36 schematically shows how the molecules are filled in the confined space. It is easy to blend the molecules with these inorganic materials to obtain different hybrids of organic/inorganic blends by solution or melt mixing. However, it is difficult to control the uniformity of the pores or layer spaces in the matrices, meanwhile, it is more difficult to ensure that all the testing molecules are located in the pores or layers without leaving the molecules outside. This is however critical in constructing a uniformly confined system to study.

Figure 2.36 Confinement environments with porous or layered inorganic materials as templates (a) Schematic representation of molecules confined in the layered clay; (b) Schematic representation of molecules confined in porous glass.
2.5.2 Microphase separation of immiscible block copolymers

According to the macromolecular nomenclature of the IUPAC Commission, a block copolymer is defined as a polymer with molecules of a linear arrangement of blocks. The monomeric units in one block are constitutionally or configurationally different from the monomer units in its adjacent block.\textsuperscript{149} As synthetic techniques developed, block copolymers with different architectures, such as diblock, triblock and star block copolymers, can be obtained. Some typical block copolymer architectures are schematically shown in the Figure 2.37. Recently, more complicated block copolymers, such as miktoarm (mixed-arm star) block copolymers, have also been designed and synthesized (shown in Figure 2.37).\textsuperscript{150-152}

Among the variety of the block copolymer architectures, diblock copolymers are the simplest one. Even for the simplest diblock copolymers, they can be further classified into different types because the blocks in the copolymer can be in different physical states such as crystalline, amorphous or liquid crystalline phases.

(a) Both blocks are in amorphous phases;
(b) One block or both are in crystalline phases;
(c) One block or both are in liquid crystalline phases.

Since the physical state can be changed by varying temperature, solvent and other conditions, these classifications are not absolute, and they can also changed from one phase to the other depending on the surrounding environmental conditions.
If two distinct blocks in the block copolymers are thermodynamically incompatible, the dissimilar blocks prefer to phase segregate. However, the blocks are linked by covalent bonds, so the phase separation in block copolymers cannot occur on a
macroscopic scale, which is different from the macrophase separation in polymer blends on the scale of micrometers. The phase separation in block copolymers is on the nanometer scale due to the chemical linkage between the blocks, and it is called microphase separation.\textsuperscript{153,154}

Two competing factors control the microphase separation process of block copolymers: enthalpy and entropy. In general, the dissimilar blocks prefer to phase segregate, so the enthalpic process of demixing favors phase separation in order to minimize interfacial area. When the process of the demixing occurs, the junctions between the blocks have to be located in the region of the interface, then the chain configuration will be constrained. Therefore, the entropy of the system will be reduced since the density must be unchanged.\textsuperscript{153,154} This entropic factor favors phase mixing in order to maximize chain conformational entropy. The extent of segregation in the block copolymers is a compromise result of these two competing factors.

There are several physical parameters which determine the phase behavior of AB diblock copolymers: the overall degree of polymerization ($N$), the Flory-Huggins segment interaction parameter ($\chi$), the volume fraction of one component ($f$), the monomer volumes ($v_A$ and $v_B$) and the segment lengths ($b_A$ and $b_B$).\textsuperscript{153} The interaction parameter $\chi$ has the temperature dependence of $\chi = A/T + B$, where $A > 0$ is the enthalpy part, and $B$ the entropy part.\textsuperscript{155} A reduced parameter $\chi N$, which expresses the balance of enthalpy and entropy, is often used to estimate the extent of segregation in block copolymers. The transition from a homogeneous melt to heterogeneous ordered microphase-separated domains is called the order-disorder transition (ODT).
Three regimes have been defined depending on the extent of segregation of the blocks: the weak ($\chi N \approx 10$), intermediate ($\chi N \approx 10-100$), and strong segregation ($\chi N > 100$) regimes. In the weak segregation limit (WSL), the composition profile is approximately sinusoidal at the phase boundary. As $\chi N$ increases, the profile becomes sharper, with a narrower interface between the blocks. In the strong segregation limit (SSL) the domains contain essentially pure components, and the phase behavior in the SSL depends largely on the composition of the copolymer.

A phase diagram constructed based on the experimental observations of a series of polystyrene-$b$-polyisoprene (PS-$b$-PI) diblock copolymers (in SSL regime) is presented in Figure 2.38. Different experimental techniques including transmission electron microscopy (TEM), small angle X-ray scattering (SAXS), and small angle neutron scattering (SANS) have been utilized to identify ordered micro-phase morphologies. As shown in Figure 2.38, there are bcc spheres ($Im \bar{3}m$, BCC), hexagonal cylinders (HEX), double gyroid ($Ia\bar{3}d$, DG), hexagonal perforated layers (HPL), and lamellae (LAM). With the help of certain external forces, like mechanical shearing, and electric fields, the ordered block copolymers can be macroscopically oriented.

Since immiscible diblock copolymers can form diverse ordered morphologies, such as lamellae, double gyroid, cylinder and sphere, on the length scale of a few nanometers, if one block is crystalline (or liquid crystalline), it is possible to confine the crystalline (or liquid crystalline) polymer in the nanometer space due to the microphase separation of the block copolymers.
2.5.3 Methods to produce thin films

There are different techniques to make polymer thin films which include solution casting, spin-casting, Langmuir-Blodgett and self-assembly monolayer methods. Here we briefly summarize these methods.
2.5.3.1 Solution casting method

The simplest method is solution casting. The procedure is to cast the polymer solution on a substrate which normally sits horizontally. This method is very sensitive to vibration of substrate, and the evaporation rate of the solvents. Reproducibility of the film quality is generally poor.

2.5.3.2 Spin-casting method

This method is developed by the microelectronics industry for making resistant protective layer with a micrometer thickness. The solution is put on a substrate which spins at an adjustable speed before or after the solution is dropped on. By varying solution concentration, spinning speed, the thickness of the thin films can reach 20 nm. There are problems of pin holes and instability when the thickness is below 20 nm. Dewetting processes are also an issue during the drying process after spinning.\(^{176-181}\)

2.5.3.3 Langmuir-Blodgett technique

This method is to deposits a single layer or a multilayer of amphiphilic molecules on a substrate from a subphase which is normally water. The first scientific study of a monomolecular layer was carried out by Benjamin Franklin who spread oil onto a pond and observed that one teaspoon of oil could have a calming influence over half an acre of water.\(^{182}\) Modern investigations into monomolecular films began with Anges Pockels.\(^{183}\)
She prepared the first monolayer at the air-water surface. Langmuir further developed the technique used by Pockels to study monomolecular films, and found the area occupied by the molecules like acids was independent on the hydrocarbon chain length. The results infer that only the hydrophilic head groups are merged in the subphase (usually water), and the hydrocarbon is in the air in an extended chain conformation.\(^{184}\) Blodgett first conducted a study on the deposition of multilayers of long chain carboxylic acid onto a solid support.\(^{185-187}\) This is the historical reason why monolayer and multilayers transferred from a subphase-air interface to a substrate are called Langmuir-Blodgett films.

People also utilized this method to deposit block copolymers onto a substrate. However, the polymer or copolymer should have extraordinary geometrical or amphiphilic anisotropy when the LB method was applied to construct the monolayer or multilayer.\(^{188-190}\) In fact, the uniformity of the film cannot be controlled well when a monolayer of PEO-\(b\)-PS was transferred to a silicon substrate from a water-air interface by the LB method.\(^{191}\) Schematic drawings of molecules on the subphase-air, pressure-area isotherm and deposition of a monolayer from the air-water interface to substrate are shown in the Figure 2.39.

2.5.3.4 Self-assembly monolayer technique

This method forms a film which is attached to a substrate by physisorption or covalent bonding. This method is also applied to make polymer brushes, which will be summarized in Section 2.8.1.
2.6 Self-organization, crystallization and vitrification in the amorphous-crystalline diblock copolymers

Since immiscible diblock copolymers can form diverse ordered morphologies, such as lamellae, double gyroid, cylinder and sphere on the length scale of a few
nanometers, and if one block is crystalline, it is possible to confine the crystalline polymer in 1-dimensional (1D), 2-dimensional (2D) or 3-dimensional (3D) geometries by using lamellae, hexagonal cylindrical and spherical microphase separated morphologies. In the current and following subsections, the crystallization behavior of crystalline blocks is summarized.

In order to make the case simpler, we narrow down the chemical structure of the crystalline diblock copolymer by constructing one crystalline block and one amorphous block. This amorphous-crystalline diblock copolymer can be divided into two classes based on the miscibility of the two blocks: (1) The two blocks are miscible; (2) The two blocks are not miscible in the amorphous state.

2.6.1 Miscible amorphous-crystalline diblock copolymers

There are not many miscible amorphous-crystalline polymer system reported in literature. Poly(ethylene oxide)-b- poly(methyl methacrylate) (PEO-b-PMMA) is one of the examples of this case. The existing report focused on the study of crystallization kinetics, and melting point depression. It was found that the crystallization rate of PEO (in PEO-b-PMMA with a molecular weight of 18.6 kg/mol - 22.2 kg/mol) is decreased 3-4 fold compared to the PEO homopolymer, and the melting point of the PEO in copolymer is depressed 2-3 ºC. No morphologies after crystallization of the PEO blocks were reported.
2.6.2 Immiscible amorphous-crystalline diblock copolymers

Three different physical transitions occur in immiscible crystalline-amorphous diblock copolymers: (1) Self organization of the block copolymers which is represented by the ODT transition; (2) Vitrification of the amorphous blocks; and (3) Crystallization of the crystalline block. These three processes may compete or overwrite one another during the formation of the final nano-phase morphology and crystals at different conditions, crystallization temperatures for example. Although these three processes possess different thermodynamic and kinetic origins, we can use three temperature parameters to describe their inter-relationships the order-disorder transition temperature, $T_{ODT}$, the glass transition temperature of the amorphous blocks, $T_{g}^{a}$, and the crystallization temperature of the crystallizable blocks, $T_{c}$ (which is always lower than the melting temperature, $T_{m}$, of the crystalline blocks). The two types of crystallization for the crystallizable blocks can be defined as “unconfined crystallization” and “confined crystallization” based on the relationship between $T_{ODT}$, $T_{g}^{a}$ and $T_{c}$ for the diblock copolymer. The conditions for these two classes of crystallization are summarized in the following two subsections. These conditions have been referred to elsewhere.\cite{193,194}

2.6.2.1 Unconfined crystallization

If crystallization takes places in the block copolymer within the disordered or weak segregation regime, i.e., $T_{ODT}$ is in the vicinity of $T_{c}$, the tendency for microphase separation is relatively weak and the crystallization is the stronger driving force to
determine the final morphology. When $T_g^a$ is much lower than $T_c$, the viscosity of the system is relatively low, and so the amorphous blocks do not restrict the crystallization process, and the crystallization will overwrite the existing phase morphology (no matter whether it is a disordered or ordered morphology). It is thus called unconfined crystallization. It can be further classified into two cases based on whether the crystallization process starts in the disordered phase or the ordered phase, as shown in Figure 2.40. Lamellar morphology (LAM-C) is always formed after crystallization disregarding the initial morphology in the melt for this unconfined crystallization.

![Diagram](image_url)

**Figure 2.40** Schematic of the unconfined crystallization from: (a) disordered and (b) ordered phase.\(^{194}\)
It is “unconfined crystallization from the disordered phase” when the three transition temperatures meet the criteria $T_c > T_{ODT} \gg T_g^a$. At high temperatures, the system is in the disordered melt, and crystallization of crystalline blocks starts taking place in the disordered melt, the lamellar crystalline phase forms during the crystallization process. After the crystallization, further decreasing temperature cannot make order-disordering process to occur because of the fixed morphology of the lamellar crystalline phase, even when the $T_{ODT}$ has been reached. When the temperature reaches $T_g^a$, the amorphous block starts to solidify. The schematic of this process is shown in Figure 2.40a.194 The unconfined crystallization from the disordered phase has been reported by different research groups.195-198

“Unconfined crystallization from the ordered phase” occurs when the transition temperatures meet the $T_{ODT} > T_c \gg T_g^a$ criteria. The system undergoes the order-disordering transition first to form the ordered microphase separated morphology. Crystallization starts within the ordered phase when the temperature decreases to $T_c$. The crystallizable blocks crystallize to form the lamellar crystalline structure, and the original ordered phase morphology can be overwritten by this process since the temperature of the system is still much higher than $T_g^a$. Upon further decreasing the temperature to reach $T_g^a$, the amorphous blocks are vitrified. The schematic of this process is shown in Figure 2.40b. The unconfined crystallization from the ordered structure has also been widely studied.196, 199-204
2.6.2.2 Confined crystallization

On the other hand, if the order-disorder transition and vitrification of amorphous blocks takes place at temperatures higher than the melting point of the crystalline blocks, the crystallization occurs in a confined environment. The crystallization can be completely (hard) confined in the preexisting disordered or ordered morphologies in a crystalline-amorphous diblock copolymer if \( T_g^a \) is higher than \( T_c \).  \cite{123, 140, 144, 193, 205-217}

The amorphous blocks may also construct a soft-confined environment for the crystalline blocks when the tendency for phase segregation is sufficiently strong and/or crystallization kinetics is fast even though the \( T_g^a \) is lower than the \( T_c \).  \cite{141, 200, 206, 218-222}

As shown in Figure 2.41a, when \( T_g^a \) is higher than \( T_c \) and \( T_{ODT} \), the vitrification of amorphous block occurs first, therefore the order-disorder transition cannot take place. The block copolymer is thus forced to stay in the disordered state. However, the crystallizable block may still crystallize because of a fluctuation-induced disordered structure (\( D_{CF} \)).  \cite{156}

The frozen thermal concentration fluctuations have a short-range order and confined crystallization within the disordered morphology is still possible.

If \( T_{ODT} > T_g^a > T_c \), the order-disorder transition occurs first, then the amorphous blocks vitrify before the crystallization starts. The ordered phase morphologies are then fixed due to the vitrification of the amorphous blocks. Therefore, the crystallization of the crystalline block takes place in the ordered nano-confined space. The crystallization process thus takes places in the hard confinement environment constructed from the glassy amorphous blocks. A schematic view of this process can be seen in Figures 2.41b.
If the tendency to microphase separate is very strong during crystallization, the \( T_{ODT} \) is much higher than \( T_c \), it is possible that the initial ordered phase morphologies in the melt state are preserved after crystallization even though the \( T_g^a \) is lower than the \( T_c \). This is called soft-confined crystallization as shown in Figure 2.41c.

\[
\begin{align*}
&\text{(a) } T_g^a > T_c \text{ and } T_{ODT} \\
\text{Confined crystallization from disordered phase.} \\
\text{Disordered melt} &\quad T_g^a \quad \text{Amorphous vitrification} \quad T_c \\
\text{Confined crystallization} &\quad \text{Within the disordered morphology} \\
\text{Ordered morphology} \quad T_{ODT} &\quad \text{Hard confinement}
\end{align*}
\]

\[
\begin{align*}
&\text{(b) } T_{ODT} > T_g^a > T_c \\
\text{Hard Confined crystallization within ordered phase.} \\
\text{Disordered melt} &\quad T_{ODT} \quad \text{Ordered morphology} \quad T_g^a \quad \text{Amorphous vitrification} \quad T_c \\
\text{Hard-confined crystallization} &\quad \text{within the ordered morphology}
\end{align*}
\]

\[
\begin{align*}
&\text{(c) } T_{ODT} >> T_c > T_g^a \\
\text{Soft Confined crystallization within ordered phase.} \\
\text{Disordered melt} &\quad T_{ODT} \quad \text{Ordered morphology} \quad \ldots \quad T_c \quad \text{Soft-confined crystallization} \quad \text{within the ordered morphology} \quad T_g^a \quad \text{Amorphous vitrification}
\end{align*}
\]

Figure 2.41 Schematic of the confined crystallization: (a) from disordered; (b) hard confined and (c) soft confined from ordered phase. 194
2.7 Crystal orientation in the confined space through microphase separation of block copolymers

Microphase separated block copolymers can form various ordered phase structures on the length scale of a few tens of nanometers, and the crystallization in each domain is thus confined to nano-space. Furthermore, the orientation of these microphases of block copolymers can be aligned at the macroscopic level by means of mechanical shearing or other routines, which help to study the orientation of the crystals in these nano-confined spaces.

The structural hierarchies in crystalline-amorphous block copolymers are schematically described in Figure 2.42 at different length scales (from large to small length scale). Usually, the bulk sample is macroscopically isotropic and comprised of randomly oriented grains, which is called a poly-domain structure. The size of the grain is usually on the scale of a few micrometers, which is the first level of the structure hierarchies. In each grain, the microphase separated domains are oriented. These oriented domains in each grain are the second level with a length scale of a few tens of nanometer in size (nano-domains). The crystals (at the third level of the structural hierarchy) form in the nano-domains of the crystalline blocks. Theses crystals form in the confined space, their size is dependent on the confinement condition and crystallization conditions. Each crystal in a nano-domain is made from a crystal unit cell, which is the fourth level of the structural hierarchy with sizes on the length scale of less than 2 nm for general polymer crystals.
Level I
Grains:
1000 \( nm \) to 10000 \( nm \)

Level II
Nano-Domain:
\(~ 50 \( nm \)\)

Level III
Crystal Size:
\(~ 10 \( nm \)\)

Level IV
Crystal Lattice:
\(< 2 \( nm \)\)

\[ \sin \beta = 0.656 \( nm \) \]
\[ b = 1.304 \( nm \) \]

Figure 2.42 The structural hierarchies on different length scales in crystalline-amorphous block copolymers.\textsuperscript{37}
Lamellar morphology is the simplest confinement geometry which has a 1-D confinement effect on crystallization, because lamellae have one small dimension (lamellar surface normal) and two large dimensions. Different crystal orientations were reported for different block copolymers crystallized at different conditions. The crystal $c$-axes were reported to be parallel to, perpendicular to, or inclined to the lamellar surface normal ($\hat{n}$). Solution grown PEO-$b$-PS single crystals have chains parallel to the lamellar normal. Through a detailed investigation and careful experimental design, it was demonstrated that the PEO crystal orientation in one PEO-$b$-PS block copolymer with a lamellar phase morphology changes with crystallization temperature as shown in Figure 2.43.

\[
\begin{align*}
TC &< -50 ^\circ C \\
-50 ^\circ C &\leq TC \leq -10 ^\circ C \\
-5 ^\circ C &\leq TC \leq 30 ^\circ C \\
TC &> 35 ^\circ C
\end{align*}
\]

Figure 2.43  Schematic of the different crystal orientation of PEO blocks in PEO-$b$-PS diblock copolymers within different $T_c$ regions.
If a block copolymer has a cylindrical morphology where the cylinder phase is formed by crystalline blocks, then the crystallization of the crystalline block occurs in the cylinders with a 2D confinement, since the cylinders have only one large dimension (the cylinder axis) and two small dimensions. A PEO-\(b\)-PS block copolymer (\(f_{PEO}=0.26\)) with a cylindrical morphology was carefully designed and synthesized.\(^{194}\) This block copolymer meets the hard confinement criteria \(T_{ODT} > T_g > T_m \). Using a combination of synchrotron 2D SAXS and WAXD techniques, the c-axis orientation of the PEO crystals within the nano-cylinders was found to change from random, to inclined, to perpendicular with respect to the cylinder axis as the \(T_c\) was increased.

The crystal orientation in other confined geometries constructed by the microphase separated block copolymer was also investigated.\(^{219,227,228}\) The crystal orientation was reported to change with crystallization conditions.\(^{227}\)

2.8 Tethered chains and polymer brushes

Tethered polymer chains are defined as a class of polymers which are anchored by one end onto a surface or an interface, while polymer brushes refer to an assembly of polymer chains which are densely tethered by one end to a surface or an interface.\(^{229-232}\) When tethering is sufficiently dense, the polymer chains are crowded and forced to stretch away from the surface or interface to avoid overlapping. These stretched configurations are found under equilibrium conditions in the polymer brushes system, and neither a confining geometry nor an external field is required. There is no clear boundary which distinguishes polymer brushes from tethered chains, and most people
prefer to use polymer brushes to describe the chains attached to substrate or interface with one end no matter whether the chains are stretched or not. These two terms are now interchangable in the literature, so are they in this dissertation.

Polymer brushes can be used to describe many polymer systems in different environments as shown in the Figure 2.44. The interface at which the polymer chains are attached to is not limited to a solid substrate. In fact, it could be any sort of interface including liquid-liquid, liquid-air, melt-melt, or solution-solution interfaces.

Figure 2.44 Schematic representation of examples of polymer systems comprising polymer brushes.
Since one chain end is attached to the interface, and the chain conformation can be stretched due to the high tethering density. This is different from polymers with two free chain ends, therefore the tethered polymer chain systems have been drawing extensive scientific interest. The first theoretical study was by Alexander$^{233}$ and de Gennes$^{234}$ in the late 1970s and early 1980s. Additionally, the properties of the surface or interface modified by the polymer brushes have also significantly changed, which leads to the broad application of polymer brushes in different areas, including adhesion, lubrication, colloidal dispersion, and environmentally sensitive controllers (chemical gate)$^{235-246}$

2.8.1 Traditional approaches to construct polymer brushes

Different approaches have been reported to fabricate polymer brushes, each of which has specific advantages and potential problems. There is not a single approach that stands out as the best compared to the others.

Polymer chains can be attached to the surface or interface through chemical bonding or physical absorption (physicosorption). In physicosorption, the polymer chain ends or one block in the block copolymer absorbs onto a suitable substrate through physical interactions. Long chain aliphatic acid molecules have carboxylic acid end groups, which can absorb to hydrophilic substrates, while the hydrophobic aliphatic chains are repelled from the hydrophilic substrate. Different blocks in amphiphilic block copolymers such as polystyrene-b-poly(methacrylic acid) (PS-PMA) have different preferential absorption on to substrates depending on the properties of the substrates. PS
blocks prefer to absorb onto hydrophobic substrates, while PMA blocks favor hydrophilic substrates.

On the other hand, covalent attachment is enabled through chemical bonding between the polymer chain and substrate. The chemical bond attachment can be accomplished by either “grafting to” or “grafting from” approaches. In a “grafting to” approach, preformed end-functionalized polymer molecules react with an appropriate substrate to form polymer brushes. The “grafting from” approach can be accomplished by generating immobilized initiators on the substrate followed by polymerization.

Compared to the polymer brushes through other approaches, polymer brushes fabricated by the “grafting from” approach are more attractive due to the high density of initiators on the surface and a well-defined initiation mechanism. Progress in polymer synthetic techniques also makes it possible to produce polymer chains with controllable lengths. Nevertheless, the molecular weight and distribution of the polymer brushes are still issues even with the “graft-from” approach, since the monomer diffusion plays an important role during the chain propagation process.

2.8.2 Polymer brushes constructed by single crystal engineering of block copolymers

A single crystal of an amorphous-crystalline block copolymer can be grown from dilute solution. Solid lamellar crystals are formed due to the crystallization of crystalline blocks, simultaneously, amorphous blocks are planted on the lamellar crystal surface because they are excluded from the crystal lattice. Yet they are chemically bond to the crystalline blocks. Therefore, the amorphous blocks become a type of polymer
brush. These polymer brushes were used by DeMarzio to calculate the thickness of the amorphous layer and crystal layer.\textsuperscript{259}

2.8.3 Theoretical prediction and experimental study on polymer brushes

Tethering density (\( \sigma \)) is defined as the number of tethering points in a unit area, and it is an important parameter to describe polymer brushes. Statistically speaking, \( \sigma \) represents how close the tethered chains are from one another. However, it can not tell when the chains need to adjust their conformation due solely to dense tethering, because the chain conformation is dependent on the molecular weight and surrounding environmental conditions such as temperature, solvent quality and other factors. Thus reduced tethering density (\( \tilde{\sigma} \)) is more generally used. Reduced tethering density is defined as \( \tilde{\sigma} = \frac{\sigma}{\pi R_g^2} \), where \( R_g \) is the radius gyration of an unperturbed polymer chain under a specific set of conditions. Therefore, the physical meaning of \( \tilde{\sigma} \) is the number of tethered chains in the area occupied by one unperturbed polymer chain under a specific set of conditions. It is thus molecular weight (MW) and solvent independent when \( \tilde{\sigma} \) is used to describe the crowdedness of the polymer brushes. Based on \( \tilde{\sigma} \), three regimes are used to describe the polymer brushes the non interaction regime, the cross over regime, and the highly stretched regime.

When \( \tilde{\sigma} \) is very small, the tethered polymer chains are away from each other, and cannot feel the existence of the other chains (non interaction regime). As \( \tilde{\sigma} \) increases and reaches to some value, tethered polymer chains start to touch their neighbors. When \( \tilde{\sigma} \)
further increases, the chains starts to be overcrowded, and the repulsive interaction among tethered polymer chains is so strong that they have to stretch away from the surface to release the interaction. The stretched conformation of tethered polymer chains could be formed when $\tilde{\sigma}$ reaches to some critical value (highly stretched regime).

2.8.3.1 Non-interaction regime

In the non-interacting regime, the tethered chain does not interact with its neighbors. The intra-chain interaction and the interaction among tethered chains and the surface (interface) are the factors affecting the conformation of the tethered chains, which is shown in Figure 2.45: (a) A coil conformation (mushroom) in a good solvent with a non-attractive surface-polymer interaction; (b) A pancake conformation in a good solvent with strong attractive surface-polymer interactions and (c) A globule conformation in a poor solvent with non-attractive surface-polymer interactions.

The renormalization group theory was used to calculate the chain conformation by treating each chain as an isolated chain without interchain interaction. Calculated results indicated that for a system with strong attractive polymer-surface interaction, the segmental concentration was high near the surface with a quick decay towards the tethered chain-solvent interface. The chain then adopted a pancake conformation. For the case of a strongly repulsive polymer-surface interface, the segmental concentration at the interface was zero despite the physical connection of the chain to the substrate and the segmental concentration maximum was located at a distance of $R_s$ from the solid substrate, so the chain fits a top-sit random coil model. For the cases with polymer-
surface interaction between the two extreme cases described above, the segmental concentration profiles were between the two extreme forms. This renormalization group theory is applicable to the experimental results when $\bar{\sigma} < 5$.

Figure 2.45 Possible conformation of a single tethered polymer chain at low reduced tethering density: (a) coil (good solvent, no-attractive surface-polymer interaction), (b) pancake (good solvent, strong attractive surface-polymer interaction), (c) globule (bad solvent, no-attractive surface-polymer interaction)
2.8.3.2 Highly stretched regime

The highly stretched regime was described by scaling law\textsuperscript{233, 234, 262, 263} and self-consistent field (SCF) theories.\textsuperscript{229, 264-273} The first theoretical analysis of tethered polymer chains in the highly stretched brush regime was reported by Alexander,\textsuperscript{233} which was further developed by de Gennes’ publication about the scaling theory of polymer adsorption.\textsuperscript{274} The scaling theory of tethered polymer chains was then further elaborated by de Gennes\textsuperscript{234} and Cantor.\textsuperscript{275}

The Alexander model considers polymer chains of uniform lengths with polar heads. The dominant attraction between the flat surface and the polymer chains is due to the polar head, if the substrate surface does not adsorb other parts of the polymer chain except for the polar head. This polar head adsorption is representative of chemically tethered polymer chains if the polar head’s size is negligible and the head-substrate attraction is very strong.

The parameters used to described tethered chains are: (a) The number of statistical segments in the tethered chain is $N$; (b) the size of each segment is $a$; (c) the average distance between the two nearest tethering points is $d$ (therefore the average covering area $S = d^2$, and the tethering density $\sigma = S^{-1} = d^{-2}$); (d) the thickness of the polymer chain layer (with or without solvent) is $L$.

In the Alexander model, all the free chain ends are assumed to be located at the polymer-solvent interface. In the same plane, all polymer brush chains have the same end-to-end distance. The segment concentration inside the polymer chains layer is assumed uniform as $\varphi = Na^3 / d^2 L = Na^3 \sigma L$. 

75
The overall free energy of one tethered polymer chain can be expressed as:

\[ f = f_{\text{interface}} + f_{\text{interpolymer}} + f_{\text{el}} \]  
(2.2)

Since the interaction between the segment and substrate surface is negligible as assumed in the model, the first term on the right hand side (r.h.s.) of equation 2.2 can be ignored.

\[ f_{\text{interpolymer}} = 0 \]  
(2.3)

The second term on the right hand side of equation 2.2 can be expressed according to the “Flory approximation” (\( \nu \) is the excluded volume parameter):

\[ f_{\text{interpolymer}} \sim kT\nu N \phi \frac{kT\nu N^2 a^3 \sigma}{L} \]  
(2.4)

The third term on the right hand side of equation 2.2 is the entropy penalty due to the deviation of the chain conformation by its ideal random-walk. According to the scaling theory, this term can be expressed as:

\[ f_{\text{el}} = \frac{3}{2} kT \left( \frac{L^2}{R_o^2} + \frac{R_o^2}{L^2} \right) \]  
(2.5)

Where \( R_o \) is the radius of the unperturbed ideal random coil. In the case of the highly stretched conformation, \( L >> R_o \), the second term on the right hand side of equation 2.5 can also be ignored.

All numerical coefficients are treated as 1 to simplify the further scaling analysis. Thus the overall free energy of single tethered polymer chain should be:

\[ f \sim kT \left( \frac{\nu N^2 a^3 \sigma}{L} + \frac{L^2}{R_o^2} \right) \]  
(2.6)
The most favorable layer thickness (equilibrium thickness $L_{eq}$) can be obtained by minimizing $f$ with respect to $L$ and the result for good solvents is:

$$L_{eq} \sim N^{1/3}a^{5/3}\sigma^{1/3}$$

(2.7)

From the calculation, the equilibrium thickness for the highly stretched polymer brushes is linearly dependent on the degree of polymerization ($N$) as shown in equation 2.7. The scaling relation between the chain dimension ($L$) and $N$ is stronger than that of the polymer chain random coil in a good solvent ($R_g \sim N^{0.6}$). Another important relation shown in equation 2.7 is the power law between $L_{eq}$ and $\sigma$ ($L_{eq} \sim \sigma^{1/3}$). It has been thought to be a unique property of polymer brushes and has been verified by experimental observations.$^{276,277}$

The tethered polymer chains in $\theta$ and poor solvents show the same $L$ dependence on $N$. In the bulk state of tethered polymer chains, however, the layer thickness can be calculated as $L \sim N^{2/3}$ based on the constant density concept.

Since the highly stretched chain has a strongly anisotropic chain conformation, the $L$ has to be much larger than the unperturbed chain size characterized by $R_g$. Furthermore, the average distance ($d$) between the neighboring tethering points has to be much smaller than $R_g$, which means that $(\bar{\sigma} = \pi R_g^2 / d^2)$ is much larger than 1. This is a pre-requisite for the application of the scaling theory. However the theory cannot predict where the highly stretched regime starts. Kent$^{261}$ showed the observed results did not fit the prediction of the scaling theory even when $\bar{\sigma}$ was as high as 12.

The size dependence of tethered polymer chains and of the corresponding random coil size is listed in Table 2.2. The difference between them is clearly shown in the table.
Table 2.2  Polymer sizes versus degrees of polymerization under various conditions

<table>
<thead>
<tr>
<th>Conditions</th>
<th>Tethered polymer chain (highly stretched regime)</th>
<th>Free polymer chain</th>
</tr>
</thead>
<tbody>
<tr>
<td>In good solvent</td>
<td>$L \sim N$</td>
<td>$R_g \sim N^{3/5}$</td>
</tr>
<tr>
<td>In $\theta$ solvent</td>
<td>$L \sim N$</td>
<td>$R_g \sim N^{1/2}$</td>
</tr>
<tr>
<td>In poor solvent</td>
<td>$L \sim N$</td>
<td>$R_g \sim N^{1/3}$</td>
</tr>
<tr>
<td>In the bulk state</td>
<td>$R_g \sim N^{2/3}$</td>
<td>$R_g \sim N^{1/2}$</td>
</tr>
</tbody>
</table>

The scaling theory assumes the tethered chains have the same end-to-end distance, and the free chain ends are located in the same plane. Analytical SCF theories (aSCF) were introduced to allow the chain ends to distribute themselves throughout the brush layer in the late 1980s. So the aSCF model was closer to reality compared to the scaling theory by releasing the assumption that the all free ends are in the same plane. The aSCF theories assume that the tethering density is high enough to be laterally homogeneous (mean-field treatment) and assumes the segment density and free chain end density are solely a function of the distance away from the tethering surface. In order to simplify the calculation, all the polymer chains are required to possess the most probable conformation, which implies that there are no back-folding chains.

The aSCF model for highly stretched brushes has its own problems since this model has a serious simplification that all the chains are in the most probable conformations. Fluctuations around this conformation are not taken in account, therefore the chains are not allowed to back-fold. In reality, there is no special reason to forbid back-folding conformations. The numerical SCF theory (nSCF) was developed. The nSCF model allows a few chains to fluctuate from their most probable conformations.
to allow back-folding while a majority of the chains still possess the most probable conformation. The chain conformation in scaling theory, aSCF theory and nSCF theory is shown in Figure 2.46.

Figure 2.46  Polymer chain conformation in different theoretical calculation models. (a) scaling theory. (b) aSCF and (c) nSCF.
In aSCF theory, the segment density is at the maximum at the tethering surface (interface) because all the tethered chains start from there. Then the segment density starts to decrease when the distance away from the tethering surface reaches a certain value, because the short chains reach their maximum size (length) and stop contributing segmental density. Nevertheless, the brush height calculated based on free energy from aSCF has the same expression as the one based on scaling theory, $L_{eq} \sim N\sigma^{1/3}$. But the segmental density profile vs. the distance away from the tethering density is quite different from scaling theory as shown in Figure 2.47. The nSCF also gives the same expression between $L$, $N$ and $\sigma$, $L_{eq} \sim N\sigma^{1/3}$, however, the segmental density profile is different from scaling theory and aSCF theory. The maximum of the segmental density is no longer located at the tethering surface due to the back-folding.

Figure 2.47 Predicted segment density distribution of a non-adsorbing tethered polymer chain in (a) box model of Alexander/de Gennes; (b) aSCF model; and (c) nSCF model. All the curves are drawn schematically.
2.8.3.3 Intermediate tethering density regime (crossover regime)

The intermediate regime is located where there is some interchain interaction, but it is not strong enough to cause the stretched chain conformation. Theories concerning the intermediate regime are relatively few and less successful. The scaling theory and the SCF theories were used to describe the intermediate regime, but they are not as successful as they are in the highly stretched regime. In the 1990s, single chain mean field theory (SCMF), was proposed by Szleifer and Carignano to describe this regime. In the SCMF theory, the interaction of the “central chain” with the surrounding polymer and solvent molecules is taken into account with a mean-field approximation. In the SCF model, interactions between segments are treated by a mean-field approach, and inter-chain segment-segment and intra-chain segment-segment interaction are not differentiated, while they are treated differently in the SCMF model. The single chains are generated with their intra-molecular interaction and the boundary conditions. The inter-chain interactions are treated as the boundary condition. This difference between these two models leads to a significant difference in the predictions of chain conformation and interaction. The thickness of the tethered polymer layer \( h \) predicted by the SCMF theory was compared with experimental observation. The data are shown in Figure 2.48. One broad transition was observed, which is called the “mushroom to brush transition” by the authors. The relationship between the scaled thickness of the tethered chains by the \( R_g \) of unperturbed chain \( (h/R_g) \) and \( \bar{\sigma} \) \( (\sigma^* \text{ was used instead of } \bar{\sigma} \text{ by Kent}) \) can be expressed as:

\[
\frac{h}{R_g} \sim \bar{\sigma}^{1/4} \quad (2.8)
\]
Figure 2.48 Mushroom to brush transition represented by the scaled height of the layer as a function of the reduced surface coverage, $\sigma^*$, in a log-log representation. The transition occurs in a wide range of reduced surface coverage around $\sim 1$. The exponent $1/4$ is obtained instead of the $1/3$ which is predicted by the scaling theories and SCF theories for the highly stretched brushes. It is still interesting to find that the linear fit starts at $\tilde{\sigma} = 2-3$ as shown in Figure 2.48, which cannot be the onset of the highly stretched regime, therefore this transition should still be within the crossover regime. The tethered chain thickness is less dependent on the tethering density and possesses a different scaling relation. In a good solvent, the relation between $R_g$ of unperturbed chain and $N$ is $R_g \sim N^{3/5}$, so the thickness of tethered chain can be expressed by equation 2.9 based on equation 2.8.

$$h \sim R_g \tilde{\sigma}^{1/4} = R_g (\sigma R_g^2)^{-1/4} = \sigma^{1/4} R_g^{3/2} \sim \sigma^{1/4} N^{9/10} \quad (2.9)$$
The exponent 9/10 is slightly smaller than the value 1 predicted by the scaling theory and SCF theories, which implies that the SCMF model is less dependent on molecular weight and that the polymer chains would have a less stretched conformation. The interchain interactions are also calculated by the SCMF theory and compared with the experimental results. In the regime of $\tilde{\sigma}<8$, the prediction agrees with the experimental data well. When $\tilde{\sigma}$ is greater than 8, an increasing difference between the prediction by SCMF and the experimental data is found. It was concluded that SCMF can only be applied to the crossover regime ($1<\tilde{\sigma}<8$).

The SCMF theory can describe the tethered polymer chains in a broad reduced tethering density region ($1<\tilde{\sigma}<8$) well, while Kent showed that the experimental data could not fit into the predicted results by the scaling law and SCF theories even at $\tilde{\sigma}$ up to 12. This suggests that the boundary between crossover (intermediate) regime and highly stretched brushes regime should be located at a $\tilde{\sigma}$ value greater than 12.

As a summary of the theories concerning tethered homo-polymer chains, three regimes can be identified the non-interacting, the crossover, and the highly stretched brush regime with increasing reduced tethering density as shown in Figure 2.49. Two boundaries, the onset of chain overcrowding and the onset of highly stretched brushes, are expected. These onsets must be verified experimentally. So far no experimental results clearly show these two boundaries. One of the objectives of this dissertation is to study the onsets of tethered chain overcrowding by direct experimental observation.
Figure 2.49. Schematic representation of three regimes of the tethered polymer chains.\textsuperscript{296}
3.1 Synthesis and characterization of PEO-\textit{b}-PS diblock copolymers

Some PEO-\textit{b}-PS diblock copolymers were synthesized in Professor R.P. Quirk’s laboratory \textit{via} a sequential anionic polymerization. The detailed procedure can be found in the literature.\textsuperscript{287} sec-BuLi was the initiator for the polymerization of styrene in benzene at room temperature. After 24 hours of polymerization, an aliquot of poly(styryl) lithium (PS precursor) was sampled from the reactor and terminated with degassed methanol. The living poly(styryl) lithium remaining in the reactor was end-capped with excess ethylene oxide for copolymerization. The product was precipitated into hexane. The PEO homopolymer was removed from the crude polymer through liquid column chromatography with microcrystalline cellulose and methanol as eluent solvent.

The molecular weight of the PS precursor was characterized by size exclusion chromatography (SEC) calibrated with polystyrene standards. The number average molecular weight ($M_n$) of PEO blocks was determined by proton nuclear magnetic resonance ($^1$H-NMR), and the polydispersity of the final diblock copolymer was also
determined by SEC using universal calibration. Some block copolymers (EOS4 and EOS5 in Table 3.1) and PEO homopolymer were purchased from Polymer Source Inc., and the samples were used as received in this research. All molecular characterization data for the PEO-\textit{b}-PS diblock copolymers used in this study are listed in Table 3.1.

<table>
<thead>
<tr>
<th>Sample names</th>
<th>(M_n) (×10³ g/mol)</th>
<th>(M_{n,\text{PEO}}) (×10³ g/mol)</th>
<th>(M_{n,\text{PS}}) (×10³ g/mol)</th>
<th>(M_w/M_n)</th>
<th>(f_{\text{PEO}}^*)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Homo-PEO</td>
<td>56.0</td>
<td>56.0</td>
<td>0</td>
<td>1.03</td>
<td>1</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS1)</td>
<td>28.0</td>
<td>11.0</td>
<td>17.0</td>
<td>1.07</td>
<td>0.35</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS2)</td>
<td>17.9</td>
<td>8.7</td>
<td>9.2</td>
<td>1.06</td>
<td>0.45</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS3)</td>
<td>15.6</td>
<td>11.0</td>
<td>4.6</td>
<td>1.07</td>
<td>0.67</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS4)</td>
<td>89.6</td>
<td>31.0</td>
<td>58.6</td>
<td>1.03</td>
<td>0.33</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS5)</td>
<td>70.6</td>
<td>67.0</td>
<td>3.6</td>
<td>1.07</td>
<td>0.90</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS6)</td>
<td>20.0</td>
<td>17.0</td>
<td>3.0</td>
<td>1.04</td>
<td>0.83</td>
</tr>
<tr>
<td>PEO-\textit{b}-PS (EOS7)</td>
<td>47.8</td>
<td>40.1</td>
<td>7.7</td>
<td>1.05</td>
<td>0.82</td>
</tr>
</tbody>
</table>

* Volume fraction of PEO assuming PEO has 100% crystallinity.
3.2 Single crystal growth of polymers in dilute solution

Single crystals of PEO-\textit{b}-PS block copolymers were grown in dilute solution with a concentration of 0.01 wt\% in a mixed solvent of octane and chlorobenzene with a 1.1:1 weight ratio. The polymer samples were put into the solvent and heated above the dissolution temperature ($T_{\text{dis}}$) in a temperature-controlled oil bath. The self-seeding technique was utilized for crystal growth. The self-seeding technique is described in the following paragraph.

The polymer solution test tube was put in an oil bath with a preset temperature, $T_d$, and held for 10 min to dissolve the polymer completely. Then, the solution was switched to another oil bath at 25°C for a fast crystallization of the polymer. When the crystallization was complete (normally overnight), the test tube was then moved to another oil bath with a preset seeding temperature ($T_s$), which was normally 0.5 °C lower than the $T_{\text{dis}}$. It was kept there for 15 min (note: the self seeding process can also be carried out by slowly heating the test tube to the $T_s$ at 0.2 °C/min, for example, and then held at $T_s$ for a certain time period). Then, the self-seeded sample was quickly cooled to a preset crystallization temperature ($T_c$) in another isothermal oil bath for single crystal growth. The self-seeding process for crystallization in solution is schematically shown in the Figure 3.1.

The self-seeding temperature and time could be adjusted to control the size of the final crystal through the seed population. In this case, the self-seeding temperature is the dominating factor.
3.3 Crystal growth of homo-PEO nucleated by PEO-\textit{b}-PS copolymer single crystals

In order to study the crystallization of PEO homopolymer with single crystals of PEO-\textit{b}-PS diblock copolymers as crystallization seeds, a homo-PEO/amyl acetate solution (0.01 wt\%) was pre-prepared by dissolving the PEO fraction in amyl acetate at 65 °C for 10 min and cooled to a preset $T_c = 30$ °C for 10 min to allow the solution to reach thermal equilibrium. This $T_c$ (30 °C in the current study) was chosen to be high enough so that crystallization of the homo-PEO without self-seeding was prevented within this period of time (the period could be as long as two hours at 30 °C).
solution was controlled to allow the crystallization to only take place after the copolymer seeds were added. Drops of the solution containing the PEO-b-PS single crystals were added into homo-PEO/amyl acetate dilute solution after 10 min. The homo-PEO single crystals could then grow on the (120) growth fronts of the PEO-b-PS single crystals.

3.4 Alternating crystallization of PEO-b-PS and PEO homopolymer

The alternate crystallizations of PEO-b-PS and homo-PEO were carried out in amyl acetate dilute solution. It was necessary to know both the growth rates of the PEO-b-PS (with $M_n^{PS} = 4.6k$ g/mol) and homo-PEO ($M_n^{PEO} = 56k$ g/mol) at the given $T_c$ and concentration. We also used other homo-PEO fractions with different $M_n^{PEO}$ values ranging from 10k to 50k g/mol. The results were identical. The detailed procedure was the following: the PEO single crystals were first grown in amyl acetate at $T_c = 30 \, ^\circ$C with the self-seeding technique. Then, a quantitative amount of the PEO single crystals suspended in amyl acetate solution was transferred to a pre-cooled PEO-b-PS/amyl acetate dilute solution for PEO-b-PS crystal growth on the (120) growth fronts of the homo-PEO single crystals at the same $T_c$. After the growth of PEO-b-PS was finished, the crystals were then transferred to a pre-controlled homo-PEO/amyl acetate dilute solution, and the homo-PEO further grew at the (120) growth fronts of the pre-existing crystals at $T_c = 30 \, ^\circ$C. This sequence could be repeated to achieve the alternating PEO/PEO-b-PS crystals.
3.5 Preparation of single crystal mats

In order to prepare single crystal mats, the single crystals were grown in large test tubes. The procedure to grow the single crystals was identical to that described above. After crystallization, the solution was filtered and rinsed by the same solvent for single crystal growth several times. Then, the single crystals were rinsed with hexane before they were collected, so that the single crystals can be dried easily. The collected single crystal mats were dried at room temperature under reduced pressure.

3.6 Differential scanning calorimetry

Differential Scanning Calorimetry (DSC, TA-2000 system) experiments were carried out to study melting behavior of the PEO block in the PEO-\textit{b}-PS single crystal mats. In addition, the glass transition temperature ($T_g$) of the PS block in PEO-\textit{b}-PS single crystal mats was found. The DSC was calibrated with \textit{p}-nitrotoluene, naphthalene, and indium standards. The heating and cooling rates were 10 °C/min. The endothermic peak temperature was taken as the melting temperature ($T_m$). For PEO fractions with $M_n \geq 10^4$ g/mol, the weight percentage crystallinity was calculated using an equilibrium heat of fusion of 8.66 kJ/mol.\textsuperscript{288} For those with $M_n < 10^4$ g/mol, the equilibrium heat of fusion is 7.89 kJ/mol.\textsuperscript{289}
3.7 Transmission electron micrography

Transmission Electron Microscopy (TEM) experiments were carried out on a JEOL 1200 EX II at an accelerating voltage of 120 kV. Calibration of the electron diffraction (ED) spacing was done using the d-spacings of thallium chloride (TlCl) with their high order diffractions. Selected area electron diffraction (SAED) patterns of the samples were obtained using the TEM in order to determine crystal orientation. For the bright field (BF) imaging, the samples were shadowed by Pt/C at a shadowing angle of 30°.

The nano-patterned single crystals from alternating crystallization of PEO-\(b\)-PS copolymer and homo-PEO were stained by the vapor of a 3% RuO\(_4\)-water solution for 30 min at different humidity before TEM observation. Although both PEO and PS can be stained by RuO\(_4\), RuO\(_4\) selectively stained PEO or PS based on the different environmental conditions.

In order to study chain-folding direction of the lamellar crystals, a polyethylene (PE) decoration method was utilized. A linear PE sample with a \(M_n^{PE}\) of 12k g/mol and polydispersity of 1.2 was provided by the Phillips Petroleum Company. During the decoration, an optimal 10 cm distance between the sample and the basket was chosen in the vacuum evaporator. The PE was heated and degraded to reduce the molecular weight to \(~\)1k g/mol. Once this was achieved, the PE evaporated and deposited on the sample surfaces.
3.8 Atomic force microscopy

An atomic force microscopy study (AFM, Digital Instrument Nanoscope IIIA) was used to examine the single crystal morphology and lamellar thickness. Silicon wafers with a cleaved (100) plane were used as substrates for single crystals. The force used by the cantilever was not high enough to damage to the sample, yet able to obtain accurate surface features. The scanning rate was 1 Hz for the scan size of 10 μm, and the resolution was 512 × 512. The operation and resonance frequencies were ~ 290 kHz. The scanner was calibrated with the standard grid in both lateral size and height. With a heating stage coupled on the AFM, the morphological change of the single crystal lamella was captured in situ during the melting process of the crystals.
CHAPTER IV

CHARACTERIZATION OF SINGLE CRYSTALS AND SINGLE CRYSTAL MATS

Through the self-seeding technique, the single crystals grown in dilute solution can be well-controlled with high reproducibility. The detailed procedures are described in Chapter III. The crystal size can be practically controlled by the self-seeding temperature \( T_s \) and self-seeding time \( t_s \), which controls the population of the seeds in the solution, nevertheless, \( T_s \) is a dominant factor from the thermodynamic perspective and in real practice. Since the size of seeds are normally very small compared to the size of the final crystals if a suitable self-seeding procedures are followed, the single crystal size can be very uniform after crystallization, because the crystals start to grow simultaneously from the seeds. Normally similar crystals are obtained by applying the same procedures, so it is easy to produce similar crystals at different times when needed. The samples used in this chapter are homo-PEO, EOS1, EOS2, EOS3, EOS4, and EOS5 as listed in Table 3.1. The sectorization, thickness, and ED pattern of the single crystals were studied by AFM and TEM. Some single crystal mats were collected, and their
melting points, glass transition temperatures were characterized by DSC. Most importantly, the three-layer, sandwiched structure of block copolymer single crystals was proven by experimental observations. The thickness of the PEO layer and PS layers in each single crystal was calculated. The morphologies of the single crystals were also recorded in situ by AFM during the melting process.

4.1 Morphology and electron diffraction of single crystals

Figure 4.1 shows the images of diblock copolymer single crystals and PEO homopolymer single crystals with bright field (BF) TEM. The samples were shadowed by Pt/C to enhance the contrast. ED patterns are made with an electron beam parallel to the lamellar crystal surface normal (\(\hat{n}\)). The single crystal was grown at 31 °C. The enlarged micrograph and ED pattern of the EOS2 single crystal are shown in Figure 4.2, and the indices of the diffraction spots are assigned in this figure. The two pairs of strongest diffraction spots are attributed to the (120) planes. The lifetime of the PEO homo-polymer single crystal under the electron beam (120 kV accelerating voltage in the current study) is very short, and the crystal structure is destroyed within several seconds, thus, ED spots for PEO single crystals diminish shortly after the crystal is exposed to the electron beam even at a very low dosage. For the PEO-\(b\)-PS block copolymer single crystal, the PEO crystal layer is sandwiched by PS layers. The PEO crystal layer is
Figure 4.1 TEM BF images of the single crystals (scale bar for 2 μm). The single crystals of block copolymers are grown at 31 °C in mixed solvent, while the homo-PEO single crystal is grown at 35 °C amyl acetate. (a) EOS1; (b) EOS2; (c) EOS3; (d) homo-PEO.

protected by the PS layer to some extent, and the lifetime of block copolymer single crystal under electron beam, EOS2 for example, is relatively longer. Thus, the weak diffraction spots like the (110) and high order diffraction like the (240), (040), (200) can
be recorded by a longer exposure time. Only (hk0) diffractions ([00l] zone) were observed when the electron beam is parallel to \( \hat{n} \), indicating that the PEO stems are parallel to \( \hat{n} \). The ED pattern of the homo-PEO single crystal is identical to those of the PEO-\( b \)-PS diblock copolymer single crystals. Therefore, the PEO crystal structure is identical in both the homo-PEO crystal and block copolymer crystals. From the corresponding orientation of the BF image and ED, it can be seen the single crystals are laterally bound by the (120) planes.

In Figure 4.1, it is also seen that lamellar crystals are always obtained from the block copolymers when they are grown in dilute solution, even though the composition of the diblock copolymers changes, and these diblock copolymers would exhibit different phase morphologies after microphase separation in the bulk state. For example, bulk EOS3 is in a disordered state (lamellae after crystallization),\(^\text{193}\) while EOS2 in the bulk has a lamellar morphology,\(^\text{123}\) and EOS1 has a HPL phase morphology in the bulk.\(^\text{227}\)

As shown in Figure 4.2, one can often to find a protruding spot marked as A in the center of the single crystal. Although foreign dust or an impurity during the TEM sample preparation can also make such an effect on the TEM images, it is reasonable to attribute this type of spot to the seeds initiating the crystallization because of the extremely high frequency at which the protruding spots are located at the center of the crystal. The thickness of these protruding spots is larger than the average lamellar
crystal thickness, which can be explained by the fact that the seeds are formed at higher temperatures ($T_s$) than the crystallization temperature ($T_c$).

Figure 4.2  TEM BF morphology and ED pattern of EOS2 single crystals (scale bar for 2 µm). Mark A: probable seed; Mark B: Border lines due to sectorization.

The sector boundary lines can also be easily found and are marked as B in Figure 4.2, which result from the different folding directions in the different sectors (“folding domains”). The protruding sectorization lines could be the result of non-planar lamellar
crystals like PE single crystals collapsing (Figure 2.3). Nevertheless, the degree of non-planarity should be small, since there are no pleats on the crystal surface of the thousands of PEO single crystals observed. It is interesting that these sectorization lines on the surface of single crystals can be observed even when the PEO crystal layer is covered by the amorphous PS layer.

By changing the composition of the block copolymer, solvent, crystallization temperature or any combination of these, truncated lamellar crystals can also be observed, which are shown in Figure 4.3. In these crystals, the b-axis is truncated, which is different from PE single crystals where the a-axis is truncated in truncated

![Image](image1.png)

Figure 4.3 TEM BF morphology and ED of truncated single crystals (scale bar for 2 μm) (a) EOS4 grown at 31 °C from chlorobenzene/octane solution; (b) EOS5 grown at 36 °C from amyl acetate solution.
lozenge-shaped PE single crystals. It was reported that the ratio of a/b axis of the PE single crystal changes with the crystallization temperature and solvent.\textsuperscript{291-293} The lateral habit change is related to the change in the growth rate along different directions due to a change in the crystallization conditions. The folding energies along the (200) and (010) planes in the PE crystal are different, which may partially account for the truncated lozenge-shaped crystals, and for different lateral habit at different crystallization conditions.\textsuperscript{291} It is natural to believe that the lateral habit of homo-PEO or block copolymer crystals changes with crystallization conditions as well. The detailed study is not discussed in this dissertation.

BF TEM images do not precisely provide a real three-dimensional image of the crystals. Atomic Force Microscope (AFM) is thus utilized. By using the tapping mode, the force between the tip and crystal surface can be minimized to avoid damaging the crystal surface like scratching and indentation, yet contact between the AFM tip and crystal surface is well maintained. It is easy to obtain thickness information of the single crystals precisely from a 3-D AFM image via single scan analysis or step analysis. The AFM images of the EOS2 single crystal grown at 31 °C from a chlorobenzene/octane (CLB/OCT) mixed solvent with 1/1.1 weight ratio are shown in Figure 4.4. The thickness of this crystal is 18.8 nm. The EOS1 has a similar morphology and the overall thickness of the EOS1 single crystal (grown at 31 °C in mixed solvent) was 22.3 nm.
Figure 4.4  EOS2 single crystal and thickness analysis  (a) AFM topography 3D image of single crystal grown at 31 °C in mixed solvent; (b) Top view (2D) image of single crystal shown in (a); (c) Height analysis on single crystal shown in (a) and (b).
4.2 DSC study on the PEO-b-PS single crystal mats

A single crystal can be studied microscopically with BF TEM and AFM for morphological observations and electron diffraction (ED) for 3-D structural information. But a single crystal cannot be studied with x-ray diffraction techniques on a macroscopic scale. Nevertheless, single crystal mats (single crystals aggregates) can be studied macroscopically with DSC scans. The detailed procedure to collect single crystal mats is described in section 3.5 of Chapter III.

The single crystal mats that we collected were analyzed by NMR, and the results showed that the composition in the single crystal mats is similar to the original material before crystallization. This indicates that fractionation during crystallization is not an issue during our crystallization. Lotz reported that molecular fractionation occurs after crystallization in solution.\textsuperscript{80, 81} The reason for the difference between our data and Lotz’s data could be the following: (1) the block copolymers we used have a much narrower molecular weight distribution than those used by Lotz,\textsuperscript{80, 81} and our samples were purified with very strict procedures; (2) the solvent we use is different from the solvents which Lotz used.

Single crystal mats of EOS1 and EOS2 were studied by DSC with a heating rate of 10 °C/min. The DSC scans are shown in Figure 4.5. The crystals were grown at 31 °C in the mixed solvent. The melting temperatures of EOS1 and EOS2 single crystals
grown at 31 °C is 57 °C, and 59 °C respectively. The glass transition temperature of PS ($T_g^{PS}$) in the EOS1 and EOS2 block copolymer bulk samples were reported in our published papers.$^{123,227}$ The DSC scans of EOS1 and EOS2 bulk samples are shown in Figure 4.6 and Figure 4.7. The $T_g$ in the EOS1 bulk sample is 70 °C, and 62 °C for the $T_g^{PS}$ of the EOS2 bulk sample.

Figure 4.5 DSC scans of EOS1 and EOS2 single crystal mats. (a) EOS1 single crystal mats; (b) EOS2 single crystal mats.
Figure 4.6  DSC scans of EOS1 bulk sample at scanning rate of 10 °C/min. The insert represents the glass transition regime of PS with an enlarged heat flow (x18).

Figure 4.7  DSC scans of EOS2 bulk sample at scanning rate of 10 °C/min. The insert represents the glass transition regime of PS with an enlarged heat flow (x17).
4.3 Morphology change of single crystals during melting

We do not intend to study the $T_g$ of the PS single layer in the diblock copolymer single crystals in detail. However we can directly observe how the morphology of the single crystal changes with different $T_g^{PS}$ during heating process using TEM and AFM. Figure 4.8 shows the in-situ AFM topography images of the EOS1 single crystals (crystallized at 31 °C in the mixed solvent) during heating. The data shows that the

![AFM images at different temperatures](image)

Figure 4.8 In-situ AFM study on the morphology evolution of EOS1 single crystal during heating process.
single crystal can maintain its morphology at 60 °C for at least 30 minutes. At this
temperature, the PEO block layer is in the molten state. It is further shown that the
single crystals can maintain their original morphology at 65 °C for at least 10 min.
Further increasing the temperature destroys the single crystal shape, and holes start to be
observed. As shown in Figure 4.9, the BF TEM and SAED experimental data confirm
that there is no crystal diffraction when the temperature is higher than the melting
temperature of the PEO layer (57 °C) because the PEO block crystal is melted, yet the
morphology of the single crystals is well maintained when the temperature is below 65 °C.
Please note the $T_g^{PS}$ in the EOS1 bulk sample is about 70 °C, so it is not unreasonable to
conclude that the $T_g^{PS}$ in the EOS1 single crystal does not vary far from 70 °C.
Similarly, the morphological evolution of the EOS2 single crystals (grown at 31 °C in the
mixed solvent) was also studied by TEM and AFM, and the results are shown in Figure
4.10 and Figure 4.11. It is evident that the morphology of the EOS2 single crystal is
destroyed when the temperature reaches 60 °C, which can be attribute the lower $T_g^{PS}$
($T_g^{PS}$ in EOS2 bulk sample is 62 °C). It is also worthy to look at the morphology when
the temperature is higher than 62 °C (100 °C for example), the characteristic dewetting
morphology of a thin liquid-like film on the substrate was formed. It can be interpreted
as a dewetting process through a spinodal decomposition mechanism.\textsuperscript{176-181}
Figure 4.9  TEM BF images and ED pattern of EOS1 single crystals after annealed at different temperatures for 5 minutes. (a) 40 °C. (b) 50 °C. (c) 60 °C. (d) 65 °C. (e) 70 °C. (f) 75 °C. (g) ED pattern for lamellae shown in a and b.  (h) ED pattern for lamellae shown in c, d, e, f.
Figure 4.10  In-situ AFM study on the morphology evolution of EOS2 single crystal during heating process.
Figure 4.11 TEM BF images of EOS1 single crystals after annealed at different temperatures for 5 minutes. (a) 50 °C. (b) 60 °C. (c) 65 °C. (d) 70 °C.

4.4 Evidence for PS/PEO/PS sandwich structure of diblock copolymer single crystals

It was reported that 90% of PE chain ends are located at the fold surface of PE single crystals.\textsuperscript{71} It is reasonable to consider the amorphous PS block as excluded from the PEO crystal lattice during the crystallization of PEO block. Statistically, each PS
block has a 50% chance to go to either folding surface of the PEO lamella.

Thermodynamically, generating even fold surfaces for PEO lamellar crystals is favorable to stabilize the crystal. Otherwise, curved or scrolled crystals would form due to the uneven crowdedness of the PS layers at the fold surfaces, which results in uneven surface tension. In reality, the block copolymer single crystal lamella is planar in shape, which supports the idea that the PS blocks are evenly distributed on each basal surface of the PEO lamellae. After the solution evaporation and solidification of the PS chains, the PEO lamellae are sandwiched by two PS amorphous layers. This sandwiched structure was proposed by Lotz for PEO-$b$-PS block copolymer single crystals, and this model was applied to analyze the chain conformation of the amorphous block on the crystal lamellar surface.

This sandwiched model structure for amorphous-crystalline block copolymer single crystals is commonly accepted, yet there is no experimental evidence reported. Two experiments were designed to provide the experimental evidence to prove the sandwiched structure.

4.4.1 Polymer decoration method

The PE decoration method is a simple yet useful way to gather chain folding information on single crystal fold surfaces. Figure 4.12a shows the PE-decorated
homo-PEO single crystals, which shows the PE oligomer extended-chain crystals are oriented in different directions in the four sectors of the PEO single crystals. The relationship between the PEO chain folding direction and the PE rods was analyzed in detail by Cheng et al.\textsuperscript{78} The key message delivered here is that the fold surface of the PEO single crystal is regular. For the PEO-\textit{b}-PS block copolymer single crystals, on the other hand, the decorating PE crystal rods on the copolymer crystal surface are randomly oriented as shown in Figure 4.12b, and the orientation is isotropic and undistinguishable in different sectors of the single crystal. Two more types of crystals were grown to further prove this. For example, homo-PEO single crystals were grown first, and then, the homo-PEO crystals initiated the crystallization of block copolymers, so we can then obtain hybrid single crystals of homo-PEO single crystals bounded by block copolymer single crystals and vice versa. The hybrid single crystals of block copolymers bound by the homo-PEO crystal can be made by switching the crystal growth sequence (Alternating the crystal growth will be discussed in detail in a later chapter.). These two types of hybrid crystals are decorated by vaporized PE oligomers, and observed under TEM. The TEM micrographs are shown in Figure 4.12c and Figure 4.12d. The homo-PEO part and block copolymer part can be distinguished by the thickness difference of the lamellae in the hybrid crystals through the showing features in Figure 4.12. Decoration results show that the folding surface on the homo-PEO crystal is regular, while the folding surface of the PS block covered surface is not.
These results suggest that the PEO block crystal layer in the block copolymer single crystals was covered by PS blocks. Since the deposition of the single crystals on
the carbon film for TEM observation from solvent is random, there is no reason that the
single crystals selectively choose one specific basal crystal surface to attach to the carbon
film than another. Therefore, both basal surfaces of PEO crystal layer in the PEO-\textit{b}-PS
block copolymer single crystals are covered by an amorphous PS layer, which is the
sandwiched structure we confirmed.

4.4.2 AFM scanning method

Since PEO and PS are quite different polymers with different physical properties,
such as viscoelasticity at different temperatures, by applying the tapping mode we can
observe an AFM phase image scan to distinguish the PS and PEO parts of the crystals.
If there is actually a 3-layer “sandwiched” structure, the only way to find out is along the
lateral surface of the crystal lamella. Our experimental design is to tilt the crystal
lamellae, and use AFM to scan the crystal lateral surface. Furthermore, with a hot stage
coupled to the AFM, we can enhance the contrast between the PEO and PS in the AFM
phase image by melting PEO while keeping PS in the glassy state. At 60 °C, PEO melts,
but PS is still in the glassy state for the EOS1 single crystal. The AFM phase image of
the EOS1 crystal at 60 °C is shown in Figure 4.13. Three layers can be clearly
distinguished from the lateral surface of the lamella.
4.5 PEO crystal layer thickness in diblock copolymer single crystals

There are different ways to measure the crystalline thickness of the crystal layer in block copolymer crystals: (1) Small Angle X-ray Scattering (SAXS) coupled with a crystallinity measurement can be used. From SAXS, the long d-spacing in the single crystal mats can be measured, and the PEO layer can be calculated by volume fraction of PEO. Therefore, the thickness of the overall PEO layer can be obtained. The crystal layer thickness can be further calculated from the crystallinity and overall PEO layer thickness. In order to run SAXS, we need to use single crystal mats. How to eliminate
the interface between PS layers from the neighboring single crystals (even voids) is the key to obtain precise results. (2) Longitudinal acoustic mode (LAM) Raman spectroscopy\textsuperscript{294} can be applied to measure the crystal layer thickness in single crystal mats. However, the extremely strong absorption from PS forbids the application of this method on PEO-\textit{b}-PS block copolymer single crystals. (3) Calculate based on the Scheerer equation from Wide Angle X-ray Diffraction (WAXD).

\[ t = \frac{K \cdot \lambda}{B \cdot \cos \theta} \quad (4.1) \]

where \( t \) is the correlation length, \( K \) is the structure parameter determined by the instrument and sample property, \( \lambda \) is the wavelength of the X-ray, \( B \) is the half-peak width in the unit of radian, and \( \theta \) is the incident angle of the X-ray. Normally \( t \) is the correlation length between crystallographic defects, and is not equivalent to the thickness in the respective crystallographic direction based on which \( t \) is calculated. However, it is reasonable to assume that there are very few defects in the lamellar single crystals along the lamellar basal surface normal direction (\( \vec{n} \)). Therefore the calculated \( t \) in \( \vec{n} \) direction is close to the real crystal thickness. \( K \) can be calibrated by homo-polymer single crystals.\textsuperscript{295} By applying this method, a diffraction peak with acceptable intensity needs to be found that contains lamellar thickness information (c-axis in PEO crystal), and the orientation of this crystal plane is randomly distributed. Unfortunately, it is difficult to find this diffraction in PEO crystal mats. (4) Calculation from the overall
thickness of the single crystal. This method is applied in the current research. It is worthy to point out that the thickness of the PEO crystal layer in the block copolymer single crystals will not change whether or not they are suspended in the solvent or dried after solvent evaporation, although the size of the PS layer may change dramatically, which depends on what environment PS chains stay in, for example, a good solvent or a theta solvent.

The thickness of the PEO block single crystal ($d_{\text{PEO}}$) can be obtained by using the equation $d_{\text{PEO}} = d_{\text{OVERALL}} \times V_{\text{PEO}}\%$, while the overall thickness of the block copolymer ($d_{\text{OVERALL}}$) can be measured easily from AFM. We assume that the density of the two PS block layers is identical to that of the amorphous PS bulk ($\rho_{\text{PS}} = 1.052$ g/cm$^3$). The densities of the PEO crystal ($\rho_{\text{PEO}}^c$) and amorphous PEO ($\rho_{\text{PEO}}^a$) are identical to the bulk densities of 1.239 g/cm$^3$ and 1.124 g/cm$^3$, respectively, at room temperature. Since the PEO crystal structure in the single crystal as determined by the SAED experiments is identical to that in the bulk, we do not expect any deviation of the $\rho_{\text{PEO}}^c$ in the single crystals from the bulk. Furthermore, the PEO blocks in this system possess 95% crystallinity based on the DSC study on the single crystal mats. This leads to little deviation caused by the assumption of $\rho_{\text{PEO}}^a$. The $d_{\text{PEO}}$ can thus be estimated to a first-order approximation.

$$d_{\text{PEO}} = d_{\text{OVERALL}} \times \frac{M_n^{\text{PEO}}}{M_n^{\text{PS}}} \left(\frac{W_{\text{PEO}}^c\rho_{\text{PEO}}^c + W_{\text{PS}}^a\rho_{\text{PS}}^a}{W_{\text{PEO}}\rho_{\text{PEO}}^c + W_{\text{PS}}\rho_{\text{PS}}^a} + M_n^{\text{PS}} / \rho_{\text{PS}}\right)$$  \hspace{1cm} (4.2)
From the step-height analysis of the topography image of the single crystals shown in Figure 4.14, the overall thicknesses of the EOS1, EOS2 and EOS3 single crystals grown at 31 ºC are 22.3 nm, 18.8 nm and 17.0 nm. The PEO crystal layer thicknesses calculated from Equation 4.2 are 7.9 nm, 8.4 nm and 11.4 nm for these single crystals, respectively. We used these PEO-b-PS single crystals as seeds to further grow a homo-PEO crystal fraction. The added homo-PEO molecules can only nucleate on the lateral (120) planes of the PEO-b-PS single crystal to grow a homo-PEO single crystal.

The initial thickness of the homo-PEO lamellar crystals connected to the PEO block crystal can readily be measured by AFM, and serves as direct evidence of the $d^{PEO}$ in the PEO-b-PS single crystal. The observed homo-PEO initial lamellar thicknesses were indeed identical to the $d^{PEO}$ calculated from the equation. Therefore, the $d^{PS} = 2.8$ nm for $M_n^{PS} = 4.6k$ g/mol, 5.2 nm for $M_n^{PS} = 9.2k$ g/mol, and 7.2 nm for $M_n^{PS} = 17k$ g/mol, respectively. Note that this method needs to take the edge thickness into account, in particular, for the PEO-b-PS with $M_n^{PS} = 17k$ g/mol (see Figure 4.14). Sometimes, while depositing the crystals onto a hard silicon wafer surface, the homo-PEO single crystal may slip down to the substrate surface. The difference observed in AFM experiments is thus equal to $2d^{PS}$. However, based on the thickness of the homo-PEO crystal, we can still calculate the $d^{PS}$, and they are also identical to the calculated data. In order to avoid this slippage, the single crystals were deposited on a lightly cross-linked viscoelastic rubber substrate surface.296
Figure 4.14 EOS1 single crystal and thickness analysis (a) 3-D AFM topography image of single crystal grown at 31 °C in mixed solvent. (b) Step-height analysis on the crystal shown in (a).

4.6 Concept of single crystal engineering

As discussed above, PEO-b-PS single crystal can be described as a PEO thin layer of nanometer thickness sandwiched by two PS nano layers as shown in Figure 4.15. It thus introduces us a new experimental design to make a uniform crystalline PEO nano-layer which is confined between two PS glassy walls. Furthermore, the melting
Figure 4.15  Schematic view of three-layer sandwiched structure of PEO-\textit{b}-PS diblock copolymer single crystal lamella. One PEO crystal layer sandwiched by two PS amorphous layers.

and crystallization process of the PEO block layer can occur within the confines of this unique environment if we design the composition of the block copolymer properly to make the $T_g^{PS}$ high enough (like EOS1). The thickness of the PEO crystal layer in the PEO-\textit{b}-PS block copolymer single crystals changes with the crystallization temperature, and this affects the conformation of the PS chain. Since PS chains are tethered to the PEO crystal layer surface, the PS chains are considered to be polymer brushes. The tethered PS chains are uniformly distributed on the tethering substrate macroscopically. Furthermore, the PEO-\textit{b}-PS was synthesized with a very narrow molecular distribution
before the polymer brushes are formed, so the tethered PS chains have almost uniform length. Uniform PS brushes (uniform distribution and uniform chain length) can be constructed through this approach, which cannot be realized by traditional methods for polymer brush fabrication.\textsuperscript{247-258} Thus, it provides a good opportunity to study polymer brushes for both theoretical calculations and experimental observations.

All these applications are based on one fundamental research topic, single crystal growth in dilute solution, yet we can expand this research topic into new fundamental research and application areas. We propose a term, single crystal engineering, for these applications of single crystals. This is the major contribution of this thesis to the field of polymer crystallization.
CHAPTER V

CRYSTAL STRUCTURAL EVOLUTION IN A SINGLE PEO NANO-LAYER CONFINED IN BETWEEN TWO THIN POLYSTYRENE GLASSY WALLS

Polymer phase transitions that take place confined in nanometer length scale geometries may exhibit different transition behaviors from those in the bulk. One approach utilized to construct nano-confined environments involves the use of diblock copolymers as templates. As long as the matrix phase possesses a high glass transition temperature \( (T_g) \) and the other component can self-order to form crystals having a lower melting temperature \( (T_m) \) compared with that \( T_g \), a tailored nano-confined crystallization can be achieved. PEO-\(b\)-PS diblock copolymers with a lamellar morphology after microphase separation can generate thin PEO films with nanometer thicknesses confined in between two glassy PS layers if the molecular composition of the copolymer is suitable. In order to study the crystal structure and orientation evolutions in the copolymer bulk sample, we need to generate single domain phase morphologies, namely, achieve macroscopic orientation of the phase morphologies utilizing a mechanical shearing technique. In mechanically aligned bulk samples, however, morphological defects such as grains, subgrains and dislocations do form as shown in the Figure 5.1.
morphology studied, for example, the cross-talk occurring between neighboring PEO layers always affects the PEO crystallization behavior in this confined environment. An ideal case would be to construct a confined single lamella environment with one PEO nano-layer sandwiched by two PS glassy-nano walls without defects.

Figure 5.1  Defects in copolymer bulk samples (a) Boundaries and defects in the microphase separated block copolymer.297 (b) Schematic view of the defects in the lamellar morphology of block copolymer.

This is the aim of this chapter, which is to study the crystallization behavior of a single PEO nano-layer confined in between two glassy PS layers. The Langmuir-Blodgett technique was used to make structurally ordered thin films for amphiphillic small molecules, oligomers, and copolymers with highly asymmetric compositions.186 Devereaux191 used the LB technique to make thin films of an
extremely asymmetric PEO-b-PS ($M_n^{PEO} = 3.6k$, $M_n^{PS} = 47.7k$, PEO is only 7 wt% in copolymer), yet the film was not uniform, and the structure of the film was not mentioned by the authors. The authors pointed out that only dots instead of films can be formed by this LB method when the percentage of PEO was over 10 wt%.

Spin coating is another method to prepare thin films. However, de-wetting and uncontrolled layer compositions are problems that exist when trying to make this sandwiched layer system.\textsuperscript{298,299} Figure 5.2 shows an AFM image of a spun cast film of EOS1 with a spherulitic structure in the thin film. The geometry of this thin film is obviously not the sandwich structure we need. However, this unique geometry of one PEO nano-layer sandwiched by two PS layers can be constructed through single crystal engineering as described in Chapter IV.

![Figure 5.2](image)

Figure 5.2  Morphology of EOS1 spin-cast film (2 wt% EOS1 in benzene) (a) AFM topography image; (b) Schematic drawing of the sandwich structure to achieve.
5.1 Unique confined space constructed by single crystal engineering

Single crystal lamella of EOS1 grown at 31 °C in a dilute solution of mixed solvent were characterized in Chapter IV. The sandwiched structure with the PEO layer between the two PS layers was shown by TEM and AFM. The thickness of the PEO layer and PS layers is thinner than 10 nm (7.9 nm for the PEO layer; 7.2 nm for the PS layers). The $T_g^{PS}$ is higher than $T_m^{PEO}$ (57 °C), which meets the ideal case of a single PEO nano-layer confined in between two PS glassy walls. Since the PEO layer is a single crystal lamella formed in dilute solution, there should be no defects comparable to the grain boundary or mis-packed layer defects in the lamellar phase of bulk block copolymers. Therefore, the melting and crystallization behavior of a PEO nano-layer without defects could be studied. EOS1 ($M_n^{PEO} = 11$ kg/mol, $M_n^{PS} = 17$ kg/mol) was used as the experimental material, and the single crystals were grown at 31 °C in dilute solution using the mixed solvent (chlorobenzene/octane with a 1/1.1 weight ratio).

5.2 Crystallization of a single PEO nano-layer confined in between two PS glassy walls

After the PEO-$b$-PS single crystal lamella was heated to 65 °C to completely melt the PEO crystal, the sample was quenched to different re-crystallization temperatures ($T_{rc}$). A self-seeding experiment was conducted when $T_{rc}$ was higher than 0 °C. Since X-ray diffraction is not sensitive to one single PEO nano-layer, the crystallization of the PEO layer was investigated using ED experiments in TEM.
5.2.1 Crystallization kinetics of the confined PEO nano-layer

It is difficult to perform in situ ED studies during crystallization, therefore we do not have the intention to study the crystallization kinetics of the single PEO nano-layer in a tradition way, like measuring crystallinity change as a function of crystallization time. We have compared the relative crystallization rate between PEO single nano-layers in the current confined geometry and the bulk copolymer sample.

Figure 5.3 is the ED pattern of the PEO-\(b\)-PS lamellae recrystallized at 5 °C for 8 days after being melted at 65 °C for 5 min. Only a diffuse amorphous ring ED pattern was observed, and the same patterns were observed when the lamellae were tilted at different angles along different directions, which means that the PEO layer confined in between the two PS layers had not crystallized at 5 °C after 8 days.

Figure 5.3  ED pattern of the recrystallized EOS1 lamella after melted at 65°C for 5 minutes \(T_{rc}=5°C\), crystallization time is 8 days.
Figure 5.4 shows the DSC cooling curve of the bulk sample of the same PEO-\textit{b}-PS copolymer after melting at a cooling rate of 10 °C/min. The crystallization peak temperature is 24 °C. Therefore, the crystallization rate of the bulk sample at 5 °C is extremely fast, and it only takes a couple of minutes to finish the crystallization process. The crystallization of this single PEO nano-layer in this confinement geometry is much slower than the crystallization rate of the bulk sample.

![DSC cooling scan](image)

\textbf{Figure 5.4} DSC cooling scan EOS1 bulk sample after melted at 70°C, cooling rate is 10°C/min.

Then, the question of whether or not the melted PEO layer in this confined geometry can recrystallize comes out naturally. In order to answer this question, a set of experiments were carried out. The EOS1 single crystal lamellae were melted at 65°C for 5 min, and then, recrystallize at -40 °C or -15 °C for 2 hours. The ED patterns of the PEO-\textit{b}-PS lamellae were taken at room temperature. The results are shown in Figure
5.5. From these ED patterns, it is evident that the PEO layer confined in between two PS layers can recrystallize, however, the recrystallization temperatures have to be low enough. It was determined that the recrystallization temperature needs to be lower than 
\(-5^\circ C\) in order that the recrystallization of the PEO layer occurs within hours.

![Figure 5.5](image)

Figure 5.5 ED pattern of the recrystallized EOS1 lamella after melted at 65°C for 5 minutes. (a) at \(-40^\circ C\) for 2 hours; (b) at \(-15^\circ C\) for 2 hours. ED pattern was recorded at room temperature.

Foreign substances which can serve as heterogeneous nucleation sites were rejected from the PEO single crystal layer when the PEO-\(b\)-PS single crystals lamellae are grown in dilute solution. Therefore, during the recrystallization process, the possibility of heterogeneous nucleation in the PEO layer was extremely low after the PEO-\(b\)-PS was melted at 65 °C. Therefore homogeneous nucleation of the recrystallized PEO layer in the confined space was required, which needs a large degree of undercooling. Therefore the PEO layer in the confined space can only recrystallize at low temperatures (lower than \(-5 \, ^\circ C\)), while the recrystallization of the PEO layer is
extremely slow or cannot occur when the recrystallization temperature is high (higher than 0 °C). This is the reason why this single PEO nano-layer in the current confined geometry needs very large degree of undercooling before it starts to crystallize.

At the same time, we note that the ED patterns of PEO crystals recrystallized at different temperatures are different as shown in Figure 5.5. In other words, the PEO crystal orientation in the PEO layer in this confined geometry is different depending on the recrystallization temperature.

When we compare the ED patterns of the PEO-b-PS lamellae directly quenched to -40 °C or -15 °C with those first quenched to 5 °C for 8 days then quenched to -40 °C or -15 °C, we observed that the final ED patterns of both these PEO crystals were the same, which is shown in Figure 5.6. This further confirms that the PEO-b-PS lamellae remained in the isotropic melt after it was isothermally annealed at 5 °C for 8.

5.2.2 Dependence of PEO crystal orientation on the recrystallization temperature

As mentioned above, the crystal orientation in the PEO layer is strongly dependent on the recrystallization temperature. It is thus worthy to study the dependence of PEO crystal orientation on the recrystallization temperature.

When \( T_{rc} \) is lower than -25 °C, the ED pattern of the re-crystallized lamella exhibited two major diffraction rings as shown in Figure 5.7a. The inner ring shows a d-spacing of 0.463 nm, which is attributed to the (120) diffractions. The outer ring has a d-spacing of 0.39 nm, and it represents the overlapped (\( \bar{1}32 \)), (032), (112), (\( \bar{2}12 \)), (\( \bar{1}24 \)), (\( \bar{2}04 \)), and (004) diffractions. We have also used a tilting stage to examine the sample.
Figure 5.6  ED pattern of the recrystallized EOS lamellae after melted at 65°C for 5 minutes through different crystallization conditions and paths.

No matter what tilting angles were used, the ED ring pattern was always observed and was identical to that shown in Figure 5.7a. This indicates that at $T_{rc} \leq -25$ °C the PEO blocks re-crystallized into a number of small crystals with random c-axes orientations. Since the PEO block layer thickness is 7.9 nm, the re-crystallized PEO crystals should possess sizes smaller than 7.9 nm in each of their three-dimensions. It was reported that the transition temperature from heterogeneous nucleation to homogeneous nucleation for the crystallization of PEO is around -5 °C.\textsuperscript{300} When $T_{rc}$ is lower -25 °C, many nuclei form spontaneously. There is not much place for the growth of crystals before the crystals start to impinge each other. The crystals do not feel the layer confinement,
thus no effect on the orientation of the crystals is expected. Overall the crystals are randomly oriented in this 7.9 nm thick layer as schematically shown in Figure 5.7b, and the ED pattern can only be a ring.

Figure 5.7 Crystal orientation of recrystallized PEO at $T_{rc} < -25 \, ^\circ C$ (a) ED pattern of the recrystallized PEO when $T_{rc}$ is lower than $-25^\circ C$. (b) Schematic drawing of the chain orientation of the recrystallized PEO with respect to the original EOS1 single crystal when the $T_{rc}$ is lower than -25°C.
A more interesting case occurs when $-25 \, ^\circ\text{C} \leq T_{rc} \leq -5 \, ^\circ\text{C}$. As an example, the ED patterns of the re-crystallized lamella from the whole lamella or the selected sectors are shown in Figure 5.8 at $T_{rc} = -20 \, ^\circ\text{C}$. The ED patterns from the selected sectors are similar to that from the whole crystal lamella, but with better orientation.

Figure 5.8  ED patterns of the recrystallized PEO lamella with $T_{rc} = -15 \, ^\circ\text{C}$ with select area aperture.

It is a fiber pattern of the PEO crystal with a uniaxial c-axis. One pair of the (120) diffraction arcs has a d-spacing of 0.463 nm on the equator. Another two pairs of diffraction arcs having a d-spacing of 0.33 - 0.34 nm can be observed at 67° away from the equator. These arcs are attributed to the overlap diffraction of the (024) and ($\bar{2}24$)
The two pairs of diffraction arcs in the quadrants with d-spacing of 0.39 nm and 23° away from the equator are attributed to the overlapped diffractions of the (112), (032), (212) and (132) planes. It can be deduced that the c-axis of the PEO crystals is perpendicular to \( \hat{n} \). The PEO crystals between two PS glassy walls rotate around the c-axis. Furthermore, the c-axis is aligned along one diagonal of the original single crystal lamellae (more precisely, it is aligned along \( a^* \) of the original single crystal).

In order to explain this experimental data, we need to look back to the process of making the single crystal lamellae. During the crystallization of the PEO-\( b \)-PS in the dilute solution, the PEO block forms the lamellar crystal first, while PS block is still in the dilute solution, which is schematically shown in the Figure 5.9a. The fold surface of the PEO crystal lamella is regular (schematically shown in Figure 5.10a), which can be proven by the PE decoration on the PEO single crystal surface as shown in Figure 5.10b. The oriented low molecular weight PE crystal rods on the homo-PEO crystal surface indicate the four sectors, and the chain folding directions are along the (120) planes. After the crystallization was finished, the solvent was gradually evaporated and the PS blocks solidified and formed glassy layers on the PEO crystal surface (as shown in the Figure 5.9b). In this process, the folding information of the PEO crystal surface could be encoded into the PS layer on the molecular scale. During the melting process, the PEO crystal was melted, while the glassy PS layers have the folding surface replica of the PEO crystal on the surface (as shown in Figure 5.9c). These PEO folding surface replicas are expected to play an important role in the nucleation and crystallization of the PEO during the recrystallization process.
Figure 5.9 Schematic drawings to show the process to make PEO-\(b\)-PS single crystals from dilute solution and the melting process of PEO-\(b\)-PS single crystals. (a) sketch of PEO-\(b\)-PS single crystals suspended in the solvent; (b) sketch of PEO-\(b\)-PS single crystals after solvent evaporated; (c) sketch of PEO-\(b\)-PS single crystals with PEO layer melted.
Figure 5.10  Regular chain folding surface of PEO single crystal  (a) Folding surface sketch; (b) TEM micrograph of PEO single crystal with PE decoration.

The PEO 7/2 helix chain conformation and the PEO crystal lattice (projection along [001]) are shown in Figure 5.11a and Figure 5.11b. If we further exam the lattice parameters of the PEO crystal unit cell, there is the following relationship.

\[ 3a \sin \beta = 0.656 \times 3 = 1.968 \text{nm} \approx c = 1.948 \text{nm} \]
As shown in the Figure 5.11c, the folds of the PEO chain make regular convex spots along folding direction on the PEO crystal surface. These regular convex spots are encoded by the regular concave pits in the glassy PS layer resulting in a replicating process during solvent evaporation described above. This replica of the PEO crystal folding surface is expected to help the nucleation with PEO chain oriented along \( a^* - \) (or \( b^- \)) direction during the recrystallization process through soft epitaxy. Figure 5.12 shows the schematic drawing of the PEO crystal orientation with respect to the original single crystal lamella.

\[
a = 0.805 \text{ nm}, \quad b = 1.304 \text{ nm}, \quad c = 1.948 \text{ nm}, \quad \beta = 125.4^\circ
\]

\[3a \sin \beta = 0.656 \times 3 = 1.968 \text{ nm} \approx 1.948 \text{ nm}\]

\(a^*\) is the length of the c-axis.

Figure 5.11  PEO chain conformation and crystal lattice  (a) 7/2 helix conformation of PEO chain; (b) Projection along [001] of PEO crystal lattice; (c) schematic drawing of PEO chain orientation during recrystallization through soft epitaxy.
Figure 5.12  Crystal orientation of recrystallized PEO at \(-20^\circ\text{C} < T_{rc} < -5^\circ\text{C}\)  (a) ED pattern of the recrystallized PEO at \(-15^\circ\text{C}\).  (b) Schematic drawing of the chain orientation of the recrystallized PEO with respect to the original EOS1 single crystal when the \(T_{rc}\) is between \(-20^\circ\text{C}\) and \(-5^\circ\text{C}\).
As the $T_{rc}$ was increased to a temperature range between 0 °C and 40 °C, the ED pattern changed. Figure 5.13 shows an ED pattern of the PEO crystals re-crystallized at 30 °C. First, four pairs of diffraction spots can be observed. Two diffraction pairs have a d-spacing of 0.463 nm, which are attributed to the (120) diffractions. The other two pairs have the same d-spacing of 0.39 nm which are from the (032) and (112) or (132) and (212) diffractions.

From the ED patterns of the selected sectors shown in Figure 5.13, there are two sets of crystal orientations in each sector. We used the Cerius®2 software to generate...
PEO single crystal ED patterns of different zones. If we rotate the PEO crystal along the normal of the (120) plane to an angle of 26°, we can generate the ED pattern of the (425) zone as shown in Figure 5.14. In the real case, only the six spots within the ring can be seen because the other spots are weak. Similarly, if we rotate the PEO crystal along the normal of the (120) plane at an angle of 26°, we can generate the ED pattern of the (423) zone which is also shown in Figure 5.14. The six spots within the selected rings are the strong spots in this figure.

Figure 5.14 Calculated ED patterns of PEO single crystal in (425) zone and (423) zone based on PEO crystal lattice.
From the ED pattern of the recrystallized PEO-\textit{b}-PS at 30 °C as shown in Figure 5.13, the PEO crystal orientation in the real space can be schematically described by Figure 5.15. The PEO chains tilt 26° along the \{120\} plane. The probable reason is the seeds generated by self-seeding can remember the original crystal orientation. During the crystal growth process, the seeds cannot rotate freely because of the tethering effect of the PEO chains to the glassy walls and the confinement of the limited space (7.9 nm) provided for the PEO crystal growth. The reason for the chain tilting needs to be studied in further detail.

![Diagram](image.png)

**Figure 5.15** Schematic drawing of the chain orientation of the recrystallized PEO with respect to the original PEO-\textit{b}-PS single crystal when \(T_{\text{rc}}\) is above 0°C.
In summary, a novel approach has been proposed to construct a sandwiched PS/PEO/PS nano-thin layer system by growing a single crystal of crystalline-amorphous PEO-\textit{b}-PS diblock copolymers in dilute solution. This is the first defect-free system used to study the confinement effect of a 7.9 nm-thick single PEO layer in between two 7.2 nm-thick glassy PS layers. The PEO crystal orientation in the confined layer strongly depends on the $T_{rc}$s. The PEO fold information can be encoded by the PS amorphous layer, and this PEO fold surface replica can help the nucleation and the crystal growth during the recrystallization process with the PEO chain aligned along the $a^*$ axis of original PEO-\textit{b}-PS single crystal when the $T_{rc}$ is between -20 °C and -5 °C. Observations of the glassy behavior of the PS layers indicate that the thickness limit of a phase size is smaller than 7.2 nm.
CHAPTER VI

POLYMER BRUSHES CONSTRUCTED BY SINGLE CRYSTAL ENGINEERING
AND ONSET OF POLYMER BRUSHES OVERCROWDING

There are three regimes for polymer brushes (the non-interacting, the crossover, and the highly stretched regimes) based on the tethering density and chain conformation as schematically shown in Figure 2.48 (the thickness of the tethered chains on the substrate in solution versus reduced tethering density $\tilde{\sigma}$). However, the location of the boundaries between these regimes is not quantitatively known. In experiments, most of the results were reported in the non-interacting and crossover regimes. One study showed that the strongly stretched regime was not reached at $\tilde{\sigma} = 12$.\textsuperscript{301} Another study reported, on the other hand, tethered chains started to be stretched at around $\tilde{\sigma} = 6$.\textsuperscript{302} The reason for the conflicting experimental data reported is because the polymer brushes generated by the traditional chemical methods are not well defined (uncontrolled and immeasurable length and distribution variations). The question we ask is when the tethered chains start to get squeezed by their neighbors. The theoretical predictions and experimental observations so far have not provided a quantitative answer to this question. And this is the focus of this chapter.
In order to answer this question, it is first necessary to precisely control $\sigma$ and its local uniformity on a substrate with mono-dispersed MW tethered chains. In Chapter IV, it was pointed out that uniform PS brushes (uniformly distributed and of uniform chain length) can be constructed, and the tethering density can be adjusted by the composition of block copolymer and/or crystallization conditions. This can be easily understood from the following two simple cases. (1) Assuming the PS chain length is fixed, and PEO lamellar crystal thickness is also fixed, longer PEO chains possess more folds in order to generate the same lamellar thickness. Therefore, the folding surface area of PEO chains is dependent on the PEO chain length, and this folding surface is the area that tethered PS chains occupy. Thus it is easy to understand that the tethering density can be adjusted by the compositions of block copolymers. (2) For the same copolymer, the lamellar crystal thickness could change with crystallization conditions, for example, crystallization temperature ($T_c$), thus the average folding number for each PEO chain could change. As a result, the folding surface area of each PEO chain, which is the area each PS chain may occupy, changes with crystallization conditions. As a result, the tethering density of PS could be controlled by the crystallization conditions.

In this chapter, the PS tethering density is controlled by changing the crystallization conditions of PEO enabling the onset of chain overcrowding to be experimentally demonstrated by the uniform PS brushes. Yet, this subject can be greatly expanded, and more questions or topics are raised in this chapter. More experiments need to be carried out before the questions can be answered.
6.1 Thickness and surface free energy of lamellar crystals

As discussed in Chapter 2, the free energy change for crystallization can be expressed as Equation 6.1.

\[ \Delta G = \Delta G_c + \sum A \gamma \]  

(6.1)

where, \( \Delta G_c = \Delta H - T \Delta S \) is the bulk free energy change for crystallization, \( A \) is the surface area, and \( \gamma \) is the specific surface free energy. Since the second term is always positive, the nucleation process can be schematically presented as in Figure 2.31. The maximum in \( \Delta G \) corresponds to the critical size nucleus.

For homogeneous nucleation, assuming the critical nucleus has an orthorhombic shape with the dimensions of \( a, b \) and \( d \) (\( a = b \neq d \)), the free energy change can be expressed as in Equation 6.2.

\[ \Delta G_i = -a^2 d \Delta g_f + 4ad \gamma + 2a^2 \gamma_e \]  

(6.2)

where \( \Delta g_f \) is the bulk specific free enthalpy of the crystal without surface defects. The \( \gamma \) and \( \gamma_e \) are surface free energies for the lateral surfaces and chain-folded surfaces.

With the self seeding procedures (a special secondary nucleation shown in the Figure 6.1), the seeds have the same nature of the growing crystals, therefore, there is no net surface increase contributing to the surface energy term in the equation 6.1 when the surface ABCD is replaced by A’B’C’D’. Therefore, equation 6.2 needs to be modified to equation 6.3 for the self-seeding nucleation.

\[ \Delta G_i = -a^2 d \Delta g_f + 2ad \gamma + 2a^2 \gamma_e \]  

(6.3)
Figure 6.1  Schematic representation of secondary nucleus.

The critical nuclei size ($a^*$ and $d^*$) can be obtained as shown in equation 6.4 and 6.5 by setting the derivatives of $\Delta G_i$ on $a$ and $d$ to zero ($\Delta G_i$ is at maximum at critical nuclei size).

$$a^* = 2\gamma / \Delta g_f$$  \hspace{1cm} (6.4)

$$d^* = 2\gamma_c / \Delta g_f$$  \hspace{1cm} (6.5)

The free enthalpy change can be expressed furthermore by equation 6.6.

$$\Delta g_f = \Delta h_f - T\Delta s_f$$  \hspace{1cm} (6.6)

$\Delta h_f$ is the specific enthalpy at the equilibrium dissolution temperature $T_f$. When the degree of under cooling is not large, $\Delta s_f$ the entropy of fusion per unit volume can be taken to be temperature independent.
\[ \Delta g_f = \Delta h_f - T_d \Delta s_f = 0 \Rightarrow \Delta s_f = \frac{\Delta h_f}{T_d} \]  

(6.7)

at \( T = T_d \)

\[ \Delta g_f = \Delta h_f - T_x \frac{\Delta h_f}{T_d} = \frac{\Delta h_f}{T_d} (T_d - T_x) = \frac{\Delta h_f \Delta T}{T_d} \]  

(6.8)

at \( T = T_x \)

The degree of undercooling is defined as \( \Delta T = (T_d - T_x) \). Thus the thickness of the single crystal \( d_c \) can be expressed as equation 6.9.

\[ d_c = \frac{2 \gamma_c T_d}{\Delta h_f \Delta T} = \frac{2 \gamma_c T_d}{\Delta h_f (T_d - T_x)} \]  

(6.9)

or

\[ \frac{1}{d_c} = \frac{\Delta h_f (T_d - T_x)}{2 \gamma_c T_d} = \frac{\Delta h_f}{2 \gamma_c T_d} \times \frac{\Delta h_f T_x}{ \frac{\Delta h_f}{2 \gamma_c T_d} \times T_x} \]  

(6.10)

In the case of the single crystal of diblock copolymers in solution, the surface energy of the folding surface \( \gamma_e \) is contributed to by both normal chain folding \( \gamma_e^F \) and the tethered amorphous chains \( \gamma_e^a \). So the \( \gamma_e \) can be expressed by equation 6.11.

\[ \gamma_e = \gamma_e^F + \gamma_e^a \]  

(6.11)

where \( \gamma_e^a \) is from the tethered amorphous chains, which is related to the chain tethering density and chain conformation. Therefore, the thickness of the crystal layer in block copolymer single crystals can be acquired by the following expression:

\[ \frac{1}{d_c} = \frac{\Delta h_f (T_d - T_x)}{2 \gamma_c T_d} = \frac{\Delta h_f}{2 \gamma_c T_d} \times \frac{1}{\gamma_e^F + \gamma_e^a} \times T_x \]  

(6.12)
The slope in the plot of $1/d_c$ vs. $T_x$ for block copolymer single crystals is equal to $\frac{\Delta h_c \times \frac{1}{v_x}}{2T_a \gamma_c^\alpha + \gamma_c^\beta}$. For the same copolymer, the tethering density is affected by crystallization temperature, and the tethering density affects the chain conformation of the tethered chains. Since $\gamma_c^\alpha$ is related to the chain tethering density and chain conformation, therefore, it is natural to draw a conclusion that the slope in the plot of $1/d_c$ vs. $T_x$ could change for the same sample at different $T_a$. Vice versa, for the same copolymer/solution system, the change of the slope in the plot of $1/d_c$ vs. $T_x$ can reflect tethering density on the crystal fold surface.

In the equation 6.12, $d_c$ is the thickness of the crystal layer in the block copolymer single crystals. From the overall thickness of the crystals measured by AFM, and thickness of the crystal layer can be obtained from the overall thickness, volume fraction, and crystallinity (see the Chapter IV).

The PEO-$b$-PS copolymers with different compositions are used in this study include EOS3 ($M_n^{PEO} = 11.0 \text{ kg/mol}$, $M_n^{PS} = 4.6 \text{ kg/mol}$), EOS6 ($M_n^{PEO} = 17.0 \text{ kg/mol}$, $M_n^{PS} = 3.0 \text{ kg/mol}$) and EOS7 ($M_n^{PEO} = 40.1 \text{ kg/mol}$, $M_n^{PS} = 7.7 \text{ kg/mol}$). The characterization data of these copolymers are listed in the Table 3.1. The single crystals are grown in dilute solution of amyl acetate or mixed solvent (chlorobenzene/octane = 1:1.1 in weight) at different crystallization temperatures.
6.2 PS brushes in non-interaction regime and onset of chain overcrowding

According to equation 6.12, the slope of $\frac{1}{d_c}$ vs. $T_x$ for block copolymer single crystals is equal to $\frac{\Delta h_f}{2T_d} \frac{1}{\gamma_e^c + \gamma_e^d}$. So the tethered PS chains could affect block copolymer single crystal thickening of when the crystallization temperature increases.

Two extreme cases can be imagined: (1) the $\bar{\sigma}$ is extremely low, therefore, the tethered PS chains have a negligible effect on the thickening of the PEO crystal with crystallization temperature, this is the no-interaction regime of tethered chains; (2) If the $\bar{\sigma}$ is very high, then the PS chains are highly stretched, and this chain conformation destabilizes the PEO crystals. In fact, a single crystal with a sufficiently extended PS conformation cannot grow from solution, so this high $\bar{\sigma}$ cannot be reached with this approach. In the intermediate regime between the two extreme cases above, the repulsive interaction between the tethered neighboring PS chains squeeze the PS chains away from the unperturbed chain conformation. If the crystallization of PEO chains can overcome this unfavorable term, then the single crystal can still form, and the PS chain can affect the crystallization of PEO chains, at the same time, the PS chain conformation is affected by the crystallization of PEO chains.

The plots of $\frac{1}{d_c}$ vs. $T_x$ for EOS6 and EOS7 single crystals grown in amyl acetate are shown in the Figure 6.2. There are several features worthy to be pointed out: (1) The relationship between $\frac{1}{d_c}$ and $T_x$ for EOS 6 copolymer is linear in the $T_x$ range of 21 °C to 38 °C. (2) There are two slopes in the plot of $\frac{1}{d_c}$ vs. $T_x$ for the
EOS7 copolymer. When $T_x$ is higher than 28 °C, the $d_c$ increases at a lower rate.

(3) In the $T_x$ range of 21 °C ~ 28 °C, the slopes of $1/d_c$ vs. $T_x$ are almost the same for the two copolymers.

![Figure 6.2 Plots of $1/dc$ vs. $T_x$ for EOS6 and EOS7 block copolymers. Crystals are grown in amyl acetate.](image)

6.2.1 Non-interaction regime

The PS tethering density ($\sigma$) in PEO-$b$-PS block copolymer single crystals can be calculated by equation 6.13.

$$\sigma = \frac{1}{A^{PS}} = \frac{1}{2A_n^{PS}} = \frac{1}{2(V / d_{PEO})} = \frac{\rho_{PS}^{PEO} d_{PS}^{PEO}}{2(M_n^{PS} / N_a)} = \frac{N_a \rho_{PS}^{PEO} d_{PS}^{PEO}}{2M_n^{PS}}$$  \hspace{1cm} (6.13)
$N_0$ is Avogadro number ($6.02 \times 10^{23} \text{ mol}^{-1}$), $\rho_{PEO} = 1.239 \text{ g cm}^{-3}$. For the sample EOS6 ($M_n^{PEO} = 17.0 \text{ kg mol}^{-1}$) shown in Figure 6.2, $d_c$ increases from 7.8 nm to 11.8 nm, therefore $\sigma$ increases from 0.17 nm$^2$ to 0.26 nm$^2$. Amyl acetate is a good solvent for PS in the experimental temperature range (21 °C to 38 °C), and the observed $R_g^{PS}$ values are independent of temperature in this region. $R_g^{PS}$ is 2.1 nm for a PS block with $M_n^{PS} = 3.0 \text{ kg mol}^{-1}$ in a solution of amyl acetate. Then the reduced tethering density ($\tilde{\sigma}$) can be calculated according to the definition $\tilde{\sigma} = \sigma \pi R_g^2$, and the $\tilde{\sigma}$ of the tethered PS chains on the PEO crystal surface in EOS6 single crystals as shown in the Figure 6.2 ranges from 2.4 to 3.6. The constant slope in the plot of $1/d_c$ vs. $T_x$ implies that the free surface energy of the fold surface is constant. There is no polymer brush transition in the $\tilde{\sigma}$ range of 2.4 to 3.6. No polymer brush transitions were reported for $\tilde{\sigma} < 2.4$ in the literature. Therefore, we expect that there is no polymer brush transitions within the $\tilde{\sigma}$ range from 0 to 3.6. With $\tilde{\sigma} < 3.6$, the tethered PS chains in EOS6 single crystals grown in amyl acetate do not feel the existence of each other, thus they are in the non-interaction regime.

6.2.2 Onset of chain overcrowding

The next question is when the tethered PS chains start to feel their neighboring chains causing the PS chains to begin to be overcrowded on the PEO crystal folding surface. There are two different slopes with one transition point in the plot of $1/d_c$ vs.
for the EOS7 copolymer when the single crystals are grown in amyl acetate in the range of 21 ºC to 38ºC as shown in the Figure 6.2. The transition temperature is at around 28 ºC. Below the transition temperature, the slope in the plot of $1/d_c$ vs. $T_s$ for EOS7 copolymer is very close to that for EOS6 copolymer, which indicates the tethered PS chains cannot feel each other yet. While at $T_s > 28$ ºC, the thickness of PEO crystal in EOS7 single crystals increases at a slower rate compared to that in the EOS6 single crystals, which indicates a larger overall free surface energy ($\gamma_e$ in equation 6.12). Therefore, when $T_s > 28$ ºC, $\gamma_e^a$ starts to affect the thickening of the PEO crystals in EOS7 single crystals.

The $M_n^{PS}$ is 7.7 kg/mol in EOS7, so the $R_g^{PS}$ is 3.7 nm in amyl acetate. Therefore, the $\bar{\sigma}$ of the tethered PS chains in EOS7 single crystals ranges from 3.1 to 4.1 when the $T_s$ ranges from 21 ºC to 37 ºC. At the transition point ($T_s = 28$ ºC), $d^{PEO}$ is 9.1 nm, then the $\bar{\sigma}^*$ is 3.7. This transition point is the onset of chain overcrowding.

This transition point was also tested for another system. Single crystals of EOS3 are grown from a mixed solvent (chlorobenzene/octane=1/1.1 in weight), which is close to a theta solvent of PS. Similarly, the plot of $1/d_c$ vs. $T_s$ for EOS3 single crystals is shown in the Figure 6.3. The thickness of PEO crystal increases from 9.4 nm to 12.0 nm with $T_s$ ranging from 22 ºC to 34 ºC. The $R_g$ of PS ($M_n^{PS} = 4.6$ kg/mol) in the theta solvent is 1.8 nm. Therefore, the $\bar{\sigma}$ of the PS chains in EOS3 single crystals ranges from 3.2 to 4.1 when $T_s$ ranges from 22 ºC to 34 ºC. A transition was found at $T_s = 27.2$ ºC with $d^{PEO} = 11.1$ nm. At this transition point, the $\bar{\sigma}^*$ is 3.8, which is very close to the $\bar{\sigma}$ of the tethered PS chains in EOS7 single crystals.
close to the transition point of the PS tethered chains in amyl acetate (a good solvent for PS).

Figure 6.3 Plots of $1/d_c$ vs. $T_x$ for copolymer (EOS3). Crystals are grown in mixed solvent.

Since the $\sigma$ is solvent independent, it is reasonable that the $\sigma^*$ values for PS brushes in amyl acetate (a good solvent) and mixed chlorobenzene/octane solvent (a theta solvent) are almost identical. It has also been proven that $\sigma^* = 3.7 \pm 0.1$ is the onset of chain overcrowding in PS tethered chains on poly(L-lactide)-b-polystyrene (PLLA-b-PS) copolymer single crystals. Since PS is immiscible with PEO and PLLA, $\sigma^* = 3.7 \pm 0.1$ as the onset of chain overcrowding could be applicable only for these immiscible
systems. Whether or not it can be extended to miscible systems is not known yet at this point.

6.3 Some new research topics based on the single crystals of copolymers

Polymer brushes can be classified into different types based on the composition and chemical structural features of the tethered chains. Four types of polymer brushes are schematically shown in Figure 6.4. With traditional techniques to produce polymer brushes, it is difficult to make uniform polymer brushes with simple features like the flexible homopolymer brushes shown in Figure 6.4a. It is more difficult to prepare the specific polymer brushes shown in Figure 6.4c, Figure 6.4b and Figure 6.4d.

![Figure 6.4](image-url)  
(a) Flexible homopolymer brush  
(b) Mixed homopolymer brush  
(c) Block copolymer brush  
(d) Rigid homopolymer brushes

Figure 6.4 Different types of polymer brushes. (a) flexible homopolymer. (b) mixed homopolymer brushes. (c) block copolymer brushes. (d) rigid homopolymer brushes.
However, these special polymer brushes can be fabricated by growing single crystals of copolymers from dilute solution if we can carefully design the molecular architecture. In order to make mixed homopolymer brushes, three-arm star copolymers with one crystallizable arm can be used to generate mixed homopolymer brushes. For example, if polystyrene-star-polyethylene oxide-star-polymethyl methacrylate (PEO-PS-PMMA) can be synthesized, then, mixed polymer brushes of PS and PMMA can be made by growing single crystals of these star copolymers (shown in Figure 6.5a and Figure 6.5b). If the molecular architecture is changed to a PEO-\(b\)-PS-PMMA triblock copolymer with PEO block at one end of the chain, then block copolymer brushes of PS-\(b\)-PMMA can be constructed after a single crystal of the PEO block is grown (shown in Figure 6.5c and Figure 6.5d). If in a diblock copolymer, one block is crystalline, and the other block is rigid, like polyethylene oxide-\(b\)-polyphenylene (PEO-\(b\)-PP), this block copolymer can be used to fabricate rigid polymer brushes by growing a single crystal of this diblock copolymer (shown in Figure 6.5e and Figure 6.5f).

To demonstrate the ideas described above, single crystals of the PEO-\(b\)-PP copolymer were grown in amyl acetate at 38 °C. A TEM micrograph of the single crystals is shown in Figure 6.6. The ED pattern has a select area aperture inserted. A lamellar crystal is obtained, and the ED pattern of the copolymer crystal is also identical to that of homo-PEO crystal. The rigid polyphenylene blocks are expected to be on the basal surfaces of the PEO crystals, thus these polyphenylene blocks can be considered as rigid polymer brushes. How polyphenylene blocks arrange on the basal surface of PEO crystal is not yet known, but it is worth further studies. On the other hand, the
The morphology of PEO crystals is certainly affected by the polyphenylene blocks. The b-axis of the PEO crystal is largely truncated compared to the square shaped PEO crystals. How and why polyphenylene blocks affect the crystallization behavior of the PEO block is also worthy of further study.

Figure 6.5  Schematic draws of different types of polymer brushes constructed by single crystals of copolymers with different molecular architectures.  (a) PEO-PS-PMMA star copolymer.  (b) single crystal of PEO-PS-PMMA star copolymer mixed homopolymer brushes.  (c) PEO-PS-PMMA triblock copolymer.  (d) single crystal of PEO-PS-PMMA triblock copolymer block copolymer brushes.  (e) PEO-PP diblock copolymer.  (f) single crystals of PEO-PP diblock copolymer.
Figure 6.6  TEM micrograph of single crystal of PEO-\textit{b}-PP grown in amyl acetate at 38 °C. The ED pattern with select area aperture is also inserted.
CHAPTER VII

“CHEMICALLY SHIELDED” PEO SINGLE CRYSTAL GROWTH AND CONSTRUCTION OF CHANNEL-WIRE ARRAY WITH CHEMICAL AND GEOMETRIC RECOGNITIONS ON A SUBMICROMETER SCALE

Uniform polymer brushes, as characterized by a uniform spatial distributed and uniform chain length, can be made through the growth of PEO-b-PS single crystals. The tethering density of PS brushes is also dependent on the composition of the copolymers and/or crystallization conditions. After evaporation of solvent and solidification of the tethered chains, the PEO crystal layer is sandwiched by two PS glassy layers. Those behaviors are more or less from average results of the whole tethered chains on the crystal fold surface. In the presence of solvent, the tethered PS chain can chemically and physically affect the lateral surface of the crystal lamellae, which is the PEO crystal growth front. This phenomenon is the focus of this chapter. More specifically, we studied how the tethered chains affect the PEO crystal growth on the lateral surface. Furthermore, we developed an approach to construct a nano channel-wire array with chemical and geometric recognitions. The materials used in this research are homo-PEO, EOS1, EOS2 and EOS3 as listed in the Table 3.1. The
solvent used to grow single crystals was amyl acetate for homo-PEO, and mixed solvent (chlorobenzene/octane with weight ratio of 1.1:1) for the copolymers.

7.1 Thickness analysis of lamellar single crystals

Step height analysis of the topography images of EOS1, EOS2 and EOS3 single crystals grown at 31 ºC in mixed solvent are shown in the Figure 7.1. The overall thickness of the single crystals, including the PEO crystal layer thickness ($d_{PEO}$) in the single crystals calculated from equation 4.2 and the thickness of PS layer ($d_{PS}$), are summarized in the Table 7.1.

<table>
<thead>
<tr>
<th></th>
<th>$\Delta d$ (nm)</th>
<th>$d_{PEO}$ (nm)</th>
<th>$d_{PS}$ (nm)</th>
<th>$R^p_{g}$ (nm)</th>
<th>$\tilde{\sigma}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>EOS1</td>
<td>6.2</td>
<td>7.9</td>
<td>7.2</td>
<td>3.6</td>
<td>10.9</td>
</tr>
<tr>
<td>EOS2</td>
<td>4.2</td>
<td>8.4</td>
<td>5.2</td>
<td>2.6</td>
<td>7.7</td>
</tr>
<tr>
<td>EOS3</td>
<td>2.1</td>
<td>11.4</td>
<td>2.8</td>
<td>1.8</td>
<td>3.9</td>
</tr>
</tbody>
</table>

One interesting phenomena of the single crystals is that the thickness at the edge of the single crystals is larger than that in the center area of the single crystals. The thickness difference between edge area and surface area ($\Delta d$) is more evident when the molecular weight of PS increases (from EOS3 to EOS1). In the current cases, the $\Delta d$ is 6.2 nm, 4.2 nm and 2.1 nm. The reason for these thicker edges is that after drying the single crystal, the PS blocks are completely separated from the PEO crystal, yet near and
at the (120) edges there are smaller covering areas per PS block on the PEO crystal basal
surface compared with those in the center area.

Figure 7.1  Step height analysis on single crystals of copolymers crystallized at
30°C in mixed solvent  (a) EOS1; (b) EOS2; (c) EOS3

The mixed solvent is close to a theta solvent for PS at 30 °C, and the $R_g$ of PS in
the bulk can be calculated based on theta solvent condition. The tethering density ($\sigma$)
can then be calculated according to equation 6.13. The reduced tethering density (\( \bar{\sigma} \)) can be calculated from its definition \( \bar{\sigma} = \sigma \pi R^2 \). The \( \bar{\sigma} \) of PS chains in the single crystals are also listed in Table 7.1. The plot of \( \Delta d \) versus \( \bar{\sigma} \) is shown in the Figure 7.2. Surprisingly, the single crystals can be formed even at \( \bar{\sigma} = 10.9 \) for the EOS1 sample. At this point, the PS brushes passed the cross-regime and start to be stretched. The \( \Delta d \) increases with chain crowdedness (\( \bar{\sigma} \)) of the PS brushes.

Figure 7.2  Plot of thickness difference at the edge and center location of the single crystal (\( \Delta d \)) versus reduced tethering density of PS chains in the block copolymer single crystals.

Since the values of \( M_n^{PEO} \) in EOS1, EOS2 and EOS3 are 11k g/mol, 8.7k g/mol and 11k g/mol respectively, their average extended chain lengths with a \( 7_2 \) helix are 69.5 nm, 55.0 nm, and 69.5 nm, respectively. Based on the thickness of the PEO crystal
layers in block copolymer single crystals, each PEO block can thus on average form 6, 7, and 9 stems in these three PEO-\textit{b}-PS single crystals. Note that in the PEO crystal lattice, each PEO stem occupies an area of 0.214 nm$^2$, and each PS block tethered on the basal surface of the PEO single crystal thus needs to cover an area of 2.57 nm$^2$, 3.00 nm$^2$, or 3.85 nm$^2$ for these three diblock copolymers, respectively (note that in thermodynamic equilibrium, only 50 percent of the PS blocks are located on one side of the PEO block single crystal). The average tethering densities, $\sigma$, of the PS blocks on the basal surface of the PEO block single crystals for these three copolymers are thus correspondingly 0.39 nm$^{-2}$, 0.33 nm$^{-2}$, and 0.26 nm$^{-2}$. Since the values of $d^\text{PS}$ are 2.8 nm, 5.2 nm, and 7.2 nm for these three diblock copolymers, each PS block of the different $M_n^\text{PS}$'s occupies a volume of 7.2 nm$^3$, 15.6 nm$^3$ and 27.7 nm$^3$, respectively. In the bulk PS samples with these three $M_n^\text{PS}$'s, each PS molecule accordingly occupies a volume of 7.3 nm$^3$, 14.5 nm$^3$, or 26.8 nm$^3$, as calculated from the density data. Therefore, in the dry state of these PS block layers, the PS densities on the top and bottom do not deviate much from that of the bulk.

However, the fact that the PS block layer density is close to the PS bulk density does not imply that in the thin layers the PS blocks possess the same random coil conformation as in the PS bulk state. In the PS bulk having $M_n^\text{PS} = 4.6k$ g/mol, 9.2k g/mol and 17k g/mol, the radii of gyration ($R_g^\text{PS}$) in the bulk (i.e., in the $\theta$ condition) are 1.8 nm, 2.6 nm, and 3.6 nm, respectively.$^{34}$ Examining the $d^\text{PS}$, it is found that in the case of $M_n^\text{PS} = 17k$ g/mol and $M_n^\text{PS} = 9.2k$ g/mol, the $d_{PS}$ is equal to 2 $R_g^\text{PS}$ (7.2 nm and 5.2 nm), indicating that the PS block conformation is close to the random coil in the
bulk. While in the case of $M_n^{PS} = 4.6k$ g/mol, the $d^{PS}$ is only 78\% of the $2R_g^{PS}$ (2.8 nm vs. 3.6 nm), indicating that the PS block conformation in this case is a somewhat collapsed random coil in the PS layers.

7.2 Homo-PEO crystal growth initiated by the copolymer single crystals

We used the PEO-$b$-PS single crystals as seeds to initiate homo-PEO crystal growth on the \{120\} growth fronts in amyl acetate dilute solution (note that amyl acetate is a very good solvent for PS). Figure 7.3 shows a BF TEM image of the self-seeded homo-PEO crystal growth when the seed was formed by the PEO-$b$-PS single crystal with $M_n^{PS} = 4.6k$ g/mol.

![TEM BF image of the homo-PEO crystals on the seed of EOS3 single crystal crystallized at $T_c = 30.0$ °C in amyl acetate dilute solution. Vaporized PE decorated the crystal surface.](image)

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The four \{120\} growth fronts serve as nucleation sites to initiate the homo-PEO crystal growth. The oriented PE crystal rods on the homo-PEO crystal basal surface profile the four \{120\} sectors and the chain-folding directions are along the \{120\} planes. On the other hand, the PE crystal rods are randomly oriented on the PEO-b-PS seed surface. Furthermore, the homo-PEO crystal is also a single crystal which possesses the same crystallographic orientation as the PEO-b-PS single crystal seed.

Figure 7.4 shows a BF TEM image of a seeded homo-PEO single crystal using the $M_n^{PS} = 9.2K$ g/mol PEO-b-PS seed. It is surprising to observe that in this figure the homo-PEO can no longer grow uniformly along the \{120\} growth fronts of the PEO-b-PS single crystal seed. Rather, the four corners initiate the homo-PEO crystal

![TEM image](image_url)

Figure 7.4  TEM BF image of the homo-PEO crystals on the seed of EOS2 single crystal crystallized at $T_c = 30.0 \, ^\circ C$ in amyl acetate dilute solution. Vaporized PE decorated the crystal surface.
growth first, and then, some sites along the edges initiate growth at later times as judged by their crystal sizes. Furthermore, the four corner PEO single crystals have the same size (isochronal nucleation). They seem to be coplanar with the parent crystal (the PEO-\(b\)-PS crystal), since these four crystals do not grow toward the parent crystal. The PE decoration indicates that these individual homo-PEO crystals are facetted single crystals with \{120\} sectors. The chain-folding direction is also along the \{120\} planes. This reveals that although each homo-PEO crystal grows independently at different times, the crystallographic orientation of the seeds is preserved.

When the \(M_n^{PS}\) of the PEO-\(b\)-PS single crystal increases to 17k g/mol, the homo-PEO crystal growth can only be initiated at the four corners as observed in a BF TEM image (Figure 7.5). The \{120\} edges can no longer provide any nucleation sites.
for the homo-PEO crystal growth. Moreover, among these homo-PEO single crystals at the four corners, the one at the right up corner is bigger than the others, indicating different initiation times of the nuclei. These homo-PEO single crystals also grow toward the parent crystal due possibly to screw dislocations, and the growth back toward the parent crystal is small compared to the outward growth.

By comparing this figure with the observations in Figures 7.3 through 7.5, it is qualitatively concluded that increasing the \( M_n^{PS} \) causes the PS blocks in the PEO-\( b \)-PS single crystals to increasingly prevent the formation of nucleation and growth sites for the homo-PEO molecules on the \{120\} growth fronts.

7.3 How do the PS blocks shield the homo-PEO crystal growth

Based on experimental observations, only those tethered PS blocks which are near and at the (120) growth fronts with a long enough \( M_n^{PS} \) and the with a high enough tethering density can be laterally displaced (overcrowded) by their neighbors.\(^{296}\) The lateral repulsion is generated by the squeeze of neighboring tethered PS blocks and can accumulate to become high enough to push the PS blocks at the edges and corners to advance beyond the PEO crystal growth front. This is very similar to the “Skoulios effect”.\(^{305,306}\) The PS blocks are thus able to prevent further crystallization of the homo-PEO (the “shielding” effect). However, we put the seeds back to the PEO-\( b \)-PS solution in amyl acetate, the PEO-\( b \)-PS slowly grows again on the seeds. Why do the tethered PS block layers not stop the nucleation and growth of the PEO-\( b \)-PS? We believe that this is critically dependent upon how the local chemical environment at the
crystal growth front is constructed, and the molecular interactions of the individual
PEO-\textit{b}-PS and homo-PEO at the growth fronts.

Since the PEO-\textit{b}-PS crystallization took place in amyl acetate which is a very
good solvent for PS, the PS blocks tethered on the basal surface of the PEO block single
crystal must have conformations that are significantly more expanded then those in the
chrolobenzene/octane mixed solvent (which is close to the \(\theta\) condition). Quantitatively,
we use the simplified concept of reduced tethering density \(\bar{\sigma} = \pi R_g^2 \sigma\) to illustrate how
close the neighboring tethered PS chains are. When \(M_n^{PS}\) is 4.6K g/mol (EOS3), the
\(\bar{\sigma}\) of the tethered PS blocks in amyl acetate is 8.9. This value is higher than the value
of 3.7, which is the onset of PS block overcrowding. However, further homo-PEO
crystal growth is not shielded against on the edges and corners of the PEO-\textit{b}-PS single
crystal grown from the \(M_n^{PS} = 4.6k\) g/mol. This indicates that, in order to prevent the
homo-PEO crystal growth on the PEO-\textit{b}-PS seeds, the PS blocks require a much greater
overcrowding and much stronger repulsion by neighboring PS blocks than those provided
at the onset of overcrowding \(\bar{\sigma}^*\).

When the \(M_n^{PS}\) increases to 9.2k g/mol (EOS2), the \(\bar{\sigma}\) value is 17, and for the
EOS3 copolymer with \(M_n^{PS} = 17k\) g/mol, the \(\bar{\sigma}\) is 24. These two \(\bar{\sigma}\) values may be
within the highly stretched regime of the PS brushes. By increasing the \(M_n^{PS}\), the
repulsion force along the [120] growth directions becomes increasingly severe. The
repulsion can only be partially released at the edges and corners of the single crystals by
expanding themselves outward along the [120] directions when the PS blocks are tethered
near and at the \{120\} edges and corners.
However, the PS blocks do not physically seal the PEO growth fronts in solution. Instead, the PS block layers advance ahead of the PEO growth fronts, as illustrated by the cartoon in Figure 7.6. In the case of PEO-\textit{b}-PS crystallization, the PS blocks do not “welcome” the PEO blocks to be absorbed onto the PEO crystal growth front, but the PS blocks in the crystallizing PEO-\textit{b}-PS molecules are compatible with the tethered PS blocks on the top and bottom of the PEO single crystal surface. The PS blocks are thus

![Figure 7.6](image)

(a)

(b)

Figure 7.6  (a) Schematic illustration of the PS block layer at the edge of the “sandwiched” crystal in solution. The PS blocks are pushed by their inner neighbors toward the [120] growth direction of the edges to form a PS block layer ahead of the PEO crystal growth fronts. (b) The bottom carton represents the side view of the PEO-\textit{b}-PS crystal.
able to drag the PEO blocks to the growth front. The existing PS blocks in the PEO-\emph{b}-PS molecules, hence, play an active role to assist the PEO blocks crystallizing onto the \{120\} growth fronts. This cannot take place with the homo-PEO on its own. Only at the sites where the $\bar{\sigma}$ of the PS blocks is relatively small (such as the low $M_n^{PS} = 4.6\, \text{g/mol}$) can the homo-PEO absorb onto the PEO growth front and crystallize. This indicates that the local chemical environment, i.e., the “chemical shielding” at the growth front, does influence the PEO crystal growth and its kinetics, and this “shielding” effect becomes increasingly severe when the $M_n^{PS}$ increases as shown in Figures 7.3-7.5.

The question that follows is why the nucleation of the homo-PEO is less restricted at the corner than along the edge of the PEO-\emph{b}-PS single crystal? Assuming the $\bar{\sigma}$ values of the tethered PS blocks along the edges and at the corners are identical, the overcrowded PS blocks at the edges may be pushed by their inner neighboring PS blocks toward the [120] growth direction that is perpendicular to the edge. However, the tethered PS blocks at the corners have two choices of where to expand since two edges merge at one corner. This results in a relatively small expansion of the PS block layers at the corners. Consequently, the homo-PEO molecules are relatively less inhibited from growing at those corners. On the basis of this analysis, it is also evident that the solvent used in the crystallization should also affect the “chemical shielding” behavior since different solvents for the PS blocks generate different hydrodynamic volumes of the tethered PS blocks. This will change the value of $\bar{\sigma}$ and lead to various degrees of repulsion. We will report our ongoing research along this direction in the near future.
7.4 Alternating crystallization of homo-PEO and copolymers to fabricate channel-wire arrays with chemical and geometrical recognition

For homo-PEO single crystals, the $\sigma$ of PS is 0 since there is no PS chain on the surface, then there should be no “chemical shielding” effect on the crystal growth of copolymers. This deduction is reasonable and it is proven by the experimental data. We use homo-PEO crystal seeds to initiate the crystallization of copolymers (EOS1, EOS2 and EOS3). The data is shown in the Figure 7.7. The four $\{120\}$ fronts of the PEO crystal seeds serve as nucleation sites to initiate the crystallization of copolymers.

![Figure 7.7 TEM BF image of the copolymer crystals on the seed of homo-PEO single crystal crystallized at $T_c = 22.0$ °C in amyl acetate dilute solution. (a) homo-PEO crystals bounded with EOS3 crystals. (b) homo-PEO crystal bounded with EOS2 crystal. (c) homo-PEO crystal bounded with EOS1 crystal.](image)
A direct result of this study is a new approach to fabricate channel-wire arrays having chemical and geometric recognitions via the alternating crystal growth of PEO-\( b \)-PS with \( M_n^{PS} = 4.6 \text{ k g/mol} \) and a homo-PEO using the lateral \{120\} surfaces of the preexisting crystals as seeds in dilute solution. Figures 7.8 and 7.9 show examples of this type of array in both BF TEM and AFM images, respectively. A SAED pattern of the [001] zone is also inserted in Figure 7.8, again indicating that the PEO chains in this alternating crystal possess a parallel orientation with respect to the basal surface normal. In these two figures, there is an alternating thickness change to achieve the geometric recognition. This is because the crystal thickness of the homo-PEO is thinner to form the channels (troughs), while the PS-\( b \)-PEO part is thicker to form the wires (crests). The PS block crests provide a periodic thickness change of 2.8 nm.

Figure 7.8 TEM BF image of a single crystal constructed by alternating PEO-\( b \)-PS and homo-PEO growths. The inset is a SAED pattern of this crystal in the correct orientation.
Figure 7.9  AFM height image of a single crystal constructed by alternating PEO-\textit{b}-PS and homo-PEO growths. (a) 3-D topography image.  (b) Height analysis along the line in (a).
To precisely control the spacing size, knowledge of the growth rates of both homo-PEO and PEO-\textit{b}-PS are critical as well as the crystallization times, concentrations, and solvent types. The lowest spacing so far reached using this fabrication is 50 nm, as shown in Figure 7.10.

![AFM height image of a single crystal constructed by alternating PEO-\textit{b}-PS and homo-PEO growths with the smallest spacing of 50 nm.](image)

Figure 7.10  AFM height image of a single crystal constructed by alternating PEO-\textit{b}-PS and homo-PEO growths with the smallest spacing of 50 nm.

This channel-wire array also possesses alternating chemical recognition. Since homo-PEO is hydrophilic and the PS is hydrophobic, we are able to create an environment with alternating hydrophilic channels and hydrophobic wires with controlled spacing and thicknesses on the array surface. This may provide a new way to investigate directional absorption, diffusion, and immobilization of biomacromolecules.
on the array surface. It is also possible to increase the dielectric contrast of the arrays by selectively staining the polymers using RuO4 or other reagents, as shown in Figure 7.11. Common understanding has been that both PS and PEO can be stained via RuO4 oxidation, and staining PEO is generally viewed to be easier compared to PS. It was interesting to find that the staining power of RuO4 toward PEO and PS blocks is dependent upon the environment. When the environment has a high humidity (created by a high vapor pressure), PEO blocks are stained first, but when the environment is dry with low humidity (the sample and staining solution were protected in dry nitrogen), the PS blocks are stained first.

![Figure 7.11](image1.png)

Figure 7.11 Two TEM BF images of the crystals with RuO4 staining: (a) under a wet environment in which the PEO blocks were stained first (b) under a dry environment in which the PS blocks were stained first.
In summary, the PEO-\(b\)-PS diblock copolymers can grow “sandwiched” single crystals in dilute solution. When these single crystals are used as seeds to further grow homo-PEO, depending on the \(M_n^{PS}\) and \(\tilde{\sigma}\) of the PEO-\(b\)-PS, the PS block may act as “chemical shielding” layers to hamper or even prevent the homo-PEO crystal growth. When \(M_n^{PS} = 4.6\text{ k g/mol}\), the PS blocks are overcrowded as evidenced by \(\tilde{\sigma} = 8.9\). However, all the edges and the corners of the PEO block single crystals can serve as nucleation sites for the further growth of the homo-PEO. This indicates that the “chemical shielding” effect requires a much stronger overcrowding than the onset of overcrowding at \(\tilde{\sigma}^* = 3.7\). By increasing the \(M_n^{PS}\) to 9.2k g/mol, the nucleation sites are limited to the corners and certain locations along the edges, and finally, only the corners can act as the nucleation sites for the further growth of the homo-PEO when the \(M_n^{PS} = 17\text{ k g/mol}\). This can be illustrated by an increase of the \(\tilde{\sigma}\) value from 17 to 24. Therefore, the tethered PS blocks in amyl acetate (a very good solvent) experience very severe overcrowding and strong repulsion between the PS blocks and their neighbors. The tethered PS blocks at the edges are thus pushed by their inner neighbors toward the [120] growth direction of the growth fronts to form a PS layer ahead of the PEO crystal fronts. This advancement of the PS blocks in solution stops the growth of the homo-PEO, yet allows the further growth of the PEO-\(b\)-PS. When the single crystals of these PEO-\(b\)-PS copolymers are dried, the PS blocks solidify. The PS blocks at the edges and the corners possess less area for each PS block to cover, and therefore, the PS layers at the edges and the corners are slightly thicker compared to those in the center areas of the single crystals. As a direct result, channel-wire arrays on the submicrometer
length scale can be prepared via alternatively growing PEO-\textit{b}-PS and homo-PEO crystals. This type of single crystal possesses alternating thicknesses and alternating hydrophobic hydrophilic environments.
Polymer crystallization has been a topic of discussion for the past 50 years, and it will continue to be an active research topic in the future since chemists keep making new polymers. Traditional polymer crystallization research is more or less focused on the morphology and structure of the polymer crystals, which are certainly important. This study applies single crystals of amorphous-crystalline polymers as ideal models for some fundamental and application studies beyond the realm of classical polymer crystallization.

In this study, poly(ethylene oxide)-b-polystyrene (PEO-b-PS) diblock copolymers with different molecular weights and compositions were chosen as experimental materials. The single crystals of these copolymers have been grown from dilute solution. The single crystals of these crystalline-amorphous diblock copolymers are used as ideal models: (1) to construct nano films; (2) to construct nano confined environments for crystallization; (3) to generate uniform and adjustable polymer brushes; (4) to construct chemical and physical conditions for crystal growth. Then these models are utilized: (a) to study the crystallization behavior of one PEO nano-layer confined in between two PS layers (a unique, defects free confinement geometry); (b) to determine the transition points between polymer brush regimes; (c) to learn about the influence of the chemical
and physical environment at the crystal front during crystal growth; (d) to construct nano-wire arrays with chemical and geometrical recognitions which have potential application in nanotechnology.

By carefully designing a PEO-\textit{b}-PS diblock copolymer (for example $M_n^{PS} = 17 \text{k g/mol}$, $M_n^{PEO} = 11 \text{k g/mol}$) where the glass transition temperature of the PS layer ($T_g^{PS}$) in the single crystal is higher than the melting temperature of PEO layer ($T_m^{PEO}$), the melting and crystallization of the PEO layer (thickness is 7.9 nm) is confined in between two PS layers (thicknesses is 7.2 nm). Since the PEO layer is a single crystal, the defects in the PEO nano-layer are limited to the defects in the crystal lattice, and do not contain the morphological defects found in bulk samples. Results have shown that the PEO crystal orientation in the confined nano-layer strongly depend on the recrystallization temperature ($T_{rc}$).

PS brushes can be generated by growing single crystals of diblock copolymers in dilute solution. The PS bushes by this new approach are uniform including chain length and distribution. The tethering density of the PS brushes can be adjusted by changing the crystallization temperature. Therefore, the transition between polymer brushes regimes may be observed experimentally. It has been found that the PS brushes start to overcrowd (the onset of chain overcrowding) when the reduced tethering density of the PS brushes is $3.7 \pm 0.1$, and this value is independent of the solvent.

In the solvent, the tethered PS chains can also chemically and physically affect the lateral surface of the crystal lamellae, which is the crystal growth front. Therefore, crystal growth can be affected by the tethered PS chains. The diblock copolymer single
crystals are then used as seeds to grow homo-PEO single crystals in amyl acetate. By changing the PS chain length, the tethering density of the PS brushes change. As the $M_n^{PS}$ of the block copolymers increases ($M_n^{PEO}$ is relative with 11k g/mol as the reference value), the homo-PEO crystal growth is increasingly hampered along the $\{120\}$ lateral surface of the PEO-$b$-PS single crystals. When the $M_n^{PS}$ of the block copolymer is 17k g/mol, only the four corners of the PEO-$b$-PS single crystal can still act as nucleation sites. The four edges are chemically “shielded” by the tethered PS blocks. This indicates that increasing the $M_n^{PS}$ leads to a higher reduced tethering density of the PS blocks on both basal surfaces of the PEO-$b$-PS single crystals. The repulsion generated among the tethered PS blocks caused the PS blocks located near and at the edges to advance along the [120] direction. Novel channel-wire arrays on the submicrometer length scale having chemical and geometric recognitions can be fabricated via alternating the crystal growth of PEO-$b$-PS and homo-PEO. This fabrication provides robust, and precisely controllable arrays with spacings down to 50 nm.

Thus this study opens new research topics in the polymer crystallization field, and these research topics are fundamental with a direct impact on applications using polymer brushes. That is the contribution of this study to the science of polymer crystallization.
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