GRADIENT MUTILAYERED FILMS &
CONFINED CRYSTALLIZATION OF POLYMER
NANOLAYERS BY FORCED ASSEMBLY COEXTRUSION

by

Michael Ponting

Submitted in partial fulfillment of the requirements
for the degree of Doctor of Philosophy

Dissertation Advisers: Professor Baer and Professor Hiltner

Department of Chemical Engineering

CASE WESTERN RESERVE UNIVERSITY

May, 2010
We hereby approve the thesis/dissertation of

Michael T. Ponting

candidate for the Ph.D. degree *

(signed) Eric Baer

(chair of the committee)

Gary Wnek

Anne Hiltner

Chung-Chiun Liu

(date) 3/17/10

*We also certify that written approval has been obtained for any proprietary material contained therein.
Dedication

To wife, Kim, and my parents, Karen and, Harry
# TABLE OF CONTENTS

<table>
<thead>
<tr>
<th>Section</th>
<th>Page</th>
</tr>
</thead>
<tbody>
<tr>
<td>LIST OF TABLES</td>
<td>ii</td>
</tr>
<tr>
<td>LIST OF FIGURES</td>
<td>iii</td>
</tr>
<tr>
<td>ACKNOWLEDGEMENTS</td>
<td>vii</td>
</tr>
<tr>
<td>ABSTRACT</td>
<td>ix</td>
</tr>
</tbody>
</table>
| CHAPTER 1
POLYMER NANOSTRUCTURES BY FORCED ASSEMBLY: A REVIEW OF PROCESS, STRUCTURE, AND PROPERTIES | 1    |
| CHAPTER 2
GRADIENT MULTILAYER FILMS BY FORCED ASSEMBLY COEXTRUSION     | 35   |
| CHAPTER 3
FORCED ASSEMBLY CONFINEMENT OF POLYCAPROLACTONE: EFFECT OF CONFINING SUBSTRATE | 70   |
| APPENDIX
TUNABLE POLYMER LENSES                                        | 118  |
| BIBLIOGRAPHY                                                 | 144  |
LIST OF TABLES

CHAPTER 2

2.1 Even and uneven split layer multiplier die dimensions and effective splitting ratios 60

CHAPTER 3

3.1 Characteristics of PCL/PS Nanolayered Films 103
3.2 Characteristics of PCL/PMMA and PCL/PC Multilayered Films 104

APPENDIX A

A.1 Materials used in the fabrication of tunable lenses 138

A.2 The first two sections present results of surface fits to measured surfaces as a function of plunger displacement \( \Delta L \). The standard deviation of the differences between data points and the fit is given in microns, and all other parameters are outlined in the text. The last section presents focal length information, both predicted and observed back focal lengths, and the resulting overall focal lengths. Uncertainty in the observed focal length is 0.5 mm. 139
LIST OF FIGURES

CHAPTER 1

1.1 (Left) Two component multilayer system comprised of extruders, pumps, feedblock, multiplying dies, surface layer extruders, and exit die. (Right) Schematic illustration of layer multiplication by cutting, spreading, and recombining the melt stream.

1.2 (Top) Three component microlayer system with tie layer extruder. (Bottom) Schematic illustration of five to nine layer multiplication with a tie layer (T) separating the A and B layers.

1.3 The MFI viscosity match of PS/PP for determining microlayer coextrusion conditions.

1.4 (Top) Schematic illustrating the difference in polymer flow streamlines based on multiplier die length. (Bottom) The effect of increasing multiplier die length from 15 to 70 cm on layer uniformity.

1.5 (Top) Cross-section AFM of 32 layer PS/PMMA 1-D photonic film with LDPE surface layers. (Bottom) Comparison of measured and modeled transmission spectra of two stacked 32 layer PS/PMMA films with 86 nm average layer thickness.

1.6 (Top) Schematic of the DFB laser film of R6G doped SAN25 and THV. (Bottom) Lasing emission from the nanolayered DFB laser.

1.7 (Left) Reflection spectrum as a function of wavelength at designated strains for an elastomeric 128 layer PU/Pebax tunable photonic crystal. (Right) Optical reflective peak position as a function of strain for tunable photonic crystal.

1.8 Cross-section AFM image of PC (light) and PMMA (dark) layer films with (Top) 50/50 composition and 60 nm layers, (Bottom Left) Offset 80/20 composition, and (Bottom Right) Offset 90/10 composition.

1.9 Effect of composition on composite SAN17/PMMA film refractive index. Varying relative composition of SAN17/PMMA in the nanolayered film altered the refractive index of the composite nanolayered film leading to the production of novel gradient index lenses.

1.10 (Top) Optical Micrograph of 128 layer 50/50 PC/PMMA film cross-section with 1 µm layers. (Bottom) AFM of 4096 layer 50/50 PC/PMMA film cross-section with 30 nm layers.

1.11 The glass transition temperature of layered PC and PMMA layers as a
As individual layer thickness is reduced into the nanoscale, increasing layer interphase contributions result in a convergence to an average Tg for PC and PMMA.

1.12 2D WAXS extrusion direction patterns and AFM cross-section images exhibiting lamellar orientation in PS/PEO layered films with nominal PEO layer thickness of (a) 1 μm, (b) 300 nm, (c) 75 nm, and (d) 25 nm.

1.13 Oxygen permeability of polyethylene oxide (PEO) layer as a function of PEO layer thickness in PEO/PS and PEO/EAA micro- and nanolayer films. Oxygen permeability tests were conducted at 23 °C and 0% relative humidity.

CHAPTER 2

2.1 Two component multilayer system layout of extruders, melt pumps, feedblock, multiplying dies, surface layer extruder, and exit die. Layer multiplication from two to four layers is illustrated by cutting, stacking, spreading, and recombining melt streams.

2.2 (a) Conventional even and (b) uneven split layer multiplier die. Uneven split layer multiplier die produces two layer thicknesses as compared to one with conventional layer multiplication.

2.3 Schematic illustration of step-by-step construction of a 10X gradient layer thickness distribution multilayered film by coextrusion through a series of four uneven split layer multiplying dies.

2.4 Cross-section optical micrograph of a 32 layer PS/PMMA gradient layer thickness film with a 10X difference between the thickest and the thinnest layers.

2.5 (Top) 128 step-layer thickness distribution and (Bottom) Resultant comparison between the analytically modeled and the experimentally measured optical reflection spectra from a 128 multilayer PS/PMMA film.

2.6 (Top) Cross-section atomic force microscopy image of 128 gradient layer film with a 10X layer thickness distribution produced by coextrusion through a series of two even and four uneven multiplier dies. (Bottom) Comparison of analytical prediction and experimentally measured 600+ nm wide reflection band from 128 gradient layer THV/PS multilayer film.

2.7 (Top) Super-lattice gradient layer thickness distribution of a 128 layer film coextruded through a series of four even and two uneven split multiplier dies. (Bottom) Comparison of an analytically modeled and experimentally measured dual reflection band spectrum from a 128 layer “superlattice” distribution PMMA/PVDF blend multilayer film.
2.8 Optical microscopy images of 256 gradient layer 50/50 v/v PS/SEPS film. (Top) Film surface micrograph of thicker layers exhibiting crazes at 90° to the film deformation direction. (Bottom) Film surface micrograph of thinner layers exhibiting large shear bands and smaller crazes that terminate into shear bands as a result of deformation.

2.9 (Left) 128 gradient layer 50/50 PS/THV foam-delaminated film exhibiting layer thickness dependent layer buckling. (Right) Effect of PS layer buckling wavelength with layer thickness in 128 gradient layer 50/50 PS/THV foam-delaminated film.

CHAPTER 3

3.1 Two component multilayer system layout of extruders, melt pumps, feedblock, multiplying dies, surface layer extruder, and exit die. Layer multiplication from two to four layers is illustrated by cutting, stacking, spreading, and recombing melt streams.

3.2 AFM phase images of partial cross sections of coextruded PCL/PS multilayered film with; (A) 16 μm-thick PCL layer, (B) 1900 nm-thick PCL layer, (C) 400 nm-thick PCL layer, and (D) 75 nm-thick PCL layers with arrows indicating the PCL layers.

3.3 Extrusion direction WAXS and SAXS patterns exhibiting increased PCL orientation as layer thickness decreases from 1900 nm to 75 nm in PCL/PS multilayered films. Orientation of PCL suggests layer confinement induces the formation of high aspect ratio single crystal lamellae in thin nanometer scale layers.

3.4 Increase toward in-plane PCL layer orientation by reducing layer thickness in PCL/PS multilayer films

3.5 Effect of layer thickness on effective PCL layer oxygen permeability in PCL/PS multilayered films. Oxygen transport measurements were conducted on as-extruded films at 23°C and 0% relative humidity.

3.6 Confined PCL layer crystalline phase orientation from ED WAXS patterns and effective PCL layer oxygen permeability exhibit good correlation in PCL/PS multilayer films. Correlation between the structural and property behavior of the confined PCL layers suggesting that lamellae orientation results in the oxygen barrier enhancement in PCL/PS multilayered films.

3.7 Extrusion direction 2D WAXS patterns of PCL/PS, PCL/PMMA, and PCL/PC multilayer films at various PCL layer thicknesses.

3.8 Effect of confining amorphous substrate on confined PCL layer crystal orientation against PS, PMMA, or PC layers. Increasing PCL-confining layer substrate interactions reduced the amount of PCL crystalline phase orientation at similar layer thicknesses.
3.9 Effect of layer thickness on PCL layer oxygen permeability. Reducing PCL layer thickness against PS or PMMA layers resulted in a decrease of oxygen permeability in the extruded films at 23°C and 0% relative humidity.

3.10 Correlation between confined PCL layer crystalline phase orientation and oxygen permeability confirm similar lamellae orientation mechanism for gas barrier enhancement in PCL/PS and PCL/PMMA multilayered film systems.

3.11 (Left) PCL layer remelting quenching or recrystallization temperature window. (Right) Extrusion direction WAXS patterns of melt recrystallization or quenching temperature on 40 nm PCL layer crystalline phase orientation in multilayered PS (top) and PMMA (bottom) films.

3.12 Remelted quenched or recrystallized 40 nm PCL layer orientation function as a function of temperature for PCL/PS and PCL/PMMA multilayered films. Sharp transitions from “edge-on” to “flat-on” crystal orientation were witnessed based on recrystallization conditions/environment.

3.13 (Top) Extrusion direction WAXS patterns of melt recrystallization or quenching temperature 100 nm PCL layer crystalline phase orientation multilayered against PA12 (top), PP-g-MA (bottom). (Bottom) Comparison of PCL (200) orientation function as a function melt recrystallization or quench temperature against different polymer substrates.

APPENDIX A

A.1 Fabrication and assembly of variable focal length lens. (a). Fabrication of deformable membrane, (b). Assembly of variable focus length lens, (c). Final injection and cure of PDMS lens core. Final diagram labeled with dimensions of lens tested in this work.

A.2 Schematic of the mechanism for variable focal length. Pushing a plunger a distance $\Delta L$ causes the deformable elastomer within the lens to expand out against the pliable outer membrane. Dashed lines indicate plunger and surface locations before compression. Little compression is necessary; the maximum $\Delta L$ cited here is 1.28 mm.

A.3 Plot of surface profiles as interpolated from fitted measurements. Dotted lines represent lens mount.

A.4 Images acquired at two different zoom states of the lens. The magnification of the object in these images differs by a factor of 1.8.
ACKNOWLEDGEMENTS

I would like to thank my research advisors, Prof. Anne Hiltner and Prof Eric Baer, for contributing to a very rewarding graduate research experience. I truly appreciated the opportunity to learn and work in such a highly interactive, cutting-edge research environment. The foundational research concepts and professional development opportunities afforded to the students in the research group are truly invaluable. The opportunity to work in the National Science Foundation funded CLiPS STC was truly a unique experience that was rewarding technology, professionally, and socially. I would also like to thank my dissertation committee members Prof. Gary Wnek and Prof. C.C. Liu for not only their time, but for contributing to my technical knowledge and entrepreneurial spirit during my time in the Case Chemical Engineering Department.

The generous financial and technical support on my collaborative projects with DARPA and the Naval Research Laboratory is gratefully acknowledged. Optical Engineering “crash courses” from Dr. James Shirk, Dr. Guy Beadie, and Dr. Richard Lepkowicz were greatly appreciated and instrumental in developing a truly interdisciplinary, and I felt very successful, GRIN lens program. I would like to specially acknowledge my past “Lens Group” teammates Huiwen Tai, Yi Jin, Akshay Kamdar, and Tomasz Kazmierczek.

Many thanks go to the Baer-Hiltner research group members, past and present, for their advice, help and cooperation along my graduate school journey. The people and relationships forged during my time at Case have truly added to
my experience. To Peter Dias, Adi Ranade, Yi Jin, Haopang Wang, Ravi Ayyer, Tomasz Kazmierczek, Akshay Kamdar, Ravi Ayyer, Devang Khariwala, Deepak Langhe, Joel Carr, Shannon Armstrong, Yaya Lai, Adriane Miller, Henry Millimen, Jong Keum, Tiffani Abernathy, Pat Simmons and Mariah Miles thank you for making everyday unique and interesting.

I would like to thank my wife, Kim, my parents, Harry and Karen, my brothers, Matt and Ryan, and my sister Erin for their support, interest, understanding, and stubbornness (“When are you going to graduate?”) for their unwavering support of my work and studies. Finally, a heartfelt thanks is also dedicated to my friends and colleagues who took an interest in my work, you have no idea how personally rewarding it was to discuss my ideas and work with you.
CHAPTER 1: A review of recent progress of micro- and nanolayer coextrusion for polymeric systems with good layer uniformity is described. Coextrusion through a series of layer multiplying die elements has enabled the production of film containing tens to thousands of layers with individual layer thicknesses from the micro- to the nanoscale. Improvements in layer uniformity are discussed through optimization of layer multiplying die design, selection of viscosity matched polymer systems, and incorporation of coextrusion surface layer capabilities. Coextrusion of layered polymer films with individual layer thicknesses in the nanoscale has resulted in the production of novel systems with improved properties. Nanolayered polymer films were utilized to develop an all-plastic laser, to fabricate gradient refractive index lenses, and to investigate gas barrier enhancement of crystalline polymer nanolayers confined to induce a high aspect ratio, in-plane, single-crystal-like lamellar structure.

CHAPTER 2: Forced assembly polymer coextrusion utilizes layer multiplication to produce films with tens or thousands of microns to nanometer thick layers. The development of novel uneven split layer multiplying dies has produced gradient multilayer films with at least a 10X difference between the
thickest and thinnest layers. Coextrusion through a series of equal and uneven split multiplier dies allows for flexibility in the unique design of layer thickness distributions by: (1) altering the multiplier offset and (2) changing the sequence of a series of uneven split multiplying dies with different splitting ratios. This new technology has created highly reflective, multilayered photonic films with gradient layer thickness distributions exhibiting, as examples, a 600 nm wide reflection band and dual optical reflection bands within a single film. Also, gradient multilayers exhibit unique mechanical behavior. A layer thickness dependent craze to shear banding deformation mechanism was observed. In addition, gradient controlled buckling was observed across a single film due to foaming-induced layer delamination.

CHAPTER 3: Polycaprolactone multilayered films were produced exhibiting highly oriented confined crystallization as a result of reducing individual layer thicknesses from the micron to the nanoscale. WAXS/SAXS measurements of crystalline PCL layers exhibited a thickness dependent confinement mechanism from unoriented spherulites (micron layers) to high-aspect ratio, single or stacked lamellae (nanolayers) oriented parallel to the layer boundary. Highly oriented, single lamellae PCL layer films exhibited more than a two order of magnitude reduction in oxygen gas barrier as a result of the increased diffusion path length tortuosity around the high aspect ratio lamellae crystals with large estimated lateral dimensions up to 5 µm. The effect of the confining layer on PCL properties was examined by coextrusion of PCL against a series of amorphous materials, PS, PMMA, and PC with increasing chemical compatibility
in micro- and nanolayered films. Increasing PCL and confining material interaction from a non-interacting PS to more interactive PMMA glassy confining substrate resulted in a decrease of confined crystalline layer orientation and oxygen permeability in thicker layers while broadening the temperature transition window from edge-on to in-plane lamellae in melt recrystallization experiments. An extreme case of nanolayering PCL against a highly interacting miscible confining layer, PC, resulted in no layer thickness effect on PCL crystalline phase orientation in coextruded multilayered films. Confinement against another crystalline polymer, such as polyamide or polypropylene, resulted in affinity for PCL to crystallize as edge-on lamella at ambient temperatures. A subsequent shifting of to higher melt recrystallization temperatures was necessary to induce the edge-on to flat-on orientation transition as a result of the crystalline confining layer substrate.
Chapter 1
Polymer Nanostructures by Forced Assembly:
A Review of Process, Structure, and Properties

1.1 Introduction

Polymeric structures and composites with properties superior to those of the individual components have been developed using various techniques including: polymer blending, block-copolymerization, and multilayer coextrusion. Layer-multiplying coextrusion represents an advanced polymer processing technique for combining two or more polymers in a layered configuration with controlled architecture. It is a continuous processing technique capable of economically producing films with up to thousands of layers with individual layer thicknesses from the micro- to the nanoscale.

Originally developed in the 1970s by the Dow Chemical Company,[1-5] early examples of synergistic polymer combinations in microlayered film systems included colorful iridescence,[6-8] crumple resistant gas and water barrier,[9] and increased ductility and impact strength which originate from changes in polymer deformation mechanisms as the layer thickness is reduced.[10-12] More recently, layered polymer films with micron-thick layers have seen increasing usage in composite films for packaging with improved gas barrier,[13] and increased mechanical toughness.[14,15] Commercialized technologies stemming from layered films with unique optical properties include highly reflective light
filters[16, 17] and polarizers.[18] As layer-multiplying coextrusion continues to evolve toward the nanoscale, opportunities arise to discover unique properties controlled by interfacial or confinement induced phenomena.

The advances in layer-multiplying technology and their application to novel nanolayered polymeric material systems with improved properties are discussed in this article. The process is described with emphasis on recent improvements in layer uniformity and quality through optimized multiplying die design, polymer selection for matching rheology, and incorporation of polymeric surface layers. Based on these recent processing modifications, layered polymer systems with individual layer thicknesses ranging from microns down to tens of nanometers have been successfully coextruded.
1.2 Coextrusion of Micro- and Nanolayered Polymer Systems

Micro- and nanolayer coextrusion, the enabling technology of the National Science Foundation Center for Layered Polymeric Systems (CLiPS), utilizes a process of forced assembly through sequential layer multiplication to fabricate thin alternating layers of two or three polymers. The uniqueness of the coextrusion process lies in the combination of conventional coextrusion of two or more polymers in a layered feed-block with additional layer multiplication accomplished through a series of multiplier dies. This design creates a highly flexible, novel process for producing polymeric films with tens to thousands of layers. When the number of layers in a thin polymer film approach the thousands, individual layer thicknesses are reduced from the micron to the nanometer scale. This nanometer layer thickness can approach the radius of gyration of the individual polymer molecule. This highly ordered and constrained composite layered structures can enable the discovery of new phenomena which include the formation of totally interphase materials, a result of polymer chain interdiffusion on the scale of individual layer thicknesses, and confined crystallization, a procedure that induces frustrated crystallization and unique orientations in thin nanolayers due to spatial layer confinement. Through the production of these novel layered structures, discoveries relating to the physical and chemical properties of two or more nanolayered polymer compounds have been studied and utilized to develop systems with new and exciting properties.
Layer multiplication exploits the viscoelastic nature of polymer melts. A two component coextrusion system consisting of two ¾ inch single screw extruders with melt metering pumps, an (A/B) two layer coextrusion feedblock, a series of layer multiplying die elements, two laminating surface extruders, and an exit tape or film die is illustrated in Figure 1.1. The inclusion of metering pumps into the coextrusion system enables an added degree of control over the relative thickness ratio of the layered polymers as they enter the A/B layered feedblock. From the feedblock, the two polymer layers enter a series of layer multiplication dies each of which doubles the number of layers through a process of cutting, spreading, and stacking the viscoelastic melt. A series of n multiplying elements combines two polymers as 2(n+1) alternating layers as shown in Figure 1.1 which specifically illustrates how two-component coextrusion through a series of three multiplier elements increases the number of layers from 2 to 16. Coextruded polymers with up to eleven multiplier dies have produced films with 4096 layers and individual layer thicknesses below 10 nm.[19] Samples consisting of 2 to 4096 layers have been extruded in 1 to 2 mm tapes or film as thin 12 µm.

Added versatility in the coextrusion of dissimilar polymers with poor adhesion can be addressed by utilizing a three-component coextrusion system that incorporates an additional polymer as a tie layer (T) in an ATBTA sequenced feedblock. Combining the layer multiplication dies with a third tie-layer extruder allows for the introduction of thin adhesive or barrier layers into the multilayered polymer tapes and films as shown in Figure 1.2. Layer multiplication of three
polymers in the ATBTA configuration through a series of \( n \) multipliers yields \( 2(n+2)+1 \) layers.

Improvements in layer uniformity and continuity have been addressed by matching polymer viscosities, by optimizing the layer multiplier die design, and by incorporating surface layers on the layered structure prior to film spreading. Layer uniformity and continuity strongly depend on the viscosities of the individual layered components. Poor viscosity matching can result in the lower viscosity polymer encapsulating the other by forming a slip film between the higher viscosity polymer and the multiplier die wall.[20] Interfacially driven layer instability and break-up may also result during layer multiplication if the two polymer melt streams possess a relatively large viscosity mismatch.[21] To maximize layer uniformity and overall film quality, polymers are extruded at a viscosity-match temperature and within a viscosity window determined by the coextrusion pressure (upper limit) and the melt strength (lower limit). Polymer viscosity is determined as a function of temperature using a Kayeness Galaxy 1 melt flow indexer at a low shear rate, 10 sec\(^{-1}\). A low shear rate is selected to simulate polymer flow conditions in the layer multiplication dies. A typical plot of polymer viscosity against temperature, Figure 1.3, illustrates a good viscosity match at 260\(^{\circ}\)C for coextrusion of polypropylene (PP) and polystyrene (PS).

Design modifications to the multiplier elements were conducted to achieve a more uniform layer thickness distribution.[22] Based on model analysis, two multiplier
designs were compared to investigate the effect of the layering pathlength, denoted as L and illustrated in Figure 1.4, on layer uniformity. Both designs utilized an identical approach of cutting, spreading, and stacking during layer multiplication. Design I, L=15 cm, had a sharp spreading transition and short landings. Design II, L=70 cm, possessed more gradual, rounded transitions and longer landings. The difference between the length spreading ratio BB′/AA′ and the stacking length ratio CC′/AA′ was reduced from 40% in Design I to 2% in Design II as a result of the longer die landing. The effect of multiplier design on layer uniformity was tested by coextrusion of a viscosity-matched polycarbonate (PC) and poly(methylmethacrylate) (PMMA) film. A 16 layer film with a 50/50 PC/PMMA composition was coextruded through a series of three Design I or Design II multiplier dies. To observe the individual layer uniformity from each multiplier design, cross-sections of the film were cut and polished with wet silicon carbide paper on a metallurgical wheel with individual layer thicknesses measured by polarized light microscopy, Figure 1.4.

The longer pathlength of the Design II multiplier dies resulted in much better layer uniformity, average layer thickness 69 ± 8 µm, as compared to the Design I, average layer thickness 71 ± 17 µm. Additionally, the smaller difference in the spreading and stacking path lengths of Design II dies eliminated the thick to thin tapering of layer thickness across the width of a single layer in films produced from Design I. Based on superior performance, Design II was utilized to obtain the structures discussed in this paper.
Further advances in film uniformity, in surface finish, and in overall flexibility in the design of layered polymer structures is accomplished through the addition of post multiplication surface layers. A 3/4 inch single screw extruder and melt pump unit provide an upper and lower polymer layer on the layered polymer stream, Figures 1 and 2. This eliminates wall drag on the layered core during the final film spreading in the exit die. Sacrificial surface layers, i.e. top and bottom layers that can be peeled from the layered polymer core post-extrusion, significantly increase the layer uniformity and film surface quality.[24] Flexibility in the selection of an additional permanent surface layer provides another opportunity for improving mechanical, gas or water barrier, or optical properties of the layered system.

Recent processing advancements including a better understanding of polymer viscosity requirements for coextrusion, the optimization of layer multiplication die design, and the addition of surface layers have enabled extension of layer-multiplying coextrusion to the nanoscale. In addition, successful coextrusion with as little as 50 grams of a specially synthesized material has demonstrated the nearly limitless design space available to fabricate polymer systems that possess novel optical, thermal, and gas barrier properties as a result of the hierarchical and scaling phenomena unique to individual polymer layers with nanoscale thicknesses.
1.3 Nanolayered Polymer Systems with Improved Properties

Coextrusion of layered polymer films with individual layer thicknesses down to the nanoscale have resulted in the production of novel systems with improved properties. Nanolayered polymer films were utilized to develop an all-plastic polymer laser, to fabricate gradient refractive index lenses, and to investigate gas barrier enhancement of crystalline polymer nanolayers confined to induce a high aspect ratio, in-plane, single-crystal-like lamellar structure.

1D Photonic Crystals and All-Plastic Lasers

Films with alternating layers of significantly different refractive indices and periodic nanolayer thicknesses approaching the quarter wavelength of light exhibit strong constructive optical reflections. Traditionally, reflective Bragg stacks have been produced by spin-coating inorganic materials with differing refractive indices.[25] Coextrusion of nanolayered polymers provides a method for continuous, low cost fabrication to extend highly reflective photonic technology to light weight polymer materials. Optically reflective layered polymer films, referred to as 1D photonic crystals, were fabricated on the two component coextrusion system using the surface layer extruders and four multiplier die elements to produce 32 layer PS (Styron 615 APR) and PMMA (Plexiglas VM-100) films.[26] The PS (n=1.585) and the PMMA (n=1.491) were selected based on their difference in refractive index (Δn=0.09) and compatible
melt viscosities. To provide optimal PS/PMMA layer thickness uniformity, thick (13 µm) sacrificial low density polyethylene (LDPE 6201) surface layers were coextruded with the 2.8 µm thick photonic PS/PMMA layered core. An AFM cross-section image of a microtomed 32 layer PS/PMMA photonic film with well defined nanolayers, 86 nm ± 14 nm, is shown in Figure 1.5. The quality of the 32 layer 1D photonic crystal was evaluated by comparing the observed transmission spectrum with the simulated spectrum obtained by the matrix method of Vasicek[27] for a non-absorbing multilayer assembly of known refractive indices. A plot comparing the measured and simulated primary reflection band, Figure 1.5, displayed excellent agreement between not only the location of the primary reflection band, but also the intensity and the band width. A 1D photonic PS/PMMA film with a peak reflection slightly greater than 600 nm appeared as an orange to red colored film, however, flexibility in the coextrusion process allowed for altering the layer thickness to produce photonic films with other visible, ultraviolet, or near-infrared reflection bands.

The ability to design and rapidly fabricate many kilometers of highly reflective photonic crystal film enabled the development of advanced optical applications including potentially mass producible, all-plastic lasers. An all-plastic distributed Bragg reflector (DBR) laser was constructed by sandwiching a dye-doped active core layer between two highly reflective 128 layer PS/PMMA photonic crystal films with the reflection band designed to match the emission maximum of the dye.[28] Operation of the all plastic DBR laser was achieved through photo
excitation ($\lambda_a=532$ nm) of a Rhodamine 6G (R6G) laser dye (MW=546 g/mole) doped in a PMMA monolith layer. The emitted light ($\lambda_e=565$ nm) was reflected and redirected by the 1D photonic PS/PMMA film. Operation of the DBR all-plastic laser was successfully accomplished under a threshold of 90 $\mu$J/cm$^2$ with a slope efficiently of 19.3%.

A second all-plastic laser, a distributed feedback (DFB) design consisting of a single microlayered 1D photonic crystal film with active lasing dye chromophores in one layer, was successfully produced[29], Figure 1.6. In contrast to the DBR laser which required laminating 1D photonic crystal films to a dye-doped active layer, the DFB laser was produced in a single roll-to-roll microlayer processing step. Films with 128 alternating layers of a poly(styrene-co-acrylanitrile) with 25% wt. acrylonitrile content (SAN25) and a fluroelastomer terpolymer of vinylidene fluoride, hexafluoropropylene, and tetrafluorethylene (THV) (Dyneon 220G) were coextruded with sacrificial LDPE (DOW 620I) surface layers. The SAN25 ($n=1.57$) and the THV ($n=1.37$) were selected for coextrusion based on a substantial difference in refractive index ($\Delta n=0.20$) and a good viscosity-match. The SAN25 was doped with 1.5 wt.% R6G dye. The THV had sufficiently low dye solubility to prevent diffusion of the R6G from the SAN25 layer. Coextrusion of SAN25 and THV layers 95 nm thick enabled the 1D photonic crystal reflection and the R6G fluorescence band to overlap and produced DFB lasing upon excitation with a Nd:YAG+OPO laser ($\lambda_e=535$ nm). Lasing of the nanolayered SAN25/THV DFB laser occurred with efficiencies as high as 8%.
with excitation thresholds as low as 100 μJ/cm². The high performance and potential low cost of continuous roll-to-roll microlayered DFB lasers demonstrated the technological usefulness of layer-multiplication already in practice in a range of passive devices.[18]

Nanolayer coextrusion of 1D photonic crystals is not limited to rigid glassy polymers. Highly elastic, tunable photonic crystals were produced through coextrusion of 128 layer films utilizing polyurethane (PU) (n=1.55, Pellethane 2355-95AE) and Pebax (n=1.48, Pebax 2533) elastomers.[27] Tunable 1D photonic crystals differ from the glassy PS/PMMA films in that very low stresses are necessary to induce reversible stretching or elongation of the elastomers. Elongation of the film decreases the overall film thickness and layer thickness, Figure 1.7, thereby changing the peak position of the reflection band. Transmission spectra of 128 layer PU/Pebax elastomeric photonic crystals were collected at increasing strain from 0 to 1.25. Stretching the elastomeric film to a strain of 1.25 resulted in a reversible reflection band shift from 600 nm (orange/red) to 400 nm (blue). The relationship between the applied strain, ε, and peak reflection, λ, is predictable based on geometric modeling of the film thinning during stretching. The reversibly tunable elastomeric 1D photonic crystals are another example of nanoscale layer thicknesses enabling a novel optical behavior in microlayered films that may lead to the development of new optically based strain sensor technology.
Variable Refractive Index Films for GRIN Lenses

Microlayer coextrusion provides additional flexibility by controlling the relative thicknesses of the A and B layers. Through coextrusion at off-set compositions, the relative thickness of PC and PMMA layers was varied from 1:1 at a 50/50 composition to 9:1 at a relative 90/10 composition, Figure 1.8.

The ability to vary the relative composition in a nanolayered polymer film with individual nanolayer thicknesses well below the quarter-wavelength of light allowed for creation of transparent layered films with designable refractive indices. A series of 4096 layer polymer films of PMMA (Plexiglas V920) and a styrene-acrylonitrile copolymer with 17% acrylonitrile content (SAN17) (Lustran) were coextruded at 1% composition intervals.[30] The refractive index of each of the 101 nanolayered PMMA/SAN17 films was measured and the results are plotted against overall film volume percentage of SAN17 in Figure 1.9.

Coextrusion of nanolayers less than the quarter-wavelength of light eliminates reflection as light passes from one layer to the next, which enables the nanolayers to act as a composite structure while remaining transparent to the visible eye. Varying the overall PMMA:SAN17 composition in the nanolayered film varies the composite film refractive index as a weighted average of the constituent polymers. Coextrusion of PMMA/SAN17 at 1% compositional intervals produced small, 0.0009 differences in the refractive index. Stacks of 101 films, each of different refractive index based on PMMA/SAN composition, were
compressed under heat and pressure to produce a thick polymer sheet with a gradient in refractive index (GRIN) equal to the difference in refractive index of the nanolayered films. For variation of PMMA/SAN17 nanolayered films from 0/100 to 100/0 compositions, a difference in refractive index of 0.09 was created. Subsequent shaping and polishing of this thick polymeric GRIN sheet produced polymeric GRIN lenses with a bio-inspired parabolic refractive index distribution. Improved optical image contrast and larger lens field of view resulted when GRIN lenses were compared with monolithic polymer or glass lenses of similar geometric shape.[30,31] Flexibility to create GRIN optics through stacking the variable refractive nanolayer films has enabled the design and production of nanolayered polymeric GRIN optics with unheralded freedom in the refractive index distribution. This breakthrough may enable lighter, higher powered optical information and imaging systems.

**Nano-Confinement of Glassy and Crystalline Polymers**

When two polymers are brought into contact, the interface is not perfectly sharp. The interphase between immiscible polymer blends can be considered a third phased with its own characteristic properties.[32] Layer-multiplying coextrusion provides an opportunity to study the interphase through coextrusion of nanolayer films with individual polymer layer thicknesses approaching the 5 to 10 nm theoretical polymer interphase thickness.[33] Processing of 50/50 composition PC/PMMA multilayer films with layer thicknesses ranging the micro- to
nanoscale was accomplished by increasing the total number of film layers from 128 up to 4096, **Figure 1.10.** As individual layer thicknesses approach the interphase dimension, a new material is created that is totally interphase.[34] This totally interphase material was examined by utilizing DSC thermograms to track the Tg of PC and PMMA layers as a function of individual layer thickness, **Figure 1.11.** When the individual layer thickness of the PC and PMMA was greater than 100 nm, the Tg value agreed with the constituent bulk values of 144°C (PC) and 112°C (PMMA) were measured. Decreasing layer thicknesses below 100 nm caused a gradual shift of the two Tgs toward a single value. A single Tg was measured when the layer thicknesses were 10 nm or less, suggesting the transformation of the material from constituent layers to a totally interface material.[19] Layer-multiplying processing to produce polymer films with very thin layers provides for an opportunity to explore and create polymer materials with novel composite properties based on high interfacial interactions and confining nanolayer phenomena.[34-36]

Layer-multiplying coextrusion provides a flexible processing tool to decrease individual layer thicknesses through the microscale and approaching the nanoscale dimensions of individual polymer molecules. Crystalline polymers confined in ultrathin spin-coated layers,[37,38] or microphase separated block structures containing at least one crystallizable block,[39] have produced specific crystal orientations and unique lamellar morphologies. One dimensional confinement of crystalline polymers by layer-multiplying coextrusion provides an
advantage over the preceding techniques in the ability to achieve long range, defect free nano-confinement in films with thousands of individual layers. As a result of the structural plurality of the confined crystalline layers in a composite film, the use of conventional polymer analysis techniques can be utilized to probe structure-property relationships.

A series of layered polymer films of alternating polyethylene oxide (PEO) (Polyox) and either PS (Styron 615) or poly(ethylene-co-acrylic acid) (EAA) (Primacor) were coextruded.[40, 41] The layer thickness of PEO was systemically decreased from 10 µm to 10 nm, the reported thickness of PEO crystalline lamellae, by tuning the relative composition of PEO/PS or PEO/EAA and increasing the overall number of film layers from 9 to 1025. Cross-section AFM images of microtomed PEO/PS layers with individual PEO layer thickness ranging from 1 µm to 25 nm were examined to elucidate structural implications of confinement on the PEO layer crystalline structure, Figure 1.12.

Truncated spherulites, resembling the bulk PEO crystallization habit, were prevalent in thicker, microscale PEO layers. In the 300 nm layers, confinement by PS appeared to highly constrain the growth direction of the PEO lamellae resulting in a preferential orientation in the layer plane. Further reduction of layer thickness to 75 nm resulted in PEO layers crystallizing as in-plane stacks of three to five long lamellae. Finally, in 25 nm layers, the PEO was confined to crystallize into very long, in-plane, single crystal-like lamellae sandwiched
between thick PS layers. To confirm the observed increased PEO lamellar orientation when confined in very thin nanolayers, wide angle X-ray scattering (WAXS) patterns were measured in the extrusion direction (ED), Figure 1.12. In good agreement with the AFM images, PEO (120) WAXS reflection patterns exhibited increasing equatorial orientation from the two arc pattern in 1 µm PEO layers to highly oriented fiber-like spot patterns in 25 nm layers. The sharpness of the diffraction spots in the 25 nm PEO layer WAXS pattern suggested that PEO crystals were well oriented in-plane in the PEO confined layer.

The effect of in-plane orientation of large PEO single crystal layers on the oxygen permeability of PEO/EAA and PEO/PS nanolayer films was tested in a Mocon OxTran® permeability unit at 23°C and dry conditions. Effective PEO layer oxygen permeability as a function of layer thickness was calculated from the measured oxygen flux using the series transport model for layered structures, Figure 1.13.[41]

As PEO layer thickness was reduced below a micron, a smooth decrease in effective PEO oxygen permeability with decreasing layer thickness was measured. A minimum effective PEO layer oxygen permeability of 0.0025 barrer was measured for confined, highly oriented 25 nm PEO layers. This was nearly 150 times lower than the bulk PEO permeability, 0.38 barrer. The large improvement in confined PEO layer oxygen barrier was attributed to the large
size, estimated to approach 5 microns, of the gas impermeable, single crystal-like, in-plane lamellae induced through nanolayer confinement.
1.4 Conclusions

Layer-multiplying coextrusion was demonstrated as a polymer processing technology capable of producing films with up to thousands of layers with layer thicknesses in the micro- and nanoscale. Production of nanolayer films was demonstrated with improved layer uniformity stemming from optimization of layer multiplier die design, selection of viscosity matched materials, and incorporation of surface layer capabilities. Design of ‘uneven’ split layer multiplier dies enabled the coextrusion of a wide variety of layer thickness distributions. Layered films with improved properties were successfully coextruded based on nanoscale structure-property relationships. Optical properties of nanolayer polymer films were utilized to produce an all-polymer laser, tunable photonic materials for sensors, “super lattice” dual reflection peak films, and novel GRIN lenses. Coextrusion of a semi-crystalline polymer in 25 nm thick layers led to gas barrier enhancement based on a layer confinement induced crystalline phase orientation. The ability of layer-multiplying coextrusion to produce synergistic composite structures by a continuous process with only minimal material quantities continues to make it an attractive tool for rapid development of a broad range of future polymeric materials and composites based on novel structure-property relationships.
1.5 References

Figure 1.1: (Left) Two component multilayer system comprised of extruders, pumps, feedblock, and mulltiplying dies, surface layer extruders, and exit die. (Right) Schematic illustration of layer multiplication by cutting, spreading, and recombining the melt stream.
Figure 1.2: (Top) Three component microlayer system with tie layer extruder. (Bottom) Schematic illustration of five to nine layer multiplication with a tie layer (T) separating the A and B layers.
Figure 1.3: The MFI viscosity match of PS/PP for determining microlayer coextrusion conditions.
Figure 1.4: (Top) Schematic illustrating the difference in polymer flow streamlines based on multiplier die length. (Bottom) The effect of increasing multiplier die length from 15 to 70 cm on layer uniformity.
Figure 1.5: (Top) Cross-section AFM of 32 layer PS/PMMA 1-D photonic film with LDPE surface layers. (Bottom) Comparison of measured and modeled transmission spectra of two stacked 32 layer PS/PMMA films with 86 nm average layer thickness.
Figure 1.6: (Top) Schematic of the DFB laser film of R6G doped SAN25 and THV. (Bottom) Lasing emission from the nanolayered DFB laser.
\[ \lambda_{\text{reflected}} = 2(n_1d_1 + n_2d_2) \]

Figure 1.7: (Left) Reflection spectrum as a function of wavelength at designated strains for an elastomeric 128 layer PU/Pebax tunable photonic crystal. (Right) Optical reflective peak position as a function of strain for tunable photonic crystal.
Figure 1.8: Cross-section AFM image of PC (light) and PMMA (dark) layer films with (Top) 50/50 composition and 60 nm layers, (Bottom Left) Off-set 80/20 composition, and (Bottom Right) Off-set 90/10 composition.
Figure 1.9: Effect of composition on composite SAN17/PMMA film refractive index. Varying relative composition of SAN17/PMMA in the nanolayered film altered the refractive index of the composite nanolayered film leading to the production of novel gradient index lenses.
Figure 1.10: (Top) Optical Micrograph of 128 layer 50/50 PC/PMMA film cross-section with 1 µm layers. (Bottom) AFM of 4096 layer 50/50 PC/PMMA film cross-section with 30 nm layers.
Figure 1.11: The glass transition temperature of layered PC and PMMA layers as a function of individual layer thickness. As individual layer thickness is reduced into the nanoscale, increasing layer interphase contributions result in a convergence to an average T_g for PC and PMMA.
Figure 1.12: 2D WAXS extrusion direction patterns and AFM cross-section images exhibiting lamellar orientation in PS/PEO layered films with nominal PEO layer thickness of (a) 1 μm, (b) 300 nm, (c) 75 nm, and (d) 25 nm.
Figure 1.13: Oxygen permeability of polyethylene oxide (PEO) layer as a function of PEO layer thickness in PEO/PS and PEO/EAA micro- and nanolayer films. Oxygen permeability tests were conducted at 23 °C and 0% relative humidity.
Chapter 2

Gradient Multilayer Films By Forced Assembly Coextrusion

2.1 Introduction

Multilayered polymer systems are produced to satisfy stringent technical requirements for high value-added applications such as gas barrier films [1,2] mechanically robust systems [3,4], and optical applications.[5,6] These polymer systems are conventionally produced by multilayer coextrusion, a process which combines multiple polymers using a multilayered feedblock. Recent developments in coextrusion technology have led to the production of multilayered polymer films with designed “chirped” or graded layer thickness distributions which exhibit enhanced optical reflection properties.

Multilayer structures with “chirped” or a graded layer thickness are commonly found in nature.7 These naturally occurring graded layer structures exhibit vibrantly colored optical surface reflections in organisms such as beetles [8], crabs [9], and fish [7] stemming from the interaction of light reflected from the gradient structure. Light reflections through a layered stack of differing refractive index media are a function of incident light angle, wavelength, and layered stack thicknesses.[8] These metallic-like, colored, structural reflections result from an constructively and destructively interfering contributions of the individual layers which comprise the graded layered structure.
Optically reflective gradient layer thickness polymer films are produced commercially utilizing specially designed multilayer feedblocks.[10-12] These coextrusion feedblocks are fabricated to produce a multilayered polymer film with a specific number of layers and set layer thickness gradient distribution. Multilayered polymeric mirrors[13] and films with 400 nm wide optical reflections peaks[14] have been produced by this approach.

Forced assembly coextrusion is a low-cost, highly flexible alternative approach to multilayered film polymer processing utilizing solely a multilayered feedblock. Forced assembly coextrusion combines conventional coextrusion of two or more polymers in a two-layered feedblock with additional layer multiplication capabilities achieved by extrusion through a series of multiplier dies. This processing design creates a highly flexible, novel process capable of producing polymeric films with tens or thousands of layers.[15-17] The synergistic combination of two or more polymer materials into these layered structures is not limited solely to optical effects. Mechanical effects of reducing the layer thickness in multilayered films have been demonstrated to increase film fracture strain, impact strength, and ballistic performance.[18,19] A change in the polycarbonate/ poly(styrene-acrylnitrile) copolymer multilayered film deformation mechanism from craze opening, in 30 micron layers, to micro-shear banding and yielding, through several adjacent one micron layers, was reported as an effect of layer scaling.[20,21]
This chapter describes the extension of forced assembly coextrusion to produce multilayered polymer films with gradient layer thickness distributions. Flexibility in the design and sequencing of novel uneven split layer multiplier dies was utilized to produce films with different magnitude, i.e. the ratio of thickest to thinnest individual polymer layers, and different gradient layer thickness distribution profiles. Coextrusion through a series of novel uneven split and conventional layer multiplying dies was utilized to produce families of gradient multilayered films with individual layer thicknesses ranging from the micro- to the nanoscale to elucidate the scaling effects of gradient layer thickness distributions on the optical and the mechanical properties in these novel polymer systems.
2.2 Materials and Methods

Forced Assembly Coextrusion System

A two component coextrusion system consisting of two ¾ inch single screw extruders with melt metering pumps, an (A/B) two layer coextrusion feedblock, a series of layer multiplying die elements, a laminating surface extruder, and an exit film die was utilized, Figure 2.1. The inclusion of metering pumps into the coextrusion system enabled an added degree of control over the relative thickness ratio of the layered polymers as they entered the A/B layered feedblock. From the feedblock, the two polymer layers were fed through a series of layer multiplication dies. Each layer multiplier doubles the number of layers through a process of cutting, spreading, and stacking the layered viscoelastic melt. A series of \( n \) multiplying elements was utilized during this work to combine the two polymers as \( 2^{(n+1)} \) alternating layers, Figure 2.1.

Layer uniformity and continuity depend heavily on the viscosity of the individual layered components. To maximize layer uniformity and overall multilayered film quality, polymers were coextruded at a viscosity-match temperature and with laminating surface layers. Polymer viscosity was determined as a function of temperature using a melt flow indexer (Galaxy I Model D7054, Kayeness Inc., Honeybrook, PA) at a low shear rate, 10 sec\(^{-1}\), to simulate flow conditions during layer multiplication coextrusion. A common material coextrusion temperature
was selected based on similar relative material viscosities within a processing window bounded by the coextrusion pressure (upper limit) and the material melt strength (lower limit). Coextruded film uniformity, film surface finish, and overall flexibility in the design of thin nanolayered polymer films were accomplished through the addition of post multiplication surface layers. A surface layer extruder, consisting of a \( \frac{3}{4} \) inch single screw extruder and melt pump unit, provided an upper and lower polymer layer on the multilayered polymer stream. Sacrificial surface layers, i.e. top and bottom layers that were easily delaminated from the microlayered polymer core post-extrusion were utilized in this work to increase the layer uniformity while providing a structural support for encasing nanolayered core films as thin as 12 microns. It should be noted that although only sacrificial surfaces layers were utilized in this study, flexibility in the selection of a permanent surface layer polymer provides an additional opportunity for improving mechanical, gas or water barrier, or optical properties of the multilayered tape and film systems.

**Design of Layer Multiplying Dies**

Layer multiplying dies were designed with uneven split feed channels, [Figure 2.2](#). Coextrusion through a layer multiplying die with uneven feed channels, i.e. \( A \neq B \), resulted in layer multiplication from two to four layers. However, the uneven split, spread, and recombination of the polymer melt streams through this die resulted in the formation of a two thicker layers from channel A as compared
to those from channel B. To illustrate the effect of offsetting the multiplier flow channel width, predictions of the uneven layer multiplication through these multipliers was simulated based on achieving an equivalent extrusion pressure drop inside each die flow channel. Extrusion pressure drop inside the multiplier was estimated utilizing the Hagen-Poiseuille relationship for pressure drop through a square channel[22], Equation 1:

\[ P_i - P_o = \frac{12 \times \mu \times L \times Q_i}{H \times W_i^3} \]  

(1)

where \( P_i - P_o \) is the pressure drop across the multiplier die, \( \mu \) represents the layered melt viscosity, \( L \) is the die channel length, \( Q \) is the volumetric flow rate of polymer, \( H \) is the flow channel height, and \( W \) is the offset channel width. Equation 1 was solved for the relative polymer flow rate through an uneven split multiplier die by setting an equivalent internal die pressure drop across the cross-section width of channels A and B. The actual uneven split ratio of the offset layer multiplier die was then be calculated from the relative channel flowrates by Equation 2

\[ \text{split ratio} = \frac{Q_A}{Q_A + Q_B} : \frac{Q_B}{Q_A + Q_B} \]  

(2)

Substitution of the known uneven split multiplier die channel widths allowed for calculation of an actual split ratio for the uneven layer multiplying dies which was
significantly more extreme than the relative physical multiplier dimensions, Table 2.1. In order to construct several gradient layer thickness distributions, four new uneven split layer multiplying dies were machined with relative offset A/B flow channel widths of 51/49, 52/48, 54/46, and 58/42%.

**Coextrusion of Gradient Layer Thickness Polymer Films**

A 32 gradient layer coextrusion experiment was conducted to confirm the uneven multiplier die functionality and calculated pressure equilibrated split ratios. Coextrusion of a 32 gradient layer thickness Polystyrene (PS) (Styron 615, The Dow Chemical Company) /Polymethylmethacrylate (PMMA) (Plexiglas VM-100, Arkema Inc.) film was designed to validate the forced assembly approach for producing gradient layer thickness films. A coextrusion trial through the series of the four fabricated uneven split layer multiplying dies, Figure 2.3, was predicted to construct a gradient layer thickness distribution within the polymer film by doubling the number of layer thicknesses as the melt stream passes through each individual die. The resulting 32 gradient layer film should be constructed of sixteen different thickness layer doublets. The magnitude of individual layer thickness differences between the thickest and thinnest layer should also approach 10X as a result of coextrusion through this series of four uneven split layer multiplication dies.

Optically reflective 128 gradient layer thickness films were produced by forced assembly coextrusion through a series of conventional and uneven split layer
Gradient multilayer films with 256 layers were produced to investigate the scaling effects of layer thickness on the deformation behavior in composite multilayer films. A 256 gradient PS (Styron 685, The Dow Chemical Company)/styrene-ethylene propylene-styrene triblock copolymer (SEPS) (Kraton G1730, Kraton Polymers Inc.) multilayer film was coextruded utilizing a series of three even and four uneven split multiplier dies to produce a 10X magnitude layer thickness gradient containing layers ranging from ~1µm to 100 nm.

A 128 layer PS/THV multilayer film with a 10X magnitude layer thickness gradient was coextruded to investigate a thickness dependent buckling of plastic/elastic layers. Inline foaming of the PS layer was accomplished by addition of 1.5% wt. of a commercial carbon dioxide blowing agent (Safoam® RIC50-FP, Reedy International Corp., Keyport, NJ). The relative composition of the PS and THV material was held constant at a 50/50 v/v ratio.
Characterization

Characterization of the 32 gradient layer PS/PMMA films was investigated by optical microscopy (OM). The coextruded gradient layer film was embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were microtomed at -100 C under a liquid nitrogen cooled atmosphere with an Ultramicrotome (MT6000-XL from RMC, Tucson, AZ). Film cross sections were prepared perpendicular to the film plane and imaged directly by OM (Olympus BH-2 optical microscope, Olympus America Inc., Melville, NY).

Optical transmission spectra of reflective 128 gradient layer films were measured using a SD2000 Fiber Optics Spectrometer (Ocean Optics Inc., Dunedin, FL). All measurements were carried out under unpolarized light at 0° incident angle and at ambient temperature. 128 gradient layer PS/THV film structure was examined with atomic force microscopy (AFM) utilizing the previously described sample preparation and microtoming procedure. Film cross sections were prepared perpendicular to the film plane and imaged directly by AFM with a commercial scanning probe microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) operated in the tapping mode. Measurements were performed at ambient conditions using a rectangular type Si probe with spring constants 50 Nm$^{-1}$ and resonance frequencies in the 284-362 kHz range. The tip radius was 10 nm.
PS/SEPS films with 256 gradient layers were analyzed by optical microscopy with images in the upright position and transmittance mode to observe changes through the film thickness. Uniaxial tensile bars were cut along the extrusion direction of the film according to ASTM D 638 and deformed to 2% strain to examine the characteristic deformation zones through the film thickness (z-direction).[23] The films were analyzed normal to the surface of the specimen in the tensile bar neck region to determine if differences in the failure mechanism result from the reduction of layer thicknesses through the gradient film.

Foamed PS/THV 128 gradient layer film cross sections were prepared perpendicular to the film plane and imaged directly by OM as previously described. PS/THV film density was measured via a submersion technique utilizing a density kit attachment and Excellence XS analytical balance (Mettler Toledo, Greifensee, Switzerland).
2.3 Results and Discussion

Producing Gradient Thickness Films

A 32 layer, 10 mil PS/PMMA gradient multilayer film was extruded utilizing a series of the four uneven split layer multiplier dies in order of increasing offset split ratio, Figure 2.3. The resins were chosen for coextrusion on the basis of matching viscosities at a common coextrusion temperature, a requirement for Forced assembly coextrusion layering. Micrographs of the film cross-section were examined to compare the predicted and measured layer thickness distribution in the gradient film, Figure 2.4. As predicted, the cross-section micrograph of the 32 gradient layer PS/PMMA film contained an order of magnitude difference, 30 to 3 µm, difference between the thickest and thinnest individual layers. In addition, good agreement between the simulated and measured 32 gradient layer thickness distribution was witnessed.

Forced assembly coextrusion and uneven split layer multipliers are not limited to large magnitude layer thickness gradients. Combining the four previously described uneven split layer multipliers with conventional 50/50 even split layer multipliers allows for the coextrusion of films with larger number of layers and different layer thickness distributions. The sequence or order of a combined series of the uneven and even split multipliers will affect layer thickness distribution produced within a coextruded multilayered film.
The ability to rearrange and intermix uneven and even split multipliers enables processing of a wide range of gradient layer thickness distributions by the forced assembly processing technique. The combination of these technologies enables quick and economical experiments to investigate structure-property relationships in families of gradient layer thickness distributions without machining additional multilayered feedblocks. The flexibility of the uneven split layer multipliers was next utilized to investigate the optical effects produced by varying the gradient layer thickness distribution in 128 layer multilayered polymer films.

**Optically Reflective Gradient Nanolayered Films**

Stemming from the difference in refractive index, visible reflections from multilayered film structures are produced when the individual polymer layer thicknesses approach 100 nanometers. This photonic phenomenon has been previously investigated and modeled for uniform thickness layered polymeric films.[6] Extension of analytical predictions for optical reflections for multilayered polymer films with gradient layer thicknesses distributions have been developed by Francon[24], Vasicek[25], and Shrenk[26]. This method first defines the incremental phase angle, $\Phi_i$ contributions of each individual polymer layer as

$$
\Phi_i = \frac{2\pi n_i d_i}{\lambda},
$$

(3)

where $d_i$ and $n_i$ represent the layer thickness and refractive index, respectively. A matrix approach describing the optical behavior of each layer can be expressed as
\[
\begin{pmatrix}
q_1 \\
q_2 \\
q_n
\end{pmatrix}
= \begin{pmatrix}
q_{11} & q_{12} \\
q_{21} & q_{22}
\end{pmatrix}
\begin{pmatrix}
\cos \Phi_i & j \frac{\sin \Phi_i}{n_i} \\
j n_i \sin \Phi_i & \cos \Phi_i
\end{pmatrix},
\]

(4)

where \( j = \sqrt{-1} \). Through definition of each layer thickness, \( d_i \), and refractive index, \( n_i \), any two component multilayer film layer thickness distribution can be described by a complex 2 x 2 matrix \((Q)\) which represents the matrix product of \(N\) individual layer matrices \((NQ)\):

\[
(Q) = (q_1 q_2 q_3 q_4 \ldots q_N)
\]

(5)

The multilayered film reflection spectrum for normal incident light in an air, i.e. refractive index = 1.0 medium, is then expressed as

\[
R = \left[ \frac{(Q_{11} + Q_{12}) - (Q_{21} - Q_{22})}{(Q_{11} + Q_{12}) + (Q_{21} + Q_{22})} \right]^2
\]

(6)

Utilizing this model as a guide, the effect of varying the gradient layer thickness distribution was investigated as a means to develop films with novel optical reflective properties.

Three different 128 layer gradient layer thickness distributions were coextruded to examine optical effects of gradient multilayered films. Forced assembly coextrusion of a 128 multilayer 50/50 v/v PS/PMMA 0.5 mil thick film, with a \(\Delta n = 0.08\), was processed utilizing a series of five conventional and one uneven 51/49 split multiplier, Figure 2.5. Coextrusion through the multiplier series described should produce a film containing a “step-distribution” consisting of two layer thicknesses. The effect of adding a second layer thickness in a nanolayered...
PS/PMMA film was modeled to widen the optical reflection peak to 90 nm, **Figure 2.5.** Experimentally obtained UV-vis optical reflection spectra of the 128 PS/PMMA gradient multilayer films in fact exhibited a strong reflection from 520 to 680 nm. The minimum measured transmission of this film approached the model predicted zero percentage level. The 160 nm span of reflected wavelengths was considerably larger than the model predictions. The increased reflection width was contributed to strong secondary reflection peaks suggesting layer thickness deviations were present in the multilayered film structure.[6] The 160 nanometer wide reflection band produced with only a single uneven split layer multiplier, exhibited greater than a 3X increase in optical reflection band width over previously coextruded uniform layer thickness PS/PMMA films.[6] Polymer multilayered films with optical band gaps of a couple hundred nanometers have potential applications as optical filters or reflectors and in optical communications devices.

A second 128 gradient layer 50/50 v/v PS/THV film, $\Delta n=0.19$, was coextruded utilizing a combination of two conventional and four uneven split layer multipliers sequenced in order of increasing split ratio. Increasing the number of uneven split layer multipliers will increase the number of additional layer thickness in a multilayered film, which in turn should further widen the optical reflection band of the composite multilayer film. An AFM cross-section of the 128 gradient layer PS/THV film structure showed excellent comparison of the predicted and coextruded layer thickness distribution, **Figure 2.6.** In contrast to the 32 gradient layer PS/PMMA film which also showed a 10X magnitude
gradient with four uneven split multipliers, inclusion of two conventional layer multipliers before the uneven split multipliers increased the number of film layers to 128 and decreased individual layer thicknesses from the micron to the nanometer scale. Nanometer scale gradient multilayer PS/THV films exhibited optical reflections over the entire measurable spectrum of visible light (> 600 nm). The 600 nm wide band, Figure 2.6, may actually extended farther below 400 nm (UV) and above 1000 nm (near IR) however, the UV-vis spectrometer utilized in this work was limited to a measurement range of 400 to 1000 nanometers. The intensity of the measured reflection, approximately 20% transmission, was slightly lower than the modeled transmission spectrum potentially suggesting additional film reflectivity may be present due to coextrusion induced orientation effects in the THV layers not accounted for in the analytical models. Gradient layered polymeric films with wide-band reflections over the entire visible light spectra have potential applications as light reflectors in solar collectors and waveguide type materials.

Forced assembly coextrusion processing allows for tuning the relative volumetric polymer ratios in a layered film. By tuning melt pumps in the coextrusion system, a 128 gradient layer 60/40 v/v PMMA and PVDF blend/PS film, $\Delta n=0.13$, was coextruded. This 128 layer film utilized four conventional multipliers and two uneven split multipliers, 51/49 and 52/48. The combined effect of an unbalanced 60/40 feed ratio with uneven split layer multipliers creates a dual “super lattice” gradient layer thickness distribution within a single multilayered film, Figure 2.7. The simulated optical effect of designing an internal “super lattice” distribution in
a multilayered film with a significant difference in polymer refractive indices was the formation of two distinct reflection peaks at 500 and 600 nanometers. Experimental UV-vis transmission spectra of the coextruded “super lattice” films exhibited excellent agreement with analytical predictions for the dual peak positioning and intensity, 10% transmission. Dual reflection peak “super lattice” films have potential applications in the production of special optical filtering and sensory devices. The flexibility to rearrange and intermix the uneven and the even spilt layer multipliers enables processing of a wide variety of layer thickness distributions that may lead to the production of novel polymeric structures for optical filters and information storage devices while potentially leading to studies of new mechanical property phenomena.

**Mechanical Deformation of Gradient Multilayered Films**

Layer-multiplying has been shown to be advantageous in producing systems with increased material toughness by reducing the constituent layer thicknesses.\(^{18-20}\) Previous work by Sung et al.\(^{[20,21]}\) showed that decreasing the individual layer thickness in a series of polycarbonate (PC)/SAN multilayer films led to a change in the SAN layer deformation from crazing to shear banding. Thin layers of polystyrene (PS) confined by a block copolymer also experienced a change in deformation mechanism. Recent work by Korley et al.\(^{[27]}\) using confinement by an elastomeric styrene/saturated ethylene-propylene block copolymer (SEPS) demonstrated that the change in the deformation mechanism occurred at a critical layer thickness, demonstrating thin layer yielding as reported by Michler.\(^{[28]}\)
Gradient multilayer PS/SEPS films were produced to refine the transition from brittle crazing to ductile shear banding. A 256 multilayer film of PS/SEPS, was coextruded utilizing a series of three even and four uneven split layer multiplier dies arranged in order of increasing offset ratio. The resulting 100 μm thick, 50/50 v/v PS/SEPS film contained a 10X gradient in the nominal layer thickness from 1 μm to 100 nm. A dogbone shaped tensile bar was cut from the gradient layered film along the film extrusion direction according to ASTM D638. The specimen was then deformed under uniaxial tension to a strain of ~2%. The two sides of the strained film were examined by optical microscopy, Figure 2.8. The side of the film with thick 1 μm PS layers exhibited crazes that propagated at 90° to the applied stress direction. In contrast, images of the side with thin 100 nm layers exhibited some long shear bands that extended at a 45° angle to the applied stress direction and many, much shorter surface crazes. Upon closer examination, the short surface crazes terminated in small shear bands similar to those observed in PC/SAN film with thin uniform layers.[21] The transition in the PS deformation from crazing to cooperative crazing and shear banding was indicative of increased cooperative interaction between the layered materials as a result of the reduced layer thickness. The effect of layer scaling on the deformation mechanisms in a single gradient thickness PS/SEPS film was similar to that witnessed previously in a series of 49, 194, 388, and 776 uniform layer PC/SAN multilayer films.[20,21] Thus, gradient multilayers facilitated the rapid investigation into the layer thickness dependence using a single polymer film. It is envisioned that the gradient multilayer technology utilizing uneven split layer
multilayer dies will enable more rapid and efficient investigation of layer scaling
effects compared to uniform thickness multilayered films.

**Layer Buckling of Gradient Multilayered Films**

The effect of layer thickness on buckling in a single 128 gradient layer THV/PS film was investigated. Layer buckling has been observed in stretched and recovered uniform layer thickness multilayered films containing alternating plastic/elastomeric layers.[29-31] Wave-like layer buckling patterns result in elastic/plastic multilayered films during the elastic recovery of the stretched film steaming from a retraction of elastomeric layers and lateral relaxation of plastic layers to relieve residual tension. A linear dependence between the plastic layer buckling wavelength, $\lambda_r$, and layer thickness, $t$, was exhibited previously in 3 layer plastic/elastomeric films by Hu et al.[29] A relationship describing the loss of stability upon buckling can be expressed as a summation of forces and moments around a rigid layered surrounded by two elastomeric layers.[32-34] Assuming ideal elastic behavior, no Poisson’s ratio effect and negligible shear deformation at the interface allows for use of the expression

$$E_p I \frac{d^4 y}{dx^4} + F \frac{d^2 y}{dx^2} + 2 \frac{\pi w E_R}{\lambda_r} y = 0$$

(7)

where $E_p$ is the compressive modulus of the rigid PS layer, $I=wt^2/12$ is the second moment of area of the rigid layer cross-section about the axis of buckling, $w$ is the $z$-dimension of the film, $t$ is the rigid layer thickness, $y$ is the displacement of the rigid layer, and $F$ is the longitudinal compressive force on the rigid layer.
Elastomeric material contributions to Equation 7 include the lateral force from the two elastomeric THV layers on the rigid PS layer, $2(\pi wE_R/\lambda)y$, due to the Young’s modulus, $E_R$. From this relationship it has been shown[32] that a layer thickness dependent critical buckling point relationship can be described in the multilayered composite by

$$\lambda_{r,c} = \pi \left[ \frac{4E_p}{3E_R} \right]^{1/3} t$$

which can be tested by experimentally measuring the rigid buckled layer wavelength as a function of layer thickness. A resultant plot of the critical buckling wavelength, $\lambda_{r,c}$, as a function of layer thickness should result in a linear relationship corresponding to a modulus ratio of $E_p/E_R$. Evaluation of this relationship in a gradient layer thickness polymer film offers a unique opportunity to trace layer thickness dependent PS layer buckling wavelengths within a single film multilayered film.

Gradient multilayered films of plastic/elastic PS/THV with a 10X difference between the thickest and thinnest layers were produced to investigate this previously reported thickness dependent buckling behavior. A 128 gradient layer PS/THV film was coextruded utilizing a series of two even and four uneven split layer multiplying dies arranged in order of increasing offset. Chemical blowing agents were added to the PS layer to induce foaming during coextrusion. Foaming the gradient multilayer structure reduced by nearly one-half, from 1.501 to 0.759 g/cm$^3$, the overall film density. A cross-section optical micrograph of the
coextruded PS/THV film, Figure 2.9, exhibited layer delamination and subsequent layer-buckling as a result of the foaming process. The resultant layer delamination by foaming induced layer buckling most probably as local interfacial layer strains due to foam cell growth surpassed the adhesive force of the THV/PS layers allowing the rubbery/plastic THV/PS to recovery as small packets of layers upon cooling. As seen in the micrograph, Figure 2.9, the thicker PS/THV layer packets exhibited longer buckling wavelengths, $\lambda_1$ and $\lambda_2$, as compared to the thinner layers, $\lambda_5$ and $\lambda_6$. PS layer buckling wavelengths as a function of layer thickness were measured across the gradient layer film, Figure 2.9. The buckled gradient layer films exhibited a trend of linearly decreasing layer-buckling wavelengths with PS layer thickness similar to that observed from a series of 3 layer films by Hu[29]. Extraction of the best fit linear slope value for this relationship was $\lambda/t=7.0 \pm 0.5$ which corresponded to an $E_P/E_R$ value of $8.5 \pm 2.1$ from Equation 8. The experimentally determined ratio was slightly lower compared to a literature reported $E_P/E_R$ ratio of 12.0.[35,36] A slight reduction in the experimentally induced buckled layer wavelength may have resulted due to lower strain rates stemming from foaming induced delamination as compared to traditional mechanical tensile strain induced buckling. The ability to control layer buckling and layer delamination through inline foaming of designed gradient layer thickness distributions within a single film could provide a powerful tool for the future development of mechanically robust, light weight materials through multilayer coextrusion.
2.4 Conclusions

Gradient layer thickness polymer films were created through the combination of novel uneven split layer multiplying dies and forced assembly coextrusion processing techniques. Fabrication of gradient layer thickness films with up to a 10x difference between the thickest and thinnest film layers were produced in 32 and 128 multilayered polymer films. The highly flexible nature of forced assembly coextrusion and the ability to combine a series of conventional even and novel uneven layer multiplier dies has allowed for production of variable shape and magnitude gradient layer thickness distributions. 128 gradient multilayered films with novel wide or dual band optical reflection properties were produced to demonstrate the potential of this new platform technology to rapidly identify and develop several novel optical gradient layered polymeric materials by merely rearranging a series of layer multiplying dies.

Mechanical deformation and buckling behavior related to the individual layer thicknesses within a gradient layer thickness multilayer film was demonstrated. A 256 multilayer PS/SEPS film with a layer thickness distribution from one micron to 100 nm was processed illustrating a layer thickness dependent mode of mechanical deformation. The shift of the brittle SAN layer deformation mechanism from crazing, in thicker layers, to short crazes terminating with micro-shear bands, in thin sub-micron layers, demonstrated how gradient layer thickness films can be exploited to study layer scaling phenomenon within a single polymer film. Additionally, a layer thickness dependent buckling behavior in a gradient
PS/THV film was illustrated through layer delamination brought about by foaming. This result represents the first time a single multilayered film could be utilized to track the reduction of the PS layer buckling wavelength with the reduction in the individual film layer thicknesses. The prospect of rapid investigating of layer scaling effects across a 10X range of layer thicknesses within a single multilayered coextrusion trial provides a powerful research and development tool for future investigations of novel structure-property relationships across all polymeric multilayered systems.
2.5 References


Table 2.1

Even and uneven split layer multiplier die dimensions and effective splitting ratios

<table>
<thead>
<tr>
<th>Layer Multiplier Die Design</th>
<th>Flow Channel Dimensions</th>
<th>Pressure Equilibrated Splitting Ratio</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>Height (mm)</td>
<td>Channel Width (mm)</td>
</tr>
<tr>
<td>Even Split</td>
<td>13.5</td>
<td>6.75 6.75</td>
</tr>
<tr>
<td>Uneven Split - A</td>
<td>13.5</td>
<td>6.83 6.67</td>
</tr>
<tr>
<td>Uneven Split - B</td>
<td>13.5</td>
<td>6.97 6.53</td>
</tr>
<tr>
<td>Uneven Split - C</td>
<td>13.5</td>
<td>7.22 6.28</td>
</tr>
<tr>
<td>Uneven Split - D</td>
<td>13.5</td>
<td>7.83 5.67</td>
</tr>
</tbody>
</table>
Figure 2.1: Two component multilayer system layout of extruders, melt pumps, feedblock, multiplying dies, and stacking, spreading, and recombining melt streams. Surface layer extruder, and exit die. Layer multiplication from two to four layers is illustrated by cutting, stacking, spreading, and recombining melt streams.
Figure 2.2: (a) Conventional even and (b) uneven split layer multiplier die. Uneven split layer multiplier die produces two layer thicknesses as compared to one with conventional layer multiplication.
Figure 2.3: Schematic illustration of step-by-step construction of a 10X gradient layer thickness distribution multilayered film by coextrusion through a set of four uneven split layer multiplying dies.
Figure 2.4: Cross-section optical micrograph of a 32 layer PS/PMMA gradient layer thickness film with a 10X difference between the thickest and the thinnest layers.
Figure 2.5: (Top) 128 step-layer thickness distribution and (Bottom) Resultant comparison between the analytically modeled and the experimentally measured optical reflection spectra from a 128 multilayer PS/PMMA film.
Figure 2.6: (Top) Cross-section atomic force microscopy image of 128 gradient layer film with a 10X layer thickness distribution produced by coextrusion through a series of two even and four uneven multiplier dies. (Bottom) Comparison of analytical prediction and experimentally measured 600+ nm wide reflection band from 128 gradient layer THV/PS multilayer film.
Figure 2.7: (Top) Super-lattice gradient layer thickness distribution of a 128 layer film coextruded through a series of four even and two uneven split multiplier dies. (Bottom) Comparison of an analytically modeled and experimentally measured dual reflection band spectrum from a 128 layer “superlattice” distribution PMMA/PVDF blend multilayer film.
Figure 2.8: Optical microscopy images of 256 gradient layer 50/50 v/v PS/SEPS film. (Top) Film surface micrograph of thicker layers exhibiting crazes at 90° to the film deformation direction. (Bottom) Film surface micrograph of thinner layers exhibiting large shear bands and smaller crazes that terminate into shear bands as a result of deformation.
Figure 2.9: (Left) 128 gradient layer 50/50 PS/THV foam-delaminated film exhibiting layer thickness dependent layer buckling. (Right) Effect of PS layer buckling wavelength with layer thickness in 128 gradient layer 50/50 PS/THV foam-delaminated film.
Chapter 3

Forced Assembly Confinement of Polycaprolactone: Effect of Confining Substrate

3.1 Introduction

Self-assembled structures possess a preferred size dimension, usually in the nanometer scale, over which formation and ordering occurs. An example of self-assembly in polymers is chain crystallization to formation lamellae crystals. Lamellae tend to form structures 20 nanometers or less in the crystal width or thickness direction and can grow to several hundreds of nanometers in length. Under isotropic melt conditions, lamellae further organize into a spherulitic morphology.[1] However, when confined in 2D domains with thicknesses comparable to small multiplies of the lamellae size scale, polymer crystallization structures have exhibited hampered crystal growth and a preferential lamellae crystal orientation.[2] Confinement of thin polymer layer crystallization have been traditionally studied by multiple techniques which include layered spin-coating [3,4], Langmuir-Blodgett methods [2], and between the microphase separated domain morphologies in block copolymer systems.[6-11] The development of the structure-property relationships under conditions of confined crystallization has been restricted to small amounts of materials, which are inaccessible by traditional bulk mechanical or gas transport polymer characterization techniques, due to various processing limitations in these conventional techniques. Whether limited by solution-polymer concentrations, polymer-substrate interactions, or the length scale of covalent bonds between
polymer blocks, a clear understanding of changes in confined crystalline material properties is prohibited.

An alternative melt processing layer multiplying coextrusion approach to produce polymer confinement between tens or thousands of micro- or nanometer thick layers have recently been conducted.[12,13] Nanolayer coextrusion provides a unique opportunity to replicate the nanolayered materials over square meter scale areas of polymer film that enable traditional analytical structure-property characterization. Nanolayer confinement by layering multiplying coextrusion has been utilized to induce high aspect ratio, single-layer, in-plane lamellae crystals of polyethylene oxide (PEO) confined against poly(ethylene-co-acrylic acid) (EAA) or polystyrene (PS).[14-16] Reducing individual PEO layer thicknesses from the micro- to nanometer scale induced anisotropic lamellae orientation parallel to the PEO/PS or PEO/EAA layer interphase. At layer PEO layer thicknesses approaching the crystalline lamellae thickness, the effect of this highly oriented PEO crystal phase structure contributed to a two order of magnitude decrease in oxygen permeability, of the PEO layer.

The ability to mass produce gas barrier enhanced, highly ordered crystalline polymer nanolayers could lead to the development of many new applications for existing polymer materials. Benefits including increased gas barrier and possible mechanical reinforcement warrant further investigations to identify and develop an understanding of material and processing variables which control and promote the phenomenon of confined crystallization in coextruded nanolayer films. The
development of the relationship of polymer material properties to film structure and properties requires exploration and examination of additional confined layered systems. This paper reports on experiments to extend the results of layer multiplying confinement of PEO to new polycaprolactone (PCL) multilayered polymer film systems.

Further exploration of the confined PCL layer and the confining substrate relationship will be conducted to elucidate additional material interactions which may affect the layer confinement mechanism. It has been well documented that polymer-polymer interactions can significantly affect blends[17-20] and multilayer film properties.[21-25] Extension of these relationships to include the case of confined crystalline layers will be examined through coextrusion of PCL against a series of amorphous and crystalline substrates. A case of increasing the interaction parameter between the confined PCL layer and an amorphous substrate will be investigated in relation to the PCL layer orientation and oxygen permeability as a function of layer thickness. Substitution of the amorphous substrate for a crystalline material will also be investigated in terms of the resultant PCL layer properties.

3.2 Materials and Methods

Polycaprolactone (PCL) with a reported molecular weight of 120 kg/mol [26] (Capa 6800, MFI =7.3 g/10min, 190°C/2.16 kg) was obtained from Perstorp UK
Polystyrene (PS) (Styron 615APR, MFI =14.0 g/10min, 200°C/5.0 kg, ASTM D1238) was obtained from The Dow Chemical Company. Poly(methyl methacrylate) (PMMA) (Plexiglas VM, MFI =14.5 g/10min, 200°C/5.0 kg, ASTM D1238) was obtained from Arkema Inc. Polycarbonate (PC) (Makrolon 2205, MFI=35.0 g/10min, 300°C/1.2 kg) was obtained from the Bayer Corporation. Both PMMA and PC were dried under heat and vacuum before processing.

Multilayered films with alternating PC L and PS, PMMA, or PC layers were fabricated using a forced assembly layer multiplication coextrusion process.[27-29] The extruders, multiplier elements, and die temperatures were set to ensure matching viscosities of the two polymer melts during coextrusion processing. Films with 17, 257, and 1025 alternating PC L and PS, PMMA, or PC layers were coextruded. The composition ratio was varied as (PCL/PS, PMMA, or PC) (v/v) 75/25, 50/50, 25/75, and 10/90. For each composition and number of layers, several film thicknesses, ranging from about 180 to 25 μm, were produced through variation of the rotation speed of a cast film take-off roll set at a temperature of 140°F. The nominal layer thicknesses for each sample were calculated from the number of layers, the composition ratio and the film thickness (Table 1). Nanolayered PS and PEO control films were also extruded under identical processing conditions as the multilayered samples. Coextruded films were stored at ambient temperature in sealed bags to prevent moisture absorption.
The layered film structured was investigated by atomic force microscopy (AFM). The layer film was embedded in epoxy (5 Minute Epoxy, Devcon, Rivera Beach, FL) and cured for 24 hours at room temperature. Cross sections were microtomed at -100°C under a liquid nitrogen cooled atmosphere with an Ultramicrotome (MT6000-XL from RMC, Tucson, AZ). Film cross sections were prepared perpendicular to the film plane and imaged directly by AFM with a commercial scanning probe microscope (Nanoscope IIIa, Digital Instruments, Santa Barbara, CA) operated in the tapping mode. Measurements to visualize the layers and their internal crystalline morphology were performed at ambient conditions using a rectangular type Si probe with spring constants 50 Nm\(^{-1}\) and resonance frequencies in the 284-362 kHz range. The tip radius was 10 nm. Phase and height images of the cross sections were recorded simultaneously.

The multilayered film density was measured at 23°C according to ASTM D1505-85. A 2-water/water-calcium nitrate solution gradient column with a range of 1.0–1.15 g/cm\(^3\) was calibrated with glass floats with known density. Small pieces of film (2x2 mm\(^2\)) were placed in the column and allowed to equilibrate for 24 hours before measurement. At least three pieces of each sample were measured to determine each multilayered film density as reported in Table 3.1.

PCL crystallinity was measured by DSC thermograms obtained on a Perkin-Elmer (Boston, MA) Series 7 differential scanning calorimeter (DSC) at a heating/cooling rate 10°C min\(^{-1}\). The crystallinity of the PCL control was 48 wt %
calculated from the melting enthalpy using the heat of fusion ($\Delta H^o$) of 139.5 J/g for PCL crystals.[30] The crystallinity of the PCL layers was calculated based on the melting enthalpy of the PCL layers ($\Delta H_{m,PCL}$) and the PCL weight content in the films (Table 3.1).

Small-angle X-ray scattering (SAXS) and wide-angle X-ray scattering (WAXS) patterns were obtained by aligning the incident X-ray beam parallel to the normal direction (ND), the extrusion direction (ED), or the transverse direction (TD) of the film. The SAXS measurements were carried out using a rotating anode X-ray generator (RU 300, 12 kW, Rigaku, Woodlands, TX) equipped with two laterally graded multilayer optics in a side-by-side arrangement, giving a highly focused parallel beam of monochromatic Cu KR radiation ($\lambda = 0.154$ nm). The monochromatic X-ray beam, operated at 40 kV and 80 mA, was collimated using three pinholes. The diameter of the X-ray beam at the sample position was approximately 700 $\mu$m. For the collection of ED and TD SAXS patterns, because the thickness of the films (50-250 $\mu$m) was smaller than the collimated X-ray beam, the X-ray beam was aligned at an angle of $\sim$3° relative to the ED and the TD to avoid total reflection. The critical angle for the total reflection is usually on the order of a few tenths of a degree. In order to collect ND SAXS patterns, the X-ray beam was aligned along the direction parallel to the ND. Two dimensional (2D) SAXS patterns were collected by using a 2D gas filled multiwire detector (Rigaku) with a spatial resolution of 1024 x 1024 pixels. The X-ray exposure time for ED, TD, and ND SAXS patterns was 9 h. The sample-to-detector
distance was 1.5 m and the scattering vector $q$ was calibrated using a silver behenate (AgBe) standard, which has the (001) peak position at $q = 1.076 \text{ nm}^{-1}$. A photodiode beam stop placed in front of the area detector allowed monitoring of the intensity of the direct beam. All SAXS images were corrected for background scattering and sample absorption. The WAXS measurements were performed using the same rotating anode X-ray generator. The collimated beam size was 0.5 mm. The 2D patterns were collected with a Bruker AXS (Madison, WI) HI-STAR area detector. The sample-to-detector distance was 74 mm and the diffraction angle was calibrated using a CaF$_2$ standard.

Oxygen flux $J(t)$ at 0% relative humidity, 1 atm pressure, and a temperatures of 23°C ($\pm 0.1^\circ\text{C}$) was measured with a MOCON (Minneapolis, MN) OxTran 2/20 unit. The instrument was calibrated at 23°C with NIST-certified Mylar film of known oxygen transport characteristics. The polymer film specimens were carefully conditioned in the instrument, as described previously.[31] The permeability $P$ was calculated from steady state flux $J$ as

$$P = \frac{J}{\Delta p}$$

(1)

where $l$ is the film thickness and $\Delta p$ is the difference of the oxygen partial pressure across the film (1 atm). For each film, the average $P$ and error bar from a minimum of two specimens were reported, Table 3.1.
3.3 Results and Discussion

Selection of PCL as a Confined Material

Forced assembly nanolayer confinement of PEO was previously described to exhibit anisotropic crystal orientation leading to increased gas barrier with individual layer thickness reduction down to the width of an individual lamellae.[14-16] Identification of additional semi-crystalline polymer candidates to reproduce and thereby better understand material and processing variables which affect this multilayer confinement phenomenon are of significant interest. Semi-crystalline polymer material properties that may affect the layer confinement induced orientation phenomenon were identified and included relative crystallinity, melting point, and crystalline morphology. Based on these initial criteria, Polycaprolactone (PCL) was selected for study in multilayer coextrusion confinement experiments based on a similar crystalline melting point, bulk spherulitic crystallization habit, and material processing temperature. PCL does differ significantly from PEO in regard to several material properties including a significantly lower modulus, a lower crystallinity if around 40%, and thinner individual lamellae, a 15 nm thickness[32,33], compared to 25 nm for PEO[16].

PCL/PS Multilayered System
The effect of reducing layer thickness on the PCL crystalline structure was observed by confinement in micron to nanometer thick PCL/PS multilayered films. Cross-section AFM micrographs of PCL/PS films showed that in all cases, the PCL and PS layers were continuous with thicknesses corresponding to calculated nominal layer thickness based on the overall multilayered film thicknesses and number of film layers. From the AFM images, Figure 3.2, the crystallization habit of PCL layers gradually transitioned from bulk-like spherulitic structures in thick, 16 μm, to single orientated lamellae in thin 75 nm layers. Crystallization in 16 μm PCL layers, Figure 3.2a, exhibited bulk-like 8 to 10 μm diameter spherulites. Further reduction of the PCL layer thickness resulted in a transition of PCL crystalline morphology from spherulites to truncated spherulites in 1.9 μm layers, Figure 3.2b. The impinged spherulitic structures seen in these thinner layers appear to nucleate at the layer boundary and grew radially in the layer thickness direction as a result of the layer confinement. These discoid-like structures were composed of individual lamellae approximately 15 to 20 nm thick. Further reduction in the PCL layer thickness to 400 nm, resulted in a transition to stacks of individual lamellae orientated parallel to the layer interface with radial growth restricted to the layer thickness direction. Some tilting in the layered lamellae was observed. Confinement of PCL to 75 nm layers, Figure 3.2c approaching the dimensional scale of individual lamella, resulted in highly oriented single or double stacks of very long lamellae growing parallel to the layer direction. Single or stacked PCL lamellae thickness remained constant similar to that seen in bulk or thicker layered structures. It is of note that
the overall PCL crystallinity in the AFM layered structures images appeared to remain similar to measured bulk PCL values, approximately 40%, irrespective of individual layer thicknesses in the PCL/PS multilayered films.

A crystalline structural transition from bulk-like spherulites to highly ordered single or double stacked lamella with decreased layer thickness exhibited by PCL confined by PS was nearly identical to that witnessed in the previously described PEO/EAA and PEO/PS multilayered systems.[14-16] As previously stated, PCL is significantly less crystalline, 40% compared to PEO with X_c=70%, with a smaller spherulite diameters, 25 µm as compared to 80 to 100 µm, then PEO[15]. These crystalline polymer material property differences do not appear prohibitive in greatly affecting the layer confinement process of inducing orientation through reduction of layer thicknesses. This suggests that selection of future material candidate studies may not be restricted solely to highly crystalline polymers with a determination of a minimum level of material crystallinity required to form highly oriented in-plane crystalline lamellae still to be determined.

**PCL Lamellar Orientation by WAXS/SAXS in PCL/PS Films**

The extrusion (ED) and normal (ND) direction WAXS patterns from PCL bulk control films exhibited isotropic diffraction rings. The innermost reflection (scattering angle 2θ = 21.3°) consisted of the reflections from the PCL (110) planes and the second ring (2θ = 23.5°) contained the (200) reflection.[34] PCL/PS multilayered films exhibited the same reflections in additional to an
amorphous halo from the PS layer at \(2\theta = 18.7^\circ\), Figure 3.3. The WAXS patterns measured in the TD were indistinguishable from the ED, only ED patterns are presented. ND WAXS patterns for the PCL/PS system were isotropic irrespective of layer thickness suggesting no orientation of spherulitic or orientated lamellae resulted during processing and material crystallization. The ED WAXS pattern of a PCL/PS multilayered film with 1.9 \(\mu\)m PCL layers exhibited a broad equatorial arch suggesting only slight orientation most probably related to truncation of PCL spherulites witnessed in the AFM images. Reduction in the PCL layer thickness to 400 nm resulted in a significant increase in lamellae orientation parallel to the layer interface as exhibited in the sharpened, shorter equatorial arcs witnessed for the (110) and (200) reflection planes. ED WAXS patterns of 75 nm thick PCL layers further shortened the equatorial arcs of the (110) and (200) reflections indicating a nearly parallel lamellae orientation which was in good agreement with the single long lamellae imaged in Figure 3.2d.

The progression of PCL lamellae to orient from isotropic (bulk) to parallel, in-plane lamellae (nanolayers) qualitatively follows the behavior exhibited by PEO multilayers confined by PS or EAA. A confinement induced orientation on the PCL lamellae was evident in relatively thick layers up to 5\(\mu\)m. Initial indications of layer confinement effects was seen in WAXS patterns in thick layers, up to 5\(\mu\)m, two orders of magnitude thicker than the individual lamellae thicknesses was consistent with previous results in the PEO systems. However, the sharpness of the equatorial PCL (110) and (200) reflections, though greatly reduced as
compared to bulk materials, does not approach the spot-like fiber pattern seen in
25 nm PEO films.[15] The slightly lower orientation seen in the PCL films may
result from the increased amount of amorphous material, as compared to PEO,
present in the layer which may impair more perfect lamellae orientation.

The ED SAXS of the PCL/PS multilayered films exhibited increased meridional
intensity with decreasing PCL layer thickness, Figure 3.3. The strong meridional
intensity in the ED SAXS patterns indicated that the normal of the lamellar fold
surface was predominately oriented toward the ND of the multilayered film.
Even with background scattering intensity from the film surface and layer
interfaces exist, the appearance of strong spots in the 75 nm PCL layers was quite
distinctive indicating high levels of in-plane lamellar orientation in these thin
nanolayers. The WAXS and SAXS patterns were consistent for prediction
increased in-plane orientation as the PCL layer thickness was reduced. From the
SAXS patterns, a corresponding long period was calculated as $15.4 \pm 0.2$ for PCL
which corresponded quite well with the AFM images and literature values.[8,33]

An orientation function was calculated to quantitatively determine the effect of
reducing layer thickness on PCL crystalline orientation. The Herman’s
orientation function[34], utilizing azimuthal intensity distributions of the PCL
(110) reflection measured from ED WAXS patterns, was calculated as $f_{110}$ by the
relationship
\[
\langle \cos^2 \phi_{110} \rangle = \frac{\int_0^\pi I_{110}(\phi) \cos^2 \phi \sin \phi \, d\phi}{\int_0^\pi I_{110}(\phi) \sin \phi \, d\phi}
\]  

(2)

which upon integrations can be expressed as

\[
f_{110} = \frac{3\langle \cos^2 \phi_{110} \rangle - 1}{2}
\]

(3)

where \( I_{110}(\varphi) \) represents the corrected scattering intensity of the PCL (110) reflection at the azimuthal angle \( \varphi \). The normal of the film plane is set to be \( \varphi = 0^\circ \) and the film plane corresponds to \( \varphi = 90^\circ \); then \( \varphi_{110} \) is the angle between the normal of the film plane and the normal of the (110) plane. From the definition of the Herman’s orientation function, \( f_{110} = 1.0 \) indicates that the normal of the (110) plane is perfectly perpendicular to the layer normal, whereas \( f_{110} = 0 \) is a perfectly isotropic or random orientation and \( f_{110} = -0.12 \) is 33° to the layer normal. The calculated orientation function values, \( f_{110} \), from ED WAXS patterns of PCL layers as a function of layer thickness were plotted in Figure 3.4. An initial increase in orientation parameter from purely isotropic to slightly oriented/truncated spherulites was seen as the PCL layer thickness was decreased below 5 \( \mu m \). A continual increase in the PCL layer orientation approached an apparent maximum value of 0.75 as the layer thickness approached 100 nm.
Subsequent layer thick reductions below 100 nm produced no significant increase in the orientation of the PCL lamellae. The apparent maximum orientation of the sub-100 nm coextruded PCL layers corresponds to in-plane lamellae with only a slight slant or tilt. As previously mentioned, the inclusion of more amorphous material in the PCL layers appears to have prohibited ideal, \( f=1.0 \), in-plane orientation in the nanolayers, a condition met in previously published work of the more highly crystalline PEO layers.[14,16]

**Gas Permeability of Confined PCL/PS Multilayer Films**

The effect of confinement induced crystalline phase orientation on composite multilayer film gas permeability was investigated by measuring the oxygen permeability of a series of PCL/PS multilayer films with layer thicknesses ranging from 11.9 \( \mu \)m down to 25 nm. The PCL layer thickness was varied by changing the film thickness, relative PCL/PS composition, and the overall number of layers in the coextruded film, **Table 3.1**. A series model can be utilized to calculate the oxygen permeability of the multilayered composite film utilizing a two component expression like

\[
P_{\text{Film}} = \left( \frac{\phi_{\text{PCL}}}{P_{\text{PCL}}} + \frac{1-\phi_{\text{PCL}}}{P_{\text{PS}}} \right)^{-1}
\]  

(4)

where \( \phi_{\text{PCL}} \) is the volume fraction of PCL, and \( P_{\text{PCL}} \) and \( P_{\text{PS}} \) is the oxygen permeability of bulk PCL and PS materials respectively. Similar to experimental
observations of PEO by Wang et al.[14] PCL/PS multilayered films with PCL layer thicknesses less than 5 µm resulted in oxygen permeability much lower than predicted by the layered series model. Rearrangement of Equation 4 produces an expression which was used to determine the effective oxygen permeability of one of the material constituent layers, PCL, by

\[
P_{PCL,eff} = \phi_{PCL} \left( \frac{1}{P_{film}} - \frac{1 - \phi_{PCL}}{P_{PS}} \right)^{-1}
\]

(5)

as a function of the measured composite film permeability, \(P_{film}\), constituent volume fractions \(\phi_{PCL}\), and layer thickness independent PS layer permeability, measured at 2.2 barrer.

Utilizing Equation 5, a plot of the effective PCL layer permeability as a function of layer thickness was constructed, **Figure 3.5**, from measured PCL/PS multilayer film oxygen permeability data, **Table 3.1**. A continuous reduction in the effective PCL layer oxygen permeability was seen in multilayered films with less than a 5 µm thick PCL layer. Above the 5 µm threshold, the effective PCL layer oxygen permeability value equal to that of the PCL bulk polymer. Below this threshold, a nearly linear reduction of the effective PCL layer permeability of 5 µm to 100 nm thick layer thickness was measured. Further reduction of the PCL nanolayers below 100 nm resulted in a steep drop in the effective PCL layer permeability. The lowest permeability, highest oxygen barrier films, was achieved in this region with a maximum gas barrier exhibited in 40 nm PCL layers. Confined
crystallization of PCL in 40 nm layers, $P_{\text{PCL,eff}} = 0.003$ barrer, resulted in effective oxygen permeability values more than 300 times lower than the bulk values, $P_{\text{PCL bulk}} = 0.97$ barrer. Subsequent reduction of PCL layers to thicknesses less than 40 nm resulted in an increase in film and effective PCL layer oxygen permeability as layer break-up resulted in the multilayer films. It was surprising that at similar confined multilayer thicknesses, 40 – 45 nm, and against a common PS substrate layer, PCL layers exhibited twice the oxygen barrier as compared to previously reported PEO layers[14], 0.003 as compared to 0.007, irrespective of lower crystalline volume fractions, 40% to 70%, and orientation function values as compared to the PEO/PS multilayered film system. A potential explanation for this result may be explained by a consideration of the lamellae orientation and morphology necessary to achieve a 300 times lower permeability in the PCL layers.

Examination of the effect of PCL layer lamellar morphology as the principle driving force for decreased multilayer film oxygen permeability was explored through structural based gas permeability models. The decreased oxygen permeability as a function of layer thickness was attributed to the orientation of crystalline lamellae in the PCL layers. A plot of the Herman’s orientation function versus the effective PCL layer permeability displayed a correlation between an increase in the degree of in-plane lamellae orientation and a reduction in PCL layer gas permeability, Figure 3.6. An estimation of the lateral dimensions of the in-plane oriented PCL lamellae crystals was described using a
Cussler model[35-37] which describes the relationship for the gas permeability of a polymer composite with a dispersion of impermeable platelets by

\[ P = P_M \left[ 1 + \frac{\alpha^2 \phi^2}{4(1-\phi)} \cos^2 \theta \right]^{-1} \]  

(6).

Equation 6 describes the permeability of the composite, \( P \), in terms of the matrix material permeability, \( P_M \), the volume fraction of impermeable platelets, \( \phi \), the platelet aspect ratio, \( \alpha \), and the angle between the flux and normal to the platelets, \( \theta \). The lateral dimension of the in-plane, PCL lamellae crystals can be estimated by solving Equation 6 for \( \alpha \) by considering the lamellae impermeable and the lamellar fold surfaces permeable amorphous regions where gas molecules permeate around the interlamellar boundaries. The volume fraction of the PCL crystals, \( \phi \), was determined by

\[ \phi = X_{C,PCL} \times w_{PCL} \times \frac{\rho}{\rho_{C,PCL}} \]  

(8)

Where \( X_{C,PCL} \) is the crystallinity of the PCL layer measured by DSC, Table 3.1, \( w_{PCL} \), is the weight fraction of PCL in the layer, \( \rho \) is the measured PCL/PS film density, and \( \rho_{C,PCL} \) is the PCL crystal density[38], 1.17 g/cm\(^3\).

The lateral dimension of the highly oriented PCL lamellae crystals were calculated from Equations 6 and 7 and reported in Table 3.1. The calculated
aspect ratio for the oriented in-plane PCL lamellae ranged from 130 to 345 as the layer thickness was reduced from 65 to 20 nm. A corresponding in-plane lamellae crystal lateral dimensions of 2 to greater than 5 μm results when considering the reported PCL lamellae thickness is 15 nm. Inclusion of such large aspect ratio crystals appears reasonable as AFM cross-section of thin PCL layers appear continuous over the entire span of micron scale images. The calculated PCL in-plane lamellae aspect ratios were slightly higher when compared to those previously reported for PEO in-plane lamellae crystals.[14] The higher PCL crystal aspect ratio is hypothesized to result from a lower multilayered film crystallization temperature as compared to PEO. A measured multilayer film crystallization peak at 25° C was measured for PCL/PS films as compared to 39° C for PEO/PS films. The lower crystallization temperature would allow for longer periods of crystal growth as the film is cooled as it exits the coextrusion process. The higher crystallization temperature of the PEO films would initiate an earlier quench of crystalline material growth as compared to PCL to potentially limit the size of the in-plane lamellae crystals during coextruded film cooling.

Effect of Amorphous Substrate on Confined PCL Layer Properties

A study into the structure-property effects of increasing polymer interactions in a confined crystallization system was undertaken in two additional multilayered PCL systems. PCL multilayered films were produced with the amorphous
confining layer changed from the highly non-interacting substrate of PS, $\chi_{PCL-PS}=0.168$, to an intermediate PMMA, $\chi_{PCL-PMMA}=0.017$, and miscible PC, $\chi_{PCL-PC}=0$, substrates. A series of 257 layer PCL/PMMA and PCL/PC films were coextruded to produce a series of PCL layer thicknesses ranging from 900 down to 30 nm, Table 3.2, for comparison with the previously described PCL/PS system. Upon film cooling off the coextrusion line, vitrification of the PS, PMMA, and PC confining substrate occurred before PCL crystallization due to the substrate material $T_g$ greater than the PCL crystallization temperature. PCL crystallization against a vitrified confining layer in all three systems should maintain an equivalent thermally hard confinement environment that is effected only by material interactions during crystallization. Structure property investigations of the effect of varying PCL-substrate interactions as a function of layer thickness were investigated utilizing similar WAXS and oxygen permeability experimental probes as previously described for the PCL/PS multilayered system.

The effect of PCL-substrate polymer interaction on layer confinement was examined by comparing ED WAXS of PCL/PS, PCL/PMMA, and PCL/PC multilayered films at 750, 100, and 30 nm nominal PCL layer thicknesses, Figure 3.7. A transition of PCL layer crystal habit from spherulite to oriented in-plane lamellae as a function of layer thicknesses was previously described in a non-interacting PCL/PS multilayered system. Crystalline orientation of PCL/PMMA films, which possessed an increased chemical interaction relative to PCL/PS, displayed a similar confinement induced crystallization transition from spherulitic
to oriented in-plane lamellae by decreasing the PCL layer thickness. However, a comparison of the ED WAXS patterns of the PCL/PS and PCL/PMMA system at 750 and 100 nm nominal layer thicknesses clearly demonstrate a wider equatorial (110) and (200) arcs indicative of lower PCL layer orientation in the PCL/PMMA films. The thinnest PCL layers, 30 nm, exhibited short equatorial arcs consistent with highly oriented in-plane PCL lamellae regardless of a PMMA or PS confining material. It is plausible that increasing the PCL-confining substrate interaction may actually retard the formation of crystalline lamellae by reducing enthalpic gains through minimization of repulsive interactions between the layer surfaces resulting in a more gradual transition of crystalline habit with reduced layer thicknesses.

Highly interacting, miscible PCL/PC multilayered films systems exhibited even less crystalline layer orientation as compared to PCL/PMMA or PCL/PS films. The (110) PCL reflection appeared isotropic in 500 layer samples while sub-100 nm thick layers failed to show any ordered crystalline reflections. Due to increased surface area to volume ratios of the multilayered structure; it was not unexpected that interdiffusion between the miscible PCL and PC layers ultimately result in an amorphous structure similar to that observed in PCL/PC blends.[20] However, it is interesting to note that samples with thicker layers, i.e. 500 nm, never displayed PCL layer crystalline reflections of a preferred orientation. In the PCL/PS and PCL/PMMA system, micron scale thick PCL layers still exhibited some degree of orientation. The lack of any significant orientation in the PCL/PC
films suggests that some type of boundary, sharp or diffuse, must exist to induce orientation in multilayered systems.

As seen in Figure 3.7, the PCL/PMMA (110) and (200) equatorial reflections from in-plane lamellae are significantly broader at 750 and 100 nm layer thicknesses. A more quantitative comparison of the effect of layer thickness on orientation in the PCL/PS and PCL/PMMA multilayered systems was conducted utilizing azimuthal scan of the (110) PCL reflection. These scans were subsequently utilized to calculate a lamellae orientation function over a range of layer thicknesses for all three multilayered systems; PCL/PS, PCL/PMMA, and PCL/PC following the procedure previously outlined. A comparison of the effect of layer thickness on the PCL layer orientation was plotted for each of the three multilayered systems in Figure 3.8. Increasing the PCL-substrate interaction from PCL/PS to PCL/PMMA multilayer films resulted in a general shifting toward a requirement of thinner layers for induction of PCL layer in-plane orientation. For 1 μm to 200 nm PCL layers confined by PMMA, a layer thickness approximately one half that of the PCL/PS system is required to achieve similar degrees of the confined layer orientation. A convergence in the relationship of PCL layer thickness and lamellae orientation for the PCL/PS and PCL/PMMA system appears to begin at 100 nm culminating in a nearly identical level of PCL layer orientation in the thinnest, 30 nm layers. These highly oriented thinnest layers exhibit orientation levels approaching entirely in-plane lamellae which would be required, regardless of layer interactions, by the spatial limitation
of placing a 15 nm thick crystalline lamellae in a 20 to 40% crystalline 30 nm polymer layer. As previously mentioned, the miscible PCL/PC multilayered system did not exhibit any confinement induced crystalline phase orientation as a function of layer thickness prior to the becoming an entirely amorphous material in sub-100 nm layered films. Due to the lack of confinement induced orientation in multilayer PCL/PC films, subsequent characterization of these films was omitted.

As a result of determining a substrate dependent PCL layer orientation as a function of layer thickness, the structurally dependent oxygen permeability of the PCL/PS and PCL/PMMA multilayered systems should exhibit distinct differences. The oxygen permeability as a function of PCL layer thickness was measured for the PCL/PMMA films to compare with the previously reported PCL/PS systems, Figure 3.9. As PCL layer thicknesses were decreased, the effective PCL layer oxygen permeability decreased in both the PCL/PS and PCL/PMMA multilayered systems. As previously described, the non-interacting PCL layered against a PS substrate first exhibit increased oxygen barrier when individual layers were reduced below 5 μm. Further reduction of the layer thickness produced a continuous decrease in the effective PCL oxygen permeability down 0.003 barrer in 35 nm layers. Reflecting the reduced crystalline phase orientation measured by WAXS, PCL/PMMA multilayered films did not exhibit a decreased effective PCL layer oxygen permeability in layers greater than 600 nm thick. A reduction in the range of layer thickness over
which confinement induced structural and property modifications are prevalent may very well be related to chemical attractions and interactions of the layered polymer materials. Further reduction of the PCL layer thickness in the PCL/PMMA films did result in a continual decrease of the confined layer down to a minimum effective oxygen permeability value, 0.003 barrer at 30 nm, identical to the PCL/PS system. The relationship between the confined PCL crystal orientation and oxygen permeability was compared for the two multilayered systems, Figure 3.10. Correlation between the PCL layer crystalline phase orientation function and oxygen permeability overlapped regardless of confining layer material. This suggests that an identical layer confinement mechanism, a transition in the crystallization habit of PCL from spherulitic to in-plane orientation, with decreasing layer thickness was present. A reduction of PCL oxygen permeability to a common value and orientation regardless of substrate may be indicative of a physical limitation on the size of the in-plane lamellae possible in films produced solely through multilayer coextrusion processing.

Experimental observation of the confinement mechanism of the two multilayered PCL systems as a function of ambient temperature was performed through a post extrusion thermal treatment of the multilayered films. There was a temperature window between $T_{m,PCL}$ and $T_{g,PS}$ or $T_{g,PMMA}$ in which the PCL layers could be melted within the confinement of rigid glassy layers. Subsequent cooling at different ambient conditions allowed for investigation of the crystallization habit of confined PCL against the different substrates as a function of crystallization or
quenching temperature. ED WAXS patterns 40 nm PCL layers that were remelted and isothermally quenched or recrystallized against PS or PMMA rigid layers are shown in Figure 3.12. A quantitative comparison of the temperature dependent remelted and quenched or recrystallized sample orientation was preformed by plotting the PCL orientation from the ED WAXS patterns as a function of temperature for the PCL/PS or PCL/PMMA system, Figure 3.12. As reported previously for PEO confined nanolayers[14], the quenching or crystallization temperature is paramount for controlling the crystalline orientation of the PCL layer. At low temperatures, -20°C and below, PCL confined by PS exhibited an edge-on orientation. A transition in the PCL layer orientation from edge-on to in-plane was seen by increasing the ambient temperature during crystallization from -10 to 0°C. Above 0°C, 40 nm thick PCL layers crystallized as rather highly oriented in-plane lamellae. The transition from edge-on to in-plane lamellae orientation with increased ambient temperature suggests a strong kinetic dependence on confined layer orientation.

Remelting and quenching or recrystallization of 40 nm PCL layers against a more interacting substrate, PMMA, resulted in a slightly broader temperature dependent transition from an edge-on to in-plane confined crystalline lamellae structure. Rapid quenching of PCL against PMMA resulted in slight, however significantly lower, edge-on orientation. A broader transition of confined PCL layer orientation from the slightly edge-on toward a strong in-plane orientation resulted when ambient quenching temperatures were increased from -20 to 10°C. Melt
recrystallization at isothermal conditions at 25°C and above displayed strong in-plane reflections of similar magnitude to the PCL/PS systems. The result of increased layer interactions in the multilayered film appeared to retard the formation of edge-on lamellae at lower temperatures while broadening the temperature window by which the transition to in-plane lamellae. One can envision a scenario of increased polymer chain entanglements and a thicker layer interphase prohibiting high orientation in rapidly quenched samples to inhibit the rapid formation of high edge-on orientation at low ambient temperature as seen in the PCL/PMMA multilayered films.

*Effect of Crystalline Substrate on Confined PCL Layer Properties*

Identical to the previously described melt recrystallization technique utilized for PCL/PS and PCL/PMMA layered films, a post extrusion thermal treatment of PCL/PA12 and PCL/PP-g-MA multilayered films was conducted to investigate effects on the confined crystallization mechanism when PCL was layered against a crystalline substrate. Again, exploitation of a temperature window between $T_{m,PCL}$ and $T_{C,PA12}$ or PP-g-MA allowed for the PCL layers to be melted within the confinement of the crystalline confining layers. Subsequent cooling at different ambient conditions allowed for investigation of the crystallization habit of confined PCL against the different substrates as a function of crystallization or quenching temperature. ED WAXS patterns of 100 nm PCL layers that were remelted and isothermally quenched or recrystallized against PA12 and 90 nm
layers quenched or recrystallized against PP-g-MA are shown in Figure 3.13. Following the previously described procedure for PCL/amorphous layers, a quantitative comparison of the temperature dependent remelted and quenched or recrystallized sample orientation was preformed by plotting the PCL orientation from the ED WAXS patterns as a function of temperature for the PCL/PA12 or PCL/PP-g-MA system, Figure 3.13. At quenching temperatures below the crystallization temperature of PCL, 25°C and below, PCL confined by PA12 or PP-g-MA exhibited an isotropic or a slightly edge-on orientation. A transition in the PCL layer orientation from isotropic or slightly edge-on to in-plane was induced by again increasing the ambient temperature during crystallization from -25 to 45 or 50°C. At 45° or 50°C, the PCL layers crystallized as highly oriented in-plane lamellae. In comparison to PCL confined by the amorphous PS or PMMA layers, confinement with a crystalline polymer substrate appeared to significantly shift the edge-to in-plane lamellae transition from -10 or 0°C to much higher crystallization temperatures, 45 or 50°C.

A shift toward nearly 40°C higher crystallization temperatures to induce a PCL lamellar transition of edge-on to in-plane orientation suggests that inclusion of a crystalline confining layer introduces additional thermodynamic or kinetic parameters to confined crystalline layer behavior. Crystallization nucleation at the nanolayer interface has been witnessed in confined crystalline PEO layered films. Transcrystallization off the crystalline confining layer interface may present an explanation for affinity for PCL to go edge-on at or below 40°C.
Chatterjee and Price[39,40] previously examined the heterogeneous nucleation of crystalline polymers, including PCL, sandwiched against various substrates in 3 layer laminates. Melting and subsequent recrystallization of PCL against a variety of crystalline polymers, including isotatic PP, HDPE, LDPE, POM, iPS, Nylons 6 or 66, and inorganic, including gold and aluminum, substrates induced solely transcrystalline or a mixture of transcrystalline and spherulite crystallization in the PCL laminate layer. Increasing crystallization temperature above an experimentally determined Transcrystallization range, reported as 45-52°C for PCL, resulted in a gradual transition from transcrystallization to spherulitic crystallization behavior. In good agreement with our experimental results for the nanolayered PCL/PA12 and PCL/PP-g-MA systems, Chatterjee et al. previously found transcrystallization to be independent of crystalline unit cell similarity or, similar to the work of Koutsky[41], the substrate surface energy. In good agreement with these previous findings, melt recrystallization of PCL nanolayers against crystalline PA12 or PP-g-MA substrates require crystallization temperatures above this transcrystallization temperature range, at which time heterogeneous nucleation of the PCL layer may follow to achieve the flat-on orientation demonstrated for PCL at these temperatures in the PCL/amorphous substrate systems. It should be noted that crystallization temperatures above the proposed transcrystallization region, 45-52°C, lies on the upper limits to induce polymer crystallization limiting experimental trials around 50°C.
3.4 Conclusions

Polycaprolactone multilayered films were produced exhibiting highly oriented confined crystallization as a result of reducing individual layer thicknesses from the micron to the nanoscale. Similar to prior results with coextruded polyethylene oxide films, WAXS/SAXS of PCL layers verified a similar layer thickness dependent crystallization confinement mechanism from unoriented spherulites (micron layers) to high-aspect ratio, single or stacked lamellae (nanolayers) oriented parallel to the layer boundary. Highly oriented, single lamellae PCL layer films exhibited more than a two order of magnitude reduction in oxygen gas barrier as a result of the increased diffusion path length tortuosity around the high aspect ratio lamellae crystals with large estimated lateral dimensions up to 5 µm. Interestingly, a requirement of high polymer layer relative crystallinity does not appear to be vital to achieve large improvements in confined multilayered material oxygen barrier, as the enhanced gas barrier via crystal orientation occurred at similar magnitudes in PCL/PS and PCL/PMMA layers with 29 to 40% relative crystallinity to 70% crystalline PEO/PS layered films. The mechanism of increased diffusion path length around highly oriented, large aspect ratio crystals suggests that future investigations to uncover and explore additional polymer candidates exhibiting confined crystallization may be extended to include less crystalline polymer candidates which may include polypropylene or polyethylene.
The investigation of confined crystallization in PCL nanolayer film systems was extended to investigate the effect of the confining layer material on PCL layer orientation and properties. The effect of the confining layer was examined by coextrusion of PCL against a series of amorphous materials, PS, PMMA, and PC with increasing chemical compatibility in micro- and nanolayered films. Increasing PCL and confining material interaction from a non-interacting PS to more interactive PMMA glassy confining substrate resulted in a decrease in confined crystalline layer orientation and permeability in thicker layers during the transition from bulk traditional 3D (micron thick layers) and truncated spherulites and tilted stacked lamellae (down to 100 nm thick layers). Similar confined crystalline layer orientation and oxygen permeability occurred regardless of substrate in PCL/PS or PCL/PMMA systems in the thinnest PCL layers, less than 100 nm, indicating crystallization under high confinement was not effected, most likely due to close proximity of the crystallizable chains in the thinnest nanolayers. The effect of PCL recrystallization temperature in 40 nm layers against PS or PMMA layers also exhibited a sharper transitions for “in-plane” to “edge-on” lamellae orientation in the non-interacting PS system suggesting a higher degree of confinement is exhibited in more non-interacting or sharp interphase multilayered systems. As expected, an extreme case of nanolayering PCL against a highly interacting miscible confining layer, PC, resulted in no layer thickness effect on PCL crystalline phase orientation in coextruded multilayered films.
Coextrusion of 90 to 100 nm PCL layers confined against PA12 or PP-g-MA crystalline layers exhibited a tendency to crystallize edge-on or isotropic orientation unless melt-recrystallized at temperatures approaching 50°C. High melt recrystallization temperatures are hypothesized to result from a need to overcome transcryallization of the PCL at the layer interfaces. The temperature dependence of the confined PCL layer orientation as a function of substrate material illustrates the importance of selecting a confining layer with sufficient thermal properties to provide a vitrified substrate against which material crystallization will accounting for effects due to polymer chain interaction or transcryallization between the materials.
3.5 References


31. Sekelik, D.J.; Stepanov, E.V.; Nazarenko, S.; Schiraldi, D.; Hiltner, A.; Baer,


33. Sun, Y.S.; Chung, T.M.; Li, Y.J.; Ho, R.M.; Ko, B.T., Jeng, U.S.; Lotz, B.


Table 3.1
Characteristics of PCL/PS Nanolayered Films

<table>
<thead>
<tr>
<th>Number of Layers</th>
<th>PS/PCL Composition (v/v) (wt/wt)</th>
<th>Film Density (g/cm³)</th>
<th>Film Thickness (µm)</th>
<th>Nominal Layer Thickness (nm)</th>
<th>f₁₁₀</th>
<th>Film P(O₂) (barrer)</th>
<th>P_{PCL,eff} (barrer)</th>
<th>X_{C,PCL} (wt%)</th>
<th>α</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS</td>
<td>100/0 100/0</td>
<td>1.045±0.001</td>
<td>51</td>
<td>--</td>
<td>--</td>
<td>2.200 ± 0.200</td>
<td>--</td>
<td>--</td>
<td></td>
</tr>
<tr>
<td>PCL</td>
<td>0/100 0/100</td>
<td>1.136±0.001</td>
<td>51</td>
<td>--</td>
<td>--</td>
<td>0.970 ± 0.030</td>
<td>--</td>
<td>48</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>50/50 49/51</td>
<td>178</td>
<td>11900</td>
<td>11900</td>
<td>-0.03</td>
<td>1.397 ± 0.001</td>
<td>1.02</td>
<td>44</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>25/75 24/76</td>
<td>51</td>
<td>1630</td>
<td>4900</td>
<td>0.16</td>
<td>0.990 ± 0.020</td>
<td>0.84</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>17</td>
<td>75/25 74/26</td>
<td>58</td>
<td>5520</td>
<td>1840</td>
<td>0.14</td>
<td>0.982 ± 0.029</td>
<td>0.37</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>257</td>
<td>25/75 24/76</td>
<td>153</td>
<td>300</td>
<td>900</td>
<td>0.26</td>
<td>0.155 ± 0.001</td>
<td>0.12</td>
<td>42</td>
<td></td>
</tr>
<tr>
<td>257</td>
<td>75/25 74/26</td>
<td>137</td>
<td>780</td>
<td>260</td>
<td>0.63</td>
<td>0.056 ± 0.001</td>
<td>0.04</td>
<td>41</td>
<td></td>
</tr>
<tr>
<td>257</td>
<td>50/50 49/51</td>
<td>51</td>
<td>180</td>
<td>180</td>
<td>0.67</td>
<td>0.059 ± 0.006</td>
<td>0.03</td>
<td>40</td>
<td></td>
</tr>
<tr>
<td>1025</td>
<td>50/50 49/51</td>
<td>1.086±0.002</td>
<td>66</td>
<td>65</td>
<td>0.81</td>
<td>0.027 ± 0.003</td>
<td>0.013</td>
<td>42</td>
<td>125</td>
</tr>
<tr>
<td>1025</td>
<td>50/50 49/51</td>
<td>1.085±0.002</td>
<td>51</td>
<td>40</td>
<td>0.81</td>
<td>0.007 ± 0.001</td>
<td>0.007</td>
<td>42</td>
<td>250</td>
</tr>
<tr>
<td>1025</td>
<td>50/50 49/51</td>
<td>1.087±0.001</td>
<td>38</td>
<td>35</td>
<td>0.77</td>
<td>0.005 ± 0.001</td>
<td>0.003</td>
<td>45</td>
<td>270</td>
</tr>
<tr>
<td>1025</td>
<td>90/10 89/11</td>
<td>1.066±0.001</td>
<td>25</td>
<td>180</td>
<td>0.83</td>
<td>0.109 ± 0.003</td>
<td>0.011</td>
<td>41</td>
<td>360</td>
</tr>
</tbody>
</table>
Table 3.2
Characteristics of PCL/PMMA and PCL/PC Multilayered Films

<table>
<thead>
<tr>
<th>Number of Layers</th>
<th>PMMA/PCL Composition (v/v)</th>
<th>Film Thickness (μm)</th>
<th>Nominal Layer Thickness (nm)</th>
<th>f_{110}</th>
<th>Film P(O₂) (barrer)</th>
<th>P_{PCL, eff} (barrer)</th>
<th>X_{ε,PCL} (wt%)</th>
</tr>
</thead>
<tbody>
<tr>
<td>PMMA</td>
<td>100/0</td>
<td>51</td>
<td>--</td>
<td>--</td>
<td>0.200 ± 0.001</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PCL</td>
<td>0/100</td>
<td>51</td>
<td>--</td>
<td>--</td>
<td>0.970 ± 0.030</td>
<td>--</td>
<td>48</td>
</tr>
<tr>
<td>25/75</td>
<td>25/75</td>
<td>158</td>
<td>300</td>
<td>900</td>
<td>0.47</td>
<td>0.200 ± 0.001</td>
<td>1.027</td>
</tr>
<tr>
<td>25/75</td>
<td>25/75</td>
<td>102</td>
<td>195</td>
<td>585</td>
<td>0.46</td>
<td>0.181 ± 0.001</td>
<td>0.681</td>
</tr>
<tr>
<td>50/50</td>
<td>50/50</td>
<td>102</td>
<td>390</td>
<td>390</td>
<td>0.29</td>
<td>0.085 ± 0.001</td>
<td>0.164</td>
</tr>
<tr>
<td>75/25</td>
<td>75/25</td>
<td>160</td>
<td>900</td>
<td>300</td>
<td>0.40</td>
<td>0.048 ± 0.002</td>
<td>0.032</td>
</tr>
<tr>
<td>75/25</td>
<td>75/25</td>
<td>86</td>
<td>510</td>
<td>170</td>
<td>0.63</td>
<td>0.053 ± 0.005</td>
<td>0.045</td>
</tr>
<tr>
<td>75/25</td>
<td>90/10</td>
<td>145</td>
<td>990</td>
<td>110</td>
<td>0.53</td>
<td>0.055 ± 0.003</td>
<td>0.041</td>
</tr>
<tr>
<td>90/10</td>
<td>90/10</td>
<td>84</td>
<td>585</td>
<td>65</td>
<td>0.71</td>
<td>0.034 ± 0.005</td>
<td>0.007</td>
</tr>
<tr>
<td>90/10</td>
<td>90/10</td>
<td>38</td>
<td>270</td>
<td>30</td>
<td>0.76</td>
<td>0.022 ± 0.003</td>
<td>0.003</td>
</tr>
<tr>
<td>PC</td>
<td>100/0</td>
<td>51</td>
<td>--</td>
<td>--</td>
<td>1.59 ± 0.064</td>
<td>--</td>
<td>--</td>
</tr>
<tr>
<td>PCL</td>
<td>0/100</td>
<td>51</td>
<td>--</td>
<td>--</td>
<td>0.970 ± 0.030</td>
<td>--</td>
<td>48</td>
</tr>
<tr>
<td>50/50</td>
<td>50/50</td>
<td>127</td>
<td>490</td>
<td>490</td>
<td>0.435 ± 0.006</td>
<td>0.252</td>
<td>5</td>
</tr>
<tr>
<td>50/50</td>
<td>50/50</td>
<td>86</td>
<td>330</td>
<td>330</td>
<td>0.437 ± 0.012</td>
<td>0.253</td>
<td>4</td>
</tr>
<tr>
<td>50/50</td>
<td>50/50</td>
<td>51</td>
<td>200</td>
<td>200</td>
<td>0.390 ± 0.008</td>
<td>0.222</td>
<td>4</td>
</tr>
<tr>
<td>25/75</td>
<td>25/75</td>
<td>71</td>
<td>140</td>
<td>420</td>
<td>0.411 ± 0.010</td>
<td>0.128</td>
<td>0</td>
</tr>
</tbody>
</table>
Figure 3.1: Two component multi-layer system layout of extruders, melt pumps, feedblock, multiplying dies, cutting, stacking, spreading, and recombining melt streams.
**Figure 3.2:** AFM phase images of partial cross sections of coextruded PCL/PS multilayered film with; (A) 16 μm-thick PCL layer, (B) 1900 nm-thick PCL layer, (C) 400 nm-thick PCL layer, and (D) 75 nm-thick PCL layers with arrows indicating the PCL layers.
Figure 3.3: Extrusion direction WAXS and SAXS patterns exhibiting increased PCL orientation as layer thickness decreases from 1900 nm to 75 nm in PCL/PS multilayered films. Orientation of PCL suggests layer confinement induces the formation of high aspect ratio single crystal lamellae in thin nanometer scale layers.
Figure 3.4: Increase toward in-plane PCL layer orientation by reducing layer thickness in PCL/PS multilayer films
Figure 3.5: Effect of layer thickness on effective PCL layer oxygen permeability in PCL/PS multilayered films. Oxygen transport measurements were conducted on as-extruded films at 23°C and 0% relative humidity.
Figure 3.6: Confined PCL layer crystalline phase orientation from ED WAXS patterns and effective PCL layer oxygen permeability exhibit good correlation in PCL/PS multilayer films. Correlation between the structural and property behavior of the confined PCL layers suggesting that lamellae orientation results in the oxygen barrier enhancement in PCL/PS multilayered films.
Figure 3.7: Extrusion direction 2D WAXS patterns of PCL/PS, PCL/PMMA, and PCL/PC multilayer films at various PCL layer thicknesses.
Figure 3.8: Effect of confining amorphous substrate on confined PCL layer crystal orientation against PS, PMMA, or PC layers. Increasing PCL-confining layer substrate interactions reduced the amount of PCL crystalline phase orientation at similar layer thicknesses.
Figure 3.9: Effect of layer thickness on PCL layer oxygen permeability. Reducing PCL layer thickness against PS or PMMA layers resulted in a decrease of oxygen permeability in the extruded films at 23°C and 0% relative humidity.
Figure 3.10: Correlation between confined PCL layer crystalline phase orientation and oxygen permeability confirm similar lamellae orientation mechanism for gas barrier enhancement in PCL/PS and PCL/PMMA multilayered film systems.
Figure 3.11: (Left) PCL layer remelting quenching or recrystallization temperature window. (Right) Extrusion direction WAXS patterns of melt recrystallization or quenching temperature on 40 nm PCL layer crystalline phase orientation in multilayered PS (top) and PMMA (bottom) films.
Figure 3.12: Remelted quenched or recrystallized 40 nm PCL layer orientation function as a function of temperature for PCL/PS and PCL/PMMA multilayered films. Sharp transitions from “edge-on” to “flat-on” crystal orientation were witnessed based on recrystallization conditions/environment.
Figure 3.13: (Top) Extrusion direction WAXS pattens of melt recrystallization or quenching temperature 100 nm PCL layer crystalline phase orientation multilayered against PA12 (top), PP-g-MA (bottom). (Bottom) Comparison of PCL (200) orientation function as a function melt recrystallization or quench temperature against different polymer substrates.
Appendix A:
Tunable Polymer Lenses

A.1 Introduction

Today’s technology is driving the need for lighter, simpler, and more compact optical devices, yet the requirements for image quality are only getting more stringent. Zoom capability, for example, is still desirable in even the smallest devices. Typical zoom lens systems need lens groups to move back and forth to adjust the image size. At a certain package size, one simply runs out of room to move lenses enough to magnify an image. Even for larger cameras, an alternative to mechanical motion would be beneficial by reducing engineering complexity. A fundamental shift in the design of zoom systems can occur if one considers variable lenses: mutable lenses which alter their shape or index distribution to produce focal length changes, without translational movement. This paper describes the fabrication and optical performance of an all-solid-state variable focal length lens developed to address these needs.

One need not look far for an example of a variable lens: the human eye changes its shape and refractive index in order to achieve dynamic focus [1]. Several research groups have embarked on biomimetic research projects in order to emulate the processes of the human eye. There has been work using voltage-controlled liquid crystals as active optical elements, for standard imaging systems as well as for fiber coupling [2-5]. Other variable lenses have been based on
Microfluidics enables the controlled injection of fluid into chambers with deformable membranes [6-8]. Fluid re-distribution can also be initiated mechanically to produce variable lenses [9-11]. Recent work shows lens properties of a controlled liquid drop shape, with no membrane [12]. A similar shape change based on different physics is found by taking advantage of electrowetting, in which an electrically induced change in surface-tension changes the surface curvature of liquid microlenses [13-16].

In contrast to the liquid tunable lenses, an all-solid-state polymer lens more closely mimics the nature of the human eye lens. Solid-state lenses can more readily withstand fluctuations in temperature, pressure, and motion than liquid based lenses and offer a more robust approach to tunable optical systems. To our knowledge, very little research has been published in this arena. Thermopolymers have been used recently to create a tunable microlens and lens array [17, 18]. In that device, adjusting the temperature of the thermooptical polymer within the lens can change the focal properties.

This work discusses the development and characterization of an all-polymer tunable lens, in which pressure applied to a membrane containing a compliant cross-linked polymer gel causes symmetric shape changes to the outer surface. A detailed description of lens fabrication, detailing the materials used in the construction, their properties, and how they are assembled into the lenses is presented. An analysis of lens shape change, including direct measurements of
the surface profiles as a function of applied pressure, is discussed. The focal length is measured as a function of applied stress and correlated with the tunable surface shape as a model to predict lens focal length change.

A.2 Materials and Methods

A novel lens manufacturing procedure was developed to fabricate solid state deformable composite lenses. Composite, variable focal length lens designs were created through the production of individual optical components: a flexible, elastomeric lens membrane, a reservoir of cross-linked gel-like polymer beneath the membrane, hard plastic backings, and static hard plastic lenses. Fabrication of lenses through assembly of the individual components provided an advantage in their flexibility to be aligned and integrated in several different geometries to form a lens of tailored static and variable optical power. A general description following the fabrication of the optical components and composite lens is shown in Figure A.1.

Composite, variable focal length lenses were constructed using a combination of deformable and rigid polymeric materials. An elastomeric styrene-ethylene/butylene-styrene (SEBS) block copolymer was provided by Kraton Polymers (Kraton® G1657). A room temperature, cross linkable, two-part polydimethyl siloxane (PDMS) was provided by Dow Corning Corp. (Sylgard® 184). Poly (methyl methacrylate) (PMMA) was provided by Atofina Chemicals,
Inc. (Plexiglas V920). The SEBS copolymer and PMMA resins were received in pellet form and used without further modification. The cross-linkable PDMS was received as a viscous fluid and cross-linked at a w/w ratio of 40:1.

The deformable elastomers and rigid PMMA materials were selected based on material optical properties (refractive index, transmission, and high clarity). The refractive indices of the Kraton and PDMS were measured at three wavelengths, Table 1, using a commercial instrument (Model 2010 Prism Coupler, Metricon Corporation, Pennington, NJ). Also reported are the indices interpolated from standard data on PMMA [19]. In addition to optical requirements, elastomers were selected based on an ability to reversibly change shape with pressure. Reversible expansion of the elastomeric membrane was ensured through application of tuning strains less than the elastic deformation limit of the SEBS rubber. It is estimated that the maximum strain on the lenses in this paper was 18%, as compared to the irreversible strain limit which lies between 30% and 40%.

Soft, deformable meniscus shaped lens membranes were created via compression molding of SEBS elastomer, Figure A.1(a). A sheet of SEBS was placed between a plano-convex and plano-concave glass lens which were housed and aligned in a metal holder. An additional metal spacer of designated height was placed around the lens holders to regulate the thickness of the deformable lens
shell. The assembly was molded at 120°C for 15 minutes under slight pressure, cooled in-situ, and removed from the holder assembly.

Rigid lenses of desired geometry were fabricated via compression molding of PMMA sheet utilizing the commercial glass lens and lens holder design previously described to manufacture deformable SEBS lens membranes. The flexibility of this manufacturing method allowed for variation in the glass shape and geometry to produce PMMA lenses of corresponding shape and geometry. In this study, plano-convex and plano-concave PMMA lenses of various radii of curvature were fabricated via this method for inclusion in the composite, variable focal length lenses.

The PMMA lenses were aligned and attached to an optically smooth, flat molded PMMA backing for ease of incorporation into the final composite lens design. An ultra violet crosslinking optical adhesive (Dymax OP-29V, Dymanx Corp., Torrington CT) was applied between the lens and flat backing. Upon exposure to UV light, the lens and backing assembly were irreversibly attached.

Soft, SEBS elastomer spacers were created via compression molding of virgin resin pellets at 190°C under 10,000 lbf for 5 minutes, Figure A.1(a). A metal spacer was utilized to assure a final sheet thickness of 4 mm. Circular spacers were cut from the flexible sheet using custom machined die punches of designated diameter. A second mechanical punching of the circular spacer resulted in the creation of soft rings using a second die punch of smaller diameter. 25 and 20 mm
diameter circular die punches were utilized to create ring-like, soft, SEBS spacers for the variable focal length lens designs described in this work.

Composite, variable focal length lenses were created through the alignment and adhesion of the previously described optical components. As shown in Figure A.1(b), the multi-step assembly procedure began with the adhesion of the SEBS spacer onto the SEBS deformable meniscus lens membrane. Adhesion was completed via a two-part bonder/activator cyanoacrylate glue (Loctite®, Henkel Corporation, Avon, OH). An additional adhesion of the rigid PMMA lens and backing followed.

PDMS monomer was mixed with a cross-linking agent at a w/w ratio of 40:1. The elastomer was injected, via syringe, through the SEBS spacer and into the air filled cavity of the composite lens, Figure A.1(c). A second syringe was inserted through the SEBS spacer to allow for the displaced air to vent from the lens cavity during injection. The elastomer filled composite lens was allowed to cross-link at room temperature for three days before optical testing and analysis were performed.

Concave-convex, double convex, and plano-convex lens designs have been successfully fabricated using the methods outlined in Figure A.1. In this paper the mechanical and optical characterization of this paper of one of these: the double-convex lens depicted in Figure A.1(c). This lens combined a plano-convex poly (methyl methacrylate) (PMMA) lens, R=25.8 mm, with a tunable
elastomeric lens membrane, $R=38.6$ mm. The PMMA is rigid; the variable focal length is provided by elastomer side only. The PMMA and tunable lens membrane were designed to have diameters of 15 mm. The styrene-ethylene/butylene-styrene (SEBS) lens spacer was 4 mm thick with an inner and outer diameter of 20 and 25 mm respectively. After assembly, the double-convex lens design had an overall thickness of 8 mm.

### A.3 Results and Discussion

#### Tunable Lens Actuation

The lenses were designed to vary focal length based on a change in the deformable membrane shape with applied pressure, Figure A.2. Pressure to deform the lens is applied through surface contact with rigid rings. Squeezing the rings together displaces the soft, deformable crosslinked PDMS lens center. The pressure is converted into expansion of the SEBS membrane, resulting in a shape change of the outer surface. As the surface expands its average radius of curvature is reduced.

Experimental induction of the SEBS membrane shape change was achieved using lens mounts. The mounts were designed with the membrane side of the lens held fixed against a circular aperture. A threaded retaining ring secured the lens from the back side, against the hard PMMA backing. Once engaged, the retaining ring
could be further rotated inducing a uniform compressive force on the soft lens, which would drive the shape change of the deformable membrane.

The front aperture dimensions of the lens mount for all lens surface measurements was 3 mm thick with a diameter of 10.5 mm. The thread for the retaining ring required 1.56 turns to compress the lens by 1 mm. A typical linear force required for maximum reversible lens compression was 10 N.

Full optical simulations of the lenses have been performed, but their basic operation can be illustrated by simplified equations. Considering the biconvex lens to be comprised of two lenses, a PMMA lens and a tunable lens, the focal length of the system $F_{\text{Composite}}$ can be approximated by Equation 1

$$\frac{1}{F_{\text{Composite}}} \approx \frac{1}{F_{\text{PMMA}}} + \frac{1}{F_{\text{Tunable}}}$$ \hspace{1cm} (1)

The focal length of the tunable lens is proportional to its radius of curvature $R$. If an uncompressed lens with a radius of curvature $R_0$ results in a tunable-part focal length of $F_0$, then the system focal length can be approximated by Equation 2:

$$\frac{1}{F_{\text{Composite}}} \approx \frac{1}{F_{\text{PMMA}}} + \frac{R_0}{F_0 R}$$ \hspace{1cm} (2)
The shape change is reversible so long as the applied strain is within the elastic limit. The limit in tunable lens curvature occurs when the plunger is fully depressed. The minimum radius of curvature is practically limited to half the diameter of the optical aperture.

**Determination of Lens Surface Profiles**

Lens surface profiles were measured directly using a non-contact, raster-scanned depth measurement device. Three-dimensional maps of lens surfaces were measured by rasterscanning a range finder (Model Acuity AR200, Schmitt Measurement Systems, Inc. Portland, Oregon) across the face of the lens. The range finder operated by triangulating the position of a laser beam scattered off the surface. The device could measure distances up to 6.35 mm with a root-mean squared measurement error of 5.8 μm, determined by running the profiler over a flat laser mirror set at a slight (3.4 deg) angle from normal incidence. The translation stage actuators had specified linear positioning repeatability better than 1 μm. Points across the surface were acquired on a 150 μm grid.

A consequence of the measurement geometry is that areas of the lens surface near the mount aperture were inaccessible to proper depth measurements. Two effects contributed to this loss of data: 1) obstruction of the profiler laser spot by the lens mount, and 2) multiple reflections of the laser between the lens surface and surrounding mount. Both of these effects can be traced to the fact that the lens is recessed from the mount surface: when viewed from an oblique angle (required
for triangulation) the aperture side walls permitted a view only of an elliptical portion of the lens, and near the edges the profiler laser beam would reflect onto the walls and produce multiple spots.

To discriminate against edge effects, data near the edge were masked out. To discriminate against outliers, a spherical fit was performed to the remaining data and points deviating from the fit by more than a certain threshold were ignored. The threshold was typically 200 μm, 35x greater than the measurement uncertainty, and not less than 100 μm. To test the accuracy of the measurement, an Edmund Optics NT45-084 glass lens was scanned. The manufacturer reports the 12 mm diameter lens has a surface with a 9.42 mm ± 1% radius of curvature. When scanned and fitted, the data showed a value of 9.54 mm radius of curvature with a standard deviation of 8.2 μm for the residuals.

Measurements were obtained for a variety of compression values, spanning a broad range of curvatures. The resulting datasets were compared against models for the surface shape, with the goals of predicting optical performance and providing physical insight into the membrane dynamics. The overall results of the data fitting are presented in Table A.2, with an explanation of the parameters to follow.

First, the surface curvature scans were fit to a spherical profile. A spherical surface is described by an equation with one constant $c$:
\[ z = \frac{c(x^2 + y^2)}{1 + \left(\sqrt{1 - c^2(x^2 + y^2)}\right)} \]  

(3)

where the vertex of the spherical surface is located at \((x, y, z) = (0, 0, 0)\), the radius of curvature is \(R = 1/c\), and the surface curves upward into the space \(z > 0\).

In order to fit this curve to experimentally-determined data points, three additional parameters \((x_0, y_0, z_0)\) are necessary to represent the location of the vertex, for a total of 4 fit coefficients. The results of the spherical fits are presented in Table A.2. The radius of curvature shows a clear, monotonic decrease with increasing compression, \(\Delta L\). The membrane deforms to accommodate the pressure induced on the partially cross-linked polymer reservoir. The measured radius of curvature was reduced by nearly a factor of 4 for a total compression of only 1.12 mm.

Initially, the lens assumes a more spherical shape with compression. At compression values of \(\Delta L = 0.32\) to 0.80 mm, the standard deviations are near the instrument limit of 8.2 \(\mu\)m, as determined by measuring a commercial-quality control lens. At the highest compressions the deviation from a sphere increases rapidly. Much of this residual deviation is near the lens edges, suggesting a systematic departure from a spherical surface at large compression. This is not surprising given the lens mount geometry and reduced curvature. The plunger aperture is 10.5 mm in diameter; as the radius of curvature approaches half this (5.25 mm) the edges can be expected to deviate from spherical.
The spherical fits of Table A.2 provided a first order measure of the focal length of the variable lens. More sophisticated models for the shape of the surface were applied in order to track the optical aberrations and to give a better understanding of how the membrane deforms. To extend the surface model beyond a simple sphere, one choice is to employ a polynomial expansion such as Zernike polynomials, which are commonly used in the analysis of optical aberrations. Instead extension of the data analysis with a biconic surface was performed which should provide more physical insight into the membrane shape. The biconic surface is described by

$$z = \frac{c_x x^2 + c_y y^2}{1 + (\sqrt{1 - (1 + k_x) x^2 - (1 + k_y) y^2})}$$

(4)

which deviates from a sphere via a conic constant \(k\) and furthermore allows for astigmatism through separate values for the curvature \((c_x, c_y) = (1/R_x, 1/R_y)\) and conic constant \((k_x, k_y)\) along each axis \(x \& y\). The advantages of this description include the fact that it requires relatively few parameters to describe the surface (four) and that a clear, physical meaning can be ascribed to each one. In particular, physical intuition suggests that the surface shape will be stretched almost linearly near the lens aperture. This would suggest a cross section more hyperbolic than circular, which is precisely what the conic constant \(k\) allows one to model. Along either axis, the physical meaning of the conic constant \(k\) can be described loosely by saying at values of \(k > 0\) the surface curves away more
sharply than for a sphere, while for values of $k < 0$ the surface curves away more shallowly than for a sphere. More precisely, the curve is a hyperbola for values of $k < -1$, a parabola for $k = -1$, an ellipse for $-1 < k < 0$, a circle for $k = 0$, and an oblate ellipsoid for $k > 0$. It should be pointed out that fitting these data requires several more degrees of freedom than the four mentioned here. The experimental axes $(x,y,z)$ in the lab frame were related to the principal $(X,Y,Z)$ axes of a biconic lens through the incorporation of additional translational (3) and rotational (3) degrees of freedom in the actual surface fit.

The results of biconic surface curvature fits are shown in Table A.2. As anticipated the conic constants for most of the fits are negative, suggestive of hyperbolic shapes where the center of the membrane is spherical while the edges trail off nearly linearly towards the inner boundary of the plunger. As the compression increases, however, there is a shift towards higher conic constants until, at the highest compression, the constant flips sign. We speculate that at this high compression the center of the membrane is reaching a saturation point in its expansion, causing it to flatten out some and make the edges look steeper by comparison. An important point is that ahead of that transition region the lens surface is very well described by a sphere, which should translate to good optical performance.

To gain a deeper understanding of the deformation behavior of the dynamic surface, one would have to consider the strain distribution on the surface that is
likely balanced biaxial at the center and gradually becomes uniaxial at the edges. Furthermore, one would expect the magnitude of the strain to be greater at the center [20]. This strain distribution, the stress strain behavior of the material in both biaxial and uniaxial loading, and the boundary conditions imposed by the rigid rings during deformation would all contribute to the deformation behavior. A deformation analysis considering these parameters is possible, especially with the aid of finite element methods, but is beyond the purpose and scope of this paper.

Conic constants describe the deviation of a surface from a sphere. The biconic fit also enables us to describe the asymmetry, or astigmatism, of a lens. We can investigate the degree of astigmatism by computing the difference in height along orthogonal directions across the lens surface. The data show that the lens surface goes through a minimum astigmatism near $\Delta L = 0.64$ mm, at which point the maximum deviation of one curve from the other is $10 \mu$m out at the lens edge. Since the averaged sag at this point is 1.3 mm, this represents a relative astigmatism $< 1\%$. The largest astigmatism is measured for a low-pressure case $\Delta L = 0.16$ mm. Here is measured a maximum deviation from symmetry of $57 \mu$m out of a total sag of 0.52 mm, for a relative astigmatism of $11\%$.

Shown in Figure A.3 are cross-sections of the lens profile under different amounts of strain. The data presented are generated from spherical curve fits and are graphed in a coordinate system in which the outer face of the lens mount lies
along y=0. The data points within a single curve are accurate with respect to one another, but different curves may be offset horizontally by up to 0.3 mm as a result of the uncertainty in accurately registering the edge of the aperture mount.

As the strain/pressure is increased the lens surface wells up to form a boundary with greater and greater curvature. The maximum displacement of the central surface is about 2 mm. Not shown are the curves for ΔL = 0 and 0.16 mm. Below ΔL = 0.32 mm, the mount did not fully engage the lens surface. The surface was in contact only on one side of the aperture, which helps to explain the higher standard deviations of the low-compression surface fits in Table A.1.

Future work correlating the volume redistribution of the tunable lens as a function of elastic membrane response and plunger position may be considered to better predict optical behaviors of these novel, solid state tunable lenses.

**Tunable Lens Optical Properties**

To test the optical performance of the lens, images of simple objects were projected onto a CCD camera. To measure back focal lengths, a 2.5 cm tall printed “Y” was placed 1 meter away from a camera. The lens was mounted on a translation stage in front of a camera. The back focal length was measured by recording the stage position at which the image was in focus, measuring the distance between the camera plane and the lens mount, and accounting for the surface deformations induced by the lens compression. The software used to
model the optical properties of the lens was ZEMAX, written by the ZEMAX Development Corporation, Bellevue, WA. Inputs into the model were spherical fit results from measurements of both sides of the lens, including the pressure-induced center thickness changes mentioned above.

Object and image distances were compared to optical calculations carried out in a standard optical design software package. The results of the spherical surface fits in Table A.1 the geometry of the various lens components from Figure A.1, and the refractive indices as reported in Table A.2 were used as inputs to the software. Measurements were carried out at several lens compression values to see how the lens performed at different focal lengths. Table A.1 shows a comparison of fitted and measured back focal lengths. The agreement is excellent, suggesting that the principal properties of these lenses can be well-understood from a detailed knowledge of their composition and shape change. Based on this good agreement, the calculated effective focal length is reported as a function of the compression $\Delta L$. The focal length, and therefore the optical power, of the lens varied by nearly a factor of two with a $\Delta L$ of only 1.28 mm. This is directly verified by comparing the image sizes recorded for each compression value: for a distant object the magnification is proportional to the focal length.

A metric for the optical power in a lens is the diopter, defined as $1/\text{focal length}$ in inverse meters. This metric is most useful when comparing lenses of a similar aperture. Because of the inverse relationship, small changes to small focal lengths
can correspond to large diopter changes, but systems with small lenses necessarily operate in a different regime than systems with larger lenses. For our lens with its 10.5 mm aperture, we observe a tunable variation of 30 diopters, which represents a significant change in optical power. For example, the human eye can effect a change of only ~4 diopters [1]. The change in optical power of the lens described here is similar to that reported in the referenced literature for tunable lenses with a comparable diameter. Of the reported lenses with apertures of 5 mm or greater, only three have a greater change in optical power. Two 5 mm aperture lenses [11, 13] were reported to exhibit tunable changes of 52 and 45 diopters respectively. A change in power of 150 diopters was reported for a 20 mm diameter lens [7] but this was achieved by adjusting two optical surfaces simultaneously.

Quantitative assessments of the image quality of the lenses, such as measurements of the modulation transfer function, are beyond the scope of this introductory paper. Sample images are presented in Figure A.4. Qualitatively, the image quality tracked the behavior observed in the surface profile fits: trailing off at the extremes of compression but quite good over a large range in the middle. Images in all cases were easily recognizable and, by eye, free of distortion. At the lower end of the compression range the quality is expected to improve with a more symmetric initial lens construction. (Preliminary efforts along this direction have already shown improvement at low compression.) At the upper end of the range the quality is limited not by issues of lens construction but rather by the inherent aberrations of highly curved optical surfaces. Nonetheless, there are at least two
ways in which the upper end of the range could be addressed, both related to the many degrees of freedom afforded by the construction of these lenses. They are: 1) the use of higher-index materials in the lens, and 2) utilizing the conic constants of the surface membrane to correct for aberrations. Higher-index materials would allow for greater focal length changes with less curvature. This automatically entails less aberration for the same power change: less curvature results in less aberration. The conic constants can also help. For highly-curved surfaces, a negative conic constant helps reduce spherical aberration. By tailoring the mechanical properties of the membrane one could achieve a membrane that could adopt target deformation characteristics as a function of compression – improving optical quality as a result.

A.4 Conclusions

In conclusion, we have demonstrated a general technique for making variable focal length lenses. Their construction is easily generalized to compound lenses which can have negative focal lengths, positive focal lengths, or lenses that can switch between positive and negative, which is required for high zoom ratios with stationary lenses. Based on the compression of a reservoir or sac of gel-like polymer, the convex lens surface is formed by an elastic membrane that expands outward in response to the applied pressure. Experimental surface profiles of the elastomeric membrane were fitted to spherical and biconic shapes to predict lens focal length and image properties as a function of compression. As a result of the
surface profile measurements, predictions of the optical behavior were in very good agreement with the observed data. By compressing the reservoir only 1.3 mm we changed the focal length of the lens by a factor of 1.9. Dynamically-magnified images generated by the lens show the usefulness of these lenses as working optical elements and have led to preliminary demonstrations of unique camera designs.

A.5 References

Table A.1
Materials used in the fabrication of tunable lenses

<table>
<thead>
<tr>
<th>Material</th>
<th>Trade Name</th>
<th>Lens Component</th>
<th>Refractive Indices</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td></td>
<td>532 nm</td>
</tr>
<tr>
<td>SEBS Rubber</td>
<td>Kraton G1657</td>
<td>Deformable membrane &amp; spacer</td>
<td>1.4938</td>
</tr>
<tr>
<td>PDMS Elastomer</td>
<td>Slygard 184</td>
<td>Elastomer core</td>
<td>1.4149</td>
</tr>
<tr>
<td>PMMA</td>
<td>Plexiglas V-920</td>
<td>Static lens</td>
<td>1.4955</td>
</tr>
</tbody>
</table>
Table A.2

The first two sections present results of surface fits to measured surfaces as a function of plunger displacement $\Delta L$. The standard deviation of the differences between data points and the fit is given in microns, and all other parameters are outlined in the text. The last section presents focal length information, both predicted and observed back focal lengths, and the resulting overall focal lengths. Uncertainty in the observed focal length is 0.5 mm.

<table>
<thead>
<tr>
<th>$\Delta L$ (mm)</th>
<th>$c$ (mm$^2$) $R$ (mm)</th>
<th>$\text{Stdev (\mu m)}$</th>
<th>$c_x$ (mm$^2$)</th>
<th>$c_y$ (mm$^2$)</th>
<th>$k_x$</th>
<th>$k_y$</th>
<th>$\text{Stdev (\mu m)}$</th>
<th>$\Delta L$ (mm)</th>
<th>Pred. (mm)</th>
<th>Obs. (mm)</th>
<th>F.L. (mm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>0.00</td>
<td>0.0366</td>
<td>27.32</td>
<td>10.71</td>
<td>0.0402</td>
<td>0.0336</td>
<td>-10.00</td>
<td>6.14</td>
<td>9.32</td>
<td>0</td>
<td>24.6</td>
<td>24.9</td>
</tr>
<tr>
<td>0.16</td>
<td>0.0384</td>
<td>25.79</td>
<td>12.95</td>
<td>0.0452</td>
<td>0.0354</td>
<td>-8.00</td>
<td>4.80</td>
<td>9.28</td>
<td>0.32</td>
<td>23.3</td>
<td>24.1</td>
</tr>
<tr>
<td>0.32</td>
<td>0.0507</td>
<td>19.72</td>
<td>9.16</td>
<td>0.0553</td>
<td>0.0558</td>
<td>-8.59</td>
<td>-7.44</td>
<td>8.49</td>
<td>0.64</td>
<td>18.9</td>
<td>17.6</td>
</tr>
<tr>
<td>0.48</td>
<td>0.0737</td>
<td>13.57</td>
<td>9.51</td>
<td>0.0829</td>
<td>0.0814</td>
<td>-5.40</td>
<td>-3.63</td>
<td>7.86</td>
<td>0.96</td>
<td>14.8</td>
<td>14.6</td>
</tr>
<tr>
<td>0.64</td>
<td>0.0943</td>
<td>10.60</td>
<td>8.83</td>
<td>0.1006</td>
<td>0.1027</td>
<td>-1.80</td>
<td>-2.24</td>
<td>7.29</td>
<td>1.28</td>
<td>12.9</td>
<td>13.0</td>
</tr>
<tr>
<td>0.80</td>
<td>0.1069</td>
<td>9.43</td>
<td>7.57</td>
<td>0.1147</td>
<td>0.1173</td>
<td>-1.13</td>
<td>-1.44</td>
<td>6.75</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>1.12</td>
<td>0.1381</td>
<td>7.24</td>
<td>13.05</td>
<td>0.1321</td>
<td>0.1344</td>
<td>0.50</td>
<td>0.35</td>
<td>11.69</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
Figure A.1: Fabrication and assembly of variable focal length lens. (a). Fabrication of deformable membrane, (b). Assembly of variable focus length lens, (c). Final injection and cure of PDMS lens core. Final diagram labeled with dimensions of lens tested in this work.
Figure A.2: Schematic of the mechanism for variable focal length. Pushing a plunger a distance $\Delta L$ causes the deformable elastomer within the lens to expand out against the pliable outer membrane. Dashed lines indicate plunger and surface locations before compression. Little compression is necessary; the maximum $\Delta L$ cited here is 1.28 mm.
Figure A.3: Plot of surface profiles as interpolated from fitted measurements. Dotted lines represent lens mount.
Figure A.4: Images acquired at two different zoom states of the lens. The magnification of the object in these images differs by a factor of 1.8.
BIBLIOGRAPHY

Chapter 1


**Chapter 2**


**Chapter 3**


**Appendix A**


