# CHAPTER 3

EXPERIMENTAL MATERIALS AND METHODS

3.1. Materials

Poly(ε-caprolactone)s (PCL) with different molar masses were purchased from Polymer Source, Inc. and were used as received. The chemical structure of the PCL repeat unit is shown in Figure 3.1. Number average molar mass (M_n), weight average molar mass (M_w), and polydispersity index (PDI = M_w/M_n) values measured by size exclusive chromatography and provided by Polymer Source, Inc. for the PCL samples are listed in Table 3.1. All polymers will be referred to by their M_w value provided by Polymer Source Inc. or by the code P1-P5 provided in Table 3.1. For most experiments presented in this thesis, spreading solutions were prepared by dissolving the samples in chloroform (HPLC grade) at concentrations of ~ 0.4 - 0.5 mg·g^{-1}. In Chapter 8, spreading solutions for various PCL samples were prepared at concentrations of ~ 0.1 - 0.2 mg·g^{-1} for addition experiments.
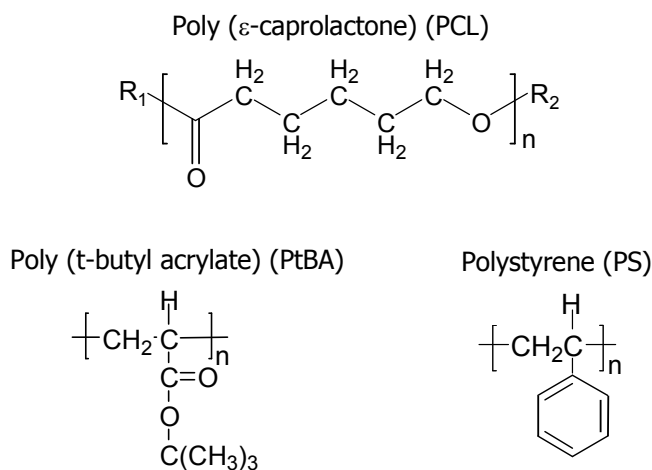
Figure 3.1. Chemical structures of the repeating units for materials used in this thesis.

Table 3.1. Molar mass data for PCL samples.

Sample	#	M_n	M_w	PDI
		kg·mol^{-1}	kg·mol^{-1}	
P1934-CL^b	P1	3.5	5.2	1.49
P1302-CL^a	P2	8	10	1.25
P3281-CL^c	P3	11	13	1.18
P5050-CL^a	P4	13	15.5	1.19
P1297-CL^a	P5	36	42.8	1.19

a.	$R_1 = -OCH(CH_3)_2, \ R_2 = -H$
b.	$R_1 = -OCH_2CH_3, \ R_2 = -H$
c.	$R_1 = -OCH(CH_3)CH_2OCH_3, \ R_2 = -H$

$^{a, \ b, \ c}$End groups for PCL samples from Polymer Source, Inc.

Amorphous poly(t-butyl acrylate) (PtBA) and polystyrene (PS) samples with different molar masses were purchased from Polymer Source, Inc. and were used as received. Chemical structures of the PtBA and PS repeat units are shown in Figure 3.1. Spreading solutions of blends were prepared by dissolving either PCL/PtBA or PCL/PS blends in chloroform (HPLC grade) with concentrations of ~ 0.4- 0.5 mg·g^{-1} at room temperature. Number average molar mass (M_n), weight average molar mass (M_w), and polydispersity index (PDI = M_w/M_n) values of the PtBA and PS samples provided by Polymer Source, Inc. are listed in Table 3.2 and Table 3.3, respectively.

Table 3.2. Molar mass data for PtBA samples.

Sample	M_n	M_w	PDI
	kg·mol^{-1}	kg·mol^{-1}	
P1036-tBuA	14.4	15.3	1.06
P1600-tBuA	23.8	25.7	1.08
P1148-tBuA	37	39.2	1.06

Table 3.3. Molar mass data for PS samples.

Sample	M_n	M_w	PDI
	kg·mol^{-1}	kg·mol^{-1}	
P1779-S	0.7	0.74	1.06
P1772-S	1.47	1.56	1.06
P489-St	20.8	22.2	1.07
P468-St	62.6	64.4	1.03
PS207	207	217	1.05

3.2. Experimental Set-up of the Langmuir Trough and BAM

Isotherms and *in situ* morphologies of Langmuir films were obtained with a standard Langmuir trough (500 cm^2 and 700 cm^2 NIMA Technology, 601BAM) equipped with a Brewster angle microscope (BAM, MiniBAM, NanoFilm Technologies, Ltd., Linear resolution $\leq$ 20 μm). The instruments are housed in a Plexiglas$^®$ box to maintain a relative humidity of 70–75% and a dust free environment. The Plexiglas$^®$ box and instrument are placed on a floating optical table with black curtains on all sides to minimize stray light and mechanical vibrations (Newport RS-2000 & I-2000). The Langmuir trough constructed of Teflon$^®$ is hydrophobic and can be cleaned with dichloromethane or chloroform without damaging the trough. The barriers are made of a

hydrophilic acetal resin polymer (Delrin[®]) and need to be cleaned with isopropanol as halogenated solvents will damage the barriers. The Langmuir trough was filled with ultrapure 18.2 MΩ water (Milli-Q Gradient A-10, < 5 ppb organic impurities). The highly hydrophobic Teflon[®] trough supports an approximately 1 mm brim of water above the top of the trough edges. Before spreading the monolayer, the barriers were automatically moved toward each other thereby concentrating dust and surface-active contaminants in the center of the trough. A pipet connected to a vacuum pump was used to suction off surface-active contaminants. This cleaning procedure was repeated several times. The barriers sweep the water surface during compression of the monolayer to vary the surface area as illustrated in Figure 3.2.

The Π-A Isotherm equation shown in the figure:

$$\Pi = \gamma_0 - \gamma = \frac{F_{obs,0} - F_{obs}}{2(L+t)\cos\theta} = \frac{F_{obs,0} - F_{obs}}{2L}$$
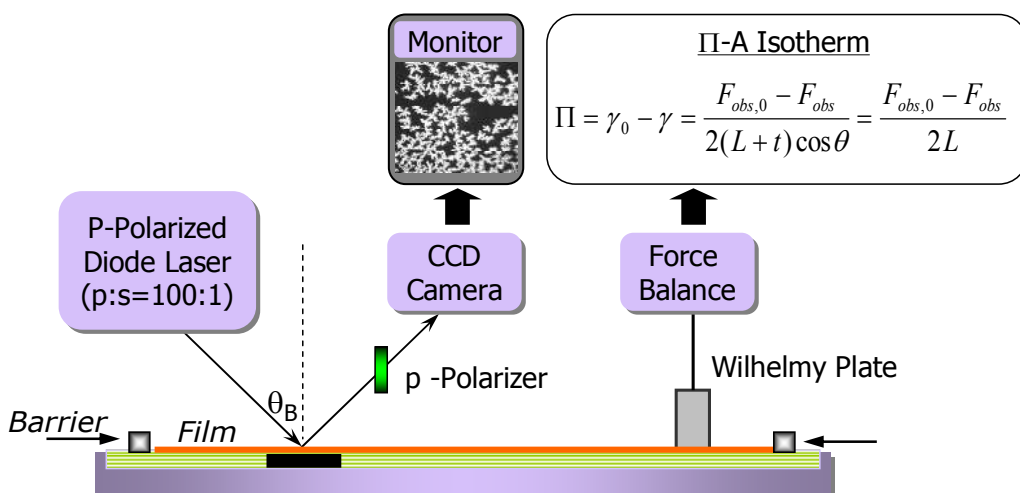
Figure 3.2. Schematic illustration of a Langmuir trough equipped with BAM.

A measured mass of spreading solution based on the desired initial area per molecule was spread onto the cleaned surface using a micro syringe (Hamilton). About 20 ~ 30 min was allowed after spreading to ensure the volatile solvent, chloroform, evaporated before all isotherm measurements. Surface tension (γ) and surface pressure (Π) were obtained by the Wilhelmy plate technique to ± 0.2 mN·m^{-1} during all isotherm measurements. A completely wetted filter paper plate (contact angle $\theta = 0^{\circ}$) was used as a Wilhelmy plate in the NIMA Mini-BAM trough. The experimental temperature was controlled at 22.5 $^{\circ}$C for all experiments using a circulating bath (Neslab RTE-111) unless otherwise noted. Surface pressure-area per monomer (Π-A) isotherms were recorded by a computer which controlled the barrier positions and provided a read-out of the surface pressure from the balance as illustrated in Figure 3.2.

BAM studies were carried out simultaneously with isotherm measurements. The reflected laser beam was projected onto the detector window. When monitoring the morphologies of Langmuir films, a black plate was placed in the bottom of the subphase to minimize scattering from refracted light reflected by the white Teflon$^{\circledR}$ surface. The BAM images were taken by a charge coupled device (CCD) camera and were viewed on a black and white monitor (Philips) as seen in Figure 3.2. Image data was transferred to a connected computer with a video card (Accurion) and analyzed using imaging software packages (National Instruments). BAM micrographs utilize an optimal brightness rather than an absolute intensity scale. While this BAM feature yields the best possible contrast, care must be taken when comparing two images, as a bright object in one image may be dark in a subsequent image if a brighter object enters the field of view.

3.3. Π-A Isotherms from Constant Compression Rate Experiments

During compression Π-A isotherm experiments, the barriers were compressed at a specific and fixed rate. Compression isotherms were used to determine the areas per monomer where various phase transitions occur. For most Π-A isotherms presented in this thesis, the samples were compressed at either 8 or 20 $cm^2 \cdot min^{-1}$. The compression rate is also indicated in each chapter. Other compression rates were also used depending on the goal of the experiments. The film's static dilational elastic modulus, $\varepsilon_s = -A(\partial\Pi/\partial A)_T$, can be calculated from the Π-A isotherms.

3.4. Hysteresis Loops: Compression and Expansion Π-A Isotherms

During hysteresis experiments, each sample was compressed at a constant compression rate to a designated minimum trough area and was immediately expanded at the same barrier speed back to the initial maximum trough area. The hysteresis loops can be used to make inferences about the stability and reversibility of various phases and phase transitions, respectively, that are present for the Π-A isotherm. Simultaneous BAM measurements provide morphological information about the phase transitions.

3.5. Isobaric Area Relaxation Experiments

Isobaric (constant Π) area relaxation experiments were performed for monolayers in supersaturated states to explore the nucleation and growth of PCL crystals in PCL-based polymer blends. These experiments started after the monolayers were compressed to a desired target Π at a constant compression rate. Then, the surface area (A) – time (t) relaxation isotherm was recorded. Various target pressures in the supersaturated monolayer regime were chosen to study the effects of Π on the morphological evolution of PCL crystals during isobaric area relaxation experiments.

3.6. Successive Addition Experiments

Compression isotherms represent dynamic Π-A data. In contrast, successive addition isotherms can be used to study the surface properties of monolayers approaching "equilibrium" states. In Chapter 8, successive addition isotherms are used to estimate the crystallization window (supersaturated monolayer regime) for PCL with various molar masses. During successive addition experiments, the trough area was held at a constant value. The surface area per monomer value was varied by making successive additions of PCL solution onto the water surface. In the monolayer regime, the monolayer was allowed to relax for 8 ~ 12 minutes and the corresponding "equilibrium" Π was recorded. Once the nucleation of crystals was observed, Π was recorded ~ 20 minutes after each addition.

3.7. Morphological Characterization of Langmuir-Schaefer Films

Silicon wafers (100) used for spincoating were obtained from Waferworld, Inc. The silicon substrates were boiled in a 1:1:5 (by volume) solution of ammonium hydroxide: hydrogen peroxide: ultrapure water (18.2 MΩ, Milli-Q Gradient A-10, Millipore, <5 ppb organic impurities) for 1.5 h. After the substrates were rinsed with copious amounts of Millipore water and dried with nitrogen, they were immersed in a 30:70 (by volume) solution of hydrogen peroxide : concentrated sulfuric acid for ~ 3 h. Next, the substrates were rinsed with Millipore water, and dried with nitrogen. The clean substrates were then hydrophobized by treating them with HF (J. T. Baker Inc., 1:7 buffered etch oxide) and NH_4F (J. T. Baker Inc., 40% solution) solutions. Langmuir films of PCL or PCL-based polymer blends formed at the air/water (A/W) interface were transferred onto the cleaned silicon substrates that were first covered with a spincoated polystyrene layer (1

wt % PS in toluene at a spinning rate of 3000 rpm for ~ 60 s) using the Langmuir-

Schaefer (LS) method as illustrated in Figure 3.3. The spincoated polystyrene layer

between the silicon substrate and the LS transferred PCL crystals is thick enough to allow

us to see 7 to 8 nm thick crystals with visible light because of interference effects at

visible wavelengths arising from differences in optical path lengths between the PS layer

and the PS+PCL crystal for light reflected from the film/air and film/substrate interfaces.

A compression rate of 8 or 20 $cm^2 \cdot min^{-1}$ was used to obtain the desired transfer pressure.

The transfer pressure for each different experiment is specified in each chapter.
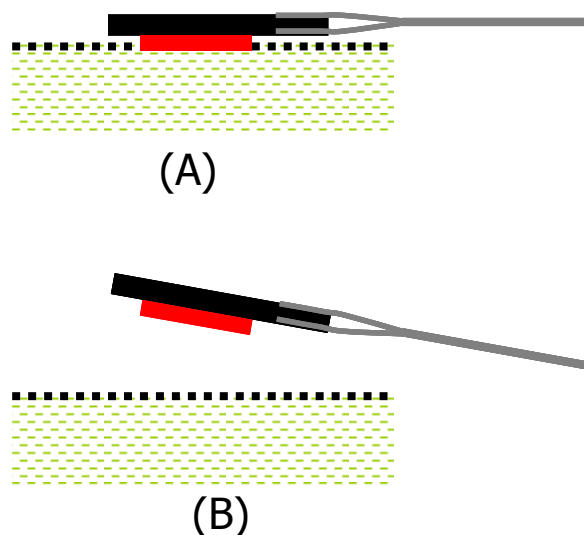
Figure 3.3. Schematic illustration of Langmuir-Schaefer transfer.

The *ex situ* morphological studies were then preformed on transferred one-layer LS

films using an optical microscope (OM) operating in reflection mode (Axiotech Vario

100 HD, Carl Zeiss, Inc.). The transferred LS-films were air-dried for at least 24 hours

prior to scanning them in the tapping mode with a Nanoscope III AFM (Dimension 3000

scope with a Nanoscope IIIa controller, Digital Instruments, set point of ca. 0.6). AFM

images are reported without any image processing except flattening.   PCL crystal

samples for electron diffraction studies were transferred onto a carbon coated copper grid

at a surface pressure of ~ 11 mN·m^{-1}. A JEOL TEM-2010 electron microscope (Japan)

equipped with a CCD camera operating at 200 kV was used to obtain electron diffraction

patterns of PCL crystals.