

## CHAPTER 1

### OVERVIEW OF THESIS

One of the most intriguing subjects in polymer physics is the crystallization of semicrystalline polymers from a random-coil state to a well-ordered crystalline state. The crystallization process of polymers commonly occurs far from equilibrium conditions and strongly depends on processing conditions such as the crystallization temperature, shear deformation, etc. as well as the initial state of polymer samples from which nucleation starts. Like polyethylene, poly ( $\epsilon$ -caprolactone) (PCL) has been widely studied as a model system for investigating polymer crystallization mechanisms. PCL 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. Previous studies of PCL's crystalline properties include: shear induced crystallization,<sup>1</sup> molar mass dependent crystallization,<sup>2</sup> and highly oriented surface induced crystallization.<sup>3</sup> Spherulitic crystal structures were commonly observed in these cases. Once semicrystalline PCL is constrained in thin film geometries, the confinement of the polymer chains can significantly alter properties such as molecular mobility,<sup>4,5</sup> the glass transition temperature,<sup>6,7</sup> chain orientation,<sup>8-10</sup> etc. For instance, the interfacial interactions between films and substrates may alter the transport properties of polymer molecules to the growth fronts of crystallizing lamellae, thereby altering growth rates, morphologies and melting temperatures for crystals grown in thin films.<sup>8-23</sup>

For previous studies of PCL crystallization in thin film geometries, the samples are usually prepared on solid substrates by spincoating and the film thicknesses are

controlled by varying the concentration of the polymer solution or the spinning rate.<sup>8-10</sup> On solid substrates, the cooperative motion of polymer chains directly affects chain folding and consequently the crystallization rate and morphology.<sup>8-10</sup> Furthermore, surface defects on solid substrates can affect the nucleation and growth mechanism for crystal growth.

However, at the air/water (A/W) interface, the ultrapure water minimizes surface defects, providing a model surface for probing nucleation and growth of PCL crystals in Langmuir films.<sup>24</sup> In addition, PCL Langmuir films formed at low surface pressures are very uniform, approaching monomer thickness. In this thesis, PCL crystallization along with other phase transitions in PCL-based polymer blends are extensively studied as Langmuir films at the A/W interface.

Chapter 2, an introduction and review, provides important background information, including phase transitions in Langmuir monolayers, concepts of polymer crystallization, thin film crystallization, miscibility of polymer blends, diffusion of polymer chains, diffusion-limited growth of crystals, etc. Pertinent literature about PCL-based systems is reviewed and included in this chapter. Techniques for studying Langmuir films such as surface pressure-area per monomer ( $\Pi$ -A) isotherm studies, Brewster angle microscopy (BAM), and atomic force microscopy (AFM) are also summarized in this chapter.

Chapter 3, materials and experimental methods, is the only chapter containing a detailed description of the materials and experimental methods used in this thesis.

In Chapter 4, surface pressure induced crystallization of PCL in single-component Langmuir monolayers at the A/W interface was studied in real time by BAM.

Morphological features of PCL crystals grown in Langmuir films during the compression process exhibit butterfly-shapes with well-developed  $\{100\}$  sectors and distorted  $\{110\}$  sectors. 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 principle axes. Electron diffraction on Langmuir-Schaefer (LS) films suggests that the lamellar crystals are oriented with the polymer chain axes perpendicular to the substrate surface, while AFM reveals a crystal thickness of  $\sim 7.6$  nm.<sup>24</sup>

In Chapters 5 and 6, semicrystalline PCL was blended with amorphous poly(*t*-butyl acrylate) (PtBA) to study the influence of viscous PtBA on the morphological evolution of PCL crystals. Thermodynamic analyses of  $\Pi$ - $\langle A \rangle$  isotherms and BAM results reveal that PCL/PtBA blends are compatible as Langmuir films below the dynamic collapse transition for PCL at a surface pressure of  $\Pi_C \sim 11$  mN·m<sup>-1</sup>. For PCL-rich blends, *in situ* BAM studies reveal nonequilibrium growth of PCL dendritic crystals during compression into the metastable monolayer regime. In the subsequent plateau regime PtBA is excluded from growing PCL crystals and hinders PCL diffusion from the surrounding monolayer to the crystal growth fronts, leading to dendritic morphologies for PCL crystals. The crystal thickness of the PCL dendrite is found to be  $\sim 7$ -8 nm by AFM cross-sectional analysis. This range of thicknesses is comparable to PCL crystals grown from single-component PCL monolayers as indicated in Chapter 4. In contrast, PtBA-rich blend films suppress PCL crystallization.

Results obtained from a representative PCL/PtBA blend with a PtBA mole fraction of  $X_{\text{PtBA}} \sim 0.14$  under various experimental conditions are included in Chapter 6. Increasing compression rates for dynamic compression experiment leads to smaller dendritic crystals at similar surface area per monomer. Interestingly, the average growth rate analyses give similar growth rate data for crystals grown at different compression rates, suggesting that the apparent size differences of the crystals is only a function of the growth time, though chain organization in crystals could become poorer with increasing compression rate. Furthermore, BAM studies during isobaric area relaxation experiments at different  $\Pi$  reveal morphological transitions for PCL dendrites from highly branched symmetric dendrites, to six-arm dendrites, four-arm dendrites, seaweedlike crystals, and distorted rectangular crystals. In these isobaric experiments,  $\Pi$  is analogous to temperature in bulk isothermal crystallization studies and has a profound impact on morphological selection because of the interplay between diffusion, interfacial energy, and the anisotropy of the interfacial energy.

Chapter 7 includes extensive studies on immiscible blends of PCL and glassy polystyrene (PS) with intermediate molar masses as Langmuir films at the A/W interface.<sup>25</sup> For PCL/glassy PS blends, the surface concentration of the amphiphilic PCL is the only factor influencing the surface pressure below the collapse transition as indicated by  $\Pi$ - $\langle A \rangle$  analyses. For PS-rich blends, both *in situ* BAM studies at the A/W interface and AFM studies for LS-films reveal that PS nanoparticle aggregates formed at very low surface pressures can form networks upon further compression. The networklike structures seen in PS-rich blends suggest that the nonamphiphilic PS aggregates at the A/W interface produce domains with dipole densities that differ from pure PCL. In all

composition regimes, the amphiphilic PCL phase tends to spread and form a continuous surface layer at the A/W interface, while simultaneously improving the dispersion of nonamphiphilic PS domains. For PCL-rich blends, compressing the blend films into the supersaturated monolayer regime of the PCL component leads to the nucleation and growth of PCL crystals around PS aggregates. In this case, these small PS aggregates serve as heterogeneous nucleation centers for the growth of PCL crystals. During film expansion, BAM images show a gradual change in the surface morphology from highly continuous networklike structures (PS-rich blends) to broken ringlike structures (intermediate composition) to small discontinuous aggregates (PCL-rich blends). In contrast to PCL/glassy PS blends, it is interesting to note that PCL/liquid PS oligomer ( $M_w = 0.74 \text{ kg}\cdot\text{mol}^{-1}$ ) blends as Langmuir films show dramatically different surface morphologies. BAM studies show features that are consistent with phase separation by “nucleation and growth” as well as “spinodal” type decomposition. Additional preliminary results obtained for the PCL/PS oligomer blends as Langmuir films are provided in Chapter 9 as suggestions for future work.

In Chapter 8, PCL samples with various molar masses are examined to explore molar mass dependent nucleation and growth of crystals, crystal morphologies and melting properties in Langmuir films at the A/W interface.<sup>26</sup> At  $A > \sim 0.37 \text{ nm}^2\cdot\text{monomer}^{-1}$ , both surface pressure and surface elasticity exhibit molar mass independent behavior that is consistent with a semi-dilute PCL monolayer. In this regime, the scaling exponent indicates that the A/W interface is a good solvent for the liquid-expanded PCL monolayers.  $\Pi$ -A isotherms show molar mass dependent behavior in the metastable monolayer regime, corresponding to the onset of the nucleation of crystals. Molar mass

dependent morphological features for PCL crystals and their subsequent crystal melting are also described in Chapter 8. The competition between lower segmental mobility and a greater degree of undercooling with increasing molar mass produces a maximum average growth rate at intermediate molar mass. The plateau regions in the expansion isotherms represent the melting process, where the polymer chains continuously return to the monolayer state. The magnitude of  $\Pi$  for the plateau during expansion decreases with increasing molar mass, indicating that the melting process is strongly molar mass dependent.

Chapter 9 provides the overall conclusions for this thesis and several suggestions for future work: (1) the effects of PtBA molar mass on the morphologies of PCL dendrites grown in PCL/PtBA blends; (2) the effects of PCL molar mass on the morphological selection of PCL dendrites grown in PCL/PtBA blends; (3) growth mechanisms for PCL dendrites during isobaric area relaxation experiments; and (4) understanding phase diagrams for PCL/liquid PS oligomer blends as Langmuir films.