Block Copolymer Photonic Crystals

by

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Abstract

This thesis explores the photonic properties of block copolymer systems. One dimensionally periodic dielectric stacks are fabricated with symmetric, lamellar forming, copolymer systems: diblock copolymers, solvent swollen BCP materials, and homopolymer swollen BCP blends. Each system exhibits reflectivity in visible spectrum. These materials are also investigated for their phononic band properties by Brillouin scattering. A copolymer forming the three dimensional double gyroid at optically relevant length scales and its reflective properties are presented as well.

Experimental results document the initial observation of photonic optical properties related to the microstructure of a block copolymer. One dimensionally periodic, lamellar polymer block copolymer systems of poly(styrene-b-isoprene) are used to fabricate multilayered optical structures with a range of lamellar dimensions. The lamellar repeat of the copolymer morphology is shown to be adjustable by blending symmetric amounts of like homopolymers of lower molecular weight with the copolymer. The composition of the blends remains symmetric and the morphology is shown to remain lamellar. An isopleth of composition is examined and photonic crystals containing up to 60 wt \% homopolymer exhibit wavelength selective reflectivity from the ordered morphology. The wavelength of reflectivity is correlated with the lamellar repeat spacing and morphology.

The optical properties of solvent swollen ultrahigh molecular weight block copolymers are examined. The wavelength selective reflectivity is shown to correlate with the expected behavior of the phase segregated morphology. Deformation sensitive ordered gels are fabricated by using a non-volatile, alkyl phthalate plasticizer. The optical properties are shown to respond to the material strain. A simple demonstration of the visualization of the strain field of a deforming system is presented. In addition these gels are shown to exhibit phononic band gap behavior. The system is studied by Brillouin scattering and resonant phonons arising from the morphology are predicted and observed.

Three dimensionally periodic photonic crystals formed of a double gyroid styrene-isoprene diblock copolymer are also documented. The copolymer material is considered as formed and also after a series of processing steps. Etching of the isoprene
matrix is demonstrated yielding a free standing air-styrene double gyroid. This material is then used to replicate the matrix geometry in titania by infiltration with a sol-gel precursor and subsequent pyrolysis. The structure of the double gyroid material is examined via x-ray scattering and electron microscopy. The photonic band properties of the double gyroid structure for multiple constituent materials with a broad range of refractive indices are examined. Features in optical measurements resulting from the double gyroid structure are observed consistent with the 250nm cubic lattice parameter.

A block copolymer photonic crystal platform is outlined and presented. Acoustooptic, phononic crystal properties are noted in these materials and applications are discussed. Strategies for creating a block copolymer based material with an absolute band gap are outlined in addition to novel techniques for incorporating additives for the production of active, photonic, copolymer based materials.

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Chapter 1

Introduction

Photonic crystals enjoyed a rapid rise to the forefront of the scientific community's interest. Applications in telecommunications and the possibility of observing new physical phenomena fuelled this ascent. With the statement of the fundamental concept of the photonic band gap, a range of frequencies forbidden to propagate in a material, in 1987[2, 3], the field was poised for rapid development both experimentally and theoretically. It has remained a challenge from the beginning to fabricate the photonic crystals structures, that had been identified as having complete band gaps by a process which could realize these properties. Early researchers noticed the optical properties of self assembled colloidal structures[4, 5], and many researchers turned to self-assembly in polymer[6] and colloidal systems[7, 8] as a means to fabricate three dimensionally periodic photonic crystals. The opal, a naturally occurring gemstone mineral, served as a model for this approach as it exhibits colors arising from inherent photonic properties of its FCC close packed silica spheres. The bulk of research on self-assembled photonic crystals remains on synthetic opal based systems. This thesis is about an alternative path to self-assembled photonic crystals using block copolymers and the periodic morphologies they exhibit as photonic materials and templates for them.
1.1 Photonics and Applications

The promise of photonic materials is to provide a technological leap forward analogous to that of the semiconductor in the mid twentieth century. Most enticing is their particular application to the telecommunication industry where all-optical communication technology will dramatically expand the capacity of current networks. Their use as cladding for fiber waveguides[9] and planar waveguides[10] and for enhancing integrated optical circuits have been proposed[11]. Eventually, application of photonic materials in optical computation and even quantum information[12] are expected. This is only part of their potential as new phenomena are discovered on a fairly regular basis. The importance of these materials is largely yet to be realized, however, as photonic materials have proven difficult to manufacture in a useful form via a process which is cost effective.

Fabrication is the critical issue with regard to the eventual application of photonic crystals. The physics of their various functions is relatively well understood, although, researchers continue to invent more imaginative structures and integrate special materials to provide interesting, useful and unique properties. Photonic crystals will occupy the same role as silicon does in current electronic devices and therefore must be similarly cost effective and easy to manufacture. Many technologies being explored involve adaptations of semiconductor fabrication techniques. Complex three dimensional structures can be fabricated by assembling them a layer at a time to build up the full structure[13, 14]. Semiconductor devices are currently fabricated as complex interwoven structures fabricated in several, up to ten, layers. These technologies are applicable to fabricating photonic crystals, but the precision required, to optimize the structure and the number of layers needed for adequate photonic properties, stretches the limits of this technology. Still though, much progress continues to be made here.
1.2 Photonic Crystal Structures

A relatively new approach which shows much promise for fabricating large area, well ordered photonic crystals of appropriate thickness for application is holography[15, 16]. Recent results have produced complex, well ordered, interconnected structures which posses a band gap for higher dielectric contrasts than fabricated. No results have been published for structures showing optical properties or a complete gap but all indications are that it is just a matter of time. Holography is, however, no magic bullet, and problems such as shrinkage of the resist material, and enhancement of the dielectric properties of the resulting structures still need to be solved. In addition to the fabrication of well ordered structures practically without defects, or more precisely, with excellent defect control, holographic techniques are being developed for directly writing wave guide "circuits" into these structures. This technology holds much promise.

1.2.1 Self-Assembly and Photonic Structures

Self-assembly is decidedly different from either lithographic or holographic approaches for fabricating well ordered structures. It is an energetically driven process which arrives at an equilibrium structure based on the system having the lowest free energy of accessible states. Defects and imperfection in the structure represent increases in free energy which provide a driving force to remove them. Based on the free energy increase, a uniform structure is achieved as the free energy of the system is minimized. The system components, such as the block copolymer or the individual polymer spheres, define the structure, and the characteristics are the uniform throughout it. The driving force toward equilibrium decreases as the structure nears the equilibrium configuration, causing defects to persist in real self assembled systems. This is because either the time scale to reach the equilibrium configuration is much longer than the time scale of the observations, or the system has energetically trapped defects such that the equilibrium structure is only accessible by first increasing the free energy of the system enough to escape the meta-stable defect state[17]. The nature of these
defects is to be randomly distributed in the structure, and little control can be had over their placement or form.

The local order of self-assembled systems, however, can be extremely good. In photonic crystals with high index contrast which possess complete band gaps, it is likely that only a few repeat spacings of the ordered structure are responsible for most of the observed properties. The local order becomes extremely important in this circumstance since roughness and irregularity[18] deform the band structure and degrade the photonic performance and can even close the band gap[19]. Self-assembled photonic crystals show their greatest potential here as templates for high index contrast photonic crystals. The most popular example of a self assembled photonic crystal is that of the synthetic opal. It is a structure comprised of uniform diameter spheres, typically made of silica(e.g. natural opal) or polymer, packed on a face centered cubic (FCC) lattice. The structure shows photonic properties in the form of opalescence[20], which is the property of natural opals to reflect bright colors that change with angle. They do not possess a complete band gap for any dielectric contrast[21]. If the space between the spheres is filled with a material of sufficiently higher index, $n_1$ than that of the spheres themselves, $n_2$, (such that $\frac{n_1}{n_2} > 2.9$), a complete band gap can be opened between higher order, ($8^{th}$ and $9^{th}$), bands[22]. The relative ease and simplicity of fabrication of synthetic opals has proved enticing to many researchers. It is also possible to enhance the speed and degree of order of synthetic opals by assembling them in preformed channels, which can be done on substrates suitable for later device fabrication. The major drawback is that only close packed structures can be formed, and it requires manipulation of the particles[23] or substrate[24] directing the self assembly to form any structure other than HCP or FCC. The possibility for large scale production is good since the size of the photonic crystal is limited only by the quantity of particles on hand. The uniformity of the structure over the area of the crystal is determined by the particle size distribution, which can be as good as a few percent variation in diameter. This is a self assembly process however, and as such, defects will persist in even the most carefully prepared systems. Nevertheless, research on synthetic opal photonic materials is a vibrant field that yields interesting
results.

Block copolymers (BCPs) provide another route to self assembled photonic crystals. BCPs have long been known to form ordered morphologies when the molecular weights of the component blocks are large enough to drive microphase segregation into well defined, chemically differentiated regions[25]. This again is an energetically driven process whereby the competition between the unfavorable interaction of dissimilar polymer types and the tendency of polymer blocks to adopt a random coil configuration. Above the critical value of $\chi_{AB}N_{A+B}$, where $\chi_{AB}$ is the Flory-Huggins segment-segment interaction parameter and $N_{AB}$ is the total degree of polymerization of the polymer (both A and B blocks), the blocks segregate and the resulting domains arrange into a shape and spacing yielding the lowest energy configuration. The domains can adopt a wide variety of morphologies increasing as the constitution of the molecule becomes more complex, e.g. linear AB triblocks, star polymers, terpolymers and others. The compositionally determined morphologies of diblock copolymers that this thesis will explore experimentally are lamellae and double gyroid shown in Figure 3-1. The architecture of polymer molecules are shown to affect the morphology formed. More complex multiblock copolymers are likely to adopt a variety of core shell versions of the above mentioned "classical" morphologies[26], as well as a palette of new, more complex morphologies[27, 28]. The wide array of possible morphologies shows the flexibility of the block copolymer platform for making photonic structures.

1.2.2 Block Copolymer Photonic Crystals

The simplest photonic structure is the multilayer stack. It also happens to be the structure with the largest ratio between the wavelength at which the structure interacts with light and the dimension of the periodicity. These two features make lamellar block copolymers the most likely candidate for a first exploration of BCP photonic crystals. The spacing of a block copolymer morphology scales with a fractional power of the molecular weight, and the relaxation time of a polymer scales with the cube of it. This presents a problem, as it becomes difficult to increase the spacing while leaving the system mobile enough to relax defects out of the structure. The length
scales required are on the order of a quarter of the wavelength of light, and it has been proposed that these spacings could not be achieved by block copolymers because of the inability of polymers of sufficient molecular weight to relax into an equilibrium morphology[29]. The choice of a first experimental system is established by these considerations. For, to simply observe photonic properties from a block copolymer, a lamellar system requires the lowest molecular weight and smallest repeat spacing. A full development of BCPs as a photonic materials platform, however, necessitates the creation of a three dimensional structure either with a complete band gap or with the potential to have one.

Block copolymer systems offer many possibilities in this regard due to the range of accessible three dimensional morphologies, including the double diamond and double gyroid. These two structures are distinct from a general three dimensional morphology in that they divide space into three continuous regions: two interpenetrating networks and a matrix. This will be more fully explored in Chapter 6, but the key topological feature is that it is possible to go from any place in a block domain to any other place within the same region without leaving it. Continuity of phases facilitates material transport within each phase and allows for the removal of a single block component to create a free standing porous structure, much like the opal, and backfilling with high index, possibly non-polymeric materials to improve optical properties. The potential to easily replace one component with a desired high index material, coupled with the optical properties possible from these morphologies, make them excellent candidates for self-assembled photonic crystals. Even when the polymeric materials can be made which would form these large length scale self-assembled structures, there remains the significant challenge to have them do so. The time scales to reach equilibrium for polymeric materials with high molecular weight are estimated to be on the order of hundreds of years. Also, the relative instability of such high molecular weight polymers at elevated temperatures prohibits possible long time, high temperature annealing needed to facilitate the equilibration of the samples. While these obstacles are significant, it is important to note that reaching a repeatable non-equilibrium state which has useful properties will also enable the
application of these materials to photonics.

1.2.3 Dielectric Properties and Optical Characteristics

Fabrication of a complex or desirable structure is not enough to create a complete photonic band gap. The dielectric properties of the material must be sufficient, often extreme, to realize this. As was alluded to before, the opal structure does not in itself have a complete gap. The inverted opal structure has a narrow gap which is often not completely opened because of the inherently high dielectric contrast required. Infiltration with high dielectric additives has achieved this potential in a limited number of experiments. Similarly, the component polymer blocks of a BCP have quite modest and uniform optical properties and would, for any configuration, have to be altered dramatically in order to realize a complete photonic band gap. Useful optical properties may, however, arise out of the intrinsic systems or with mild modification, possibly by the incorporation of unique optical additives. Characteristic optical properties can be observed from the polymer structures as they are formed and will aid in determining the potential performance of the system. In the scope of this thesis, applications of both natures will be explored: for the unmodified copolymer system and for the copolymer used as a template for the assembly of other dielectric materials. Once formed, these polymeric materials have unique properties that set them apart from other photonic materials. Explorations of how their characteristics make them suitable for particular applications will be conducted. The ability to pattern additives while forming photonic crystals, the wide variety of mechanical properties exhibited by the polymeric component materials, and the morphological control of block copolymers through composition will all be analyzed as unique traits of this platform. The particular fitness of these materials to applications can then more easily be identified.
1.3 Future Applications of Block Copolymer Photonic Materials

Photonic crystals from block copolymers and other self-assembling materials will remain distinct from lithographically patterned photonic crystals as self-assembled materials will likely always contain defects. It is possible however to image a broad variety of unique properties that will distinguish their benefits. It has been shown that additives incorporated into a BCP solution will preferentially segregate within the material. These can be quantum dot, high dielectric, semiconductor particles[30], or metal particles[31]. Each of these impart enhanced dielectric contrast to the domains due to their selective positioning, which will enhance the width of band gaps in the block copolymer photonic crystals. In addition, non-linear materials, such as conducting polymers [32] or anisotropic materials such as liquid crystals [33] can impart dynamic properties to the materials which are responsive to changes in electric or magnetic fields, temperature, or exposure to light. Such responsive materials could provide novel functionality in BCP photonic materials which would also benefit from the ease of fabrication provided by the photonic host. The ability to incorporate additives within BCP photonic materials will realize the potential to make photonic coatings which are applicable in a single step, such as spin or spray on coatings, perhaps even as a paint.

The versatility of copolymeric materials is just one asset. The structure forming capabilities are unrivaled, however. The simplest copolymer architecture, the diblock, is capable of forming the double gyroid morphology, possibly more complex than any lithographic technique is capable of forming. This potential is increased dramatically by increasing the complexity of the polymer architecture. Many recent studies have been devoted to the cataloging of the ever increasing palette of morphologies accessible to terpolymer, and tetrapolymer systems. The complexity of these morphologies is an excellent demonstration of the variety and capability of block copolymers as structure forming materials. In addition to this structure forming potential, these systems have the capability to template and arrange individual active centers,
atoms, or molecules on regular lattices. Specifically, recent work involving luminescent centered star molecules[34] suggests that metal centered polymer molecules with a variety of homopolymer and block copolymer arm configurations can locate these luminescent centers topologically at the intermaterial dividing surfaces of copolymer morphologies. Furthermore, this constraint becomes tighter in copolymer systems of higher complexity. Morphologies such as the "wagon wheel" reported by Sioula and coworkers[35], locate the junctions of terpolymer, "miktoarm" star molecules on lines. More complex, star tetrapolymer systems could be engineered to locate the junctions at points on a lattice. This opens up the possibility of studying ordered arrays of isolated luminescent centers and observing such phenomena as array lasing and other coherent phenomena.

1.4 Outlook

This thesis will document the progress that has been made in making optical materials, specifically photonic crystals, from the self assembled morphologies of block copolymers. Multilayer, one-dimensionally periodic materials form the bulk of the research and have been the source of the most progress, but these results are fully applicable to the two and three dimensional cases. The potential realized for the one-dimensional model systems, stands as future challenges to be met for the two and three dimensional ones. Most important, perhaps, are the successes in creating three dimensional photonic crystals from the double gyroid materials. This is convincing evidence of the capabilities of these materials as important contributors to the fabrication technology of three dimensional photonic crystals and perhaps complete band gap materials. The results here should serve as a starting point to develop the potential of these versatile, flexible optical materials.
Chapter 2

Experimental Techniques and Methods

2.1 Introduction

The experimental techniques and sample preparation procedures used in the research presented here are collected in this chapter. Chapter 2 will serve as a central reference for the rest of the document as many experiments in later chapters were based on common experimental techniques. Where it is important or unique to a particular experiment or series of measurements, parameters or modified procedures will be noted with the results of the experiment. The techniques used fall into four categories: imaging techniques for microscopic analysis; scattering techniques for studying the structure of block copolymer materials at the Angstrom to micron length scale; spectroscopic techniques for characterizing the optical properties of these materials; and synthetic procedures for producing the block copolymers. In addition a variety of sample preparation techniques and procedures suitable to these experimental techniques were used. A concise description and references, where necessary, will be given for each.
<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$</th>
<th>A</th>
<th>B</th>
<th>PDI</th>
<th>Morphology</th>
<th>Ch.</th>
<th>Source</th>
</tr>
</thead>
<tbody>
<tr>
<td>PS-PI</td>
<td>137k</td>
<td>137k</td>
<td>275k</td>
<td>1.05</td>
<td>Lamellae</td>
<td>4</td>
<td>L.J. Fetters</td>
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<tr>
<td>PS-PI</td>
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<td>247k</td>
<td>249k</td>
<td>1.05</td>
<td>Lamellae</td>
<td>5</td>
<td>L.J. Fetters</td>
</tr>
<tr>
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<td>470k</td>
<td>560k</td>
<td>1.02</td>
<td>Lamellar</td>
<td>7,8</td>
<td>P. DeRege</td>
</tr>
<tr>
<td>PS-PI</td>
<td>750k</td>
<td>300k</td>
<td>450k</td>
<td>1.03</td>
<td>Double Gyroid</td>
<td>6</td>
<td>P. Deree</td>
</tr>
<tr>
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<td>280k</td>
<td>280k</td>
<td>1.10</td>
<td>Lamellae</td>
<td>9</td>
<td>Polymer Source</td>
</tr>
<tr>
<td>PS-PMMA</td>
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<td>280k</td>
<td>360k</td>
<td>1.15</td>
<td>Lamellae</td>
<td>9</td>
<td>Polymer Source</td>
</tr>
</tbody>
</table>

Table 2.1: Tabulated characteristics of the diblock block copolymers used in the experiments described. Important characteristics are noted. Note some polymers were not associated with reported experiments.

<table>
<thead>
<tr>
<th>Polymer</th>
<th>$M_w$</th>
<th>PDI</th>
<th>Chapter</th>
<th>Source</th>
</tr>
</thead>
<tbody>
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<td>1.06</td>
<td>Chapter 4,5</td>
<td>Pressure Chemical</td>
</tr>
<tr>
<td>Polystyrene</td>
<td>257k</td>
<td>1.04</td>
<td>Chapter 5</td>
<td>Polymer Source</td>
</tr>
<tr>
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<td>47.5k</td>
<td>1.06</td>
<td>Chapter 5</td>
<td>Pressure Chemical</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>13k</td>
<td>1.07</td>
<td>Chapter 5</td>
<td>Polymer Source</td>
</tr>
<tr>
<td>Polyisoprene</td>
<td>248k</td>
<td>1.10</td>
<td>Chapter 5</td>
<td>Polysciences</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>48.6k</td>
<td>1.05</td>
<td>9</td>
<td>Polymer Labs</td>
</tr>
<tr>
<td>Polymethylmethacrylate</td>
<td>212k</td>
<td>1.10</td>
<td>9</td>
<td>Polymer Source</td>
</tr>
</tbody>
</table>

Table 2.2: Homopolymers used in the blending experiments described in Chapter 5. Relevant characteristics are reported as well as the source of the material.

### 2.2 Polymer Synthesis

An array of block copolymers and homopolymers were used in the pursuit of copolymer based photonic crystals. Two BCP types were used; poly(styrene-b-isoprene) (SI) and poly(styrene-b-methylmethacrylate) (SMMA). A variety of molecular weights and compositions were explored as well. The characteristics of these materials, including the polydispersity index (PDI) and the source are assembled in Table 2.1 along with the chapters with which they are associated.

In addition to neat block copolymer materials, homopolymers were used to blend with the block copolymer in order to change the spacing or morphology from that of the neat BCP. Homopolymers used are listed in Table 2.2.

The homopolymers fall in to two broad classifications, high molecular weight (MW), comparable to the block MW with which they were blended, and low molecular weight, roughly one tenth or less of the molecular weight with which they were to be blended. Blending behavior of these two classes of homopolymers is different.
as will be discussed in Chapter 3. All polymers were synthesized by living anionic polymerization, and block copolymers were made by anionic synthesis with sequential addition of monomers with composition controlled by the relative amounts of monomers added.

2.2.1 Synthetic Procedure

The BCPs and HPs used were obtained from three sources. Dr. L. J. Fetters and Dr. M. Xenidou provided SI copolymers initially, the synthetic procedure by sequential addition is described elsewhere[36, 37]. The SMMA copolymers and all homopolymers were obtained commercially from one of the following suppliers of experimental polymeric materials: Polymer Source Inc., Montreal, Canada; Pressure Chemical, Pittsburg, Pennsylvania; Polymer Labs Inc., Amherst, Massachusetts; Polysciences Inc., Warrington, Pennsylvania. The synthetic procedure for each of these was also addition anionic polymerization, is described as above. The bulk of experimental SI block copolymers were synthesized in house through a modified version of Dr. Fetters’ method. The polymerization was carried out in a sealed reactor on a Schlenk line under an inert atmosphere. The living anions are sensitive to oxygen and water, both of which terminate the reaction before completion and contribute to polydispersity in the synthesized material. The Schlenk line and reactor were further contained in an inert atmosphere within a dry box manufactured by Innovative Technologies, Newburyport, MA. The dry box was nitrogen filled and equipped with molecular sieves, to remove organic vapors, activated alumina, to remove water, and metallic copper catalyst, to remove oxygen from the nitrogen atmosphere. Each of these species in the reaction atmosphere may especially interfere with the polymerization of ultra high molecular weight block copolymers, if allowed into the reaction vessel after purification of the reactants due to the extremely low concentration of initiator or living polymer end groups in the reacting solution. This “double insulation” of the reaction from oxygen and water allows for results comparable to those obtained by more complicated techniques, and allowed for versatile handling of the reaction vessel and reactants. Model materials were synthesized using this technique with molecular
weights in the range of one million kilograms per mole and polydispersities of 1.05 and better.

2.2.2 Characterization of Polymeric Materials

Each polymer material was characterized by Gel Permeation Chromatography (GPC), also known as Size Exclusion Chromatography (SEC). This technique is performed by injecting a bolus of a dilute polymer solution (a solution of a fraction of a percent by weight of the polymer material that is to be analyzed in the liquid phase of the apparatus, tetrahydrofuran (THF) in this case) in a continuous flow of the liquid phase, pure solvent through a series of columns which contain swollen polymer beads. The surface of the beads have a defined distribution of pore sizes into which the polymer molecules in the solution can travel. The lower molecular weight polymer molecules will have a smaller size in solution than higher molecular weight molecules of the same type and composition of polymer. The smaller sized molecules will tend to explore more of the pores and thus travel more slowly through the columns creating a gradient in the eluted polymer molecular weight. The refractive index, fluorescence under UV excitation and viscosity of the eluting solvent are monitored and tiny concentrations of polymer in the solvent will generate detectable changes in any of these properties. By calibrating the elution time of narrowly distributed polystyrene standards, the styrene equivalent molecular weight can be correlated with the elution time. Viscometry measurements allow for the measurement of the absolute concentration of the polymer in the eluting solvent, since it is also possible to know in advance the refractive index change associated with each species block of a BCP, this information coupled with the concentration and refractive index data, allow for the computation of the composition of BCPs. In addition, light scattering measurements can be made of the eluting solvent and correlated with the other measurements to give the absolute hydrodynamic radius of polymeric species dissolved in it, which can be related to the absolute molecular weight. This battery of tests can be used to fully characterize BCP materials. Some subset of these techniques were performed on each polymer sample to determine at least the molecular weight and polydispersity which
are included in the table.

2.3 Sample Preparation for Analysis of Block Copolymer Photonic Materials

Block copolymer, ordered, photonic materials were prepared either as solid pure polymer samples or as solvent swollen ordered gels ("solutions"), both of which had novel and interesting optical properties. Dry polymer samples were universally cast from solutions and made free of solvent by extended drying, and drying under vacuum. Both neat block copolymers and those blended with homopolymers in a variety of compositions were prepared as dry samples. Solutions were studied only of neat BCPs in different solvents.

2.3.1 Neat BCP Sample Preparation

The neat copolymers were dissolved in one of several solvents; cumene, tetrahydrofuran (THF), styrene monomer, di-octyl phthalate, and methylene chloride. Toluene was most often used, as it is a neutral solvent for SI copolymers. The dissolution was facilitated by stirring and, during it, the solution was shielded from light with aluminum foil, because it was found that the polymers would degrade in the presence of light while in solution. An antioxidant was added to the solvent used to prepare SI solutions before dissolving the polymer. The antioxidant 2,6 ditertiarybutyl-4-methyl phenol (BHT) was used at concentrations of 0.1% in the solvent. BHT is a potent small molecule antioxidant which is completely soluble in toluene and the other solvents used, and it remains dissolved in the block copolymers when dried from these solutions. It preserves these particularly sensitive polymers (due to their high molecular weight, presumably) from degradation in solution and while being stirred for dissolution. High molecular weight BCPs were usually dispersed in solution at 5% or less by weight. Higher concentrations were visibly colored indicating phase segregation. Viscosity of high concentration solutions interfered with sample preparation.
and blending, and necessitated the use of 5% by weight solutions for most initial sample preparation stages. Dissolution took place over a minimum of 24 hours to insure complete and uniform distribution of the polymer in the solvent volume.

2.3.2 BCP/HP Blend Preparation

When a blend was to be prepared, separate solutions of each component homopolymer and block copolymer were made at roughly 5% concentration by weight. The precise concentration was recorded and used for computation of blend fractions. When dissolved, prescribed amounts of each solution were added to a container such that the resulting solution contained the proper composition of polymers, and would form the desired blend when dried. This was facilitated by the common concentration, as the proportion of each component desired was roughly the same as the proportion of solution added. All blends were thus composed by weight fraction. The most common type of blend was a symmetric blend of equal parts of two homopolymers of roughly the same molecular weight added to a matching symmetric diblock copolymer (one block chemically the same as each homopolymer and an overall composition of 50% for each type) so that the overall composition of the system remained the same as the copolymer. This allowed for systematic studies of the domain spacing of the block copolymer system morphology along a 50/50 composition isopleth (symmetric amounts of each polymer type). Adding single homopolymers or non-symmetric amounts of the two homopolymers makes it is possible to study off-symmetric compositions as well and shift the morphology of the system.

An important consideration for this study is that, as the molecular weight of a polymer increases, the time that it takes to reach its equilibrium structure increases approximately as the cube of the molecular weight. This necessitates increasingly longer times to reach equilibrium for these higher molecular weight systems. It is thus essential to cast the polymer from solution at as slow a rate of solvent evaporation as is practical so as to maximally equilibrate these samples. It will be shown later that there are practical limits to this however. A casting procedure which generated reproducible samples was determined and used exclusively for dry sample preparation.
The general steps were to take the prepared neat BCP solution or blend solution and place it in a crucible, or on a glass substrate with a dropper. The substrate or crucible was then placed in an atmosphere of the vapor of its solvent, usually a loosely closed container with a reservoir of that solvent inside. Crucibles and sample vials were thus exposed to a slowly declining vapor pressure of solvent which caused the slow removal of solvent from the polymer over the course of days. These sample containers were allowed to evaporate for a period of one week to two months. At the end of the prescribed time the solvent was fully evaporated. The samples were allowed to further dry in air for a period of at least 24 hours before final optical characterization was performed. Samples monitored for this 24 hour period showed little or no drift in their optical properties.

2.3.3 BCP Solution Preparation

Solution samples were initially prepared by using one of the above mentioned stock solutions of the desired polymer. Solutions of neat photonic block copolymers were studied exclusively. In order to obtain a desired concentration from the stock solution, an initially 5% by weight polymer solution would be carefully monitored as the solvent evaporated over the course of several days, to insure near-equilibrium conditions, until the desired concentration was reached. Alternately, a prescribed amount of BCP was placed in a sample vial, the weight of which was known, and solvent was added. The absolute amount of polymer was known so the total weight of the sample could be used to very precisely calculate the by weight concentration of the polymer in the solution sample. This improved procedure was used exclusively for the samples prepared in deep, thin walled NMR tubes (Wilmad Glass Inc.) of 5mm diameter for use in Rayleigh-Brillouin scattering experiments (see Chapter 8) performed by Dr.George Fytas and Dr.Hartmut Kriegs. A modified version of this procedure was used for studying solution optical properties, as well. Once the solution was prepared as described, the unscaled tube was placed in a thermal bath such that only the portion filled with solution was submerged. A strong flow of cool air was directed across the top of the bath such that the solvent evaporating from the solution was condensed
immediately above the solution and precipitated back into it. Small amounts of solvent were lost at a steady slow rate from these solutions. The weight of the vial was monitored so that the concentration could be determined and compared to optical measurements. This technique generates solutions with uniform optical properties, suggesting that the solvent remains evenly distributed throughout the volume of the solution. In addition, the solution collects at the bottom of the tube, indicating that it is fluid enough to conform to the container and thus is relatively free of internal stress from the drying process.

2.3.4 Dry Polymer Sample Preparation

Slow solvent casting was the most common procedure for sample preparation in the experiments presented here, rather than extended annealing as is most frequently used when studying block copolymer systems, for example see Winey et al.[38]. The SI BCPs in particular were prone to degrade rapidly when annealed at temperatures of even 100°C, well below the 120°C which is commonly used for SI BCPs. This is problematic, but slow casting[39] is also used in the study of BCP systems with success. SMMA samples were annealed however since they appeared much more robust under this treatment. The standard procedure was to anneal them at 200°C for at least 24 hours and up to two weeks. 200°C is well above the glass transition temperatures of each block, 105°C and 110°C respectively, imparting significant mobility to the system. It was well below the theoretical order-disorder transition temperature for these high molecular weight block copolymers however which is not attainable due to thermal degradation of the polymer.

2.4 Measuring the Optical Properties and Microstructure of BCP PBG Materials

Samples were prepared in several ways in order to measure their optical properties and correlate them with the structure and materials properties of the samples themselves.
To this aim reflectivity was measured prior to any other characterization techniques. At times, this measurement was made in conjunction with the transmission of the samples. Spectral measurements of both types were performed on a microscope spectrograph or a CARY 5E UV-VIS-NIR spectrophotometer. The microstructure of samples as prepared was subsequently determined using non-destructive x-ray scattering techniques, including Small Angle X-ray Scattering (SAXS) and Ultra-Small Angle X-ray Scattering (USAXS). Finally, microscopy techniques were used, as the preparation required for them was often destructive of the sample. Electron microscopy was also a valuable tool for visualizing the microstructure of these photonic block copolymer materials. Cryo-microtomy and Transmission Electron Microscopy (TEM) were used to prepare and view thin sections of bulk materials, and Scanning Electron Microscopy (SEM) was used for viewing bulk and film sample fracture surfaces. SEM was also valuable for visualizing etched samples as it provided a view with perspective and allowed the determination of the degree of etching and the clarity of the etched channels.

2.4.1 The Microscope Spectrometer

The microscope spectrometer is based on an unmodified Zeiss Axioscope equipped with transmissive and reflective lighting and a view port for micrography. A collection lens, (f=1.2), was fitted to the view port via a custom fabricated adaptor. This lens collected the total light output of the port and focused it into a fiber. The fiber is connected to a Stellar Net Inc. SP2000C spectrometer equipped with a CCD detector and holographic grating. The fiber carries all light present in the reflected image of the sample to the spectrometer, where the holographic concave grating spreads by diffraction and focuses the light onto a linear CCD array consisting of discrete pixels. The spectrometer measured wavelengths from 200nm to 850nm in 1024 divisions giving a measurement resolution of 0.64nm. The manufacturers' claimed optical resolution for the system of 0.4nm exceeds that of the detector. The output of the spectrometer corresponds to the spectral distribution of light over the entire field of view of the microscope. The illumination source was a tungsten halogen lamp which
produced collimated light from the microscope objective (divergence less than 5°). It was possible to limit the field of the reflective illuminator equipped to the microscope by the use of a moveable, adjustable aperture fitted at an imaging plane in the light path of the reflection mode illuminator. Limiting the illuminated sample area effectively limited the part of the sample probed by this instrument. The aperture allowed for a circle of incident light with 1/20th the radius of the field of view, to be placed anywhere in the field of view. The objective lens of the microscope determines the collection angle of the sample/detector. Samples were generally on flat glass or silicon substrates so the microscope stage provided for positioning the substrate normal to the viewing direction which insured average normal incidence and collection for the system. When optical properties were measured from samples in NMR tubes, a jig was used which insured the right orientation of the tube relative to the stage and lens. The collection angle can be determined from the numerical aperture of the objective lens $N_o = n \sin(\theta)$ where $\theta$ is the collection angle. Generally lower power lenses have smaller numerical apertures and thus lower collection angles about normal incidence. Lower collections angles are a desirable feature in this circumstance since the optical properties of photonic crystals are dependent on the propagating direction and a small collection angle allows for the isolation of the properties for a particular propagating direction. Measurements reported in this thesis were taken with a Carl Zeiss, Neo-Fluorar 10x objective with a numerical aperture of 0.3 corresponding to a collection angle of 17° about normal. It would be possible to further limit this collection angle by the use of a mask at the primary lens surface of the objective. The selection of the diameter of this aperture in conjunction with the lens to sample distance would physically define the collection angle. This technique was not used for any reported experiments, however. Other objectives were tested as well but the clearest spectra facilitated by the small collection angle were available from the above mentioned objective. It was used universally for reported measurements.

The measurement procedure on the microscope reflectometer began with the normalizing the detector. The illumination source was turned to a standard voltage (12V) and a coated aluminum, first surface mirror was placed in the sample area.
The microscope was focused on the surface of the mirror. A raw spectrum was taken of the signal, i.e. a raw number of counts for each wavelength. This was used as the high reference spectrum, representing 100% reflectivity. The true reflectivity of the reference mirror was closer to 97% across the visible spectrum. The collection lens was then closed from the light path such that no light from the microscope was incident on it. A dark frame was captured here to account for fluctuations and thermal dark current in the CCD detector. A reference spectrum of a blank substrate or sample tube was then collected to subtract from the sample data to yield the final spectrum. The reflectivity of the blank substrates and sample tubes were approximately 10% of that of the aluminum mirror and did not depend on wavelength, in agreement with the reflection expected from the front surface of a dielectric slab. This reflectivity was about one fifth the magnitude of the peak reflectivity typically associated with the reflective polymer samples. It was general procedure to average 5-20 scans for each of these measurements to increase the signal to noise ratio of the measurement. This technique is favored over increasing the measurement time because of signal bleed into adjacent pixels and the noise characteristics of CCD devices, as well as the limited dynamic range of this sensor. Typically the noise associated with 10 averaged scans is much lower than the noise for a single scan of ten times the length. Spectro-fluorimetric measurements were also taken using this system prepared with suitable filters. A dielectric notch filter passing only 488nm light was used to limit the incident light. A dichroic mirror and low pass (yellow) filter were used to pass only longer wavelengths to the spectrometer collection lens. Long collection times were required but acceptable data was obtained with this system. No fluorimetric experiments are reported.

2.4.2 Spectral Measurements from the CARY 5E Spectrometer

A second type of reflective measurement was taken from dry block copolymer samples, but was not used for solution measurements. Diffuse reflectance from the sample
surface was obtained using the CARY 5E UV-VIS-NIR spectrophotometer supplied by Varian Inc., and located in room 13-4035 of the MIT CMSE MRSEC facility. A diagram of the optical components of this instrument are shown in Figure 2-1. This system used one of three light sources coupled with a monochromator to generate two identical collimated beams (less than 1° divergence) of monochromatic light for each wavelength measured; a sample beam and a reference beam. The sample beam was directed through a collecting sphere of the diffuse reflectance accessory. The sample was placed on the exit port of the sphere such that the beam was incident on it and any light reflected from the sample back into the sphere was directed by the sphere to a photomultiplier tube which counted the number of reflected photons. The second beam, the reference beam, was directed through a path not incident on the sample and the number of photons present in the beam was determined. The signal was the fractional intensity of the reflected sample beam to that of the reference beam. This insured that fluctuations in the light source were corrected for dynamically. A reference spectrum was collected from a diffuse reflectance reference of Halon, a compressed polyfluorocarbon powder with reflectivity above 99% over the visible spectrum. Background spectra were also taken of blank substrates or empty sample holders when substrates were not used. The sample data was collected relative to the bright signal and the appropriate background scan was subtracted from it.

2.5 Electron Microscopy and Sample Preparation

Scanning and Transmission Electron Microscopy (SEM and TEM)[40] were used in the experiments presented. These techniques and associated sample preparation techniques are elaborated below.
Figure 2-1: The above diagram of the Cary 5E UV-Vis-NIR spectrometer shows the optical path of the instrument for transmission measurements. For reflectivity measurements, an integrating sphere is incorporated into the sample area, including optics which direct the sample beam to the measurement area of the sphere and the reference beam to the sphere surface. Apart from this the optical path is identical.
2.5.1 Cryo-Ultramicrotomy Sample Preparation and Transmission Electron Microscopy

After optical characterization was complete, the samples were prepared for TEM examination by embedding bulk and thick film polymer samples in epoxy (Poly-Bed obtained from Polysciences Inc.). SI samples were fixed by exposing them to OsO₄ vapor to crosslink the isoprene on the surface and prevent swelling by the epoxy during its cure. Samples were cured in epoxy at 60C for 24 hours to fully harden the resin. SI samples were also attached to cryomicrotomy stubs with Permabond 901 metal bonding adhesive after crosslinking as mentioned above, and allowed to set for 24 hours. Samples of both types were then ready for ultramicrotomy.

Ultramicrotomed sections of all polymer samples were obtained on a Richert-Jung Ultracut 2E equipped with a cryomicrotomy stage. SMMA polymer samples were microtomed at room temperature. SI polymer samples were cryomicrotomed at a temperature of -90C to bring the isoprene domains below their glass transition and facilitate thin sectioning. Samples were microtomed to obtain 60-100nm thick sections which were either floated on water and collected on copper grids for room temperature samples, or picked up with a drop of sugar water and placed on copper grids and washed in deionized water. SI sample grids were stained by exposure to OsO₄ vapor which selectively binds with the double bonds in the isoprene making it more electron opaque for examination in TEM[41]. This improves the contrast between the styrene and isoprene domains. SMMA samples were exposed to RuO₄[42] which selectively binds with the styrene, again, to improve contrast and facilitate visualization of the microstructure. Mass loss contrast also contributed to the observation of PS-PMMA samples. The electron beam degrades PMMA such that it loses mass in the form of volatile degradation products. This loss of mass leads to thinner PMMA domains and hence a lighter appearance in the TEM image[40]. Samples were all examined with a JEOL 200CX transmission electron microscope operating at 200KV.
2.5.2 Scanning Electron Microscopic Examination of BCP PBG Materials

Bulk samples and films were also fractured in order to allow examination of the cross section, especially the regions adjacent to surfaces. Samples to be fractured were submerged in liquid nitrogen for 30 minutes to ensure that the entire thickness of the sample was well below the glass transition of both components (especially the polyisoprene). Samples were grasped with chilled pliers and fractured while still submerged. Fractured samples were mounted onto SEM stubs. A JEOL 5910 field emission gun, scanning electron microscope (FEGSEM) operating at 1-5kV was used to examine some samples, which were coated with 100 of gold/palladium by DC argon sputtering. The low accelerating voltage was useful for obtaining a more accurate visualization of the surface due to the reduced penetration of the electron beam into the sample. In addition to collecting Secondary Electron Intensity images (SEI) from samples, backscattered electron images were collected by a detector positioned around the objective electron lens opening. The electrons striking this detector have been elastically scattered directly from the spot where the incident beam strikes the sample, back nearly along their direction of incidence. Elastic scattering is more likely from heavier nuclei such as those of the stain. This type of image is referred to as a Backscattered Electron Intensity (BEI) image. BEI images were collected from samples that had been treated by exposure to OsO₄ vapor for 15 minutes to stain the isoprene domains. To eliminate specimen charging, the samples were coated with a film of thermally evaporated carbon, approximately 200 Angstroms thickness (measurement of the deposition rate is difficult since the evaporation of carbon is a relatively quick process and precludes the use of a crystal monitor). The use of carbon as a conductive coating is essential for these experiments, as it preserves the contrast due to the higher Z of the osmium nuclei in the stained domain. BEI image contrast could be masked by a gold/palladium coating. The microscope was operated at 5kV for the backscatter images. The relatively heavy osmium nuclei in the stained regions scatter more electrons back to the detector making those regions appear bright in the col-
lected image. SEI and BEI images were collected from samples with a Philips XL30 Field Emission Gun, Environmental, Scanning Electron Microscope (FE-ESEM) operating with the sample chamber filled with a 1-10 torr atmosphere of water vapor. This allowed for the removal of surface charge from the sample during microscopy and precluded the need for coating. Fractured samples were examined in the FE-ESEM without coating.

2.6 Small Angle X-ray Scattering and Ultra-Small Angle X-ray Scattering for Determination of BCP Length Scales

The microstructure of photonic block copolymer materials was probed with small (SAXS) and ultra-small angle x-ray scattering (USAXS). X-ray scattering techniques rely on the coherent scattering of monochromatic x-rays from the ordered structure of the block copolymer material. Since all of the structures studied are periodic, diffraction from the Bragg planes of their crystal lattice is expected. A fraction of the incident monochromatic beam of x-rays will be diffracted out of the beam axis at an angle, $2\theta$, in directions which are characteristic of the diffraction condition from the lattice. The direction of the diffracted beam from the beam center is characteristic of the orientation of the lattice. Many of the material samples as prepared tend to be polygranular on a length scale of the x-ray beam sampling area. Effectively, all possible, or at least many, rotational orientations of the lattice are therefore sampled by the beam as it passes through the material. The result is that characteristic directions and angles average to thin cones of diffracted x-rays which retain only information on the length scale of the diffracting lattice planes. If the grains are large, texture is occasionally observed in the scattering pattern as bright regions or spots in a ring, connoting substantial diffraction from a single, large grain. Typically the angle of this cone is measured either directly, as is the case in USAXS measurements, or by measuring the displacement of the scattered x-rays from the beam center at a known
distance, as is the case of SAXS measurements where a two dimensional scattering pattern of rings is recorded. The scattering vector, \( \mathbf{q} \), is the reciprocal space measure of the lattice spacing responsible for the reflection. The diffraction angle relates to the magnitude of \( \mathbf{q} \) in the following way:

\[
q = \frac{4\pi \sin \theta}{\lambda}
\]  
(2.1)

From this the lattice spacing, \( d \), responsible for the reflection is calculated using the relation below:

\[
d = \frac{2\pi}{q}
\]  
(2.2)

In general, each morphology has a unique scattering pattern which can be calculated based on its lattice structure. This pattern is composed of an array of spots (a linear array in the case of lamellae, but two dimensional for 2 and 3 dimensionally periodic structures such as cylinders or double gyroid). The relative magnitudes of these spots are influenced by the form factor, or shape of the domains, such that some reflections can be extinguished by form factor scattering. Such is the case of symmetric lamellae, where only odd reflections are present in a series of reflections spaced by \( q_0 \), the fundamental reflection[43]. The combination of these two factors determines a unique scattering pattern, but since patterns from polycrystalline samples such as those presented here are comprised of a series of rings at the same angular displacements as the expected spots, some degeneracy is possible. Microscopy can be correlated to scattering results for more accurate identification of the microstructure and then the scattering results are primarily used as a precision measure of the lattice spacing.

Of the two small angle scattering techniques used, there are some differences in the range of data obtained and the way in which it is collected. Apart from that, each effectively measures the same characteristics of the structure.

2.6.1 Small Angle X-ray Scattering

Small Angle X-Ray scattering[44] was performed at several facilities: X27C the high-resolution polymer beamline at Brookhaven National Laboratory (BNL), the X12B beamline, also at BNL, and the D line at the Cornell High Energy Synchrotron Source.
(CHESS). Each of these facilities used a pinhole collimated beam of monochromated X-Rays from a synchrotron source enhanced by wiggler and bending magnets respectively. The X-Ray wavelength used was roughly 1.5Å for each experiment but was determined at the time of the experiment. The X-Ray beam was approximately 200μm in size at the sample and had an angular divergence less than 1 mrad. Synchrotron sources were vital for the SAXS measurements in this research because the high degree of angular resolution and extremely small angles which were to be measured require a large sample to detector distance and extremely fine collimation, necessitating a high flux of X-Rays in order to make timely measurements. Sample to detector distances were typically 2000 mm. X27C utilized Fuji image plates as the detector. These were scanned and the images analyzed by a proprietary software package. X12B and the D line at CHESS were both equipped with a two dimensional, multi-wire, time delay line, X-Ray detector system integrated with a computer which allowed for direct digital acquisition of the scattering data. X12B utilized custom prepared data analysis software and the data from the D-line was analyzed with a the software FIT2D, a package available for free download. [45] In each of these experiments, the maximum spacing which could be directly measured was less than 100nm, and was limited by the angular extent of the beam stop eclipsing low q reflections. This was due to a convolution of the sample to detector distance and the size of the beam stop. Additionally, the the degree of collimation defined the angular resolution.

2.6.2 Ultra-Small Angle X-ray Scattering

BCP photonic crystal samples studied here often had fundamental spacings of 100 nm to 250 nm and higher. These spacings could only be measured by collecting data from higher order reflections (corresponding to smaller spacings) using conventional SAXS and extrapolating to the fundamental spacing. In order to collect data for the fundamental spacing, a Bonse-Hart camera [46] x-ray scattering geometry was used at either the UNICAT beamline 33-ID facility at the Argonne National Laboratory or X10A, the Exxon-Mobil beamline at BNL. Each of which were capable of angular measurements with a resolution of better than 0.1mrad from the beam center, i.e.
this geometry does not employ a beamstop which limits the angular extent of measurement. The angular resolution of the Bonse-Hart camera is defined by a double diffraction path for the slit collimated beam through a notched silicon crystal. The angular resolution was measured by the angular width of the beam as measured by the detector, and was on the order of 0.01° for the experiment presented here. Data was collected by a detector assembly consisting of a scintillator/photomultiplier which counts x-rays emerging from a triple bounce diffraction path through another notched silicon crystal positioned to limit the angular acceptance of the detector to a value less than the beam width, approximately 0.005°. The detector is swept through an arc to collect a linear data set of intensity versus angular position. It is important to note that the slit collimation used for this experimental geometry, as opposed to the pinhole collimation used in conventional SAXS experiments, introduces an aberration which measures additional intensity at a given angle from scattering at a larger angle. This is because the diffracted slit image creates a linear smear of rings from polygranular samples yielding measured intensity at a smaller angle than appropriate. This smearing can be corrected for by using, among others, the Lake desmearing method, a computational technique[47]. Of primary interest in these experiments are the peak positions of the scattering patterns which are found to be little changed (less than 5%) by using the desmearing routine. Desmearing was not generally applied to the data. Data was analyzed with the Origin 5.0 data analysis package from MicroCal Inc. This technique permitted the measurement of spacings up to 10 microns.

2.7 Computation Methods for Correlating Materials Properties and Photonic Properties

Computational methods were used to determine the expected properties of BCP Photonic systems once the microstructure had been determined. Most of the samples studied here were simple one dimensional lamellar materials and could be treated as lamellar stacks for these purposes. This simple geometry and composition, alternat-
ing layers of two materials with different indices of refraction, is most easily treated as a quarter wave stack for which a simple analytical solution exists. A quarter wave stack has a unique relation between the thicknesses and indices of the two materials, and in general sample properties deviate somewhat from these. A more general method of computing the optical properties of multilayer materials was employed. The transfer matrix method, proposed by Yeh and Yariv[48] allows for the calculation of the spectral characteristics, both transmissive and reflective properties, for a generalized multilayer material. Measurements of the spacing of each material in the multilayers structure are made as described above and literature values for the index of each block are used, for dry samples, to compute photonic properties using the transfer matrix method as described in Chapter 3.

Band diagrams of three dimensional structures, including the double gyroid and gyroid, will be referred to in this thesis which were computed by the plane wave method.[49, 50] Two band diagrams are presented in Chapter 6 for the double gyroid structure which were computed expressly for this work. Those band diagrams were generated by Martin Maldovan and the details of their preparation are found in Maldovan et al.[51] In general the band structure of an arbitrary photonic crystal is determined by numerically solving Maxwell’s Equations in the presence of the specified dielectric properties. The numerical calculations can take a number of forms, such as plane wave calculations, Finite Difference Time Domain (FDTD), and density of states calculations, all of which generate comparable results. FDTD, however, has the advantage of being able to observe time dependent properties.

2.8 Conclusion

These experimental procedures were ubiquitous in the following described experiments. Together they allow for thorough characterization and correlation of the microstructure and optical properties. References to experimental procedures in following chapters will be for the standard procedures described here, unless deviations from the standard procedure are indicated.
Chapter 3

Theoretical Considerations Related to Block Copolymer Photonic Materials

3.1 Founding Research

A broad variety of founding research supports this thesis in addition to collaborative work. The basis of the work presented here is the fundamental concepts of block copolymer microphase segregation leading to ordered microstructure formation and the creation of photonic crystals. These are fields of research in their own right. In this chapter, fundamental equations relating to these concepts will be derived. These founding relations will be drawn from in later chapters. In particular, the derivation of the governing equations of ordered microphase dimensions and methods for computing the optical properties of multilayered materials will be presented.
3.2 Block Copolymer Physics, Scaling Laws Relevant to Optical Properties

Block copolymer microphase separation is governed by the enthalpic repulsion of the monomer components in competition with their entropic tendency for the polymer block chains to maintain a random coil, conformation and uniform density distribution. The repulsion of unlike, A and B, monomer types is characterized by the Flory-Huggins interaction parameter $\chi_{AB}$. If the repulsion is sufficient, it is possible that the reduction in free energy due to the creation of separate domains for the block types and their associated interfaces will overcome the entropic tendency for a uniform spatial distribution or mixing of the monomer types, and a random coil conformation of the chains. This establishes a critical condition for the observation of microphase segregation. Leibler[52] found that the length of each block and the unit enthalpic repulsion ($\chi_{AB}N_{A+B}$) must exceed the critical value of 10.5 for symmetric compositions in order to observe micro phase segregation. Once segregated it is clear that the domain size will scale in some way with the size of the molecule, since the respective blocks are tied at the block junction, limiting the distance over which they can segregate. This leads to the immediate conclusion that in order to observe large length scales in microdomain formation, large molecules are required.

Once a block copolymer microphase segregates, the minimization of the free energy of the system results in ordered morphologies. The composition of the system, the architecture of the polymer, and molecular weight all affect this phase behavior[25]. The morphologies observed in linear diblock systems are shown in Figure 3-1 with the associated volume fractions of the minority component indicated. In this thesis the optical properties of two structures in particular will be studied; the lamellar and the double gyroid. The observation of visible wavelength photonic properties depends on the size scale of these morphologies, so it is useful to establish a theoretical expression of the relationship between the molecular weight and the domain spacing to provide a specification for the molecular weight of synthesized BCPs. The basic characteristic governing microphase segregation is represented by the segregation power, $\chi N$ and
in general two limits are explored when examining the domain size relative to the molecular weight. Values of $\chi N \approx 10.5$ represent weakly segregated systems as this parameter is close to the critical value and, notably, the system often has an accessible order disorder transition temperature, an ODT. For the styrene-isoprene and styrene-methyl methacrylate systems, an inverse temperature dependence is observed in $\chi$ such that the segregation power decreases as the temperature increases and systems can homogenize above the ODT.

The strong segregation limit, for $\chi N > 100$, is the other range explored theoretically. The properties of polymer systems in this limit are similar to their values at the extreme of infinite segregation power. As such these systems have no physically accessible ODT, due to chemical degradation of the polymer components at sufficiently elevated temperatures. The systems presented here have universally very high values of $N$, and thus are strongly segregated in the absence of large amounts of solvent. Specifically, values of $\chi N$ range from 180 to nearly 500. The relation between the molecular weight and the domain size is of principal interest in these strongly segregated polymer systems. Experiments in altering the domain spacing by blending homopolymer with the block copolymer are presented in Chapters 4 and 5. Modification of the spacing by adding solvent to the neat block copolymers is presented in Chapter 7. The governing relations between the domain spacing and blended composition or solvent volume fraction will be explored in the Section 3.2.2.

### 3.2.1 Scaling of Domain Spacing with Molecular Weight

The scaling of microphase size with molecular weight has been studied since the late 1960’s, an analytical solution was only arrived at later. The derivation of the properties of strongly segregated block copolymers was first presented by Semenov in 1985.[53] Among the key assumptions are that, in the strong segregation limit, the A and B polymers are completely separated into the respective domains and that monomer-monomer repulsive interactions are only significant at the interface between the two blocks. Thus the energy of the surface dividing these regions is the only enthalpic contribution to the free energy (it is convenient to think of the
Figure 3-1: This pictorial phase diagram shows the various "classical" block copolymer morphologies adopted by linear diblock systems within each specified composition range. The blue component represents the minority phase and the matrix, majority phase surrounds it. Detailed in the above diagram, the surfaces of the blue structures represent the IMDS of the copolymer morphology, the location of the block junctions. This diagram was prepared by Dr. Benita Dair.
interfacial area per block junction as a measure of this per polymer molecule repulsive contribution). Strongly segregated polymers have been shown to have very narrow interfacial regions (approximately by \( \frac{a^2}{(8\xi)^{1/2}} [54] \) for statistical segment length \( a \), and measured to be less than 30 Å [55]). This validates the narrow interface assumption, and since it does not depend on the molecular weight, the relative thickness steadily decreases for high MW copolymers, such as those studied here. This narrow interfacial region can be thought of as a surface, the inter-material dividing surface, or IMDS, which is specifically useful in visualizing complex morphologies presented in Figure 3-1.

First, an expression characterizing the entropic free energy of the system due to deformation of the chain from its random coil conformation is required. When it adopts the conformation of a random coil, the end to end displacement of a polymer on average is \( Na^2 \) where \( a \) is the statistical segment length (with the assumption that \( a_A = a_B \)). It is possible simply to model the polymer chain as a Gaussian spring according to DeGennes. It then has a free energy given by:

\[
F_{Lam} = \frac{3}{2} kT \left[ \frac{(L/2)^2}{Na^2} - 1 \right]
\]  

(3.1)

where \( L \) is the length scale of the lamellar periodicity. The asymmetry term (domain length scale over the average end to end displacement of the polymer) is the approximation of the stretching of the chain. This approach was used by Leibler [52] and is strictly valid only for weakly segregated systems. A better approximation can be made for strongly segregated systems because the degree of chain stretching is higher near the IMDS. It will be shown that the dependence on the molecular weight changes only by a constant multiplier. However, the exponent of the molecular weight dependence remains the same. In this strongly segregated region it is clear that the chain ends of each block in the system will necessarily be separated by some average distance (the block end at the copolymer junction lying at the narrow interface and the free end being in the body of the domain). This net displacement shows that the chains are on average stretched. If the presumption is made that, for a symmetric diblock copolymer with a degree of polymerization \( N \), a lamellar morphology is formed
with a lamellar repeat of $L$, characterization of the energy of the stretched chain, according to Semenov, is accomplished with two terms, the expressions for inner and outer stretching energies. The inner stretching energy is due to the stretching near the domain interface, and the outer is due to deformation in the domain body. Integrating the average displacement along the contour of the chain gives the inner and outer free energy as:

\[ U_{\text{in}} = \frac{4\pi^2 L^3}{32a^2 3N^2} \]  

\[ U_{\text{out}} = \frac{\ln(0.5)\pi L^3}{16a^2 N^2} \]  

The enthalpic contribution to the free energy of the system is given by the surface energy since in this strongly segregated system there is only contact at the surface, represented by the following equation:

\[ U_{\text{surf}} = 2a\chi^{1/2} \]  

Combining these expressions, the total free energy of the system is given by:

\[ F = \left(\frac{1}{2}V\right)^{-1} [U_{\text{in}} + U_{\text{out}} + U_{\text{surf}}] = \left[\frac{4\pi}{6} + \ln \frac{1}{2}\right] \frac{\pi L^3}{16a^2 N^2} + 2a\chi^{1/2} \]  

Differentiating with respect to $L$ and equating the quantity with zero gives the value of $L$ for which the energy of the system is a minimum. This is shown in the following equation:

\[ L = \sqrt[3]{\frac{4a^3 64\chi^{1/2} N^2}{(8\pi^2/6 + 2\pi \ln \frac{1}{2})}} \]  

This gives the dependence of the equilibrium lamellar spacing on the molecular weight and $\chi$ as:

\[ L \propto \chi^{1/6} N^{2/3} \]  

The $N^{2/3}$ molecular weight dependence was found in the earlier study by Hashimoto and coworkers in 1980.[39] This relation, coupled with another to come will later be used to determine the characteristics of the materials explored, necessary to create photonic block copolymer materials.
3.2.2 Domain Spacing of Block Copolymer-Homopolymer Blends

The general characteristics and specifically the domain spacing of block copolymer-homopolymer blends have been studied extensively, treated both experimentally[38, 1] and theoretically[56, 57]. The case of primary interest for this work is the stable ternary blend of a compositionally symmetric diblock copolymer and its associated homopolymers, as this will preserve the symmetric composition of the system and the lamellar morphology. Much of the work in copolymer blends is on binary systems of a single homopolymer and a copolymer. These results will be referred to, as they shed light on the physics of ternary blends, but the results are not directly applicable. It has been shown that swelling of asymmetric morphologies is possible and this can be applied to non-lamellar systems such as hexagonally packed cylinders and possibly, though not yet experimentally verified, the double gyroid. Ternary blends of A-B block copolymers and A and B homopolymers have been treated specifically in the case of weakly segregated systems by Janert and Schick.[56] and the issue of domain spacings in these blends was further addressed for a symmetric blends by Huh and Jo.[57] These studies focus on the weakly segregated regime but identify and study a range of the critical parameters of homopolymer volume fraction $\phi$, and the fractional relative molecular weight of the added homopolymer and its like block $m = \frac{M_H}{M_B}$. These theoretical works generally find little change in the domain spacing for blends on the symmetric composition isopleth over the entire range of homopolymer fractions and for values of $m$ up to one. These results seem to apply only to weak segregation, as more strongly segregated ternary blends show increases in spacing with homopolymer volume fraction. Values of $m$ which are less than or near 1 are the most promising for enhancement of the domain spacing, since larger molecular weights have a greater potential to macrophase separate,[58, 59] and do not enhance the processibility of extremely high molecular weight polymers as lower molecular weigh additives have the potential to do.

Experimental studies have shown dramatic increases in the spacing of lamellar systems in stable binary and ternary blends of strongly segregated copolymers and
homopolymers of a range of m values, however.[1, 59, 38] These studies reveal three types of blend behavior; "dilution", "solubilization" and "segregation" swelling. The swelling regime is dependent on the relative block weights, m. In weakly segregated systems, and systems where m is relatively low, "dilution" blending is observed. The effect of the added polymer is to produce little change in the domain spacing, for example in binary blends [38], (possibly a small decrease or increase), in agreement with what would be expected from ternary systems based on the theoretical studies mentioned above. Intermediate values of m, show solubilization swelling as in Torikai et al.[1] This is the most commonly observed behavior, and it is characterized by a volumetric dependence of the spacing on the fraction of homopolymer in the system. Finally higher values of m, studied in ternary systems show a dominance of "segregation" swelling[1], yielding dramatic increases in domain spacing.

Microscopically, each of these swelling regimes can be understood by considering the chain conformations of the BCP blocks, the area per block junction and the location of the homopolymer in the system. The "dilution" region is characterized by the even distribution of homopolymers in the system. This is similar to the first example shown in Figure 5-6, but the two homopolymers are distributed uniformly in both domain types. The homopolymer has a screening effect which generates an associated contraction of the blocks, to a more relaxed conformation. The screening also leads to an expansion of the area per block junction at the interface by reducing the energetic cost of that interface. The net effect is little change in the overall spacing with increasing homopolymer fractions. The "solubilization" regime, shown in the first example of Figure 5-6, is similar to the "dilution" regime, in that the homopolymers are evenly distributed but each only in its like domain. This allows for the coils of the blocks to relax and expand the interfacial area associated with the block junctions. The net effect is that added homopolymers in the system expand the morphology in all three directions equally, or volumetrically. The following equation describes this behavior:

$$L = \frac{L_0}{(1 - \phi)^{1/3}}$$

(3.8)

The "segregation" swelling regime, shown in the second example of figure 5-6, is sim-
imilar to the "solubilization" regime in that homopolymer is segregated to like domains. This regime is characterized by a lack of penetration of the homopolymer in each domain into the coils of the copolymer blocks. The homopolymer essentially remains segregated to the center of the domain, between the ends of blocks emanating from opposite IMDSs. The area associated with each block junction remains unchanged from the neat block copolymer case. The swelling of the domain structure is then only in the direction of the lamellar normal, in a linear fashion. This behavior is governed by a similar equation:

\[ L = \frac{L_0}{(1 - \phi)} \]  

(3.9)

The notable change of exponent shows that swelling in the "segregation" regime is most efficient in increasing the domain size for a given amount of added homopolymer, and possibly for the ultimate swelling behavior of the system.

The solubilization and the segregation swelling regimes and the transition between them were examined experimentally by Hashimoto and coworkers [60] in binary blends and later by Torikai and coworkers [1] in ternary blends. Both investigations qualitatively derived equations governing the two regimes. It was clear from their data that experimental systems followed a behavior which was a mixture of these two regimes, indicating that the systems were not behaving strictly according to one model but a combination of the two. Torikai suggested a unified model for ternary blends in agreement with their experimental data by combining the two models into a single equation

\[ L = \frac{L_0}{(1 - \phi)^{1/3}(1 - x\phi)^{2/3}} \]  

(3.10)

where \( x \) is a parameter which identifies the fraction of homopolymer that tends to be localized at the center of the domain, in accordance with the segregation model. Later neutron scattering studies [61] revealed that the homopolymer distribution was indeed mixed between these two regimes in binary blends. Furthermore, these studies confirmed the qualitative tendency for higher molecular weight homopolymers to segregate to the domain center. The transition between primarily "solubilization" and "segregation" regimes was dramatic in the Torikai study which used 150k to 180k molecular weight copolymers and a range of \( m \) values from 0.05 to 0.80. This study
showed the largest domain swelling factor was 1.5. Differences are apparent between this result and those of the study of Winey et al.[38] on binary blends, which showed a smoother transition between the two proposed types of swelling. Lower molecular weight copolymer (50k) and a broader range of m values, 0.1 to 1.3, were used in the latter study and a less dramatic swelling was observed. The Hashimoto study looked at a still lower molecular weight system (26k) and a range of m values similar to Winey and coworkers, 0.1 to 1. These studies are varied and the systems are not directly comparable but all possess physically similar transition behavior between two swelling regimes. The differences between the swelling behaviors and their dependence on m show a likely dependence of the transition value of m on the segregation power or copolymer molecular weight.

Control of the wavelength of operation of a photonic copolymer structure requires complete control of the lamellar spacing, so all of the swelling behavioral regions are of use in the production of block copolymer photonic crystals. Typically, however, BCP systems have small spacings relative to those needed for photonic applications so the emphasis of the work presented in this thesis is to increase the spacing as efficiently as possible. Thus blends component properties are targeted to be in the "segregation" swelling regime. Simply increasing the molecular weight of the added homopolymer is not enough, however. In addition to increasing domain spacing, optimization of the processibility of the blend by incorporating lower molecular weight additives is beneficial. Macrophase separation of the additive, which is associated with higher molecular weight homopolymer blended in BCPs, must be avoided because it leads to large pure homopolymer domains, random optical scattering and cloudiness. These are all undesirable optical qualities. It is important to optimize the use of additives by determining the critical value for the transition between the swelling models, in order to incorporate the lowest molecular weigh additive homopolymer possible, while achieving maximum swelling.

Shull [62] and Winey [63], and Semenov [64] theoretically explored penetration of homopolymer into the block coils of block copolymers and the effect of homopolymer molecular weight on the position of the homopolymer in ordered blend morphologies.
Shull and Winey [63] initially proposed that the penetration of the added homopolymer into the extended coils of the like blocks in the copolymer depended on the relative molecular weight. A formalism was developed involving two regimes, the wet brush (from research on BCP micelles with solvent swollen outer layers and insoluble cores), similar to the "solubilization" regime and dry brush, similar to the "segregation" regime. The distribution of homopolymer in a BCP morphology was assessed as a function of homopolymer relative molecular weight and it was clear that, at relative molecular weights of as little as \( m = 0.22 \), concentration of the homopolymer at the domain midpoint was evident. This was elaborated by Semenov in providing a critical parameter for homopolymer penetration into the brush:

\[
N_H \gg N_{Hc} \equiv \frac{N}{(\chi N_B)^{1/3}}
\]  

(3.11)

where \( N \) is the degree of polymerization of the whole copolymer, \( N_B \) is that of the block matching the penetrating homopolymer, and \( N_{Hc} \) is the critical degree of polymerization for the homopolymer. This produces a critical condition for a symmetric BCP:

\[
m_c = \frac{2}{(\chi N/2)^{1/3}}
\]

(3.12)

which is in reasonable agreement with the data presented by Winey and coworkers [38] and with Torikai et al.[1] This provides a guideline for the comparison of blending results in subsequent chapters of this work. When the homopolymer additive is much larger than this critical parameter, it is completely excluded from the like brush, and therefore localized to the domain center (or in a separate macrophase which will be addressed address below). Under this condition, maximal domain spacing increase is achieved.

### 3.2.3 Considerations of the stability of blends of block copolymers and homopolymers

The ultimate stability of ternary blends is the last point to address. It has been noted above that macrophase separation can result if added homopolymer is of similar or
larger molecular weight as the like-block of the copolymer. In the lower range of m values, it is important to know the limits of homopolymer addition which will form a blend with a stable and regular lamellar morphology. The equations presented earlier suggest that, in any swelling regime, the spacing unrealistically increases unbounded as homopolymer is added to the system. It was proposed by Lipowsky and Leibler[65] that Van der Waals interacting membranes such as those found in swollen lamellar systems, undergo an unbinding transition as the distance between them increases. As the adjacent membranes interact less strongly, they eventually lose there correlation, no longer remain parallel, and thus no longer constitute an ordered phase. This puts an upper limit on the dimensional change that is accessible in swollen ternary blends. The unbinding transition in BCP ternary blends has been specifically treated by Jant- ert and Schick,[56] who found that highly swollen lamellar phases decomposed into twin asymmetrically swollen lamellar phases which smoothly transition to disordered phases as the fraction of homopolymer is increased. The systems were weakly segregated however, and the applicability to the strongly segregated case is uncertain. Another consideration of the unbinding transition in BCP systems by Wennerstrom[66] suggests that the unbinding transition takes place much like a liquid-vapor transition below the critical point, where a correlated phase, lamellae in the symmetric composition case, coexist with an uncorrelated phase, isolated membranes, over a wide composition range. The specific situation of the ultimate stability of blended phases was also addressed by Tanaka and Hashimoto[67], who suggested that the stability of the microphase segregated, ordered lamellae at lower BCP volume fractions was enhanced by the presence of lower molecular weight homopolymer additives compared to higher molecular weight ones. In all, these suggest that there will be a real upper limit to the swelling that can be achieved, but give no guidelines for computing it. Experimental studies have reported swellings up to 1.5 times the unperturbed lamellar repeat[59](to $L = 50nm$) at a homopolymer fraction of 0.8. This suggests that blending will be effective, if properly undertaken, in increasing the lamellar spacing to optical length scales.
3.3 Calculating Photonic Properties of Block Copolymer Photonic Materials

The concept of a photonic band gap was first proposed only in 1987 [2, 3] but certainly the quarter wave stack and other multilayer materials had been made and studied extensively prior to this, as had some two and three-dimensional materials such as the naturally occurring and synthetic opal. The significance of Yablonovich's and John's work was in proposing that a range of photon energies would not be allowed to propagate in any direction in a properly structured material, i.e. the concept of an absolute photonic band gap. A gap over a limited range of modes may be forbidden to propagate in most any material with periodic and even non-periodic[2] variation in refractive index. Computational methods have been developed to determine the extent to which this gap is limited to certain directions and frequency ranges and to calculate the propagating constants. In the experiments outlined in this work, only partial gaps were achieved. It was necessary to develop some computational tools to model the photonic properties of these systems based on the physical properties measured in order to correlate the observed properties with the structure.

To a limited extent the results of later chapters, notably Chapter 6 on the double gyroid, draw interest due to the possibilities that the self assembled structures may provide a template from which significant photonic properties can be derived. It will be shown that the materials systems provide a possible route to creating a complete photonic band gap. Careful modelling of the structure and calculation of its photonic band properties show this. The computational results, most notably the existence of the complete gap in the single gyroid structure, were the work of Martin Maldovan. A brief description of the techniques used to generate these theoretical results were given in Chapter 2. While this three dimensional system is a highlight of the work presented here, much ground work was done on one dimensional materials. Indeed the concept of block copolymer photonic materials was first realized in one dimensional systems, and it was necessary to correlate the behavior of these systems with their physical properties in order to confirm the photonic properties. The transfer matrix method
Figure 3.2: A diagram of a multilayer film. The two possible polarizations are shown for incident radiation. This diagram is useful for a film with arbitrary layer thicknesses and indices of refraction as well.

outlined by P. Yeh [48] was used to calculate band diagrams for the photonic materials based on known physical parameters, and determined structural characteristics. From these diagrams the expected optical properties of the system can be determined. A simple derivation of the optical properties of the "quarter wave stack" will be outlined as well. This will provide useful equations that will be referenced periodically in the thesis.

3.3.1 The "Quarter Wave Stack"

The simplest model system that can be used to approximate block copolymer photonic crystals is the classical example of "quarter wave stack". The system, pictured in Figure 3.2 is composed of alternating layers of two different materials with indices of refraction \( n_1 \) and \( n_2 \). The layer thicknesses, \( d_1 \) and \( d_2 \), are such that the optical thickness \( n_d \) of each layer is the same, i.e. \( n_1 d_1 = n_2 d_2 \). Consider a plane wave with wavelength \( \lambda \) normally incident on a material on N layer pairs, propagating through this material at normal incidence. At each interface there is a reflection propagating
back along the direction of travel. At interfaces of low index to high index transitions, there is a phase shift of \( \pi \) associated with the reflection. For interfaces of high index to low index there is no associated phase shift. For the case where \( n_1 < n_2 \) the reflection from the face is given by:

\[
R_1 = r_i E_0 \exp i(kx - wt + \pi)
\]

where \( r_i \) is the reflection coefficient of the \( i^{th} \) interface and \( E_0 \) is the initial intensity. The reflection from the first internal interface is:

\[
R_2 = r_2 E_0 \exp i(k(x + 2n_1d_1) - wt)
\]

The reflection from the second internal interface is:

\[
R_3 = r_3 E_0 \exp i(k(x + 2n_1d_1 + 2n_2d_2) - wt + \pi)
\]

Subsequent reflections follow the same pattern. In the series of reflections, each reflection has a translation and every other reflection has a \( \pi \) phase shift. Each factor of \( 2n_id_i \) in translation amounts to a \( \pi \) phase shift for \( \lambda = 4n_id_i \). For this wavelength all reflections add constructively on the incident side of the quarter wave stack. This leads to a reflected wave of magnitude \( R = |E_0 \sum_i^N r_i| \). Assuming a lossless medium, the total reflection approaches 100% as the number of layer pairs, \( N \), increases. The reflectivity is given by the formula:

\[
R = \left[ \frac{(n_1/n_2)^N - 1}{(n_1/n_2)^N + 1} \right]
\]

In addition to the fundamental wavelength, this condition is met for higher order reflections, i.e. for any \( \lambda \) such that \( \lambda = \frac{4n_id_i}{m} \) for any positive integer \( m \). It is also important to point out that the reflections destructively interfere for other wavelengths, leading to efficient transmission over most of the incident spectrum. Therefore the normal incidence reflectance spectra of a quarter wave stack is made up of sharp peaks centered at the wavelengths \( \lambda_i = \frac{4n_id_i}{m} \).

The utility of this approach is to provide a convenient formula for estimating the reflected wavelengths expected from a known microstructure as well as to correlate
the optical features of a reflectance spectrum with a model one dimensionally periodic system. This derivation is explicitly for alternating layers of equal optical thickness, which is not the general case. In addition, the analysis is only appropriate for normal incidence. In the next section a more complex method will be developed which is capable of giving the properties of a general multilayer film for all propagating directions.

3.3.2 The Transfer Matrix Method

While the above analysis is useful for estimating the properties of the lamellar systems in this study, a more complex computation is necessary to characterize them thoroughly. The work of P.Yeh [48] can be used to accomplish this. Yeh developed the transfer matrix method for arbitrary multilayer materials in 1977. This method is applicable to an arbitrary, N, layer medium in which all the layers have a unique index and thickness. Of particular interest is the case of a two component system with asymmetric layer thicknesses. This technique also allows for the treatment of all propagating directions within the material. It can be used to generate a band diagram for BCP multilayer materials so as to fully know their optical properties and be able to rigorously compare them with measured optical properties, such as reflectance spectra. It is also possible to generate a reflectivity diagram for a specified system of a certain number of layers giving expected values of reflectivity on a two dimensional coordinates of incident angle and wavelength.

A material with alternating layers of two indices of refraction and two independent thicknesses is defined with the quantities, \( n_1, n_2, d_1 \) and \( d_2 \). To facilitate the characterization of light propagating in an arbitrary direction with respect to the material layers, a coordinate system is defined such that the layer normal is parallel to the x-direction and, because there is rotational symmetry about this axis, the z direction is along the component of the propagating wave perpendicular to the lamellar normal, as shown in Figure 3-2. The electric field in each layer is composed of a forward propagating plane wave and a reflected plane wave within each layer of the material. The amplitudes of these waves within the \( n^{th} \) layer of index \( n_1 \) can be expressed as
complex numbers $a_n$ for the forward propagating wave and $b_n$ for the reflected wave. The amplitudes in layer $n$ can then be related to the amplitudes in the previous layer of the same index, $n-1$, by the recursive matrix relation:

$$
\begin{pmatrix}
a_n \\
b_n
\end{pmatrix} = \begin{pmatrix}
A & B \\
C & D
\end{pmatrix} \begin{pmatrix}
a_{n-1} \\
b_{n-1}
\end{pmatrix}
$$

\begin{equation}
(3.17)
\end{equation}

where the matrix elements $A$, $B$, $C$, and $D$ are trigonometric expressions in terms of the components of $k$, the indices of each layer and the layer thicknesses $d_1$ and $d_2 + d_1 = L$. Only two of the components will be used, $A$ and $D$, in the computation of the band diagram. This expression relates the components of the electric field in adjacent unit cells of the multilayer structure. This can be extended to relate the components at the first layer to those at the $n^{th}$ in following relationship:

$$
\begin{pmatrix}
a_n \\
b_n
\end{pmatrix} = \begin{pmatrix}
A & B \\
C & D
\end{pmatrix}^n \begin{pmatrix}
a_0 \\
b_0
\end{pmatrix}
$$

\begin{equation}
(3.18)
\end{equation}

The method of determining the band diagram of this material is finding the Bloch wave solutions and mapping their properties. Bloch used the Floquet theorem and noted that the stratified medium leads to a propagating wave of the form:

$$
E_K(x, z) = E_K(x) \exp iKx \exp ik_{//}x
$$

\begin{equation}
(3.19)
\end{equation}

where $K$ is the Bloch wave vector and $k_{//}$ is the component of the propagating wave vector perpendicular to the lamellar normal. This sets up an eigenvalue problem in the equation:

$$
\begin{pmatrix}
A & B \\
C & D
\end{pmatrix} \begin{pmatrix}
a_n \\
b_n
\end{pmatrix} = \exp -iKL \begin{pmatrix}
a_n \\
b_n
\end{pmatrix}
$$

\begin{equation}
(3.20)
\end{equation}

The eigenvalues of this problem define the dispersion relation for the Bloch waves, in terms of $k_{//}$ and $\omega$. The following dispersion relation is obtained and used to calculate the band diagram:

$$
K(k_{//}, \omega) = \frac{1}{L} \cos^{-1} \left[ \frac{1}{2} (A + D) \right]
$$

\begin{equation}
(3.21)
\end{equation}

This equation was derived assuming that the incident radiation was polarized such that the electric field was tangential to the surface of the film, (TE). The derivation
is slightly different for the other possible polarization, where the magnetic field, of incident electromagnetic radiation, is tangential to the film surface (TM). The terms A and D are different for the TM but the above equation is valid. The coefficients A and D for the TE case are given by the following relations:

\[A_{TE} = \exp^{-ik_{1z} a} \left[ \cos k_{2z} b - \frac{1}{2} i \left( \frac{k_{2x}}{k_{1z}} + \frac{k_{1x}}{k_{2z}} \right) \sin k_{2z} b \right]\]  

(3.22)

\[D_{TE} = \exp^{ik_{1z} a} \left[ \cos k_{2z} b + \frac{1}{2} i \left( \frac{k_{2x}}{k_{1z}} + \frac{k_{1x}}{k_{2z}} \right) \sin k_{2z} b \right]\]  

(3.23)

where \(k_{iz}\) is the perpendicular component of the propagation vector in the \(i^{th}\) layer. The coefficients for the TM case differ, and are given by:

\[A_{TM} = \exp^{-ik_{1z} a} \left[ \cos k_{2z} b - \frac{1}{2} i \left( \frac{n_2^2 k_{2x}}{n_1^2 k_{1z}} + \frac{n_1^2 k_{1x}}{n_2^2 k_{2z}} \right) \sin k_{2z} b \right]\]  

(3.24)

\[D_{TM} = \exp^{ik_{1z} a} \left[ \cos k_{2z} b + \frac{1}{2} i \left( \frac{n_2^2 k_{2x}}{n_1^2 k_{1z}} + \frac{n_1^2 k_{1x}}{n_2^2 k_{2z}} \right) \sin k_{2z} b \right]\]  

(3.25)

By examining this equation for the Bloch wave vector above, it is apparent that there are two states for the K wave vector. When the term \(\frac{1}{2}(A+D)\) \(< 1\) the Bloch vector is real and represents a propagating wave. If it is greater than one, the Bloch vector becomes complex signaling an evanescently decaying wave in the medium. This is not a propagating wave in an infinite medium. If the solutions are mapped in terms of those with real wave vectors and those with imaginary wave vectors on axes of \(k_{/}\) and \(\omega\), a band diagram is produced. The edges of the bands are where \(\frac{1}{2}(A+D) = 1\) and represent crossovers between the propagating and non-propagating bands. An example of a band diagram is given in Chapter 4, Figure 4-4, for the case of a polymer multilayer of the same structure as the lamellar material examined there. The band diagram is plotted in units normalized by the lamellar repeat spacing, so it can be scaled arbitrarily, but is characteristic of the indices of the layers and the relative thickness of the two block domains.

It is important to note that the band diagram is a representation of the properties of an infinite periodic material. An evanescent wave in an infinite material is effectively forbidden to propagate, and is localized over some distance characterized by
the magnitude of the imaginary component of the Bloch wave vector. This localization is the source of distributed feedback, for example, in multilayer optical cavities. In a real multilayer film, evanescent waves are reflected in relation to the thickness of the film and the magnitude of the imaginary component. This gives rise to the reflective peaks observed in multilayer and BCP photonic crystal samples. The peak reflectivity approaches 100% over the width of the gap as the material thickness becomes effectively infinite. For the index contrasts present in typical BCP systems, a hundred or so layer pairs are required to give asymptotically perfect reflection. This is well within the fractional millimeter sample thicknesses that is typically addressed in copolymer bulk solution cast film studies.

3.4 Conclusion

As was mentioned in the first chapter, typical molecular weights for block copolymers are in the tens of thousands of kilograms per mole. If the repeat spacing of such copolymers is on the order of ten nanometers, it is clear that molecular weights at least an order of magnitude larger are necessary for photonic applications in the visible range. Above were derived the proportionality between the molecular weight and the spacing of BCPs, the work of Hadziioannou and Skoullos[68] and Hashimoto et al.[39] yield experimental proportionality constants. From the latter:

\[ L = 0.024M^{2/3}(nm) \]  \hspace{1cm} (3.26)

for SI materials, where \( M \) is the total molecular weight in g/mol of a symmetric SI polymer. It is evident from the quarter wave stack calculation that, in order to obtain a lamellar morphology which reflects visible light, a spacing \( L_0 = \frac{\lambda}{2n} \) is required. For 550nm light, and assuming typical indices of refraction for the polymers of \( n = 1.55 \), a spacing of 180nm is required. This specifies a molecular weight of 630kg/mol for a symmetric SI block copolymer to achieve this spacing. This outlines the parameters required to observe photonic properties in block copolymers. The next chapters will show the progress toward this goal.
Chapter 4

A First Block Copolymer Photonic Crystal

The work presented in this chapter benefits from materials synthesized by Dr. L. J. Fetters. The results are published as a communication to the editor in the journal *Macromolecules.*[69]

4.1 Initial Steps in Photonic Crystal Fabrication

The first photonic crystals were made by machining overlapping holes into a slab of alumina at millimeter length scales appropriate for observing reflection at microwave frequencies [70]. Current work employs the lithographic equivalent (at the micron and sub-micron length scale for IR and visible frequencies) to make dielectric structures [71]. Self assembly is distinct as a method to make photonic crystals because the periodicity is a property of the system rather than a manufactured trait. Making photonic crystals via self assembly at a periodicity suitable for frequencies in the visible portion of the spectrum can potentially be more simple and efficient than by lithographic means. Materials used include colloidal crystal arrays [72], artificial opals and inverse opals [73, 74], and hollow spherical micelles [6]. As mentioned in Chapter 2, block copolymers can self-assemble into a wide variety of periodic structures including 1-, 2-, and 3-dimensional structures [25]. Lamellar poly(styrene-b-methylmethacrylate) structures have been explored for use as optical wave guides
as well[75]. The lamellar structure is a model microphase morphology to study for demonstrating microphotonic properties in a block copolymer system because of the relatively small length scale required to observe visible light photonic properties. As computed in the last chapter, a lamellar repeat of approximately a third of the desired wavelength, for typical polymer indices of refraction, is required for reflectivity at that frequency. This requirement is smaller than that required for other morphologies, such as hexagonally packed cylinders.

4.2 Block Copolymers as Photonic Materials

There are several essential challenges to overcome in order to achieve desirable photonic crystal properties employing block copolymers. Obtaining the correct size of domains for the optical frequencies of interest is the foremost. Secondarily, long-range domain order and appropriate orientation, as well as providing sufficient dielectric contrast between the domains, are both areas to address as well. Accessing large periodicities in block copolymers is possible using very high molecular weight blocks, since the domain spacing scales at the two thirds power of the molecular weight, but early attempts at this route using SMMA diblock of approximately $10^6$ g/mol proved difficult[29]. Attaining well-ordered structures becomes increasingly difficult due to the very high viscosity, in melts and solutions, of such systems. An alternative approach is to utilize a rigid rod block for which the domain thickness varies linearly with block molecular weight. In this way, spacings into the micron range can be produced [76, 77]. A practical approach for readily available materials is to blend block copolymers with homopolymers and thus swell the microdomains. Block copolymer/homopolymer blends have been investigated both experimentally [78, 60, 38] and theoretically [79, 63]. Such blends offer tailorable domain spacings, as well as the processing advantage afforded by somewhat lower molecular weight components. The dependence of the lamellar repeat in bulk cast blends of homopolystyrene and polystyrene-b-polyisoprene block copolymers has been analyzed as a function of the percent homopolymer added and its molecular weight [59]. The lamellar thickness
Figure 4-1: The lamellar morphology of a block copolymer can be interpreted as a multilayer film. The alternating lamellae have indices of refraction \( n_1 = n_{PL} \) and \( n_2 = n_{PS} \) and layer thicknesses \( d_1 \) and \( d_2 \). In this lamellar system, a high molecular weigh block copolymer is blended with low molecular weight homopolymers matching the block types.

depends on many factors including homopolymer volume fractions and the block composition and molecular weight as described in chapter 3. In this thesis, blending has been shown to be a convenient way to almost double the equilibrium spacing of the neat block copolymer and retain a well ordered morphology, however.

### 4.3 Fabrication of Initial Block Copolymer Photonic Material

A regular lamellar morphology having a difference in the index of refraction between the respective domains is similar to a layered optical filter or quarter-wave stack (see Figure 4-1).

This chapter documents the first reported observation that a diblock copolymer/homopolymer blend, which self-assembles into a lamellar microdomain structure, can exhibit a limited angular range stop band at visible frequencies. In order
to demonstrate that a photonic crystal of any type could be made by self-assembly in a block copolymer system, a simple blending experiment was performed. The goal was to maximize the spacing of a high molecular weight block copolymer by blending it with the maximum fraction of a symmetric blend of its constituent homopolymers. The BCP was the symmetric diblock copolymer SI 137k/137k. Based on the formulas presented in Chapter 2, this polymer will have an equilibrium spacing of approximately 100 nm, giving it a reflective peak at approximately 300 nm. At this ultraviolet wavelength the polymer components are highly absorbing. The PS and PI polymers are highly transparent in the visible, but they exhibit strong absorption occurring at UV wavelengths below 350 nm and in the near-IR starting at about 3 microns. Approximately 50 wt % of the copolymer was blended with 25 wt % of homopolyisoprene, PI 13k and 25 wt % of homopolystyrene, PS 13k. The ternary blend was cast from toluene, and annealed at 180°C for 1 week in an inert atmosphere to produce films of approximately 0.5 mm thickness and 10 mm diameter. During solvent evaporation the solution first becomes pale green, then bright green-blue, and finally, when dry, predominantly blue pearlescent to an observer viewing it in ambient. When the dry film is held between a white light source and the observer, it appears red/orange. After annealing, optical measurements of film transmission and reflectance properties in the UV, visible, and near-IR spectral ranges were performed. The annealing process causes the films to become somewhat translucent, likely originating from increased scattering due to homopolymer pooling at defects and, possibly, some chemical degradation. The reflection and transmission spectra of the film are shown in Figure 4-2.

Clearly identifiable is a band of high reflectivity from about 410-525 nm and a corresponding drop in the transmission characteristics of the film in this same spectral range. Due to the strong absorption of UV radiation by both PS and PI, the transmission is near zero for wavelengths below about 330 nm. After spectral measurements were obtained, the film was sectioned and examined with TEM. Micrographs (Figure 4-3) of the material revealed a regular symmetric lamellar morphology with a period of about 130 nm.
Figure 4-2: The transmission and reflectivity spectra of the blend containing 50% of a symmetric 274k SI block copolymer with a balance of symmetric amounts of 13k homo(polystyrene) and homo(polyisoprene). The relative reflectivity is presented in arbitrary units as a function of wavelength. The transmission and reflectivity spectra are complimentary. This shows that the observed color is primarily due to the microstructure and its reflectivity, and not due to any substantial absorption in the material.
Figure 4-3: TEM micrograph of a cryomicrotomed thin section of the copolymer/homopolymer blend. The isoprene has been stained with osmium tetroxide prior to examination in the TEM making it dark in this positive image. The scale bar is 1 micron.
The lamellae are reasonably well ordered and have a dominant in-plane orientation due to the influence of the substrate and air interfaces on the lamellar organization during evaporation.[60] Small-angle X-ray scattering (SAXS) was used to assess lamellar periodicity, orientation, and long-range order. SAXS was done at the Cornell High Energy Synchrotron Source (CHESS). 1.5 Å radiation was used, and a sample-to-detector distance of 1.05 m was calibrated with a silver behenate standard. An example of the type of data pattern generated can be seen in Chapter 7, Figure 7-2. SAXS with the beam oriented parallel to the sample surfaces produces an arced pattern of two reflections, indicating the in-plane orientation. The spacings of these peaks are approximately 52 and 32 nm. Based on the mass composition of the BCP blend material, the volume fraction of each component in the structure is determined to be 46/54 PS:PI. The structure factor of this roughly symmetric lamellar composition has a structure factor which yields strong odd Bragg orders and suppresses the even reflections.[43] Assuming the 001 spacing is behind the beam stop, the two observed reflections correspond well to the 003 and 005 peaks of a lamellar sequence. Thus, the repeat spacing deduced by SAXS of approximately 156 nm is in reasonable agreement with that observed by TEM. In addition, this repeat spacing yields an approximate peak wavelength of reflectivity of 500 nm, in agreement with the observed reflectivity.

4.4 Examination of Properties of First BCP PBG

The spectral properties of the film can be understood by considering light incident over varying angles onto a system of 1-dimensional dielectric stacks of varying orientation. The lamellar structure and the difference in the layer index of refraction create a photonic crystal multilayer, a simple physical interpretation of this structure is a "quarter-wave stack". For such a structure, the stop band for normally incident light would have a midpoint wavelength of 4 times the average optical thickness (the domain thickness multiplied by the index of refraction) of a layer and a spectral width that depends on the index of refraction contrast of the layers. The wavelength of this
stop band varies with the angle of the incident light and its polarization, see Figure 4-4. The reflectivity of a film containing many grains of variously oriented lamellae will be some superposition of reflectivity from the distribution of orientations. This is especially true since all light that is forward scattered is collected as the reflected intensity, and complementarily all that which is transmitted and any angle is the transmitted intensity. So many orientations of grains within the material contribute to the detected signal, not just the grains which satisfy the normal incidence condition. Figure 4-4 shows the calculated band structure of a one-dimensional stack of layers using the refractive indices of polystyrene (n = 1.59) and polyisoprene (n = 1.51) and using the measured thicknesses of the respective layers. As is shown in the band diagram, a one-dimensional stack does not possess a complete band gap but a partial gap, the midgap wavelength of which varies with the incident angle of the light and with polarization.

The incident light has a wave vector \( \mathbf{k} \) and frequency \( \omega = \frac{ck}{n_0} \) where \( c \) is the speed of light in a vacuum and \( n_0 \) is the index of refraction of the external medium. The incident wave vector and the normal to the layers allows the specification of two independent electromagnetic modes: Transverse Electric (TE or s-polarization) and Transverse Magnetic (TM or p-polarization). The band structure \( \omega(\mathbf{k}) \) is displayed versus the magnitude of the projected wave vector parallel to the layers, \( k_{//} \). The horizontal axis is normalized frequency \( \omega \) in terms of \( \frac{2\pi c}{a} \), where \( a \) is the lamellar periodicity. Propagating states inside the material (i.e., light of these frequencies is transmitted through the material) are indicated by gray regions while the white region corresponds to evanescent modes that decay exponentially within the material. (The photonic gap lies in the narrow white region in the center of the graph.) The dotted lines bounding the gray and white regions represent the band edges. The heavy straight lines represent the light line and delineate the extent of the light cone, the range of \( \omega - k \) space accessible to light entering the material from an external homogeneous medium (in this case, air). Light incident at 90 to the film normal lies on the light line given by \( \omega = ck_{//}/n_0 \).

The effect of this partial band gap would be the rejection at any interface by
Figure 4-4: A band diagram calculated by the transfer matrix method is presented for the indices of styrene and isoprene and the relative thicknesses found in the 137/137 SI blend sample. The right side of the graph are modes for TE polarization. The left side is for TM polarized light. The grey shaded regions represent allowed propagating modes. The dotted lines are the band edges. The band gap can be seen between the second and third bands. The region between the heavy lines represents all modes accessible to light incident from outside the material (the "light lines"). The dashed line on the left side of the graph is the Brewster line, the angle where TM polarized light passes through the structure without reflection.
reflection of light with wavelengths and \( k \) vectors located in the gap region and transmission of light with wavelengths and \( k \) vectors outside of the gap. The wavelengths rejected between the second and third bands shift to shorter values with increasing angle of incidence relative to the lamellar normal, as these band edges shift to higher frequencies. For the relatively small index difference in the self-assembled BCP lamellar structure \( (\Delta n = 0.08) \), the gap is relatively narrow. A gap will open for any index difference, however. At normal incidence \((k_{\|} = 0)\) the gap width to midgap frequency ratio, \( \frac{\Delta \omega}{\omega_0} \) is approximately 0.05. The midgap wavelength for light at normal incidence to the film calculated for a repeat period \( a \) of 160 nm is approximately 500 nm and the bandwidth only 25 nm. This is the longest wavelength that is expected for this material to reflect. Experimentally a broad-band region of reflectivity between 410 and 525 nm is observed. As mentioned before, the broad reflectance spectra is primarily due to the polycrystalline nature of the lamellar morphology in this sample film. Light at normal incidence to the film encounters grains of lamellae at orientations departing significantly from normalcy. Thus, the bulk film optical properties are those resulting from a superposition of photonic microcrystals with properties similar to those calculated above. The reflectivity region of this material does show a marked broadening toward shorter wavelengths because of scattering geometries that reflect photons at off normal conditions. This superposition also affects the bulk film spectral properties as a lowered overall reflectivity of frequencies in the normal incidence stop band.

### 4.5 Conclusion

A self-assembled block copolymer lamellar morphology has demonstrated optical reflectivity arising from the photonic properties of the microstructure. It was shown that by suitable blending of homopolymers with a diblock copolymer a self-assembled lamellar structure can be obtained in which the homopolymers swell the repeat spacing into the regime appropriate for visible photonic applications. A basic treatment by transfer matrix methods has correlated the structure and materials properties with
the observed optical characteristics. Using copolymer blends not only raises the ceiling on accessible spacings for BCP systems but also imparts tunability to that spacing by varying the amount of added homopolymer. This will be explored in Chapter 5. This experiment represents the first reported observation of BCP photonic properties.
Chapter 5

Blending to Control the Wavelength of Reflectivity of BCP Photonic Crystals

The results presented in this chapter were published as part of an article in the journal Advanced Materials.[80] In addition the work benefits from the experimental assistance of R. Sharpe, and polymer materials synthesis by Dr.M. Xenidou in the lab of Dr.L.J.Fetters at Exxon-Mobil.

5.1 Block Copolymer Blends and Domain Spacing Control

In Chapter 4 the properties of a single blend of a block copolymer and two homopolymers were discussed. It was shown that the block copolymer spacing could be dramatically increased by the addition of equal amounts of matching molecular weight homopolymers and that photonic crystal properties related to the microstructure of a block copolymer were observed. The nature of these optical properties were explored and equations were presented describing the properties based on the structures and materials characteristics of the BCP system. In order to expand this work
it is necessary to study the behavior of these systems under a variety of blending conditions. In particular the ability to tune the wavelength of peak reflectivity of the block copolymer system is useful to demonstrate the flexibility of this platform for applications. In this chapter a demonstration that proper combinations of two homopolymers and a block copolymer can produce photonic materials with reflective properties spanning visible wavelengths is reported.

5.2 Fabrication of a Range of Photonic Crystals

A near symmetric poly(styrene-b-isoprene) (S/I) diblock copolymer with a total molecular weight of 391kg/mol was synthesized by anionic polymerization in benzene at 25°C. The styrene block had a molecular weight of approximately 194kg/mol and the isoprene block had a molecular weight of approximately 197kg/mol. The homopolymers used were a polystyrene, PS 13k and polyisoprene, PI 13k. The blends were made by mixing together calculated amounts of stock solutions of 100mg/ml polymer in cumene. Blends were prepared containing 100% to 40% diblock at 5% increments, with the remainder composed of equal fractions of the two homopolymers (i.e. samples contained 0-60% total homopolymer). About 0.25 ml of the resulting blended solution was dispensed onto one side of a glass cover slip 25 mm in diameter. The solution coated disks were allowed to dry in a cumene rich atmosphere for one week. The resulting samples were strongly colored and had visible grains of highly reflective material. A photograph of samples between 100% BCP and 40% BCP is shown in Figure 5-1. Samples with higher homopolymer fraction evidenced a milky appearance, but still displayed highly reflective grains. Samples were also made by rapidly drying them in roughly 10 minutes yielding approximately the same optical characteristics since at approximately 10% by weight polymer in solvent, the samples are already microphase segregated. The size of the highly reflective grains was much smaller in the rapidly prepared samples however, indicating a higher density of defects and grain boundaries. Drying them quickly is analogous to quenching them, thereby freezing in the early stage, defect-laden microstructure. Films of all the poly-
Figure 5-1: This is a photograph in ambient light of a variety of blends of block copolymer/homopolymer blends. The blue samples begin with pure 194k/197k symmetric SI copolymer, and change color slowly as the fraction of symmetric homopolymer is increased. The color shifts through green and ends with the red sample having 60% homopolymer added. The sample in the center is of a solution sandwiched between two glass plates. As the solvent dries, from the edge inwards, the sample becomes more strongly colored. This will be discussed further in Chapter 7.

Film samples of blended poly(styrene-b-isoprene) diblock copolymer, polystyrene and polyisoprene, were characterized optically. It is important to note that as they dried, selective reflection of light, giving the appearance of blue, green or red color, was seen in each sample. After drying, each sample showed a single well defined peak in reflectivity in the visible wavelength range (350-600nm) and a corresponding drop
Figure 5-2: Typical spectra for several homopolymer fractions (as labelled). Notice that the width of the peaks increases with increasing homopolymer fraction due to the associated increase in defects and disorder in the samples. The maximum reflectivity also decreases for much the same reason. These are total reflectivity spectra from the samples, representing light reflected into $2\pi$ steradians.

in the transmission profile. Similar to the sample in the previous chapter, this was taken as confirmation that reflectivity was observed and that the color and spectral properties of each sample were not due to significant absorption. In Figure 5-2, typical reflectivity curves are shown for several blend samples. The relative width of the reflectivity peaks (or transmission dips), $\frac{\Delta\lambda}{\lambda}$, varies approximately from 0.15 to 0.25, widening as the fraction of homopolymer in the blend increases.

The wavelength of the reflectivity peak versus the homopolymer content is plotted in Figure 5-3. There is a monotonic increase in the peak reflective wavelength with the fraction of homopolymer.
Figure 5-3: The dependence of the peak reflective wavelength (left axis) versus the homopolymer volume fraction is clearly linear. The lamellar spacing can be calculated from the reflective wavelength using the information contained in figure 4-4. The lamellar spacing corresponding to each homopolymer weight fraction is plotted on the right axis. The thin solid line represents an approximate mixed model, Torikai[1] based on 70% of the homopolymer segregating to the domains centers. The dashed and dotted lines represent the bounding models.
SEM of the samples confirmed that a lamellar morphology was present in the samples, with typical grain sizes of the order of several microns. The backscattered electron image (BEI) of a sample containing 40% homopolymer is shown in Figure 5-4. The bright regions correspond to the $OsO_4$ stained polyisoprene domains and the dark regions are the unstained polystyrene layers. The lamellar repeat from the micrograph is about 140nm, although the dimensions of structures in the micrograph will depend on the angle of the fracture plane relative to the lamellar normal, and expansion/shrinkage due to electron beam damage and $OsO_4$ staining. The layers appear approximately symmetric in thickness. The lamellae are seen to have a tendency to orient parallel to the glass substrate which lies at the upper edge of the micrograph. The homopolymers can be seen concentrating, or pooling at defects in the lamellar structure (in arrowed regions of Figure 5-4).

The Ultra Small Angle X-ray Scattering data for samples containing 20% and 40% homopolymer are presented in Figure 5-5. The higher order scattering peaks fall
Figure 5-5: USAXS data for the 20% and 40% samples are shown. The series of peaks are the reflections from the lamellar morphology. USAXS is an important technique for the measurement of the dimensions of this systems because it provides data about the primary, low order reflections and thus the dimensions and symmetry of the lamellar morphology.

at integer multiples of the first order peak, implying that the morphology is indeed lamellar. The relative weakness of the even order peaks indicates that the thicknesses of the styrene and isoprene lamella are approximately equal. Detailed comparison of the intensity with model calculations of peak intensities of a lamellar structure suggests that the layers are 0.52L and 0.48L thick.[43]

5.4 Discussion of Reflective Properties

A blend film of the same type of self-organized photonic crystal was presented in the Chapter 4. The alternating regions of styrene and isoprene correspond to a periodic
dielectric structure. The structure possesses a stop band for certain electromagnetic modes. These modes are rejected when incident on the surface of the material. This is observed as a reflection of these selected modes, imparting the appearance of color to the samples. As the size of the lamellar repeat spacing increases with the added homopolymer, this stop band will shift as the optical thickness of each layer is changing. A similar change could be observed if the average index of the material were increasing, though no mechanism for this is consistent with the experimental procedure presented here since the only addition to the system is homopolymer to the matching copolymer block. A thickness increase of each layer type is noted with increasing homopolymer weight fraction which correlates with the change in stop band wavelengths.

SEM images of cross sectional, fracture surfaces show that the lamellae preferentially orient parallel to the surfaces of the film and glass substrate. This allows for the attribution of the wavelength of peak reflectivity, the wavelength for which reflectivity is highest, to be characteristic of the normal incidence behavior. Disoriented grains and variations in the structure would contribute to a broadening of the reflective peak, specifically to wavelengths shorter than those of the normal incidence gap. This is observed in the samples when reflective peaks show substantial asymmetry. Reflective peaks are primarily symmetric, characteristic of samples with a general tendency for in plane order of the lamellae. The wavelength of peak reflectivity is well correlated with the lamellar spacing, which facilitates the simple expression of the lamellar spacing in terms of the wavelength of peak reflectance, $\lambda_p$. The lamellar spacing of a sample is thus given by:

$$L = \frac{\lambda_p}{(n_{ps} + n_{pe})}$$  \hspace{1cm} (5.1)

A single plot can be made to interpret the reflective data of all of samples and infer the lamellar spacing from the reflectivity data (shown on the right axis of Figure 5-2). This plot shows how the lamellar morphology repeat spacing and wavelength of reflectivity change with respect to the addition of homopolymer to the BCP blend system. The clear functional dependence gives a recipe for creating a photonic crystal of any
desired center wavelength. This is a unique property of block copolymer photonic materials, namely the length scale of this system is dependent strongly on the ratio of the three components, rather than solely on some prefabricated component, e.g. as for the sphere precursors in the case in a synthetic opal.

This relationship between the lamellar spacing and the volume fraction of added homopolymer is indicative of a certain type of swelling behavior. As discussed in Chapter 3, block copolymer blend behavior has been studied historically in much lower molecular weight diblock systems.[59] In general, swelling falls into two regimes which depend on the relative characteristics of the block copolymer and homopolymer blend components. In the particular case of ternary blends of a symmetric BCP and its two constituent homopolymers which preserve the overall composition of the system, both linear and volumetric swelling are observed. Linear swelling is characterized by the relation between the morphological length scale with the homopolymer fraction, shown in Chapter 3, similar to that which is observed in this system. Volumetric swelling would be characterized by the a one third power dependence of the length scale on the homopolymer fraction, also in Chapter 3. The hybrid relation of Torikai [1] can be used to approximate the data and get an estimate of the fraction of homopolymer segregated to the domain center. Figure 5-3, shows that 70% homopolymer accurately reproduces the behavior of this system over the full range of measured spacings.

Volumetric swelling is attributed to lower molecular weight homopolymers, and is explained by the homopolymer molecules interpenetrating the like BCP blocks and swelling them, increasing the surface area per block junction at the same rate as the distance between Inter-Material Dividing Surfaces (IMDSs). Linear swelling, attributed to higher molecular weight homopolymer additives (higher, in this case, is on the order of one tenth the block molecular weight,[64] in this experiment the homopolymer is roughly 5% of the block molecular weight), is characterized by no increase in the area per block junction on the IMDS. In order to accommodate the new material in the morphology, adjacent IMDSs must spread apart, increasing the spacing linearly with the added fraction. This is due to the fact that the higher molecular
weight additives, tend not to penetrate the like block coils and collect between the 
blocks of adjacent IMDSs. The two swelling models are pictured in Figure 5-6. It is 
suggested that there is a smooth transition between the two models as the molecular 
weight of additive is increased. The behavior of the system presented here is much 
closer to the linear model, however, which suggests that it is clearly governed by the 
high molecular weight additive behavior. This is surprising for such a low relative 
molecular weight, but since the mixing entropy scales as the inverse of molecular 
weight, it is expected that segregation will occur at progressively lower values of 
m for increasing block molecular weights. This is practically beneficial since the low 
molecular weight of the additive homopolymer will make the system more amenable to 
melt processing by reducing the melt viscosity compared to the pure, high molecular 
weight diblock. Lower molecular weight materials can have reduced glass transitions 
and melt viscosities, which will temper those of the ultra-high molecular weigh BCPs 
needed to achieve photonic properties.

5.5 Conclusion

This experiment clearly demonstrates the flexibility of this platform. It was shown 
that photonic crystals spanning the visible spectrum can be easily fabricated from 
a ternary blend of a diblock and two homopolymers. By the use of relatively low 
molecular weight additives, a significantly greater degree of processibility is imparted 
to the system, as well. Reflective films with stop bands of \( \frac{\Delta \lambda}{\lambda} = 0.15 - 0.25 \) with a 
peak reflective wavelength tunable over \( \lambda_{\text{peak}} = 350 - 600 \text{ nm} \), nearly the complete 
visible spectrum, were created by simply varying the relative fractions of the compo-
ments. These films had peak reflectivities in the range of 60-70%. This simple method 
demonstrates the ease with which large area, tunable, highly reflective, flexible films 
can be fabricated from block copolymer based materials.
Figure 5-6: Two models are shown for the position of homopolymer in microphase segregated block copolymer/homopolymer blends. For lower molecular weight additives, the homopolymer distributes uniformly in the body of the like microphase. Whereas, for higher molecular weight additives, concentration to the center of the like microphase is found.
and control light.

This chapter documents the pursuit of a BCP based three dimensional photonic crystal. A self-assembling block copolymer system is employed to form the double gyroid (DG) morphology at a length scale sufficient to interact with visible light. The optical properties of the poly(styrene-b-isoprene) diblock photonic material are compared with expected reflectivity. The block copolymer was also subjected to a UV treatment to remove the isoprene component as a method of modifying the optical properties. This process can serve as the basis for fabricating a three dimensional photonic crystal with a complete photonic band gap in the visible from a block copolymer template.

6.2 The Double Gyroid Morphology as a Photonic Crystal

In previous chapters it was proven that block copolymers offer an alternative means to produce self-assembled photonic crystals. Microphase segregation, already shown in one dimensionally periodic systems in previous chapters, can also form three dimensionally periodic structures as shown in Chapter 2. In particular, a three dimensionally periodic bicontinuous morphology known as the double gyroid is exhibited in block copolymers.[82] The structure is shown in Figure 3-2 for the 35%-39% volume fraction range and in Figure 6-1 in slightly higher detail. More complex block copolymer architectures (e.g. ABC linear triblock terpolymers [27] and miktoarm star copolymers [35]) produce correspondingly more intricate microdomain morphologies. The double gyroid morphology can possibly be harnessed to produce a 3D photonic crystal.

Three-dimensional structures offer the most challenging fabrication problems and self-assembly can be used to overcome them. The double gyroid microdomain structure is composed of two three-dimensionally periodic and continuous intertwined networks in a continuous matrix. One of the blocks of a double gyroid material could
Chapter 6

Three Dimensional Block Copolymer Photonic Crystals

The contents of this chapter were first presented as an article in the journal *Advanced Materials*. The band diagrams calculated for the double gyroid structure were prepared expressly for this thesis by Martin Maldovan. The procedure is reviewed in Chapter 2.

6.1 Utilizing the Potential of BCP Systems for 3D PBGs

One dimensionally periodic photonic crystals are an excellent demonstration of the potential of self-assembly in photonic block copolymer materials. They exhibit a variety of physical characteristics, including a range of accessible optical properties and offer a test bed for experiments in dielectric enhancement and incorporation of optical additives. One dimensional optical materials are technologically relevant as filters, coatings, and in application such as mechano-chronic film sensors explored in Chapter 7. The ultimate goal however remains a fully three dimensional material. While not necessary for the containment of light, a three dimensional material with a complete photonic band gap can form the basis of structures designed to manipulate...
Figure 6-1: This is a representation of the double gyroid morphology for the 34% volume fraction based on the level set reconstruction. The two networks are differently colored to distinguish them and indicate that they are independent. This tricontinuous structure divides space into the three contiguous regions shown. This figure was generated by Jim Hoffman and is available from the website www.msri.org.
also be etched away to provide a useful template for the formation of a three dimensionally periodic bicontinuous structure composed of the remaining low dielectric polymer scaffold and a wide variety of high dielectric materials that could be infiltrated into it. In particular, block copolymers exhibiting the double gyroid phase have been etched to form porous polymeric materials,[83] and treated to generate a free standing silica-oxy-carbide network from a silicon containing block copolymer.[84] Such etched double gyroid materials could be used as photonic crystals provided that their length scale was sufficient to interact with light.

6.3 Photonic Properties of Gyroid and Double Gyroid Morphologies

The photonic properties of the the double gyroid and other cubic bicontinuous systems that occur in self-assembling systems have recently been calculated.[51] These calculations show that for a single gyroid network structure with 17% volume of high dielectric the minimum dielectric contrast to open a complete gap is 5.2:1 which is lower than that of titania:air, and for a contrast of 13:1 the complete band gap is a robust \( \Delta \omega / \omega = 0.25 \) of the midgap frequency. The quantity \( \Delta \omega / \omega \) := \( \text{\frac{\text{high} - \text{low}}{\text{high} + \text{low}}} \) A gap map calculated for the 17% network volume fraction for a variety of dielectric contrasts, generated by the plane wave method by Martin Maldovan is shown in Figure 6-2. This shows that the gyroid structure is a desirable, and very effective morphology for making photonic crystals.

6.4 Fabrication of a Double Gyroid Photonic Crystal

The physical systems studied for this work are a styrene/isoprene and a styrene/air double gyroid structure, both based on an SI diblock with a 300kg/mole styrene block and a 450kg/mole isoprene block that is 38% styrene by volume and exhibits a double
Figure 6-2: This gap map generated for the 17% high dielectric network volume fraction, shows the gap opening at a dielectric contrast of 5.2, and a gap width of approximately 25% at a contrast of 13. The 17% network is precisely half of a 34% volume fraction double gyroid morphology observed in block copolymers. This gap map was calculated by Martin Maldovan.
gyroid morphology with styrene networks and an isoprene matrix. A map of the photonic properties calculated for the double gyroid structure [51] show that it does not exhibit a complete band gap for any composition or dielectric contrast. The structure will have partial band gaps associated with the strong Bragg scattering due to the \textit{Ia\overline{3}d} symmetry of the structure. These partial gaps can be seen in the band diagrams below, Figure 6-3 for SI double gyroid and Figure 6-4 for the etched, styrene/air structure. The gaps are indicated in the figures. The experimental photonic properties of unetched and etched double gyroid samples can be compared with expected values once the unit cell size is known since the band diagrams are normalized to that value.

6.4.1 Characterization of the BCP Photonic Double Gyroid

SAXS measurements can provide an accurate measure of the unit cell size based on correlating scattering peaks with allowed reflections of the structure. A representative SAXS pattern is shown in Figure 6-5. The sample thickness provided for a number of higher order reflections to be visible. The disorder in the sampled region causes the scattering pattern to be composed of rings as the diffracting beam averages over many possible orientation of the structure. The first seven allowed Bragg reflections for the \textit{Ia\overline{3}d} space group are the \{211\}, \{220\}, \{321\}, \{400\}, \{420\}, \{332\} and \{422\}. Radial integration of a two dimensional scattering pattern of the SI material shows 5 peaks corresponding to \textit{q} values of 0.090, 0.121, 0.180, 0.243, 0.30 \textit{nm}^{-1}. The first two reflections; the 211 and the 220 are expected to be hidden in the beam stop due to their small \textit{q} value. If the magnitudes of the other allowed peaks are compared, it is apparent that the first observed peak is consistent with the 321 reflection. The fourth allowed reflection 400 was not observed, presumably due to form factor cancellation (see Hadjuk et al.[82] for an SI double gyroid with similar composition). The fifth, sixth and seventh reflections are closely spaced and could all contribute to the observed peak which would be centered at the 422 reflection based on the expected peak intensities. Assuming this assignment is correct, a cubic lattice parameter of about 260nm is calculated [this is an average between the value for 321 and 422 peaks]. X-ray scattering measurements were not performed on the
Figure 6-3: This photonic band diagram is calculated for the 38% volume fraction double gyroid morphology. The diagram is for styrene networks and an isoprene matrix. The diagram plots the dispersion relation of propagating waves in the material. A complete gap would be indicated by a horizontal band of frequencies where no lines crossed. A singularity is where two bands approach and touch only at one point. Bragg reflections are indicated by a separation of two adjacent bands indicating forbidden states. Strong "Bragg" reflections are indicated along high symmetry directions by arrows. The actual separation of bands is small compared to the scale of these graphs and is difficult to distinguish. The letters on the bottom axis indicate special directions in the irreducible Brillouin zone of the Ia3d structure. These band diagrams were prepared by Martin Maldovan.
Figure 6-4: This is a band diagram for the double gyroid structure composed of styrene networks and an air matrix. The diagram is similar to that for S/I but there is a significant upward shift in frequency of the bands due to the overall lowering of the dielectric constant of the material. Again the "Bragg" reflections are noted with arrows. The frequency change of these reflections will indicate their presence relative to the reflections of an S/I gyroid. This band diagram was also calculated by Martin Maldovan.
Figure 6-5: This figure shows a plot of the x-ray intensity versus scattering angle in degrees of the inset SAXS pattern. The scattering pattern is from a double gyroid sample of 750k SI block copolymer cast from toluene. It shows 5 clear Bragg rings. The assignment of the first two rings to the \{321\} and \{422\} reflections of the gyroid structure yields a lattice parameter of 260nm. Successive rings are higher ordered reflections.

Cryo-microtomed sections of the SI material permit direct observation of the double gyroid morphology, the average grain size and an estimation of the lattice parameter. Figure 6-6 is representative TEM micrograph of an \(\text{OsO}_4\) stained 80nm thick section. This particular micrograph shows a projection along the [123] direction. The lattice parameter measured from micrographs of standard projections of the DG structure is 250nm. This is consistent with the X-Ray scattering results confirming the assignment of the X-Ray peaks.

\(\text{UV/O}_3\) can readily degrade and etch the polyisoprene matrix block of the copolymer, while leaving the polystyrene networks intact. An SEM micrograph of the
Figure 6-6: TEM micrograph of an 80nm thick cryo-microtomed thin section of the 750k SI block copolymer exhibiting the [123] projection of the microstructure. The isoprene matrix has been stained with osmium tetroxide, leaving the styrene networks light in this positive micrograph. The unit cell is highlighted to the left side and the long lines yield a lattice parameter of roughly 250nm, consistent with SAXS measurements. The scale bar is 500nm.
UV/O₃ etched material is shown in Figure 6-7. It can clearly be seen that the polystyrene double gyroid network morphology is well maintained after the etching process, yielding a polystyrene/air photonic crystal. This structure can be compared to Figure 6-1, which is a unit cell representation of the styrene networks at 34% volume based on a level set approximation.[85] The lattice parameter of the etched structure is found to be comparable to that of the unetched structure, so the glassy styrene networks seem not to have been altered substantially by the etching process. The middle portion of the etched film shows incomplete removal of the isoprene matrix, so longer etching times are required for its complete removal.

The spectrographic plots for the bulk S/I film and the S/air film are shown in Figure 6-8. The intensity of each plot is normalized. The wavelength of the main peak reflectivity is 327nm for the as-cast sample and the width of the peak is 70nm. In addition, the diblock sample shows less intense reflective features at 280nm and 235nm. If these features correspond to be allowed Bragg reflections for the styrene/isoprene material at normal incidence, then the wavelengths are expected to correlate with the principal {211}, {220} and {321} allowed reflections. Using the measured lattice parameter yields computed reflective peaks at 324nm, 281nm and 212nm, quite consistent with the observed values. This confirms that the double gyroid structure is indeed a photonic crystal exhibiting reflectivity at optical wavelengths.

The partially etched gyroid film exhibits reflectivity arising from both the styrene/air and styrene/isoprene structures. If the differential reflectivity between the partially etched and unetched samples is considered, the effect of etching on the reflectivity is clear. In Figure 6-8, features are indicated by arrows at 1) 286nm, 2) 261nm, and 3) 210nm, in addition to a dramatic decrease in the primary reflectivity at 327nm. This shift to shorter wavelengths of the primary reflective features of the etched double gyroid structure is a result of the material having a lower average refractive index.

This double gyroid sample is notable mostly in the possibilities it creates. Demonstration of a three dimensional self assembling block copolymer with sufficient length scale to interact with visible light is motivation to further pursue this path to the goal of creating a self-assembling block copolymer based structure with a complete band
Figure 6-7: This SEM secondary electron image of the double gyroid styrene networks remaining after UV/ozone etching, shows that the networks are intact and self supporting after processing. The dimensions of the network structure are not perceptibly changed by the processing. The scale bar is 250nm.
Figure 6-8: The reflectivity of the double gyroid block copolymer film plotted as a solid line. Features indicative of the primary expected "Bragg" reflections are indicated and labelled. The differential reflectivity of the etched structure with the unetched structure is shown by the dotted line. The reduction in the average index of the medium results in a shifting to shorter wavelengths of the "Bragg" reflections, again indicated with arrows and labelled.
gap. In order to realize this goal, progress must be made in two key areas. The first is to increase the dielectric contrast between the constituent materials and second is alter the polymer such that a single gyroid template structure is obtained. The results of Suzuki et al.[86] demonstrate a double gyroid structure with chemically distinct networks. Suzuki employed double gyroid forming triblock terpolymer. One network was composed of polyvinyl pyridine, the other is polystyrene with a matrix of polyisoprene. If such a material could be realized at sufficient molecular weight for optical applications, a single gyroid network could be etched from this material, providing a single gyroid (SG) template. This template could then be replicated in titania, which has a sufficient refractive index to open a complete gap in a gyroid, titania network/air matrix structure. To further explore this path, the infiltration into the etched double gyroid structure of a titania sol-gel precursor, titanium-tris(butoxide), was performed. The structure was then exposed to air and heated to cure the sol-gel. The infiltrated polymer/sol-gel double gyroid was then pyrolyzed to remove the polymer leaving a titania matrix, double gyroid structure. An SEM micrograph of the resulting material is shown in Figure 6-9. Unfortunately, the pyrolysis shrinks the material 40% creating a structure with no visible "Bragg" reflections measurable by reflectivity. The structure is accurately reproduced in the titania material exhibiting the feasibility of the process.

6.5 Conclusion

The block copolymer self-assembly approach for fabrication of three dimensionally periodic structures has been demonstrated. A double gyroid structure at a length scale sufficient to interact with visible light was successfully produced from a high molecular weight SI BCP. Simulations have shown that there is no complete photonic band gap in the double gyroid phase for the index contrasts realized. There is, however, reasonable agreement between the band diagram and the measured optical properties. Etching of the matrix phase of the structure was performed providing a path, via etching and subsequent infiltration, to improve the dielectric properties.
Figure 6-9: The structure resulting from the infiltration with titania sol-gel precursor and pyrolysis of the double gyroid styrene network template from the UV/ozone etch is shown in the SEM micrograph. The disorder in this sample is representative of the sample which was prepared more quickly than the sample which is pictured in figure 6-6. The scale bar is 250nm.
These steps provide the groundwork for the fabrication of a self-assembled photonic crystal possessing a complete band gap.
Chapter 7

Solution Properties of Photonic Block Copolymer

7.1 Solution Processing: an Alternate Method for BCP Microphase Dimension Control

One of the most attractive properties of block copolymer systems as photonic materials is their adjustable repeat spacing. The fundamental spacing is determined initially by the synthesis of the macromolecule, as described in Chapter 2. Described in Chapter 5 is the tuning of the spacing of BCP photonic crystals by increasing addition of homopolymer. The swelling of BCP microphase segregated morphologies of all types via homopolymer addition has a long history in research. Lamellar morphologies can exhibit an increase [1] or even a mild decrease [38] in spacing when a given block copolymer system is swollen with homopolymer such that the overall composition of the system remains the same. In the presence of a solvent, the spacing of block copolymer morphologies can decrease or increase as the concentration of solvent increases. The interaction of the polymer blocks with one another is screened by the presence of a neutral solvent, leading to a decrease in the repulsive interaction between blocks and thus a decrease in spacing.[87, 88] However, the solvent itself can exhibit some selectivity which can augment the repulsive interaction leading to a net
increase in spacing as found theoretically [89] and verified experimentally.[90, 91] The general form of the repeat spacing of a solvent swollen system is given by:

\[ d \sim d_0 \phi_P^{-\beta} \]  

(7.1)

where \( d \) is the repeat spacing, and is expressed as a function of the fraction of polymer \( \phi_P \) and an exponent \( \beta \) which is characteristic of the selectivity of the solvent, and the equilibrium repeat spacing \( d_0 \). This relation has been recently studied in low molecular weight SI systems in a variety of selective solvents [91, 89, 90] and in nonselective solvents such as toluene.[92] The wide variety of behaviors demonstrates yet another mode of adjusting the spacing of photonic materials to suit a particular application.

### 7.2 Photonic Block Copolymer Solutions

The experiments presented in this chapter are designed to follow the behavior of photonic BCPs in the presence of neutral solvents. A neutral solvent will partially shield the interactions of the blocks leading to a decrease in the layer repeat spacing. The degree of shielding will increase with the volume fraction of solvent. A more shielded system is expected to exhibit smaller spacings at equilibrium. In experiments on lower molecular weight SI systems in toluene, the value of \( \beta \) observed for toluene is 0.33.[92] The polymer materials used in the studies presented in this thesis, however, visually exhibited a swelling, that is, an increase in domain spacing, behavior when dry samples were exposed to toluene vapor. The wavelength of the reflected light increased from blue to red as the sample took up solvent. This observation is correlated with a kinetic effect observed for higher molecular weigh systems previously by Hashimoto and coworkers [92] and will be discussed below.

#### 7.2.1 Solution preparation

It is essential to closely monitor the content of solvent in a sealed sample of a high molecular weight, photonic block copolymer solution in order to determine the precise
relationship between the solvent content and the lamellar spacing. The experiment hinges on maintaining a uniform distribution of solvent throughout the sample volume as the solvent concentration was measured by tracking the weight of solvent present and comparing it to the known initial weight of polymer solution sample. The uniformity of the concentration was evaluated by the uniformity of the color of the sample. The direct relationship between the lamellar spacing and reflective color (in this case the shift of the average index of the system with solvent will be small, not so in general), it could be neutralized with the proper selection of a blend of solvents, if desired) make color a good probe of the dimensions of the system. From a measurement of the peak reflective wavelength the lamellar spacing can be determined and related to the known solvent concentration. In this way, the behavior of the system can be plotted and compared to work from literature on lower molecular weight systems.

7.2.2 Considerations for Optical Characterization

The samples were prepared and allowed to equilibrate initially for 4 weeks. At the end of this period the samples were first weighed, which allowed for the calculation of the initial sample concentration as described in Chapter 3, and then spectral measurements were made of each of the three samples. The three samples were prepared so as to have different initial concentrations, all below the apparent order-disorder concentration of 8% by weight of polymer (significantly, critical concentrations are observed in solutions of both selective and non-selective solvents [92, 89]). Below 8% concentration of polymer, no reflective peaks or features are observed, but the samples have a vaguely bluish cast. A spectra from one of the samples as initially prepared shows only weakly wavelength dependent scattering increasing at shorter wavelengths. It has been observed by X-ray scattering that, in lower molecular weight systems, at similar concentrations, weak concentration fluctuations dominate the system, rather than sharply defined, ordered morphologies.[92]

Subsequent measurements were taken after a fraction of the solvent was evaporated by placing the sample in a heated bath. After each evaporation, the samples were
again allowed to equilibrate for two weeks, even though the samples appeared uniform at the conclusion of the evaporation. The weights were recorded and the reflective spectra were taken at the conclusion of the waiting period. Reflective features first showed up in a samples with a polymer concentration of 9%. A typical reflectance spectra for a 17% solution is shown in Figure 7-1. Notably, reflective features were seen first at 410nm, not the edge of the measurable range, which indicates that it is unlikely that the peak was only first observed due to instrument wavelength limitations. Samples at 8% do not show features, which places the order-disorder concentration around 8% or 9%.

The high degree of order and the preservation of the lamellar morphology in solution is shown in the following x-ray scattering pattern (SAXS). The solution in this case was approximately 25% by weight polymer in toluene and was sealed in a kapton and aluminum sample holder. The peak positions are of the form $n2\theta$ and follow the familiar series; $q, 2q, 3q, \ldots$, indicating a lamellar morphology. The unit cell derived from the peak positions is roughly 210nm, which is consistent with the concentration. The third order (the second visible peak, the first peak is the second order partially eclipsed by the beamstop) is of similar intensity to the fourth, but successive odd orders are suppressed, demonstrating an asymmetry (46/54) of the structure which reflects that of the molecule. This scattering pattern shows that an analysis of the reflective properties of these solutions which assume a lamellar system swollen with a non preferential solvent is valid.

The peak reflective wavelength, concentration and calculated lamellar spacing are plotted in Figure 7-3. In plotting the peak wavelength or lamellar period versus the concentration, several regions become apparent. The regions are separated by vertical dotted lines in the figure. In Figure 7-3, in the low concentration region there is no identifiable morphological or spectral feature. In the mid concentration region, a clear monotonically increasing function is followed as expected from literature studies. At around 40% polymer in solvent, however, the morphological dimensions of the system begin to decrease with increasing polymer fraction. The research of Hashimoto et al.[92] was the first to describe this behavior. They attributed the inflection of the
Figure 7-1: The normal incidence reflectance spectra of a 17% by weight in toluene 480k/560k SI copolymer solution. The reflectivity is normalized relative to an aluminum mirror and exceeds it by approximately 3%. The width of this reflective peak is about 6nm, indicating that the index contrast between the two phases is low and perhaps slowly varying (rather than sharp as is expected in the concentrated styrene-isoprene copolymer).
Figure 7-2: This figure shows a plot of x-ray intensity versus scattering angle for a solution of 25% SI 470/560 in toluene. The inset is the actual scattering pattern as collected on the two dimensional image plate from which the linear plot was made. The concentric rings represent scattering from randomly oriented grains. The relative intensity of the rings indicates the symmetry of the system. The graph is a radial integration of the scattering pattern about the beam axis. The first peak position is likely modified by the beam stop edge. Successive peaks follow an n2θ spacing. The first fully visible peak is n=3. The relative intensities of the peaks are apparent.
domain spacing versus concentration profile to the vitrification of one of the blocks and the fixing of the area per junction at the IMDS. The net effect is that, as solvent is extracted from the system, reorganization of the chains and equilibration of the polymeric system is no longer possible. The dimensions of the system microstructure simply shrink as solvent is removed.

Each of these behavioral regions will have its own characteristic dependence of the spacing on the solvent content. This can be used to confirm the mechanism. Since it is impossible to assign a length scale to the low concentration regime using reflectometry, no conclusion can be drawn from this observations apart from the bluish color being associated with random, small magnitude, refractive index fluctuations in the solution. The second regime where the dependence is very regular shows the characteristic power law dependence on concentration, with an exponent of approximately 0.31. This is consistent with that observed by Hashimoto [92] in the same system but at lower molecular weight (100k). The final regime of shrinkage will follow a different power law with a negative exponent of one third if the shrinkage is affine, i.e. if the materials contracts equally in all directions. It is possible however that when one block becomes vitrified, shrinkage can predominantly occur along the lamellar normal leaving the interfacial area between blocks unchanged. This leads to a power law with an exponent of -1 for the dependence of the lamellar spacing on the solvent fraction. In actual systems, any scaling factor above this lower bounding value can be observed. The graph in Figure 7-3 shows the bounding region of this exponent and the data falls above this limit, but as is characteristic of this region, it is not well behaved. Because the shrinkage observed is a kinetic effect, the exponent is often not reproducible: successive experiments, and different materials showing slightly or significantly different behavior.

The characteristic behavior of these three regions of distinct solution regimes has been identified, fully elucidating the behavior of the photonic solution samples. Previous chapters have documented the use of blending to achieve larger spacings, a factor of two greater than the innate maximum equilibrium spacing of the material. This experiment allows for the determination, in principle, of the ultimate equilib-
Figure 7-3: The wavelength of peak reflectivity is plotted versus the concentration of polymer in a toluene solution. Data points are indicated by black and grey icons. Squares are the data which fall in the middle region and circles represent the data which fall in the "kinetically trapped" regime. The three behavioral regions are separated by dashed vertical lines. The region of concentration fluctuation on the left side of the graph shows no reflective features. The well behaved central region is shows reflective peaks well fit by the model which is indicated by the red line. The kinetically controlled region shows data which is widely scattered. The thin line in this region represents the lower bound of shrinkage, that of the linear shrinkage model.
rium spacing of materials which do not achieve their equilibrium spacing in normal casting. An important feature of the plot of reflective wavelength versus solvent fraction, is the intercept on the 100%polymer axis. This predicts the ultimate lamellar spacing experimentally. For this polymer of roughly one million kilograms per mole, the ultimate spacing is thus predicted to be 300 nm, corresponding to a reflective wavelength of 960 nm. Extrapolating this value is only a guideline, but the experimental model behavior of this system has been studied and verified by researchers at lower molecular weights. There is some reason to believe that in a system of this extreme molecular weight, that the behavior may differ, however, this lamellar repeat is consistent with the value of 240 nm predicted by the earlier derived molecular weight dependence, as well (discussed in Chapter 3, using the value given by the Hashimoto for the proportionality constant). It is quite an unprecedented dimension for a BCP system, and as yet unachieved in this one. The corresponding reflection would be in the near infrared. Combining this with the blending studies suggests that the reflective wavelength can be nearly doubled, bringing the system well within the infrared reflectivity range, and near a technological goal of 1.5µm. This as yet unrealized potential is a possible significant future development.

7.2.3 Equilibration Time in Block Copolymer Photonic Solutions

The behavior in the central region of Figure 7-3 is characteristic of an equilibrated polymer system. The functional dependence of the lamellar spacing, as observed by the peak wavelength of reflectivity, is that expected for the system at equilibrium. This range has been studied by researchers and its properties likened to those of a lyotropic liquid crystal.[93, 94] An interesting observation of the time it takes for the system to relax to an equilibrated state can be made by watching the reflectivity of a solution in this regime as it evolves with time after being compressed. In particular, a dollop of a solution of 25% by weight polymer in toluene is placed between glass slides and the reflectance is plotted as a function of time, paying particular attention
Figure 7-4: a. The reflectivity relative to an aluminum mirror is plotted as a function of the wavelength. Plots, sequential in time, of the reflectivity as a function of wavelength show the reorganization of the microstructure as reflectivity improves. Notice that the peak wavelength does not shift substantially, but the peak narrows to near ideal limits. b. The wavelength of peak reflectivity and the band width is plotted as a function of time. This second representation of the data in which the error bars represent the full width at half of the maximum amplitude of the reflectivity peak.

to the width of the peak as well as its position. Normal incidence reflectivity, in this case, is a good probe of the relative orientation of the microstructure of the material. This data is presented in Figure 7-4 below.

The position of the peak does not shift much but the material undergoes substantial reorganization over the experimental interval as evidenced by the dramatic narrowing of the reflective peak and the increase in the peak value of reflectivity. From this data it can be inferred that the lamellae are reorganizing parallel to the substrates, increasing the normal incidence reflectivity. It is important to note that the microstructure itself will change little locally, but the lamellar grains will grow and the orientation will change. The relaxation time indicated by this experiment is around 1-2 hours and gives an indication of the time required to achieve a well oriented microstructure in a technological application, such as that which will be described next.
7.3 Elastochromic Materials

The optical properties of samples in the equilibrated region are excellent. Since a very regular and reproducible dependence of spacing on solvent concentration exists there, this is potentially the most useful region of photonic block copolymer solutions. The high optical quality and narrow bandwidth provide an accurate measure of the local domain structure. Interestingly these solutions also are viscoelastic. If a solution is prepared with a non-volatile solvent, such as dioctly-pthalate (DOP), a gummy film is formed which is highly colored and resists flow. If this film is deformed by depressing a glass rod into it, a color change is observed in correspondence with the compression of the local structure.

Deformable plastic reflectors have been produced and observed before [95, 96] in multilayer materials and in colloidal crystal derived rubbery systems.[97] In the first case a multilayer was fabricated either by spin-coating alternating layers, as is the case in Kimura et al.[95] or by coextrusion of rubbery materials, as was the case in the Schrenk patent.[96] Kimura and coworkers were the only one of the two to correlate deformation with a shift in wavelength. The system was simply compressed between glass flats and the transmission of the multilayer film was measured. The second example is of a self assembled, charge stabilized colloidal crystal, infiltrated with a monomer which was then polymerized. The resulting gel exhibited diffraction which changed with deformation. This was characterized again by measuring transmission. The viscoelastic polymer multilayer system differs from the first in that it is a self organizing, rather than manufactured system, and from both in that it is a conformal coating and does not require multi-step preparation. It is simply deposited from a solution as a paint or coating.

It is possible to qualitatively correlate the deformation of this material with the local deformation of the material. By coating a flexible, black, rubber substrate with this visco-elastic film material and deforming it, the color of the film can be measured relative to its deformation. The optical measurements are taken at normal incidence relative to the surface of the film using the microscope spectrometer. A
Figure 7-5: The color of the sample shifts from green to blue as it is deformed and when the deformation is relaxed the color is recovered. The cycle is represented by the arrows: the yellow-green sample is stretched in 1 to a green color; further stretching in 2 yields a blue-green sample; continued stretching in 3 results in a color change to blue, which represents the shortest spacing of the observed colors; and finally, relaxation in 4 recovers the initial color of the sample. The cycle shown can be repeated with consistent performance.

series of photographs in Figure 7-5 shows the deformation cycle and the associated color change.

While the visual color change indicates qualitatively the degree of deformation, spectral measurements can be potentially of great importance to accurately measure the deformation precisely. The peak reflective wavelength of the material can be accurately measured and correlated with the sample deformation. A plot of the peak reflective wavelength versus the deformation is shown in Figure 7-6.

The functional dependence of this data is not exactly what is expected. A relatively simple model of linear extensional deformation suggests that the relation between the extension ratio \((\epsilon)\) and the peak reflective wavelength \((\lambda)\) should be:

\[
\lambda = \frac{\lambda_0}{\epsilon}
\]  

(7.2)
Figure 7-6: Peak reflective wavelength is plotted as a function of the measured deformation of the black rubber substrate, represented as the extension ration. The wavelength of peak reflectivity shifts to shorter values as the sample is stretched in accordance with the observed color change. The best fit functional dependence is shown by the red line. A more complex model could account for the many influencing factors in this system. The behavior is repeatable and regular.
The relationship exhibits a much shallower dependence, \((\epsilon^{-0.3} \text{ instead of } \epsilon^{-1})\). This is likely due to systematic experimental deviations from the model, rather than material behavior. Observations of the experimental system show that the thick section of reflective copolymer/DOP material is not uniformly deformed though its thickness. The top of the material is less deformed than the base attached to the rubber support. Thus the measured deformation, that of the support, is not necessarily that of the reflective material itself. This could be corrected by a thinner coating of the reflective material on the rubber support or a modified experiment in which the material is deformed directly, perhaps by compression as in the Kimura[95] study. Furthermore, a number of complicating factors may contribute to the observed changes in reflectivity. In addition to a more complex and accurate model of the deformation of the material under strain, birefringence induced by strain, reorientation of the layers under strain, and lamellar buckling or the formation of chevron patterns in the microstructure can all further complicate the model. Nevertheless, the behavior is clearly regular and repeatable, as the points are taken from several subsequent deformation cycles, making it a good measure or indicator of deformation.

An example of the possibilities which this material offers for the mapping of deformation in complex arrangements is given by the following experiment. If a small amount of a solution, the same polymer and non-volatile solvent mixture, is placed between a glass plate and a transparency, and allow it to equilibrate so that a highly colored and reflective material is obtained. The transparency can be peeled from the glass. As it is peeled a color change appears at the tip of separation, or the peel front. This is pictured in Figure 7-7.

The deformation is clearly indicated by the color shift. It would be possible to infer the precise amount of deformation by spectroscopically measuring the color at a certain point, successively in time, thereby obtaining a map of the deformation at the peel front as it propagates. Other convenient arrangements can be imagined for deformation sensing as well.
Figure 7-7: A photograph of the peeling experiment showing the deformation field of the adhesive layer between the rigid and flexible substrates. Colors representing undeformed polymer, blue slightly compressed polymer, violet to green to red as strain increases. The degrees of strain indicated can be seen following the deformation field of the peel front from right to left.
7.4 Conclusion

The versatility of block copolymer photonic materials is highlighted in this chapter through a few examples showing some useful characteristics. The solution properties of these materials may be a channel by which high quality narrow band width optical components are created, for example by using flow or electric field to align the domains [98] and then solidifying the solvent once the component is formed. The behavior in this regime also shows the potential of these materials and the ultimate reflective wavelengths which they may exhibit. It shows by the use of blending, or the use of an appropriate selective solvent it may be possible to generate photonic crystals for application in the communication bands around 1.5μm. The formation of flexible photonic gels shows additional potential for this broad class of materials. The repeatable and characteristic response to deformation is likely useful as an area strain gauge for mapping deformation fields in space and time. While demonstrated in one dimensional systems, these characteristics would be reflected in three dimensional materials as well. This further reinforces the versatility and technological potential of BCP PBG materials.
Chapter 8

Acousto-Optic Properties of Block Copolymer Photonic Crystals

This work is featured in a Physical Review Letter [99]. In addition, the Rayleigh-Brillouin scattering measurements of the photonic block copolymer samples were performed by Dr. H. Kriegs under the supervision of Dr. G. Fytas. Furthermore, complete acoustic band structures were calculated by Dr. R. Penciu under the supervision of Dr. L. Economou, although the position of the acoustic gap was calculated independently by the author.

8.1 Acoustic Stop Bands in Materials with Periodic Mechanical Contrast

While block copolymers have proven capable of forming photonic crystals, this may not be the extent of their interesting resonant structure properties. The combination of mechanical and physical characteristics typical of these materials can give rise to acoustic stop bands for phonon wavelengths commensurate to the photon wavelength of the photonic band gap in the material. Phononic crystals [100, 101] and multi-layer acoustic materials [102] have been the focus of recent investigations [103, 104, 105, 106]. They are studied for a variety of applications [107, 108], such as vibration isolation and
transducer systems. Such materials are also novel systems for the study of phonon-mediated light interactions such as stimulated Brillouin scattering. Block copolymers are capable of self-assembling into phononic crystals providing benefits to fabricating these structures at otherwise inaccessible length scales.

8.2 Examining the Ultrasonic Properties of BCP PBGs

The acoustic and phonon band properties of concentrated block copolymer solutions studied by polarized Brillouin light scattering[109] are presented in this chapter. The acoustic properties of this lamellar forming block copolymer system lie in the hypersonic (GHz) frequency range. This chapter reports the first evidence of phonon spectral features characteristic of the morphology of the block copolymer. The SI 480/560 BCP solutions were prepared in toluene and stabilized with BHT (0.1% by weight in the solvent) as described in Chapter 3. The weight percent of styrene was 46% as determined by NMR, corresponding to a volume fraction of 0.44 polystyrene. The morphology of the material as cast from toluene was lamellar determined from thin OsO₄ stained sections examined by transmission electron microscopy. X-ray data presented in Chapter 7 showed that this polymer in solution in toluene at a sufficient concentration to microphase segregate possess the same morphology, as toluene is a non-preferential solvent for the pair. It furthermore maintains the volume fraction of each layer type. Three solution concentrations were examined in this experiment. The 17% polymer content samples was strongly green opalescent. The 30% concentration was obtained by allowing a portion of the solvent to evaporate from the 17% sample. A green-yellow opalescent solution was the result of this evaporation. A third solution of 9% SI in toluene was prepared in a separate sample tube. This sample had a weak bluish cast indicating that it had not formed a microstructure. The selective reflectivity of the samples is indicative of the photonic stop band arising from the layered microstructure of the material as described in Chapters 3 and 7. Concentrations
were estimated from the peak wavelength of reflectivity using the data presented in Chapter 7.

8.3 Brillouin Scattering Results

The light scattering experiment was conducted as described in Chapter 2. The scattered light was analyzed at various specified angles, $\theta$, with respect to the illuminating beam. The scattering wave vector is defined as $q = ||\mathbf{q}_i - \mathbf{q}_f|| = \frac{4\pi n}{\lambda_0} \sin \left( \frac{\theta}{2} \right)$; where $\mathbf{q}_i$ and $\mathbf{q}_f$ are the wave vector of the incident and scattered light respectively, and $n$ is the average refractive index of the medium. In order to map the phonon dispersion relation of the block copolymer solution, scattering experiments were conducted for ten angles. For each scattering angle, the data consisted of a plot of the intensity of scattered light versus the frequency. Typical data are shown in Figure 8-1a and 8-1b for 17% and Figure 8-1c for the 9% SI polymer solution in toluene at $q = 0.025 nm^{-1}(\theta = 90^\circ)$.

The central (elastic) Rayleigh scattering peak is at the frequency of the incident beam. The inelastic light scattering represents photons with wave vector $\mathbf{q}$ scattered by interactions with phonons of wave vector $\mathbf{k}$. Typically for homogeneous media, one Brillouin doublet at $\pm \omega$ appears only at $\mathbf{q} = \mathbf{k}$. Typical behavior of a fluid is shown in Figure 8-1a for the low concentration solution (9%). It exhibits one acoustic $(\omega \propto q)$longitudinal phonon $f = \frac{\omega}{2\pi} = 5.5$ GHz at $q = 0 : 025nm^{-1}$ corresponding to an effective average medium presented by the dilute and non segregated polymer solution. The 17% SI solution displays two or three modes (Figure 8-1a,b) depending on the cell orientation relative to the scattering wave vector $\mathbf{q}$. Of the three Brillouin doublets of Figure 8-1b, cell rotation affects mainly the presence of the lowest frequency doublet (2.9GHz).
Figure 8.1: Rayleigh-Brillouin spectra obtained at $q = 0.025\text{nm}^{-1}$ for 17% (b and c) and 9% (a) SI solutions in toluene at 20°C. (a): The rich phonon spectrum for 17% is represented by a the superposition of three Lorentzians (solid lines). (b): The phonon spectrum of the same solution at a different orientation relative to the laser beam that affects only the intensity of the lowest phonon (2). (c): Only the longitudinal phonon (1) is observed at low SI concentrations. The frequency region $\sim \pm 1\text{GHz}$ about the central peak is provided by the reference beam used for the stabilization of the tandem-FP interferometer. The numbers identify the modes; 1 is longitudinal mode, 2 is the "Bragg" mode and 3 is the $q$-independent mode.
Figure 8-2: The diagram shows schematically the orientation of the lamellar axis, $z$, relative to the light scattering wave vector $q$ and the angle $\alpha$ between the lamellar surface and $q$. 
8.4 Phononic Crystal Properties of BCP-PBG Solutions Samples

In the present polycrystalline high molecular weight SI solutions, momentum conservation requires \( q = G + k \), where the reciprocal one dimensional lattice vector \( G = \frac{2\pi}{d} \), with \( d \) being the lamellar repeat spacing. The intensity of this "Bragg" phonon depends on the direction of \( q \) relative to the lamellar normal \( z \), being maximum for \( q \) parallel to \( z \) (see diagram in Figure 8-2). The resemblance to the Bragg diffraction conditions suggests the name of this new acoustic mode. Visual inspection of the sample shows large reflective grains, and the orientation dependence indicates that grains are of the order of the scattering volume (200 microns diameter). Conversely, peak(2) in Figure 8-1b can (in the sense that \( G \neq 0 \)) be utilized to determine directly the spacing \( d \) of the lamellar structure (see Figure 8-4 below). This important system parameter can be inferred from the position of the optical reflectivity peak, and can be directly measured only by ultra-small angle scattering measurements.

The highest frequency phonon (3), also absent at low polymer concentrations, is a new mode and relates to the well-ordered solutions. Cell rotation only slightly affects the frequency of this mode (roughly 3% variation, Figure 8-1b). To elucidate the nature of this mode (denoted 3 in Figure 8-1 b and c), inelastic light scattering is examined at different scattering wave vectors. Figure 8-3 shows the spectra for the 17% and the 30% SI samples at \( q = 0 : 012 nm^{-1} \) and 20 °C. Modes (1) and (2) clearly vary with \( q \), whereas the highest frequency phonon (3) shows negligible dispersion. The frequency of the "Bragg" mode (2) is found to decrease with SI concentration.

8.4.1 Phononic Band Structures: Experimental Comparison with Calculated Properties

The positions of the Brillouin peaks as a function of \( q \) are plotted in Figure 8-4. Mode (1) is the \( q \) dependent longitudinal phonon normally present in a homogenous fluid. The insensitivity of \( c = \frac{\omega}{q} (\approx 1370 m) \) to concentration changes in the examined
Figure 8-3: Rayleigh-Brillouin spectra recorded at $q = 0.012nm^{-1}$ for (a) 17% and (b) 30% SI in toluene at 20°C. The numbers identify the modes as in Figure 8-1.
range suggests low elastic constant contrast in the S and I sub-layers swollen by the common solvent. The "Bragg" mode (2) in the present one-dimensional structure is well described by

\[ f = \frac{c}{d} - \frac{cq}{2\pi} \]  

(8.1)

yielding a value for d at the intercept \( q = 0 \). The fit of the above equation to the experimental data in Figure 8-4 leads to \( d = 168\text{nm} \) and \( d = 192\text{nm} \) for the 17\% and 30\% concentration solutions respectively. A further check is the crossing of these two lines with the acoustic phonon which should occur at \( q = \frac{\pi}{d} \), i.e. at the edge of the first Brillouin zone, as observed experimentally (arrows in Figure 8-4).

The "Bragg" mode is characteristic of the lamellar spacing, provides and accurate measurement of this spacing \( d \) in situ for each concentration by either the \( q = 0 \) limit or by the crossing point. In Chapter 7, data was presented from the study of BCP solutions of the same polymer used in this experiment. A clear relationship was established between the solvent volume fraction and wavelength of reflectivity in this system. This relationship was particularly accurate in the range of concentrations examined here and allows for the accurate calculation of the solvent volume fraction of each sample from the lamellar spacing determined as measured by the wavelength of reflectivity. This provides a second measurement of the lamellar spacing \( d \), independent of that obtained from the acoustic band crossing measurement.

The highest frequency mode (3) does not appreciably vary with \( q \). The presence of the \( q \)-independent phonon at the frequency between 7-8GHz can be attributed to a morphological mode with \( k \) almost parallel to the lamellar planes composed of two optically and mechanically different materials. (It is important to note that this mode is not expected in the 9\% solution because of the diffuse, weak fluctuations between the alternating phases.) To check the interpretation of the \( q \)-independent phonon, the phonon band structure of this medium is calculated following standard techniques.[109, 110, 111] The band diagrams for this material show three lower phonon modes, a longitudinal acoustic mode, a mode with "negative" dispersion\(^1\) sim-

\(^1\)Negative dispersion in the Bragg mode results from the transfer of dispersion outside the first Brillouin zone
Figure 8-4: The phonon dispersion relations for the ordered SI-toluene samples. The open circles and squares are for the 17% and 30% SI solutions and the lines represents linear fits to the acoustic phonons. The solid circles and squares are for the optic like mode for the 17% and 30% SI solutions. The "Bragg" mode (see text) is denoted by solid triangles 17% and solid inverted triangles 30%. The solid lines are computed from the dispersion relation for the lamellar spacings 168nm and 192nm, and show the acoustic, "Bragg" and optic like phonons. The arrows on the horizontal axis indicate the edges of the first Brillouin zone in the two ordered SI solutions.
ilar to the "Bragg" mode and an optic like mode. In the limit of small elastic contrast between the layers, the frequencies of the allowed phonon modes can be estimated by plotting the uniform solution \( \omega = c|\mathbf{k}| \) where \(|\mathbf{k}| = k_x \hat{x} + k_y \hat{y} + k_z \hat{z}\) in the so called repeated zone scheme, i.e. by replacing \( k_x \) with \( k_x - G \), where \( G = \frac{2m \pi}{a} (n = 0, 1, 2, 3 \ldots) \).

The relevant system parameters to complete the theoretical calculations are the density, longitudinal phase velocity and the thickness of the S and I layers. The total lamellar repeat is extracted from the "Bragg" mode (2) in Figure 8-4 and the fractional lamellar thickness can reliably be taken to be that of the bulk block copolymer, i.e. 0.45 for the styrene layer, because toluene is a non-preferential solvent for the two component blocks as mentioned above.[112] The acoustic measure of the lamellar spacing confirms the polymer concentration in the solution obtained from the optical measurements. To obtain accurate estimates of the sound velocity in the S and I layers and further calculate the effective \( c \) in the average medium, Brillouin scattering measurements were performed to obtain the velocity of sound for a polystyrene solution (PS with 63kg/mole) and a polyisoprene solution (PI with 10.5kg/mole) in toluene over the whole concentration range.\(^2\) It was found that the commonly assumed ideal mixing for the compressibility \( M^{-1} \) (where \( M = \rho c^2 \) is the modulus and \( \rho \) is the density) overestimates \( M \) for both solutions.\(^3\) The measured phase velocities at GHz frequencies for the I and S layers are: for the 17% SI, \( c_I = 1390 \text{ m/s} \), \( c_S = 1400 \text{ m/s} \) and for the 30%SI ordered solution, \( c_I = 1410 \text{ m/s} \), \( c_S = 1450 \text{ m/s} \). Hence, the calculated effective \( c \) amounts to \( 1395 \text{ m/s} \) and \( 1430 \text{ m/s} \) for the 17% and 30% SI solutions, respectively. While the acoustic phonon in the 17% SI solution is in excellent agreement (\( c = 1380 \text{ m/s} \) in Figure 8-4) with the calculated \( c \) value, the latter is about 5% larger than the experimental value (\( c = 1360 \text{ m/s} \) in Figure 8-4). The observed softening of the acoustic phonon for the 30% SI solution might be due to relaxation times in the polymer system slowing to the time scale of the frequency of the phonon, possibly

\(^2\) At these molecular weights, roughly twice the entanglement molecular weight for each polymer type, both homopolymers have reached molecular weight independent glass transition temperatures and hence, \( c \) values

\(^3\) Experimentally, \( \frac{M_{\text{toluene}}}{M_{\text{PS,toluene}}} = 1 - 0.52 \phi \) for volume fraction \( 0 < \phi < 0.3 \) and \( \frac{M_{\text{toluene}}}{M_{\text{PI,toluene}}} = 1 - 0.57 \phi \) for \( 0 < \phi < 0.6 \) where \( M_{\text{toluene}} = 1.59 \times 10^6 \text{ dyn/cm}^2 \). Note that \( M_{\text{PS}} = 5.5 \times 10^6 \text{ dyn/cm}^2 \) and \( M_{\text{PI}} = 4.6 \times 10^6 \text{ dyn/cm}^2 \) for the bulk homopolymers. The experimental errors amount to 1%
causing less hardening with the increased concentration than expected.

As mentioned above, the low mechanical mismatch of the present one dimensional multilayers allows for the use of uniform dispersion \( \omega = c|k| \) with the replacement \( k_z \rightarrow k_z - G \),

\[
\omega = c\sqrt{(G - k_z)^2 + k_{xy}^2}
\]  

(8.2)

where \( k_z = q \sin \alpha \) and \( k_{xy} = q \cos \alpha \) and alpha is the angle between q and the lamellar surface (see Figure 8-2). Both the acoustic mode (1) \( \omega = cq \) (for \( G = 0 \)), and the "Bragg" mode (2) \( \omega = c(G - q) \) (see eq. 1 for \( G = \frac{2\pi}{d} \)), with "negative" dispersion[110] as observed in this system, are obtained for \( \alpha = 90^\circ \). For \( \alpha = 0 \), a third mode is obtained with weak dispersion beginning at \( \omega = cG = \frac{2\pi}{cd} \). This is the optic like phonon calculated in the band diagram and observed in the BCP system (3). This mode is localized in the z-direction within the layered structure present in the system. The predicted phonon mode, predominantly parallel to the lamellar planes, can be fitted to the observed optic like phonon by adjusting the angle alpha. Using the physical parameters calculated above in the model and fitting alpha, yields for the 17% concentration, a matching phonon frequency at \( \alpha = 15^\circ \), and for the 30% concentration, at \( \alpha = 26^\circ \). The moderate sensitivity of the optic like mode to the cell rotation as compared to the "Bragg" mode can result from the larger probability of finding q's parallel to the lamellar surfaces. In fact, the low alpha indicates that there is a preferential orientation of the grains along the axis of the cell rotation. The predicted optic-like mode in this BCP dispersion relation can be brought into agreement with the observed q-independent Brillouin peak observed for both concentrations.

### 8.5 Conclusion

The observed good theoretical description of the experimental dispersion relation shows that the rich phonon spectrum of layered structures can be a sensitive probe of the micromechanical properties and geometrical characteristics of ordered soft materials. Brillouin light scattering allows a direct and accurate access to the dispersion...
sion characteristics of wave propagation in mesoscopic structures as compared to the complementary inelastic X-ray scattering at shorter wavelengths and hence higher frequencies[113]. The wealth of the observed dispersion relations and consequently of the phonon group velocity opens-up a possibility of controlling the directionality of the phonon based energy flow in the light scattering geometry. This material can be studied as an active optical medium, as well, interactions between light fields mediated by stimulated Brillouin scattering. The dual nature of these materials creates a new class of periodic media with commensurate photonic and phononic band gaps.
Chapter 9

Summary and Future Work

9.1 Progress Toward a Block Copolymer Photonics Platform

It is clear that significant steps have been taken in the application of self-assembling block copolymer systems to the fabrication of photonic crystals. One dimensional systems, lamellar alternating layered media, were fabricated at length scales sufficient to interact with light. A range of spacings, and thus wavelengths of reflectivity, were achieved by employing blending and solution processing for tuning the spacing to a desired application. Both increases and decreases in the spacing of specified amounts were demonstrated showing the control possible over block copolymer ordered morphologies. Applications unique to these systems were also explored in the form of elastochromic materials. Furthermore, an interesting new page in the photonics album has been turned by combining the study of these optical systems with the commensurate phononic measurements in search of new and interesting interactions.

These are the beginnings of a vein of research which is poised to produce interesting and new scientific results as well as applications which take advantage of the unique traits of BCP systems. Work on the dielectric enhancement of block copolymer materials by the selective incorporation of high index [30] and metallic particles [31] into selected domains is underway. Rudimentary progress in the application of
high dielectric modifiers to photonic block copolymer systems were demonstrated in Fink et al.[114] Dielectric enhancement techniques promise to improve the photonic properties of these systems by widening the band gaps and increasing the reflectivity of films. This tactic generates a material which can be fabricated from a homogeneous solution, resulting in a high index contrast photonic material, from a single step process. The alternative strategy outlined in Chapter 6, involving the removal of one phase and backfilling it with high index material, is particularly suited to the bicontinuous morphologies. It allows for the complete replacement of one phase of the structure with a high index material, unlike additive filler techniques. This procedure has the greatest possibility for the fabrication of a material with an absolute band gap. Both strategies are being actively explored, each for its unique benefits.

9.2 Selective Positioning of Luminescent Species

In addition, an effort to pursue the selective positioning of optically active molecules and atomic species is underway. This provides the potential to generate arrays of site isolated, optically active, fluorescent or phosphorescent, atomic species within a photonic block copolymer matrix, an achievement uniquely suited to BCP systems. Nonlinear properties and efficient coherent emission or amplification are potential properties of such a system. Star polymer molecules with fluorescent rare earth metals at the center have been synthesized[34] and materials made available. The molecules are schematically shown in Figure 9-1.

As mentioned in Chapter 3 the block junctions are located at the IMDS of ordered diblock morphologies. As the luminescent groups in these polymer molecules can be selectively located at the block junction, it would be possible to place them specifically at the IMDS of the copolymer morphology into which the star molecules were placed. This is shown schematically in Figure 9-2. In addition it would be possible to alternatively place the luminescent centers elsewhere in the molecular architecture, thereby locating the fluorescent molecule selectively within the morphology.

The classical morphologies locate junctions at surfaces defined by the morphology,
Mixed Homopolymer Arms or Copolymer Arms

Figure 9-1: Schematic representation of the polymer architecture of a multiarm star with the possibility of mixed homopolymer arms and block copolymer arms. The metal center of the star molecule can be one of a variety including erbium, europium, ytterbium and ruthenium.
Figure 9-2: Metal centered star copolymer molecules of two varieties present in as part of a blend with diblock copolymers represented figuratively. The metal centers can be located at the IMDS defined by the morphology, or more precisely located. It may also be possible to position them within the domain in the case of copolymer arms. The drawing is rather imaginative, however, as it would require 100% bridging of the copolymer, this scenario is likely only realizable in a ter-block system.

but more complex multi component star molecules, such as that presented in Sioula et al.[35], locate junctions on lines and other architectures potentially locate them on a lattice in space. This property of ter- and tetra- block copolymers can be used to position the block junctions and therefore the luminescent centers precisely on a lattice, creating a new class of optical materials. This potential, as yet to be realized, is being actively explored by a collaboration with the research group of Dr. C. Fraser at the University of Virginia. The novel synthesis of these optically active molecules, along with work on large spacing copolymers, and novel detection techniques, notably Scanning Transmission Electron Microscopy (STEM) capable of resolving the distributions of single rare earth atoms in a BCP matrix and Near-field Scanning Optical Microscopy (NSOM),[115] provide a concerted experimental effort, sure to produce interesting new results.

It is also possible to chemically modify polymer species with luminescent dyes. Two possible strategies involve end modification and, for a higher concentration of dye, side group modification. These dye decorated homopolymers and copolymers
could then be used to fabricate photonic materials as primary or blended components. The simple inclusion of dye-functionalized polymers of only one species, selectively positions the dye in one domain. Furthermore, as was discussed in Chapter 3, the selective positioning of blended-in homopolymer at the domain center, sharpens the distribution. Research in this area has focused on the incorporation of efficient two-photon dyes, exhibiting two-photon absorption at wavelengths of 800nm and emissions in the 400-500nm range. This work is being pursued in collaboration with the research group of Dr. P. Prasad at the University at Buffalo. The selective incorporation of two photon dyes, and their positioning within a photonic copolymer morphology can provide combined benefits. The dye can be made to lie only in the high index domain, where the 800nm light will have an intensity enhancement as it propagates through the material. The effect will provide a field enhancement in the same domain as has been chosen for selectively locating the dye, and yield an increase in the two photon excitation cross section, since this depends on the square of the field amplitude. This is presented schematically in Figure 9-3. The emission properties of the dye can be modified as well by selectively tuning the photonic matrix to provide emission enhancement for the desired wavelength. This promises to provide media for efficient up-conversion or doubling of laser radiation for technological applications, as well as, provide unique experimental systems for examining low threshold lasing.

The exploration of self assembled structures for photonic properties will continue, inspired by the possibility of creating a complete photonic band gap in a morphology such as the gyroid, or by harnessing the properties of the connected diamond morphology. Morphologies yet to be engineered may provide still further ground for application in photonics.

9.3 Expanding the Palette of Available Materials

There are specific important areas which should be addressed immediately, as well. The diversity of polymer systems in which photonic properties have been demonstrated is limited. Work presented in previous chapters is exclusively in PS-PI di-
Power Distribution of $\lambda$ Excitation

Block Copolymer Blend Morphology

Dye Concentration Maximum

Figure 9-3: A figurative representation of the cooperative properties of the positioning of the dye by blending and the enhancement of the local field intensity of the excitation radiation by the photonic matrix. The upper part of the drawing represents the enhancement of the excitation wavelength, depicting the intensity maxima at alternating domain centers. The lower part of the drawing shows the corresponding block copolymer morphology and the likely dye distribution within it as the result of incorporation of a dye labelled homopolymer. Note that the stop band of the morphology would correspond to the emission of the dye, approximately half of the wavelength of the two photon excitation wavelength.
block copolymer systems. The results have been qualitatively repeated in PS-PMMA with gains in the thermal stability of the polymer but no significant new phenomena observed. Two copolymer systems of three components does not accurately reflect the broad variety of properties presently available to workers in this area. New polymer classes such as liquid crystal copolymers [33] and the use rigid rod species as blocks [76] can be used to create still larger spacings and access a broader range of wavelengths. Broadly different solubilities could be exploited to increase spacings via selective solvents. System solubilities could be changed, such as experimenting with a water soluble polymers, to access new applications. Synthetic procedures beyond new polymerization processes and monomers, can be exploited to incorporate functionality directly into the copolymer photonic material. These changes in the self assembling systems can be combined with new processing techniques in order to improve the optical characteristics of copolymer photonic materials in applications as well as create novel optical materials. Indeed, the coalescence of these research thrusts may fully realize the potential of self assembly in creating an applied optical material.

9.3.1 Brillouin Cooling in Photonic Crystals

One final note relating to the acoustic properties of these materials and the technological potential they may yield, is on the possibility of optically cooling solid materials through Brillouin scattering. As mentioned above, the fabrication of site isolated atomic metal species is being explored, among the candidates are ruthenium and ytterbium, two metal ions which are of interest in quantum information studies. An ordered array of these atoms could potentially yield some interesting coherent properties, as the interactions between adjacent atoms can be precisely tuned by adjusting the spacing through solvent or blending. Above all of this, however, is the fact that in order for researchers to possibly observe any sort of quantum coherence in this system, the coherence time must be long and this is often best achieved through low temperature. Brillouin scattering results shown in Chapter 8 present an interesting possibility. The resonant phonon is present for all scattering directions, as such if the
Figure 9-4: Schematic of optical cooling via Brillouin scattering. The incident light field is represented by the large arrow to the left. The initial, final, scattering and phonon wave vectors are indicated by $q_i, q_f, q_s$, and $q_O$ respectively. The enhancement of Brillouin scattering from a particular phonon mode can be accomplished by the use of a resonant structure. Selectively enhancing the anti-Stokes Brillouin events will lead to net energy transport out of the system and cooling.

blue shifted, higher energy, scattering events could be selectively enhanced, energy would be carried out of the system, thereby cooling it. This is schematically shown for a one dimensional resonant structure in Figure 9-4. The enhancement of this scattering could be achieved by the precise tuning of the photonic matrix as well. At its most basic level this technique may not be compatible with investigations of arrayed atomic properties, but it does represent a general strategy for the optical cooling of a patterned solid. This has only been achieved by the use of strong anti-Stokes phosphorescence from rare earth ions doped in exotic glasses. A general technique for solid optical cooling could extend the applicability of this technique and provide interesting scientific ramifications.
9.4 Conclusion

The summation of techniques and experience with block copolymers and photonic materials has yielded novel materials and properties not accessible to other systems. The exploitation of the advantages of this combination is incomplete, but the groundwork here presented shows progress toward the goal of a viable, technologically and scientifically relevant self-assembled photonic materials platform. Many tasks remain for those who take up this research but it is fertile ground for discovery.
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