

CHAPTER 4

GROWTH OF POLY(ϵ -CAPROLACTONE) CRYSTALS IN LANGMUIR FILMS AT THE AIR/WATER INTERFACE

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4.1. Abstract

Surface pressure induced crystallization of poly (ϵ -caprolactone) (PCL) from a metastable region of the surface pressure area-per monomer (Π -A) isotherm in Langmuir monolayers at the air/water interface (A/W) has been captured in real time by Brewster angle microscopy (BAM). Morphological features of PCL crystals grown in Langmuir films during the compression process exhibit four fully developed faces and two distorted faces. During expansion of the crystallized film, polymer chains slowly detach from the crystalline domains and diffuse back into the monolayer as the crystals "melt". Typical diffusion-controlled morphologies are revealed by BAM during the "melting" process as the secondary dendrites "melt away" faster, i. e. at a higher surface pressure than the principal axes. Electron diffraction on Langmuir-Schaefer films suggests that the lamellar crystals are oriented with the polymer chain axes perpendicular to the substrate surface, while atomic force microscopy reveals a crystal thickness of ~ 7.6 nm.

4.2. Introduction

Physical properties of polymers confined in thin or ultrathin films have attracted widespread interest due to their potential applications in semiconductors,^{145, 146} antireflection coatings,¹⁴⁷ electrochemical devices,¹⁴⁸ and drug delivery systems.¹⁴⁹ With decreasing film thickness, polymers in confined geometries exhibit differences from bulk behavior with respect to properties such as molecular mobility,^{4, 5} the glass transition temperature,^{6, 7} chain orientation,⁸⁻¹⁰ etc. In particular, the confinement of semicrystalline polymers in thin films may alter the transport properties of chain segments to the growth fronts of crystallizing lamellae, resulting in changes in growth rates, crystallinity, morphologies and melting behavior of crystals.¹⁰⁻²³ Thus, crystallization in thin films can provide an opportunity for the study of polymer chain organization in a confined geometry.¹⁰⁻²³

Poly (ϵ -caprolactone), a model semicrystalline polymer like polyethylene,¹¹³ is a hydrophobic polyester with a bulk glass transition temperature of $T_g \sim -60^\circ\text{C}$, a melting point of $T_m \sim 50^\circ\text{C}$, excellent biocompatibility, and low toxicity. In the past decade, PCL based systems have attracted considerable interest for controlled-release drug delivery and as scaffolds for tissue engineering that require a fundamental understanding of PCL's degradation mechanisms and crystallization properties.^{72, 73} Previous studies of PCL's crystalline properties include: shear induced crystallization,¹ molar mass dependent crystallization,² and highly oriented surface induced crystallization.³ Spherulitic crystal structures were commonly observed in these cases. The isothermal crystallization of PCL in PCL/poly (vinyl chloride) (PVC) spin-coated films with various thicknesses has recently been reported.^{8, 10} Studies by Mareau *et al.* indicated that isothermal

crystallization rates decrease when the film thickness is less than 1 μm and this behavior is independent of the composition of the blend or the crystallization temperature. Electron diffraction studies of PCL isothermally crystallized in ultrathin films (1-200 nm) suggest a flat-on orientation of lamellae relative to the substrate surface, while diffusion-controlled growth morphologies were observed for film thicknesses less than 15 nm.⁹ For the aforementioned studies, the thin films of PCL or its blends were usually prepared on solid substrates, such as silicon wafers, glass or mica by spincoating. The film thicknesses were usually adjusted by varying the concentrations of the spincoating solutions. At the air/water (A/W) interface, PCL Langmuir films formed at low surface pressures are uniform monomolecular layers, which can be thought of as the thinnest possible uniform film of PCL. The ultrapure water surface minimizes surface defects compared to solid substrates, which may affect the nucleation mechanism. While crystallization of semicrystalline polymers in thin films on solid substrates have been widely studied,¹⁰⁻²³ the nucleation and growth of PCL crystals grown in Langmuir monolayers at the A/W interface represent a unique model system. This study provides a detailed examination of the nucleation and growth of linear flexible PCL in Langmuir monolayers at the A/W interface. *In situ* Brewster angle microscopy (BAM) studies were carried out simultaneously during hysteresis experiments to monitor both crystallization and “crystal melting” processes of PCL in monolayers. Analyses of surface pressure (Π) and the static elastic moduli (ϵ_s) in terms of surface area per monomer (A) indicate possible conformational changes and phase transitions occurring in PCL Langmuir films at the A/W interface.

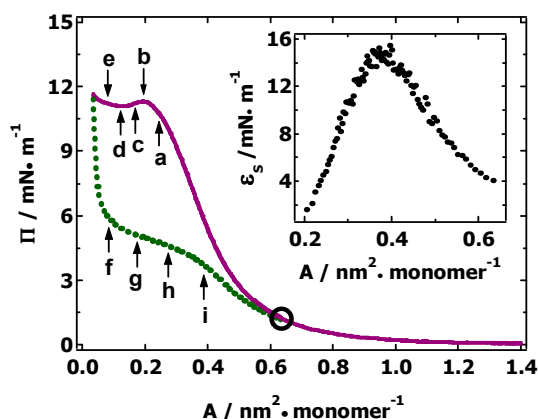


Figure 4.1. Π -A isotherm of PCL obtained at 22.5 °C during compression (solid line) and expansion (dashed line) at $0.010 \text{ nm}^2 \cdot \text{monomer}^{-1} \cdot \text{min}^{-1}$. The circle indicates the starting and end points of the hysteresis loop used for crystallization studies. A second spreading under more dilute conditions was used to measure the isotherm out to $\Pi \sim 0 \text{ mN} \cdot \text{m}^{-1}$. The letters on the graph correspond to the BAM images in Figure 4.4. The inset shows the static elastic moduli, ϵ_s , as a function of A during film compression.

4.3. Results and Discussion

Figure 4.1 shows a Π -A isotherm of PCL with a weight average molar mass of $10 \text{ kg} \cdot \text{mol}^{-1}$. The Π -A isotherm was measured at 22.5 °C with a compression and expansion rate of $\sim 0.010 \text{ nm}^2 \cdot \text{monomer}^{-1} \cdot \text{min}^{-1}$. Due to our desire to grow larger crystals, PCL was spread to an initial Π value of $1.2 \text{ mN} \cdot \text{m}^{-1}$ ($A \sim 0.63 \text{ nm}^2 \cdot \text{monomer}^{-1}$) corresponding to a homogeneous liquid-expanded (LE) monolayer for the hysteresis experiment. A separate experiment was carried out to obtain the compression isotherm out to $\Pi \sim 0 \text{ mN} \cdot \text{m}^{-1}$. The LE regime reflects the amphiphilic nature of PCL molecules as most of carbonyl groups are able to adsorb to the water subphase with the methylene groups preventing the molecules from dissolving into the subphase. Upon compression of the film, there is a

gentle rise in Π and an increase in the film's static elastic modulus, defined as $\varepsilon_s = -A(d\Pi/dA)_T$, until ε_s reaches a maximum value of $\sim 15 \text{ mN}\cdot\text{m}^{-1}$ at $A \sim 0.37 \text{ nm}^2\cdot\text{monomer}^{-1}$ as seen in the inset of Figure 4.1. At this point, it is likely that some of the carbonyl groups of the polymer backbone start to leave the A/W interface. Looking at the repeat unit structure in Figure 4.2a, and noting that “two-dimensional” (2D) monolayers of methyl esters of fatty acids become unstable at $A \sim 0.185 \text{ nm}^2\cdot\text{monomer}^{-1}$, and undergo a 2D $\rightarrow$ 3D transition upon further compression, the structure depicted in Figure 4.2b (bottom) ideally describes the monolayer structure corresponding to the maximum ε_s value at $A \sim 0.37 \text{ nm}^2\cdot\text{monomer}^{-1}$. Further compression leads to a nearly linear decrease in ε_s corresponding to the collapse of the structure in Figure 4.2b (bottom). Upon further compression, the greater rotational freedom of ester linkages around the polymer backbone could allow the formation of hairpin turns thereby allowing the chain to fold back and forth in a similar fashion to the folded chain structure of polyethylene single crystals formed from dilute solution.^{106, 115} Finally, the observable nucleation event from a “supersaturated solution,” i.e. an over-compressed polymer monolayer, was captured by BAM and corresponds to point (a) on the Π -A isotherm. These features are also consistent with the orthorhombic unit cell parameters of PCL crystals determined from X-ray data ($a = 0.748 \pm 0.002 \text{ nm}$, $b = 0.498 \pm 0.002 \text{ nm}$, $c = 1.726 \pm 0.003 \text{ nm}$).¹¹²⁻¹¹⁴ During compression to point (a), BAM shows the monolayer is homogeneous. Upon further compression from point (a) to (b) in Figure 1, the number of stable nuclei increases and crystals grow around the stable nuclei. The kink at point (b) on Figure 1, called a dynamic “collapse point” ($\Pi_c \sim 11.3 \text{ mN}\cdot\text{m}^{-1}$, $A_c \sim 0.20 \text{ nm}^2\cdot\text{monomer}^{-1}$), corresponds to the transport of polymer chains from the monolayer to

crystal lamellae as seen in Figure 4.2b (top). Thus, crystal growth becomes a dominant contributor to the phase behavior of PCL Langmuir films during the following plateau region. The above conclusion is further supported by the observation that the plateau region, corresponding to crystal growth, can be lengthened if one spreads to a higher surface pressure prior to compression.

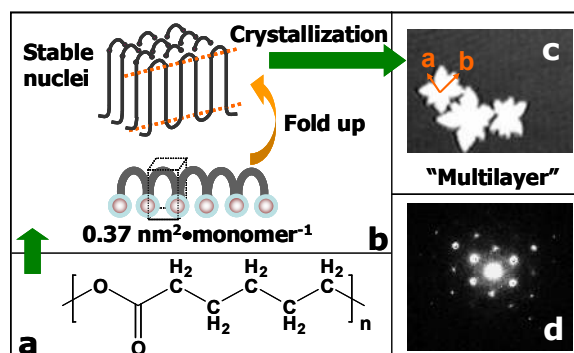


Figure 4.2. Schematic diagram of PCL crystallization at the A/W interface: (a) the PCL repeat unit, (b) a condensed monolayer prior to nucleation at $A \sim 0.37 \text{ nm}^2 \cdot \text{monomer}^{-1}$ that ultimately forms folded chain lamellae, (c) PCL crystals (this $1.28 \times 0.96 \text{ mm}^2$ image was seen upon compression), and (d) electron diffraction pattern of PCL crystals after LS transfer onto a copper grid.

Figure 4.2c exhibits the morphology of a PCL crystal grown in the plateau region. The development of symmetrically distorted hexagonal shapes could be caused by the reduced diffusion coefficient of polymer chains on the water surface. For films with thicknesses in the range of $1 \sim 6 \text{ nm}$, dendritic morphologies are observed and the shapes of the lamellar crystals are distorted with the disappearance of two of the four $\{110\}$ sectors.⁹

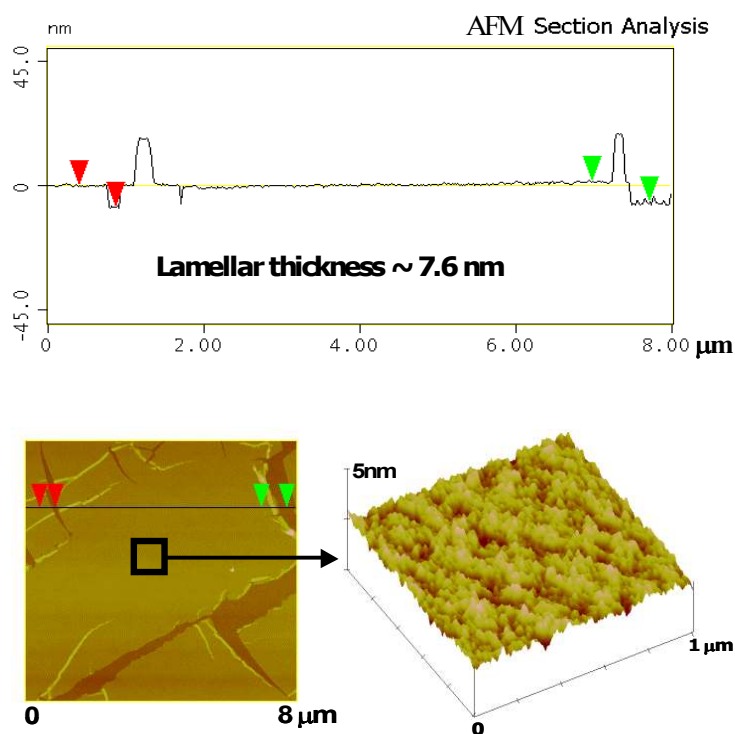


Figure 4.3. AFM images for PCL crystals on Si substrates spincoated with polystyrene. Cross-section analysis performed on the AFM height image at the edge of the crystal yields a lamellar thickness of ~ 7.6 nm.

Interestingly, atomic force microscopy images on LS films of PCL crystals formed at the A/W interface reveal a lamellar thickness of ~ 7.6 nm. One example of a AFM cross-section analysis used to deduce the crystal thickness is provided in Figure 4.3. This thickness suggests that the lamellar thicknesses of PCL crystals grown in Langmuir monolayers at the A/W interface are consistent with the lamellar thickness for flat-on PCL lamellae grown in spincoated films, even though the shear forces resulting in the distortion of hexagonal crystals at the A/W interface are different from those on a solid substrate.⁹ These factors lead to the novel morphology of PCL crystals observed in

Langmuir films as shown in Figure 4.2c. More details regarding crystal morphology are discussed later in this paper and morphologies are better illustrated in Figure 4.4. At the A/W interface, the growth of flat-on lamellae is confirmed by the electron diffraction pattern of PCL crystals transferred from the A/W interface by the LS method as seen in Figure 4.2d.

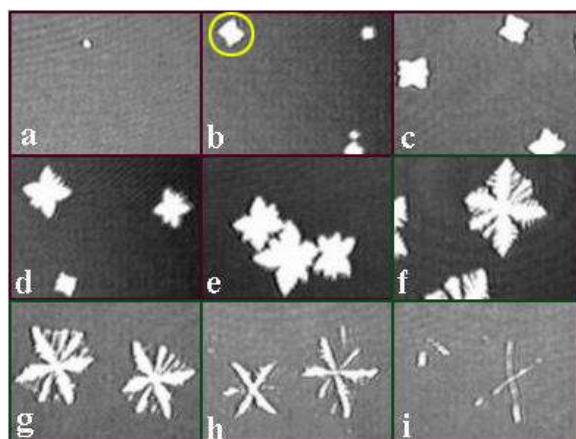


Figure 4.4. BAM images obtained during a hysteresis experiment at 22.5 °C with a compression and expansion rate of $\sim 0.010 \text{ nm}^2 \cdot \text{monomer}^{-1} \cdot \text{min}^{-1}$. Compression ($\text{Å} / \text{nm}^2 \cdot \text{monomer}^{-1}$): (a) 0.243, (b) 0.200, (c) 0.170, (d) 0.120, and (e) 0.080; and Expansion ($\text{Å} / \text{nm}^2 \cdot \text{monomer}^{-1}$): (f) 0.082, (g) 0.173, (h) 0.272, and (i) 0.387. All images are $1.28 \times 0.96 \text{ mm}^2$.

Based on the previous paragraph, the chain folds occur at the A/W interface and the crystals grow parallel to the surface with further compression. The apparent mechanism for the crystal growth at the A/W interface could be analogous to the nucleation and growth mechanism proposed by Vollhardt *et al.* for small molecule amphiphiles.^{68, 150} As seen in Figure 4.4b (circled), $10 \text{ kg} \cdot \text{mol}^{-1}$ PCL already shows anisotropic crystal growth at

very early stages. As the crystals continue to grow, this anisotropy becomes more apparent (Figure 4.4e), ultimately revealing the dendritic nature of the crystals during the early stages of expansion. The expansion process corresponds to crystal melting (Figure 4.4f). In bulk systems, dendritic structures frequently arise during crystallization from a failure to dissipate the latent heat of crystallization. However, as Vollhardt *et al.* pointed out, direct coupling of the monolayer to the subphase at A/W alleviates this problem and dendritic crystals arise from a difference in the rate of crystallization compared to the diffusion of new material to the growing crystal front.^{38, 39}

Even though the PCL crystals have irregular shapes (Figure 4.4a-e), dendritic structures are not observed during compression. However, dendritic crystal morphologies are clearly observed during the analogous crystal "melting" process. In order to observe this, the compressed film is expanded (dashed curve in Figure 4.1) and BAM is used to image the "melting" process accompanying the large hysteresis loop. During the early stage of expansion, the arrangements of PCL chains in the crystals undergo rapid relaxation as the external forces which were applied during compression are removed. The meta-stable crystals formed during compression become loose and the polymer chains attached on the unstable edges diffuse along growth fronts, leading to the dendritic morphologies as seen in Figure 4.4f. Upon further expansion, parts of PCL chains apparently fall from the unstable edges back to the water surface, which is analogous to the crystal melting process as revealed in Figure 4.4f to 4.4i. The lighter secondary dendritic branches "melt away" faster than the principal axes. At lower surface pressures (analogous to a higher melting temperature) the principal axes also melt. The contrast between the principal axes and the secondary dendritic branches is consistent with the contrast mechanism for

BAM where both thickness and refractive index differences contribute to the reflectivity of p-polarized light. Hence, even though the macroscopic measure of hysteresis is large (Π -A isotherm), the microscopic details (BAM) suggest crystal "melting" is still transport-limited. Nonetheless, the melting process is not completely reversible. During experiments for multiple cycles, the monolayer was first compressed to a trough area of 25 cm^2 and then expanded to a trough area of 485 cm^2 . After waiting for 5 min, the monolayer was compressed again to the same trough area of 25 cm^2 and re-expanded to a trough area of 485 cm^2 at the same compression rate of $8 \text{ cm}^2 \cdot \text{min}^{-1}$. BAM was used to monitor the morphological change for both hysteresis cycles. Representative images obtained at three different surface concentrations during both the first and second compression step are shown in Figure 4.5. Smaller crystals are observed during the second compression process. This feature means that the original state of the PCL monolayer at the A/W prior to the first compression of the film is not recovered at the end of the first hysteresis loop. Some locally well-ordered structures that are too small to be observed by BAM must remain at the end of the first hysteresis cycle. The presence of these locally well-ordered aggregates provide more nucleation centers during the second compression step relative to the first compression step resulting in smaller crystals. In addition, increasing the compression rate during constant compression experiments leads to more and smaller crystals as seen in Figure 4.6. Increasing the compression rate corresponds to an increase in the degree of undercooling as structural relaxation is hampered at higher compression rates. Since nucleation from the supersaturated monolayer with a higher degree of undercooling could be easier, the number of nuclei

formed increases with increasing compression rate. Such an observation is consistent with the nucleation and growth mechanism of PCL crystals grown in bulk.

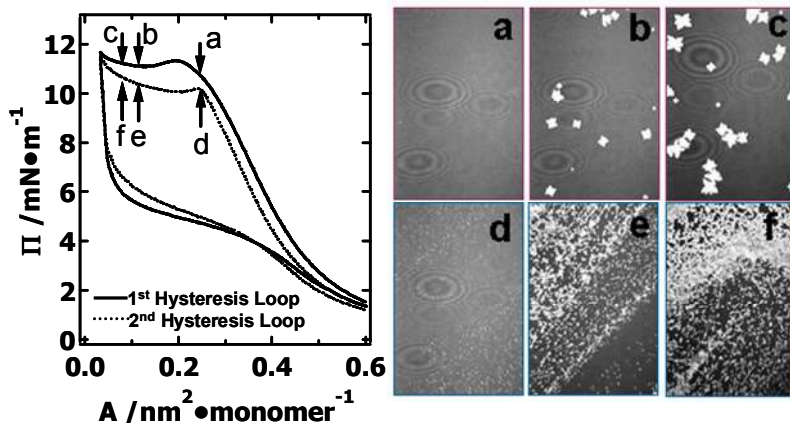


Figure 4.5. BAM images of PCL ($10 \text{ kg} \cdot \text{mol}^{-1}$) crystals during multiple hysteresis loops. The BAM images were obtained during the first and second hysteresis cycles at a constant compression rate of $8 \text{ cm}^2 \cdot \text{min}^{-1}$ and $T = 22.5 \text{ }^\circ\text{C}$. The $3.2 \times 4.8 \text{ mm}^2$ BAM images correspond to surface concentrations of (a) 0.24 , (b) 0.11 , and (c) $0.08 \text{ nm}^2 \cdot \text{monomer}^{-1}$ for the initial compression of the film, and (d) 0.24 , (e) 0.11 , and (f) $0.08 \text{ nm}^2 \cdot \text{monomer}^{-1}$ during the 2nd compression step.



Figure 4.6. Compression rate dependence of crystal growth in Langmuir monolayers at $22.5 \text{ }^\circ\text{C}$. BAM images were obtained at compression rates of: (a) 0.010 , (b) 0.013 , and (c) $0.026 \text{ nm}^2 \cdot \text{monomer}^{-1} \cdot \text{min}^{-1}$ for $A \sim 0.08 \text{ nm}^2 \cdot \text{monomer}^{-1}$. All images are $1.28 \times 0.96 \text{ mm}^2$.

4.4. Conclusions

In summary, "crystallization" processes for linear flexible PCL from Langmuir monolayers at the A/W interface have been captured in real time by BAM. Moreover, the lamellar thicknesses of PCL crystals grown in monolayers correspond to the thickness for the crossover from single crystal morphologies to dendrites observed by Mareau *et al.* in spincoated PCL films with film thicknesses less than 6 nm.⁹ Electron diffraction analysis indicates that the polymer chains in the lamellae are oriented with the polymer chain axis perpendicular to the substrate surface. The occurrence of crystallization during the "collapse" of PCL monolayers could make the system particularly suitable for studying the effects of substrate-film interactions on crystal morphology and testing models for crystallization kinetics in thin films. Furthermore, during expansion of crystallized films, the polymer chains slowly detach from crystalline domains and diffuse back into the monolayer. Typical transport-limited growth morphologies are revealed during expansion. The secondary dendrites "melt away" faster than the principal axes are able to re-dissolve at higher Π , analogous to a "lower melting temperature". The morphologies and preferred direction of crystal melting were clearly revealed in real time by BAM, suggesting further insight into the crystallization of Langmuir films could be studied through hysteresis experiments.