MAGNETIC NANOPARTICLE FIELD DIRECTED SELF-ASSEMBLY: MAGNETIC FLUX LINE MAPPING AND BLOCK COPOLYMER DRIVEN ASSEMBLY

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MAGNETIC NANOPARTICLE FIELD DIRECTED SELF-ASSEMBLY: MAGNETIC
FLUX LINE MAPPING AND BLOCK COPOLYMER DRIVEN ASSEMBLY

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ABSTRACT

Directed self-assembly of nanomaterials via external fields is an attractive processing tool for industry as it is inherently inexpensive and flexible. The self-assembly of magnetic nanoparticles in particular has gained much recent interest for applications ranging from biomedical imaging and targeted cancer therapy to ferrofluid mechanical damping devices, that rely on the state of aggregation and alignment of the nanoparticles. We utilize an oil-water platform to directly observe directed self-assembly of magnetic nanoparticles that are field ordered into two-dimensional mesostructures through the fossilized liquid assembly method. Our system consisted of polymer-coated iron-oxide nanoparticles which were assembled at the interface between a crosslinkable hydrophobic monomer oil, and water through the use of external magnetic fields, and then cured with UV light. In this study, entire magnetic flux field lines in various geometrical configurations were successfully modeled and mapped out by the magnetic nanoparticles, both in-plane and in perpendicular orientations utilizing FLA.

As the microscopic behavior of magnetic nanoparticles is known through this first study, further work can then be conducted through the assembly of block copolymer/magnetic nanoparticle nanocomposites. The morphology of neat self-
assembled block copolymers have been extensively studied and it has been proven that the molecular weight, volume fraction of the components, and the degree of segment incompatibility are the three independent parameters used to determine equilibrium morphologies. The assembled orientations of lamellar and cylindrical morphologies in particular develop specific directionalities depending on the natural interactions of the blocks with the substrate and surface. It has been shown that treatments such as UV-Ozone treatment of the substrate, mechanical shear, or electrical fields can force this directionality to be altered, however few methods have been developed to readily alter preferential morphologies through the use of magnetic fields. In order to provide preliminary results toward the validity of a magnetically driven reorientation process, systems of polystyrene-b-poly(methylmethacrylate) with varying molecular weights were loaded with up to 1% polystyrene coated cobalt nanoparticles. This study successfully showed that the particles can be loaded into the block copolymers without disrupting the morphology of the block copolymers, and also provided initial results that this method is plausible.
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Self-assembly is a key processing tool in industry as it allows for structural complexities to be built within a system in much fewer steps as compared to a serial fabrication process. This self-assembly terminology has been readily used to describe processes including non-covalent association of organic molecules in solution, the growth of semiconductor quantum dots on solid substrates (1) and it is readily used to describe the morphologies that develop in block copolymer systems. Self-assembly can also be directed through the use of external forces such as via applied shear or electric fields, and in particular in this research, magnetic fields. For example, the assembly of ferrimagnetic nanoparticles has been directed through the use of magnetic fields into two-dimensional arrays using a bottom-up methodology (2). The assembly of these magnetic nanoparticles is of interest as novel nanocomposite materials can be created, such as organic polymers hybridized with inorganic colloids used to obtain synergistic properties (3). It has been shown recently that ferrimagnetic colloids of Co and Fe have been assembled into chains when cast onto surfaces (4) (5) (6). While the chains provide
some indication that they align with the magnetic field lines, a detailed study to show the overall mapping of alignment and response in terms of chain length formation of ferrimagnetic nanoparticle assemblies within magnetic fields has not been performed to date. This detailed information about nanoparticle interactions could then lead to further composites in which the behaviors of the magnetic nanoparticles are known.

The use of nanoparticles has gained great interest recently in that these materials can generate unique size-dependent properties that vary from those seen in the bulk. These distinctive properties fluctuate depending on the individual materials, however a few examples include: improved mechanical properties, enhanced optical clarity, and superparamagnetism in magnetic particles (7). These properties essentially stem from the fact that the surface area of these small particles is a much higher percentage than when the material is in the bulk form. So, for the case of nanoparticles, contribution from the small bulk inside of the material is much smaller than the contribution from the surface.

Magnetic nanoparticles in particular have entered the spotlight with their ability to impart magnetic properties into many host materials. Magnetic particles such as magnetite have been used in medical internal applications since the 10th century A.D. by the Egyptian physician and philosopher Avicenna (8). These particles offer unique advantages over other nanomaterials as they are inexpensive to produce, physically and chemically stable, biocompatible, and environmentally safe (9). These properties lead to magnetic nanoparticles potentially being used in magnetic resonance imaging (9)
As discussed earlier, self-assembly is a name that has been given to materials in many different fields, and is readily used to describe any process where the thermodynamics/kinetics of a system ultimately determine the final ordered state of that system (if given adequate time). So, just as magnetic nanoparticles assemble naturally due to their inherent dipole interactions and attraction, much more macroscopic self-assembly can occur in a class of materials known as block copolymers. Block copolymers consist of two or more polymeric chains (blocks) which are chemically different and covalently attached to each other (17). This material is then driven to segregate into a variety of ordered structures due to the net repulsion of the immiscible blocks, similar to how immiscible homopolymers respond (17). The final thermodynamically stable microdomain pattern that develops in the bulk state is governed by the positive mixing enthalpy and low entropy of the component segments (18). As the covalent bond forbids macroscopic phase separation, the copolymer attempts to minimize interfacial energy by developing patterns with constant interfacial curvature and stretched interfacial chain configurations (19) (20). Though elaborate configurations of polymers can be created, the simplest and most extensively studied configuration is the coil-coil diblock copolymer where the molecular weight, volume fraction of the components, and the degree of segment incompatibility (expressed by the Flory-Huggins parameter, $\chi$) are the three independent parameters used to determine thermostable morphologies (21) (22).
Block copolymer development started with the discovery of termination-free anionic polymerization (21). This made the sequential addition of monomers to various carbanion-terminated (“living”) linear polymer chains possible (21). Since then much research has been put into these materials in order to harness the uniqueness and potential of these materials into applications. They currently are in commercial products such as upholstery foam, adhesive tape, and asphalt additives (23), and can be used in applications as broad as colloidal stabilization, medical implantation, microelectronic fabrication (23), fuel cells, batteries, optoelectronic devices (17), and nanolithography (18). Many of these applications stem from the rapid development of nanotechnology and nanoscience that have pushed the scale limits on modern functional devices (24). Moore observed this process occurring in the field of electronics where he predicted an exponential increase in the number of transistors per integrated circuit, where a doubling of the number of transistors per circuit occurred every two years (25). These devices are traditionally constructed using top-down lithography to pattern these elaborate structures. Many top-down production processes are currently being used to drive this miniaturization such as conventional 193nm immersion lithography, extreme ultraviolet lithography, X-ray lithography, soft lithography, and step-and-flash lithography (18). While these methods and further new “direct write” approaches are continuing to shrink length scales, there are always obstacles to beat in order to enhance resolutions while the cost of such lithographic production tools become huge and/or they could have lengthy writing times (18). A table summarizing the typical lithography top-down methods can be seen here (26):
The downfall of the classic top-down assembly process is exactly where the bottom-up self-assembly process excels. In particular with block copolymers, domain sizes ranging from 5-100 nm can be developed with good long range order for a fraction of the cost of traditional nanolithography methods. In addition to the block copolymer applications listed earlier, this bottom-up process could lead to applications in stimuli-sensitive materials (27), patterning photonic structures (28), and magnetic nanodots for addressable media (29) (30). A diagram comparing top-down and bottom-up assembly methods can be seen here (31):

<table>
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<th>Technique</th>
<th>Minimum resolution (nm)</th>
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<th>Nature of patterns</th>
<th>Intrinsic limitations</th>
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<td>UV photo lithography</td>
<td>250</td>
<td>248 nm KrF excimer laser</td>
<td>2D</td>
<td>Diffraction depth of focus</td>
<td>Easy replication</td>
</tr>
<tr>
<td>X-ray lithography</td>
<td>25</td>
<td>Soft X-ray with near 1nm</td>
<td>2D</td>
<td>Diffraction depth of focus</td>
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<tr>
<td>Interference Lithography</td>
<td>&gt;100</td>
<td>Holographic interactions between two or more lasers</td>
<td>2D, 3D</td>
<td>Diffraction depth of focus limited patterns</td>
<td>No mask easy replication</td>
</tr>
<tr>
<td>Zone plate array</td>
<td>&gt;100</td>
<td>Focused zone plates X-ray beam</td>
<td>2D</td>
<td>Zone plate fabrication</td>
<td>No mask</td>
</tr>
<tr>
<td>Near-field scanning</td>
<td>~100</td>
<td>UV or VIS laser with fiber optic probe</td>
<td>2D</td>
<td>Serial patterning</td>
<td>No diffraction limit</td>
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<td>optical lithography</td>
<td>~50</td>
<td>Focused ion beam</td>
<td>2D</td>
<td>Electrostatic interactions serial writing small field writing</td>
<td>Writing pattern</td>
</tr>
<tr>
<td>Focused ion beam</td>
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<td>High resolution large area printing relatively low cost</td>
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**Figure 1: Methods for top-down lithography**
As shown, both methods result in topographically patterned substrates, but each method has its benefits. The traditional top-down method has been discussed; however, the block copolymer method also can have its required conditions. For this method to work for lithography or for other various applications, the microdomains must be oriented perpendicular to the substrate\(^\text{(32)}\) \((33)\) \((34)\) \((35)\) \((36)\) \((37)\) \((38)\). This problem has been studied for decades and it has been shown that the morphology orientation can be controlled in a wide array of methods including surface treatments/effects, thickness control, solvent effects, mechanical alignment, electrical field alignment, and magnetic field alignment. A short summary of some of these studies can be seen here \((18)\):
These methods will be discussed in detail later. Another requirement of block copolymers for these applications is that they must be able to be easily deposited onto a substrate into a thin film (also to be discussed later). Finally then, the block copolymer must have the functional ability (specified properties, ability to be etched, etc.) in order to provide the desired result.
Polymer nanocomposites are nothing new to the commercial or academic world (e.g. tires, plastic bags, paint, etc.), yet the introduction of functional nanoparticles which have unique electric, optical, catalytic, and magnetic properties provide future opportunities in vast technologies including solar cells, photonic bandgap materials, high-density magnetic storage devices (39) (40) (41), spin-dependent electron transport devices (42), and therapeutic or diagnostic medical functions (43) (44). Yet, for these applications, the nanoparticles must assemble in a controlled fashion with nanoscale precision and selectivity (45). Block copolymers naturally are attractive then to form the continuous phase for polymer nanocomposites as they can control and guide the location of the nanoparticles into a selected domain (46) (47) (21) (48) (49) (50) (51) (52). Guiding the particles can be difficult, especially if secondary interactions are occurring between the particles, but methods have been developed to attract the particles to the desired phases such as using materials that naturally attract each other (magnetic nanoparticles with PVP (53)) or by grafting ligands of the desired assembly phase onto the nanoparticles (magnetic nanoparticles with PMMA grafted ligands to assemble in the PMMA phase (45)). These methods have been successfully researched, however at times these particles can interrupt the block copolymer by altering the domain sizes (39).

While many studies have been completed showing the assembly of nanoparticles into the self-ordered block copolymer, only recently has a single researcher published research on nanoparticles ordering the morphology of the block copolymers. That is precisely where this research will focus. Initial studies by Benkoski et al. were able to
show that magnetic nanoparticles could assemble to form macroscopic lines when under the influence of a magnetic field using a method known as fossilized liquid assembly (3). Other researchers were also able to show similar findings with other systems, yet these studies merely showed this process was possible. The first part of this study will then be to research the response of magnetic nanoparticles to an applied magnetic field. This study will fully map out the magnetic flux field lines with the magnetic nanoparticles and with this information the agglomeration/sedimentation process can also be discovered. In order to achieve this goal, 25 nm iron oxide nanoparticles with oleic acid ligands (to prevent agglomeration) will be put into the fossilized liquid assembly system under the influence of a magnetic field to observe the response of the particles to various orientations/field strengths. The physics of this process responded as expected and modeling of the system proved accurate too. With the understanding of the magnetic nanoparticle assembly process in a magnetic field, these particles will then be used to extend this research into the driven ordering of block copolymers. The use of many different processes has been shown to successfully effect the orientation of block copolymer systems such as mechanical shear, surface patterning, and electric fields, but the use of magnetic fields has been limited to very specific systems such as liquid crystals and crystalline materials. In addition to being a new method of driving orientation, this system has the potential to order thick films as the only potential limiting factor of this system is magnetic field strength and assembly time. The system for this study will consist of poly(styrene-block-methacrylate) (PS-b-PMMA) with 27 nm cobalt particles having 5k molecular weight polystyrene
ligands attached. PS-b-PMMA was chosen as it is a material of interest from an applications standpoint (38). In particular, polystyrene (PS) and poly(methylnmethacrylate) (PMMA) have significantly different photodegradation properties. PMMA is known to be a negative photoresist, so ultraviolet light or electron beam irradiation will degrade the material through chain scission (54), which allows for nanolithography to be employed on a successfully treated film. With the success of this study, other materials will be able to employ similar conditions to get the same results, but this is a starting point. The other benefit of PS-b-PMMA is that the orientations of the cylindrical domains on a silicon substrate typically form parallel to the surface (37). Therefore, with the correct conditions of magnetic nanoparticle concentration and magnet orientation/strength, the cylinders could potentially then be switched to perpendicular. In order to begin this work, this study will prove the ability of these particles to be loaded into a system without destroying the natural morphology of the block copolymer system. This will be done on many different PS-b-PMMA molecular weights and morphologies including: lamellar, cylindrical, and spherical. A similar study to this has been proven by Stafford et al., however the system employed by them lacks the attractive ligands we use and also the particles are approximately 5 times larger than ours (55). These larger particles have the potential to disrupt the long range order of the system more than small particles and makes reversal of the process very difficult.
Chapter II

MAGNETIC NANOPARTICLE FLUX FIELD MAPPING

ABSTRACT

Directed self-assembly of nanomaterials via external fields is an attractive processing tool for industry as it is inherently inexpensive and flexible. Direct observations of this process are however challenging due to the nano and meso length scales involved. The self-assembly of magnetic nanoparticles in particular has gained much recent interest for applications ranging from biomedical imaging and targeted cancer therapy to ferrofluid mechanical damping devices, that rely on the state of aggregation and alignment of the nanoparticles. We utilize in this study an oil-water platform to directly observe directed self-assembly of magnetic nanoparticles that are field ordered into two-dimensional mesostructures through the fossilized liquid assembly (FLA) method. Our system consisted of polymer-coated iron-oxide nanoparticles (25 nm) which were assembled in the vicinity of the interface between a
crosslinkable hydrophobic monomer (UV-polymerizable) oil, and water through the use of external magnetic fields, and then cured with UV light. This flash curing system effectively provides a snapshot of the assembly process and allows for direct visualization of assemblies through the use of both atomic force and optical microscopy. In this study, entire magnetic flux field lines in various geometrical configurations were successfully modeled and mapped out by the FLA magnetic nanoparticles, both in-plane and in perpendicular orientations. The assemblies showed strong directional selectivity and alignment with the flux field lines and provided evidence of strong dipole interactions which partially caused aggregate sedimentation.

BACKGROUND

Purpose/Motivation

To enable a fundamental understanding of directed assemblies of magnetic nanoparticles in an unperturbed environment, we present a full study on mapping of magnetic flux lines in polymerizable media through the use of iron-oxide nanoparticles using a fossilized liquid assembly process directed by neodymium magnets. Benkoski et al. have shown in previous studies that the fossilized liquid assembly process can allow the self-assembly of nanoparticles to occur, and subsequently freeze their positions for
real space imaging purposes (3) (56) (57). This method is advantageous as it allows for atomic force microscopy or optical microscopy to be used. Benkoski et al. used multiple nanoparticles to show the general applicability of freezing in nanoparticle structures through their intrinsic self-assembly process with minimal perturbation, including poly(methyl methacrylate) latex spheres, nonpolar polystyrene latex spheres, gold nanocrystals, dipolar CdTe quantum dots, magnetite nanoparticles, and Co nanoparticles (3) (56) (57). This method has proven to be quite robust as it allows for many variations in the experiments including: particle type, particle concentration, assembly time, and in the case of this study, magnetic field strength/orientation.

This study builds upon the work completed by Benkoski et al., with the goal of mapping out entire magnetic flux fields. Through experimentation, this study will also allow for the agglomeration and sedimentation of the magnetic nanoparticles to be explored. These two phenomena are not easy to predict and have not extensively been studied experimentally or in theory. In a typical system with magnetic particles within a magnetic field, the magnetic field gradients will eventually draw the magnetic material towards the locations with the greatest magnetic flux density. The only factor preventing this process is the repulsive forces from neighboring agglomerations. Therefore, the fossilized liquid assembly method will be used with an aqueous phase and an oil-like acrylate (DDMA) as the photopolymerizable oil phase in order to create a system to freeze the agglomerations at specified assembly times. Ferrimagnetic iron oxide particles will be dissolved into the DDMA phase, and magnetic fields will be put through the sample at different orientations and strengths to see the overall affect on
the particles. In this study it is important to realize the large number of competing effects in the system including: particle drive to the interface, particle-particle attraction, particle flux line interactions, and sedimentation effects to name a few, some of which are time-dependent phenomena.

Fossilized Liquid Assembly

The “Fossilized Liquid Assembly” (FLA) methodology allows direct monitoring of the self-assembly process, particularly, of imaging small, delicate, and highly mobile structures in a liquid medium (56). This method allows for imaging nanoparticles with varying assembly conditions including particle concentration, temperature, applied fields, and film dimensions/confinement. This method was developed by Benkoski et al. as a method to visualize submicrometer aggregates while minimizing the perturbation to the assembly process for the creation of nanoscale assemblies in two dimensions (57). The system consists of an oil-water environment, in which the basis of the method is centered on the high interfacial tension that exists between the two materials. This high interfacial tension provides a driving force for almost any nanoparticle to the interface between the materials in order to reduce this interfacial tension. Once at this interface, the particles are free to self assemble as desired to equilibrium conditions as they are free to lateral mobility. In the case of this system, the “oil” phase is in fact a photocurable monomer which allows a “snapshot” of the 2-D assembly to be taken at
the instant of UV exposure (57). Similar strategies have been developed using fluid/fluid interfaces for self assembly through the fixation of nanoparticles aggregates such as solvent casting onto solid substrates (58) (59) (60) (61), direct particle binding (62), and by gelation of the aqueous phase (63) (64) (65). The FLA method however is the first example of irreversible fixation performed through the oil phase (57). A diagram of the FLA method is shown here:

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Figure 4: Schematic of self-assembly using FLA system. (a) Nanoparticles are initially dispersed in oil (DDMA) phase and put into the aqueous phase. (b) The particles are given time to segregate to the interface (c) The assembly is "fossilized" by crosslinking the DDMA with UV light. (d) The solidified sample is removed from the water, dried, and can be imaged (56)
As seen in Figure 4, many steps go into the FLA method. Glass slides were first functionalized with 3-methacryloxypropyltrimethoxysilane (MPTMS) in order to promote wetting and adhesion with the oil phase. A thin (~100μm) oil phase, which is essentially a hydrophobic photocurable monomer known as 1,12-dodecanediol dimethacrylate (DDMA) was mixed with 2 wt % Irgacure 819 (bis(2,4,6,trimethylbenzoyl)-phenylphosphineoxide) and then cured on top of the layer of MPTMS using UV light. The reasoning for this step was so that the oil phase, when immersed in the aqueous phase, would be on the top surface of the glass slide. This was done due to the fact that glass strongly absorbs UV radiation (57), so it is much more beneficial for the nanoparticle loaded oil phase to be on the upper surface of the glass. This layer provided self-wetting so that the next filled oil phase would stick to the glass slide. If these steps were not completed the oil phase would easily dewet and rise to the water surface as the oil phase has a lower density and has a three phase contact angle (57). As mentioned, the nanoparticle filled oil-phase then can be put onto the glass slide and inserted into the aqueous phase.

An important aspect of the FLA process is that the curing of the oil phase essentially locks in a specific instant in time of the assembly process to be observed using experimental techniques such as optical microscope, AFM, etc. Yet, this benefit greatly relies on the minimization of the perturbation of the particle aggregation process and also a rapid polymerization of the oil phase. Benkoski et al. were able to prove the DDMA viscosity increases initially from 15 mPa·s as it smoothly transitions to the gel point where the viscosity becomes effectively infinite (57). This process takes
less than 1 second, however a nanoparticle in reality can diffuse over a large distance during that time frame. Making use of the Einstein relation (66), the average distance, $x$, that a particle diffuses in time, $t$, can be found as:

$$x = \frac{k_B T \gamma}{6 \pi \eta a}$$

Where $k_B$ is Boltzmann’s constant, $T$ is the temperature, $\eta$ is the viscosity, and $a$ is the particle radius (57). Essentially then, as an example, with the viscosity of water being 0.89 mPa·s, and the viscosity of the oil phase being 15 mPa·s, the particle will move between 1 and 5 $\mu$m for a 10 nm particle during curing (57). The problem with this calculation is that the equation above assumes that the viscosity remains the same for that 1 second, when in reality the viscosity of the DDMA phase is much higher during most of that period. Ignoring diffusion related distortion of the final aggregate, local curing hotspots, lateral heterogeneities during gel formation, convective currents, and the Marangoni effect, a global uniform increase in viscosity should not affect the final structures (57). With this type of curing, the polymerization typically starts at the surface and propagates downward from the exposed surface, thereby creating a network of solidification through the unpolymerized medium (67). Essentially then an experiment assembly time can be described as the time starting when the oil phase
comes into contact with the water and ends after the predetermined allowed assembly time when the UV light illuminates the sample.

Particle Assembly Physics

The basis behind the FLA method is that a high interfacial tension exists between oil and water that can localize the particles, allowing them to assemble in principle in “2D”. In order to utilize this property, an aqueous phase and an oil-like (hydrophobic) photo-curable monomer phase are used in the fossilized liquid assembly system (FLA). The interfacial tension between these two phases at 25°C is on the order of 15 mJ/m² (56). In a study by Y. Lin et al. in 2004, it was shown that nanoparticles in a system similar to this FLA system were driven to the interface in order to reduce this interfacial tension (68). Lin was able to use an argument by Pieranski (68) in order to determine the change in interfacial energy when a single particle arrives at the oil-water interface (68):

\[ \Delta E = - \frac{\pi R^2}{\gamma_{o/w}} \left( \gamma_{o/w} - \gamma_{p/w} + \gamma_{p/o} \right)^2 \]
Where $\gamma_{O/W}$ is the contribution from the interfacial energy between the oil and water, $\gamma_{P/W}$ is the interfacial energy between the particle and the water, and $\gamma_{P/O}$ is the interfacial energy between the particle and the oil.

It has been shown by Benkoski et al. (3) and Il Tae Kim et al. (69) that magnetic nanoparticles can form chains at such oil/water interfaces that align parallel to an in-plane applied magnetic flux field. When put into a magnetic field, ferrimagnetic nanoparticles (such as iron-oxide in this study) respond by creating an induced magnetic field $[H_{\text{part}}]^1$ as a function of position, $r$, in the system, mostly concentrated in the vicinity of the nanoparticle (70). A study by F. Wittbracht showed that the following dipole expression describes this magnetic field (70):

$$H_{\text{part}}^1(r) = \frac{1}{4\pi} \left( \frac{3\langle m_{\text{part}}^1, r \rangle r}{|r|^5} - \frac{m_{\text{part}}^1}{|r|^3} \right)$$

Where $m_{\text{part}}^1, r$ and $m_{\text{part}}^1$ refer to the spatially induced magnetization of the particle (part). With this expression defined, the attractive force between two magnetic nanoparticles can be defined as follows (70):

$$F_{\text{mag}}^{21} = \mu_0 (m_{\text{part}}^2 \cdot \nabla) H_{\text{part}}^1$$
Where $\mu_0$ is the permeability of the vacuum. This attraction though has a strong directionality as the particles again attempt to decrease the free energy of the system by aligning parallel to the flux field lines. In a study by Y. Sahoo et al., it was found with a magnetic nanoparticle system that there are many competing effects as to the assembly of the particles including: each particle's dipole moment to the flux field, magnetic dipole-dipole interactions, electronic polarization interactions (such as Van de Waals and Helmholtz dipole layer), thermal kinetics, the media in which the particles are in, and the ambient conditions (71). Currently, there does not exist an accurate theory that includes all of these factors (71). Sahoo et al. describe that assembly occurs at two levels. The ensemble level where there is a distribution of cluster orientations, and the cluster level where there is orientation of nanoparticles within each cluster (71). Overall then, focusing on the ensemble level, the direction of orientation of each cluster couples with an effective field ($H_{\text{eff}}$), which is the superposition of the dominant induced field, and the local mean field (71). This mean field occurs because of the polarization and orientation of the nearby clusters. The orientation of the particles in the effective field is related to the magnetostatic energy by (71) (72):

$$E_s = \frac{1}{2} M^2 N_c V + \frac{1}{2} (N_a - N_c) M^2 V sin^2(\theta) - H_{\text{eff}} MV \cos(\varphi)$$
Where $\theta$ is the angle between the magnetization vector and the easy axis, $\varphi$ is the angle between the effective field and the easy axis, $N_a$ is the demagnetization factor along the short axis, a, and $N_c$ is the demagnetization factor along the long axis, c. Therefore, in this equation it can be seen that the magnetostatic energy will be at a minimum when the cluster is aligned parallel (lengthwise) with the effective field. The overall orientation will be slightly influenced by the dipole-dipole interactions of two neighboring particles. They ideally would prefer to align head-to-tail with their easy axis along the applied field (3) (71). When this is not possible, a slightly staggered orientation is likely in order to minimize the magnetostatic energy (71).

In 2008 Benkoski et al. ran a similar study with the FLA system and they were able to determine the influence of various variables on the assembly process. The first finding was on the concentration of nanoparticles. They found that an increase in the concentration causes an increase in the number of chains per area, the contour length of the chains, and the probability of defects (56). They described that for magnetic nanoparticles, the number and lengths of the chains increases due to the dipolar particles self-assembling into chains, which are dominated by highly directional interactions (56). As the chains grow though, attractive Van der Waals interactions begin influencing the particles, and they begin to collapse into globular structures that fall out of the interface by sedimentation. This idea will be further described later. The next effect was temperature. An increase in temperature resulted in a decreased fluid viscosity, which then leads to an increase in the particle mobility. So, an increase in temperature increases the rate at which the chains assemble and an increase in the rate
at which the chains collapse (56). Time was also described in their study, and as expected by the concentration and temperature result, a longer assembly time results in longer agglomerated chains which end up collapsing out of solution (56). The assembly time does greatly influence the final structure of the nanoparticles though, as particles can only diffuse so far in a short period of time. As explained earlier, the determining equation of the average distance a particle can travel, $x$, is:

$$x = \sqrt{\frac{k_B T y}{6\pi \eta a}}$$

So, for example, a 19 nm particle in this system can diffuse an average of 15 μm in a 5 minute time period (3).

As previously mentioned, the ferrimagnetic particles within this system have many competing factors for assembly. They are driven to the interface in order to reduce interfacial tension, they are attracted to each other by dipole-dipole interactions, and they are aligned within the magnetic field in order to reduce the magnetostatic energy. This is all being done in solution, so that there is a critical point where these particles agglomerate enough that they can form clusters and fall out of solution (sedimentation). The collapse of a chain into a cluster can contribute to or accelerate the sedimentation process of a chain, primarily because the perimeter of the
iron oxide agglomeration is reduced. This clustering phenomenon was modeled by Zubarev and Iskakova, and they were able to determine a general relationship between field strength, interparticle attractions, and the number of particles needed for chain collapse to occur (73). In order to prevent the adherence of ferrimagnetic particles, typically a stabilizing layer made of surfactant molecules with a thickness of 2 nm is applied to the particles (74). This process helps to reduce the interparticle interactions so that only magnetic dipole and steric forces act between the particles, yet this cannot completely prevent agglomeration (73). The authors define $n_c$ as the number of particles needed to collapse a chain into a globule, $\varepsilon$ is the dimensionless energy of magnetic interaction between two contacting particles, and $k_0$ is the dimensionless magnetic field in the chain location (73). They were able to show that above a certain $n$, the chain will collapse into a globule as the free energy is negative. As an example, for a certain system with $\varepsilon=9-10$, the $n_c$ is found to be 50-70 particles in a zero field (73). This critical $n$ value then increases with increasing field strength, and decreases with increasing $\varepsilon$. It was also found that $n_c$ is very sensitive to the interfacial tension ($\sigma$), and that they are related to each other by $n_c \sim \sigma^3$ (73). The interfacial tension interestingly also affects the driving force of the particles to the interface, as described earlier. It was found in a study by Ten Wolde et al. that the actual value of $n_c$ for a system with $\varepsilon$ approximately equal to 9 is 90 (75). This shows a satisfactory correspondence between the simulation and the experimental study. It is important to realize that Zubarev’s study helped to determine the collapsing of a chain into a globule, whereas in this study sedimentation can be observed where agglomerates grown in length and width, causing
the assemblies to sink from the interface. Benkoski et al. observed the partial submergence of nanoparticles when their size was increased from 15nm to 25nm (56).

EXPERIMENTAL PROCEDURE

Materials and Instrumentation

DDMA (Dodecane-diol-dimethacrylate) (Sigma Aldrich), Irgacure 819 (bis(2,4,6-trimethylbenzoyl)phenylphosphine oxide) (Ciba Specialty Chemicals), HEPES (N-(2-hydroxyethyl)piperazine-N’-2-ethanesulfonic acid) (Sigma Aldrich), and 25 nm Iron Oxide nanocrystals with oleic acid ligands in chloroform (Ocean Nanotech) were used as received. Neodymium magnets (1” diameter x 3” length) were ordered from K&J Magnetics (Jamison, PA).

Sample Preparation

Glass slides were first pre-treated in order to promote good wetting and adhesion between the DDMA and the glass slide. The slides were initially put into a solution of 270 ml Acetone, 30 ml water, and 1.5 ml MPTMS. The pH of this solution
was then lowered to 4 by the addition of hydrochloric acid. This solution sat for 1 hour, and then glass slides were treated for 10 minutes in the solution. The slides were then immediately put into a 100°C oven for 1 hour and were washed with soap upon cooling to remove excess silane. Once dry, a layer of solution made with DDMA and Irgacure 819 (2% weight) was coated on the slide and cured with a UV-lamp (3835 μW/cm²). Through this process, the MPTMS treatment functionalized the surface, which is then wet by the DDMA. The purpose of this pre-treatment, as shown in Figure 4 is to prevent the oil phase from rising to the water-air interface, where oxygen in the air would scavenge the radicals in this reaction during UV curing. Ideally, the UV lamp would cure the surface containing the nanoparticles first, to immediately freeze their positions and prevent any further movement exactly at a specified time. It should be noted that the first layer of DDMA that wets the glass slide for the nanoparticle filled DDMA layer does not completely cure as the oxygen does have a chance to scavenge the free radicals in this situation. However, a thin layer should successfully be deposited and the excess is simply wiped off.

The oil-phase of the experiment consists of DDMA, Irgacure 819, and the desired concentration of iron-oxide nanoparticles. The typical weight percentages used were 2 wt. % Irgacure 819 in order to promote fast crosslinking, and 0.05 wt. % iron-oxide. This percentage of iron-oxide was decided upon through work by Benkoski et al. (3) and through experimentation. The pristine iron-oxide solution was sonicated 30 minutes before experimentation to ensure as well dispersed an initial distribution of iron-oxide particles as feasible.
The aqueous phase was made of a solution of 250 ml water, 0.6 g HEPES (which acts as a buffer), and 1.46 g NaCl which helps to prevent the oil phase from agglomerating and rising to the surface. This solution was buffered to a pH of 8 with sodium hydroxide. The interfacial tension between the oil DDMA phase and this aqueous phase is \( \sim 15 \text{mJ/m}^2 \) at 25°C (3) (56) (57).

The DDMA phase containing the iron oxide nanoparticles was then drop cast onto the treated glass slide and was placed into a petri dish filled with the aqueous solution (Figure 4). At this time, magnets (field strength varied by position) were placed at specified positions at the edges of the dish in order to create flux field lines through the interface of the oil and water. Four different arrangements were studied in the project including: north-south in-plane, north-north in-plane, north-south perpendicular, and north-north perpendicular.

The magnets were placed in their positions immediately so that an accurate assembly time could be measured. All of the samples were given 5 minutes to assemble and then were flash cured using a UV lamp. The curing time of this system was observed to be on the order of 1-2 seconds, which is similar to what was achieved by Benkoski et al with his system (3) (56) (57). As described earlier, at this small of a time scale, the particles may only diffuse short lengths, so it is likely that the assembly times that are reported are quite accurate. This diffusion length may even be exaggerated as there is a constant increase in viscosity as the crosslinking occurs, preventing much if any movement at all.
These prepared samples were then observed under a probing AFM and under an optical microscope. In work completed by Benkoski et al., nanoparticles aligned at the surface and images were easily captured using an AFM (3) (56) (57). In this experiments however, there was a competition between the agglomerated samples from settling to the bottom of the oil phase because of the large attractive forces and the drive of the particles to the interface. Due to this competition, not all of the assembly occurred at the surface. To counteract this and to get relevant images, a confocal microscope was utilized to scan multiple layers of the completed samples. These different layers were then superimposed onto one another to find the overall morphology of the assemblies at different points with different field strengths. ImageJ software was used to analyze these images. To verify the validity of the microscope images, the Maxwell simulation software (developed by Ansoft) was used to model visually with accurate dimensions and field strengths how the magnetic field lines align.

RESULTS AND DISCUSSION

Particle Interactions

Through the experiments described below, it was quite evident that competing particle effects from interparticle interactions, magnetic flux interactions, particle drive
to the interface, and particle sedimentation indeed did alter the overall DDMA/iron-oxide phase distribution. Upon scanning different time evolved samples with AFM, it was seen that as the agglomeration size of the particles increased, the particles began to sink into the DDMA phase. This result occurred directly because of the concentration of iron oxide particles used leading to particle density dependent aggregate formation. It is likely that a lower concentration would prevent the large aggregates from forming, thereby helping to keep the particles at the interface. The transition of this effect can be seen in the following AFM phase images:

Figure 5: Left: Iron-oxide concentration of 0.01% 1 micron AFM scan (5 minute assembly time), Middle-0.01% iron-oxide concentration 1 micron scan (30 minute assembly time), Right-0.05% Iron-oxide concentration 1 micron scan (5 minute assembly time)

Thus, as observed, at low concentrations (~0.01%) of iron-oxide nanoparticles, the particles align on the surface. As the chains get longer, the particles begin to sink into
the solution, and finally at 0.05% concentration few particles are on the DDMA surface. Following the work by Lin, the particles are driven to the interface in order to reduce interfacial tension (68). It can be seen between the left image and the middle image of Figure 5 that the size of the chains increases with a longer assembly time. As this occurs the force keeping the particles at the interface cannot overcome the gravity force, so the agglomerations sink. As the chains grow wider instead of longer (more globule like) the perimeter is decreased, which directly contributes to sedimentation. In the study by Benkoski et al. (3), many of the chains were present on the surface. However, in that study the ligands on their particles were much larger, thereby reducing the dipole-dipole interactions. As this interaction decreases, the number of particles needed to cause chain collapse increases (73).

The sedimentation of the agglomerations can be best described as a competition between the drive to the interface and the force of gravity. Each iron oxide particle has a perimeter of approximately 171 nm. Multiplying this value by the surface tension (15 mN/m) of the oil and water, the force holding the particle at the interface is approximately $2.57 \times 10^{-3}$ N. The weight of each particle can be calculated as $3.55 \times 10^{-16}$ grams. If half of the sphere is assumed to be in each of the fluids, taking buoyancy into account the effective weight is $2.89 \times 10^{-16}$ grams, which when multiplied by $9.8 \text{ m/s}^2$ gives the force of gravity pulling the particles/agglomerations away from the interface as $2.83 \times 10^{-18}$ N. As particles are added, the spheres turn into cylinders, which scales approximately linearly (minus the contact lines between particles). However, as the chains grow, they increase not only in length, but also width.
Therefore, while the weight continues to increase linearly, the perimeter growth is slowed. It is important to keep in mind in this argument that the surface tension is also constantly decreasing with the addition of particles as described early by Lin, which also decreases the number of particles needed to keep the particles at the interface.

Using the arguments set forth by Lin (68), the driving energetics to the interface can be calculated. The interfacial tension between the iron oxide-oleic acid nanoparticles and water can be estimated as 15.59 mJ/m$^2$ (76) and the interfacial tension between the iron oxide-oleic acid nanoparticles and the oil phase can be estimated as 2.5 mJ/m$^2$ (77). In this study, the radius of the iron-oxide particles with oleic acid ligands is 14.72 nm (as received). Therefore, the energy gain at the surface per particle coming to the interface is approximated as:

$$\Delta E = -\frac{\pi (14.72 \times 10^{-9} m)^2}{15 \text{mJ/m}^2} (15 \text{mJ/m}^2 - 15.59 \text{mJ/m}^2 + 2.5 \text{mJ/m}^2)^2$$

$$\Delta E \approx -1.2 k_B T$$

Thus, the interfacial energy drops $\sim$1.2$k_B$T per iron oxide particle driven to the interface.
In-Plane Magnetic Flux Experiments

The first completed configuration of magnets was placing the magnets in-plane with the DDMA/iron oxide solution with the attractive poles facing each other (north-south). The 25 nm iron-oxide particles were put into the DDMA/Irgacure solution at a concentration of 0.05% weight. They were given a 5 minute assembly time once the magnetic field was introduced into the system. Through the use of the Maxwell simulation software, the following figures describe the experimental design and the simulation prediction:

Figure 6: Experiment 1- North-south magnet in-plane configuration. Left- Experimental design. Right- Maxwell simulation of designed experiment (top view).

As seen in Figure 6, it is predicted that curved lines will be seen through the center region of the sample with a high concentration of particles by both of the poles. The
approximate field strength in the different positions that were studied is shown in Figure 7:

![Figure 7: North-South configuration field strengths (Gauss)](image)

The following 400X zoom confocal microscope images in their relative positions on a slide provide evidence that the magnetic nanoparticles accurately follow the relative trends in the applied magnetic field. It is important to realize in these images that the image is representative of a single 425 micron by 325 micron area on the overall 1.5” by 2” glass slide:
Figure 8: North-south in plane confocal microscope images (400X zoom)

Figure 9 overlays the simulation onto the images and it is quite evident that the iron oxide on average follows the field lines:

Figure 9: Simulation overlay of confocal microscope images (400X zoom)
It is important at this point to compare a sample prepared in a magnetic field to one prepared in the absence of one. The following figures represent an enlarged image of the middle of the image in Figure 9 and an image of a sample under the exact same conditions without the presence of magnetic field:

![Comparison of samples prepared in a magnetic field (left) and in the absence of a magnetic field (right)](image)

Figure 10: Comparison of samples prepared in a magnetic field (left) and in the absence of a magnetic field (right)

These images show that in the absence of the magnetic field, the iron-oxide particles have no overall orientation.

The images in Figure 9 were analyzed using ImageJ software to determine the average size (average number of pixels) of the agglomerations in each image. The following chart describes the results:
These results provide preliminary evidence that there is a direct relation between the magnetic field strength and the average area of the agglomerations.

To verify this observation a second test was conducted holding the magnets with the north poles facing each other. This repulsive configuration was completed in plane as in the north-south experiment. The simulation with the Maxwell software provided the following image:
This simulation makes it evident that there should be a “dead zone” in the middle of the sample and the rest of the sample should consist of curved lines diverging to avoid the center. In reality this middle of the sample is not completely void of any magnetic field, but rather is much weaker than in other positions as shown by the data collected with the magnetometer:
Figure 13: Magnetometer readings in relevant positions of a north-north magnet configuration (Gauss)

The images were again collected on the confocal microscope at 400X zoom using z-stacking to ensure all agglomerations were observed for accurate measurements. The resulting images are shown here in Figure 14:

Figure 14: North-North Configuration Confocal Microscope Images (400X)
Overlaying the Maxwell simulation for this system the following image is created:

![Image of North-North Configuration with Simulation Overlay](image)

**Figure 15: North-North Configuration with Simulation Overlay**

This sample was also observed under a 500X optical microscope too in order to get a more complete idea of the magnetic field lines:
Figure 16: 500X optical microscope images of north-north magnet configuration

Taking figure 17 and overlaying the simulation, it is evident once again that the simulation and the results match up accurately again:

Figure 17: North-north 500X optical microscope images with simulation overlay
The ImageJ software was again used on the confocal microscope images to determine the average area of the agglomerations in the different images. The results are shown in Figure 18:

![Figure 18: North-north magnet configuration magnet strength vs. average agglomeration area](image)

Figure 18 makes it evident again that there appears to be a direct relation between the magnetic field strength and the average agglomeration area. Combining the data from the north-north and the north-south configurations, Figure 19 is created:
This plot emphasizes the finding that the average agglomeration area is directly relatable to the magnetic field strength at that point. Interestingly, opposing findings were found by Sahoo et al. In their study, increasing the magnetic field strength caused a decrease in agglomeration size (71). However, the field strengths in their study were substantially larger than in this study. The largest strength in their study was 17 Teslas, whereas in the present study the largest was 2.2 Teslas.
Perpendicular Magnetic Flux Experiments

Taking the experiments in a different direction, the magnets were placed perpendicular to the sample in order to achieve alignment of magnetic nanoparticles through the thickness of the DDMA samples. The initial experiment was to hold the magnets in a north-south configuration above and below the sample. Everything in the experiment was held constant besides the magnet locations. A diagram and simulation of this experiment is shown here:

![Diagram of magnet configuration](image)

**Figure 20:** Left-Prediction of particle alignment through sample, Middle-Experiment design, Right- Simulation of north-south configuration perpendicular to sample

An important aspect to notice is the fact that the field lines are vertical going through the middle of the sample, yet they tend to curve as the radius increases. The resulting
images from the experiments from the confocal microscope after z-stacking at 400X zoom are shown here in their relevant positions:

Figure 21: North-south perpendicular magnet configuration under 400X confocal microscope

Notice in Figure 21 how the image in the middle essentially is dots which represents a vertical line of magnetic particles through the sample thickness. Due to the fact that this is a 2-D projection of the aggregates, the increased length in the outer images is a result of the increased tilt. This elongation represents a curved line of particles going
through the thickness of the sample which appear as a line when superimposed on the same plane.

The final completed experiment was then to arrange the magnets into a north-north configuration perpendicular to the sample surface. The design, prediction, and simulation are shown in Figure 22:

![Figure 22: Left-Prediction of agglomeration orientation in magnetic field top and side views, Middle- Design of experiment, Right- Simulation of magnetic field with magnets north-north perpendicular to sample](image)

This experiment relies heavily on where exactly the sample is between the two magnets. If the sample is close to the top magnet, there will be curved lines starting from the top going into the sample. If the sample is close to the bottom, the opposite will happen. If, however unlikely, the sample lies directly in between the magnets, there should once again be a “dead zone” where only small assemblies of magnetic nanoparticles are
made. In any case though, all of the particles should align in lines moving outward in a star fashion from the middle. The confocal microscope images (400X) of the sample are shown here:

![Confocal microscope images](image)

Figure 23: Confocal microscope images (400X) of north-north perpendicular magnet configuration

As predicted, the nanoparticle field lines move outward with the radius. It does appear from these images that the sample was slightly closer to the bottom magnet as the agglomeration lines curve upward as the microscope focused up through the sample.
CONCLUSIONS

We perform a complete 2D study of response, aggregation and alignment of magnetic nanoparticles to applied external fields, relevant to numerous technological applications such as biomedical applications in cancer therapy. Through the completion of this fundamental study, it has been found that magnetic flux field lines can be accurately modeled through software and can be mapped out using ferrimagnetic nanoparticles. It was found that there is a strong correlation between the magnetic field strength and the average agglomeration area of the magnetic particles. This strong attraction between particles however works to decrease the drive of the particles to the oil-water interface. Many competing forces were evident within this study, and a balance was made where the particles assembled within the DDMA phase, and not necessarily at the top or bottom surface. This assembly within the DDMA phase primarily occurred because of the competition between the drive of the particles to the interface to reduce the interfacial tension, and the gravity forces pulling the particles down. The agglomeration of the particles indeed led to accelerated sinking from the DDMA/water interface. This stems from the fact that as particles are added to the chains, the weight increases linearly. However, the perimeter scales differently depending on where the particles are added. If they are added on the ends, the perimeter also increases linearly (minus the small contact area between the particles). If the particles are added on the sides and ends, a prolated spheroid is produced, in
which the perimeter scales to the 1/3 power. This decrease in perimeter/increase in agglomeration’s weight reduces their ability to stay at the interface, and encourages sedimentation. Essentially then, the length of the chains should not matter for 1-D chains as the weight/volume and perimeter scale linearly with the number of particles. As agglomeration occurs though, this statement becomes inaccurate as the relationship between weight/volume and perimeter vary depending on their shape.
Motivation and Applications

Mixing, Alloying, and blending are all familiar terms used to describe the combination of two or more elements, compounds, or molecular species to form a single product (78). The purpose behind this is to get specific properties such as mechanical, chemical, or electrical through the incorporation of the best properties of the two components into one combination. However, the final properties of this system do not only depend on the materials themselves as the resulting phase behavior has a large influence on the properties too. While this idea classically has been used with steels or liquid surfactants, these property enhancements can also be obtained in polymer-polymer mixtures. A specific molecular architecture that can provide a vast
array of applications is a class known as block copolymers. As most polymers are inherently incompatible, stemming primarily from their entropic interactions, block copolymers provide one of the few routes to successful polymer blends. Not only can block copolymers make immiscible polymers miscible, they themselves can form macroscopic phase separated morphologies as seen here (78):

Figure 24: Representative polymer-polymer phase behaviors that can be realized with different molecular architectures. Macrophase separation (A) results when thermodynamically incompatible linear homopolymers are mixed. The covalent bond between blocks in a diblock copolymer leads to microphase segregation (C). A mixed architecture of linear homopolymers and the corresponding diblock copolymer produces a surfactant-like stabilized intermediate-scale phase separation (B). (78)
Block copolymer films are of particular interest for their compatibility capability and also because of the possibility of obtaining two dimensional patterns with very high registry and regularity (79). In bulk form, they can be used in applications ranging from drug delivery systems to structural materials (79). With many applications though, and in particular in this study, thin films of these materials are used which can provide vastly different properties than the bulk material. These films for example, allow for nanolithography to be completed to create nano-scaled templates for other applications. These applications include microelectronics, electrolyte layers for batteries/fuel cells, nanocapacitors (80) and the synthesis of conducting polymers (79). Other areas that block copolymers naturally fit into include photonic band gaps (1,2, and 3D PBG) (81) (82) (83) (84) (85) (86) (87), metallodielectric PBG (88), and tunable PBG (89), nanostructured networks (nanoporous membranes (90)), nanocomposites (BCP semiconductors (91) (92) and nanoporous waveguides (93)), and electroplating (magnetic storage (38)).

The key to block copolymers is then to control the morphology and orientation of the microphase separated blocks to ensure they align/assemble into the most beneficial arrangement for the desired system. In this study and in many applications, a vertically oriented cylindrical morphology is desired (38). Many methods have been explored in order to control the morphology (which will be described in depth later) including surface treatments, solvent effects, mechanical shear, electrical field, and magnetic fields. A table summarizing many of these methods can be seen here (81):
These methods have been proven to work in their specified systems, however not all of them work for all polymer chemical compositions or film types. One technique that has not gained a high level of research yet is the use of magnetic fields to align block copolymers. Therefore, this study will use the knowledge and findings from Chapter 2 to help provide preliminary results which will work to promote the vertical orientation of cylindrical block copolymers.
Block copolymer introduction/morphology

Block copolymers are constructed of two or more dissimilar polymer segments that are covalently bonded together. The immiscibility of the different blocks induces microphase separation of the material into ordered structures on the length scale of 5-100 nm (21) (19) (94). It has even been shown in an extreme example that small influences such as a block copolymer of polystyrene-b-polystyrene(deuterated) will phase separate at sufficiently high molecular weights (23). The phase structure that develops from this immiscibility (for coil-coil flexible polymers) primarily then depends on the molecular weight of the polymers, the relative composition of each phase, and the Flory-Huggins interaction parameter, $\chi$ (94). This interaction parameter, $\chi$, is then inversely related to temperature, so there typically is an order-disorder transition (ODT) which corresponds to the loss of microphase separation and the development of a homogeneous mixture (94).

Block copolymers can be synthesized into diverse molecular architectures in order to enhance mechanical and rheological properties such as diblock, triblock, graft, and star copolymers (95). These variances in the structures can be seen here:
The most commonly studied architecture is the A-B diblock copolymer though. These materials have a set of typical morphologies that develop depending on the length, connectivity, and mutual interactions of the different blocks as the blocks stretch and create constant interfacial curvatures (96) (20). These common microphase separated domains are spheres, cylinders, lamella, and gyroid structures which can be seen here (23):

These structures fit in good agreement with Helfand’s theoretical predictions that will be discussed in a later section (23). As seen, the composition of the AB diblock controls
the geometry of the structures (22). For essentially symmetric blocks (f=1/2), a lamellar (L) phase occurs. As slightly more asymmetries arise, a complex bicontinuous states, called the gyroid (G) phase develops. This gyroid phase consists of two interweaving threefold-coordinated lattices (97) (98). Before this phase was discovered, it was commonly thought that a double-diamond (D) structure was in fact the equilibrium phase at this volume fraction (99) (100) (101) (102) (103) (104). This phase had two fourfold-coordinated lattices (105), but it was determined that this was simply a long lived metastable formation (106) (107). Another complex structure in this volume fraction region that occurs is known as perforated lamellar (PL) (108) (109) (104). It essentially appears as a lamellar phase in which hexagonal arrangement of passages form between the layers (108). This phase typically appears when strong surface or flow fields are induced during the sample preparation (110). An example of when this phase is seen is in a block copolymer of poly(ethylene-propylene)-b-poly(ethylethylene) at a molecular weight of 9.4 x 10^4 and 65% PEP by volume (108). A final complex phase then is the hexagonally modulated layer (HML) which consists of alternating minority and majority component layers in which the thickness of the minority component domains is modulated with hexagonal in-plane symmetry. Both the HML and PL phases were found to simply be metastable phases though as they both relax to the gyroid phase upon proper isothermal annealing (110) (111). The absence of the gyroid phase in some high molecular weight materials then can simply be thought to stem from kinetic limitations as it indeed is an equilibrium phase (110). As the asymmetries continue with altering volume fractions, the minority component forms hexagonally
packed cylinder (C), and then spheres (S) that pack into a body-centered cubic lattice (22). As the volume fractions terminate to 0, a disordered phase is created.

The phase transitions between different block copolymer morphologies stem from the volume fraction of the components, however taking this idea one step further, the allowed curvature of the molecules balances the degree of stretching between the two blocks (thereby giving the permissible architectures). This balance can be seen in the following figure showing the degree of curvature <H> required for the different morphologies:

Figure 28: Area-averaged mean curvature <H> as a function of the A-block volume fraction f for each of the structures shown schematically calculated using self-consistent mean-field theory. The stable and metastable states are shown with solid and dashed
lines, respectively, and transitions are denoted by dots. As the molecules become asymmetric, structures with more curvature are preferred. (22)

Essentially then, phase changes are a competition between elastic energy of bending the interfaces and energies resulting from the constraints of interfacial separation (112). As explained by Matsen and Bates, while the mean curvature of the blocks controls the sequence of phases, the standard deviation, $\sigma_H$, governs the phase selection (22). Thomas et al. have described that interfacial tension (109) is a dominating factor in block copolymers, so in order to maintain a constant mean curvature (112), the standard deviation of the mean curvature must be zero ($\sigma_H \sim 0$). Matsen and Bates then identified a second equally important factor, which is known as packing frustration (22). This idea was first demonstrated in a lipid-membrane forming system by Gruner (112) (113), but the mechanism was adopted into block copolymers (97) (114). The mechanism essentially is the tendency to form domains of uniform thickness so that none of the molecules are excessively stretched, which causes $\sigma_H$ to deviate from zero (22). This idea can easily be seen in the cylindrical phase as shown in Figure 29 where the domains must shift slightly to accommodate hexagonal packing and the constant stretching of the molecules (22):
Figure 29: Schematic representing the stretching of polymeric chains to maintain uniform interfacial thicknesses and uniform domain thicknesses

Block copolymer Thermodynamics

Predicting the existence of the different phases possible in block copolymers was initially introduced by a series of papers by Helfand and coworkers (115) (116) (117) (118). These phases were described using the mean field or self-consistent field theory (SCFT) that permitted the quantitative calculations of free energies, composition profiles, and chain conformations (21). When it was published in 1975 though, it was supplemented with approximations which greatly reduced its effectiveness (119). Two of the main approximations were narrow interface approximations (NIA) (115), and unit-cell approximation (116). With new advances being made in the SCFT (99), exact mean-
field calculations for complex ordered nanostructures have been made. In order to make these calculations though, categories had to be developed in order to determine the strength of the phase segregation. These categories were defined by the product of the Flory-Huggins interaction parameter and the total degree of polymerization, $\chi N$. The combination of these works established that the underlying physics controlling block copolymer phase behavior involves the competition between interfacial tension and the entropic penalty for stretching polymer coils so as to fill space uniformly \cite{22}.

Two major regimes were initially determined to classify block copolymer systems, weak and strong segregation limits. In the weak segregation limit (WSL), where $\chi N$ is much less than 10, a delicate balance between energetic and entropic factors exist \cite{21} \cite{20} \cite{120}. In this vicinity the A-B interactions are quite weak so the copolymers in general are unperturbed. This leads to a sinusoidal profile of the phases with gradual fluctuations in composition. The other classic regime is the strong segregation limit (SSL), where $\chi N$ is much greater than 10. In this area the interfaces are narrow with separate, well-defined, nearly pure A and B microdomains \cite{21} \cite{121} \cite{122}. The polymers in this region try to minimize the interfacial area, but have to do so being constrained by incompressibility and under the influence of an entropic penalty for extended chain configurations \cite{121} \cite{122}. Comparisons of these two compositional profiles on a 1-D plane is shown here showing the varying sharpness of the interfaces \cite{78}:
Figure 30: Evolution of structure with the combined parameter N for a symmetric, diblock copolymer with \( f = 0.5 \). When \( N \approx 10 \), small variations in the system entropy (\( \sim N^{-1} \)) or energy (\( \sim \chi \)) leads to ordered (\( \chi N > 10 \)) or disordered (\( \chi N < 10 \)) states. A homogeneous composition profile (\( \phi_a \) versus \( r \)) results when entropic factors dominate (\( \chi N < 10 \)), whereas a strongly microphase segregated pattern characterizes the limit where energetic factors prevail (\( \chi N >> 10 \)) (78).

So, with the segregation limits determined, the earlier approaches to the SCFT were able to correctly predict the classical phases of lamellar, cylinder, and spherical (20) (122). The more complex gyroid phase was not found initially until an intermediate segregation was studied (\( \chi N \approx 20 \)). In this intermediate range, the phase sequence was accurately modeled as \( L \rightarrow G \rightarrow C \rightarrow S \rightarrow \) disordered as the volume fraction progresses from .5 to zero or one (22).
The boundaries between weak, intermediate, and strong segregations have been frequently studied throughout literature. Using the SCFT, the crossover from weak to intermediate occurs at $\chi N \sim 10.495$, or using SST predictions it occurs at $\sim 12$ (119). The intermediate to strong segregation boundary occurs when the middle of each domain becomes essentially pure. Using SST predictions, this value occurs at $\chi N \sim 50$. The self consistent field theory develops the following phase diagram of block copolymers within the strong segregation limit regime ($\chi N \sim 120$ in this case):

Figure 31: Mean-field phase diagram for conformationally symmetric diblock melts. Phases are labeled L (lamellar), H (hexagonal cylinders), $Q_{ia3d}$ (bicontinuous $Ia3d$ cubic), $Q_{im3m}$ (bcc spheres), CPS (close-packed spheres), and DIS (disordered). Dashed lines denote extrapolated phase boundaries, and the dot denotes the mean-field critical point. (119)
As seen in this image, if $\chi N$ drops enough, the entropic factors will dominate leading to a compositionally disordered phase (21). The entropic and enthalpic contributions to the free energy density scale as $N^{-1}$ and $\chi$ respectively, so the product of $\chi N$ indeed dictates the block copolymer phase state (21).

Figure 31 represented the theoretical phase diagram for diblock copolymers in the SSL regime. However, in the weak segregation limit region, a different diagram can be constructed which takes into account the much weaker thermodynamic repulsions. This diagram slightly varies whether the mean-field theory of fluctuation theory is used (20) (120) (123):

![Theoretical phase diagrams for diblock copolymers in the weak segregation limit: (a) mean-field theory, (b) fluctuation theory with N=10^4 (21)](image)

Figure 32: Theoretical phase diagrams for diblock copolymers in the weak segregation limit: (a) mean-field theory, (b) fluctuation theory with N=10^4 (21)
Image a in this figure was developed by Leibler (20) which was created by only retaining the leading harmonics in a Fourier representation of the ordered-phase composition patterns near the order-disorder transition (20). Through this explanation, it must also be considered that these phase diagrams are in terms of $\chi N$, however the Flory-Huggins interaction parameter can be described as (78):

$$
\chi = \frac{3}{16 k_B T V^2} \frac{1}{z} (\alpha_A - \alpha_B)^2
$$

where $k_B$ is Boltzmann’s constant, $T$ is temperature, $z$ is the number of neighboring contacts, $V$ is volume, $\alpha_A$ is the polarizability of polymer A, and $\alpha_B$ is the polarizability of polymer B (78). The essential correlation in this previous equation though is $\chi \sim T^{-1}$. This relationship makes comparisons between temperature and phase possible, which helps to describe the order-disorder transition temperature. Also, it can be determined then that typically, mixing is promoted as the temperature rises.

This order-disorder transition (ODT) boundary is extremely important as it governs where phase separation occurs. Above the ODT the blocks are mixed due to a dominant entropic contribution. As the temperature decreases then, the enthalpic process of demixing of the blocks occurs. This demixing is accompanied by a reduction in the configurational entropy which originates from the localizing of block-block joints at interfaces and the stretching of the polymeric chains to maintain a uniform density.
This critical temperature can be calculated using the lamellar phase free energy. In a disordered phase, where the A and B blocks are homogeneously mixed, the free energy per chain can be approximated by the A-B contact energy alone (23):

\[
\frac{F_{\text{disorder}}}{k_B T} = \chi_{AB} f_A f_B N = \frac{\chi_{AB} N}{4}
\]

Which when solved for \(\chi_{AB} N\) is equal to 10.4 (for lamellar) (23). This is quite close for the mean-field estimate explained earlier as the transition from the WSL to the intermediate segregation limit as found by Ludwik Leibler of 10.5 (20). To put this into an example, a high molecular weight sample with strongly incompatible blocks will phase separate into lamellae above \(\chi_{AB} N = 10.4\). On the other hand, a smaller more compatible block copolymer will show no microphase separation (assuming \(\chi_{AB} N\) drops below 10.4). It is important to notice again that because temperature is inversely related to the Flory-Huggins interaction parameter, many polymers pass through this ODT.
Block Copolymer Experiment/Theory Correlation

The phase diagrams shown in Figures 31 and 32 show well defined, smooth boundaries with symmetry evident around a volume fraction of 0.5. In reality though, this diagram is far too simplistic to encompass the complexities of block copolymer systems. The following is experimental data showing the theoretical and experimental results of two block copolymer systems:
Figure 33: a) Theoretical equilibrium phase diagram of a diblock copolymer using SCFT (22) b) experimental equilibrium phase diagrams of a polystyrene-polyisoprene diblock copolymer. (107) (124)

As seen in work by Bates and Fredrickson, an asymmetry develops in the experimental phase diagram. This variation occurs for a number of reasons. It occurs partially in Figure 33 because styrene and isoprene monomers have different sizes and shapes, so $a_A \neq a_B$ (which was not included in the theoretical calculations) (23). Another aspect altering the experimental phase diagram is that many times a single Flory-Huggins interaction parameter does not accurately represent the system. For example, the free-
energy cost of moving a styrene monomer from pure styrene surroundings to pure isoprene surroundings is not the same as moving an isoprene monomer from pure isoprene to pure styrene (23).

Further images from other studies continue to prove the point that a universal phase diagram for all materials may not be possible:

Figure 34: Phase diagrams associated with three values of fluctuation parameter, $N$: (a) $N=27 \times 10^3$, (b) $N=3.4 \times 10^3$, (c) $N=1.1 \times 10^3$. (107)
The asymmetry again is due to conformational asymmetry, $\varepsilon$, and fluctuations, $\bar{N}$. Bates et al. describe that the only way to possibly get a perfectly microphase separated state that lacks spontaneous curvature is to have a perfectly symmetric molecule, where the composition is exactly .5 and the conformational symmetry is 1 (107).

A final phase diagram for a block copolymer of polyisoprene-b-polystyrene was determined by Khandpur et al. (124):

![Figure 35: $\chi N$ versus $f_{PI}$ diagram for PI-PS diblock copolymers. Open and filled circles represent the order-order and order-disorder transitions, respectively.](image)

As seen in this diagram, asymmetry occurs, but also long lived metastable morphologies are documented in the form of HPL. Khandpur et al. describe the asymmetry as arising from the finite molecular weight effects that were not taken into account with Leibler’s
mean-field predictions (20). Other sources for the variance between the experimental and theoretical phase diagrams include polydispersity and deficiencies in the Gaussian Model such as nonequilibrium effects and uncertainties in molecular effects (125). Overall though, the Gaussian model is successful in providing a significant understanding of block copolymer systems.

Block Copolymer Thin Films

Thin Film Behavior

Block copolymers have gained much research interest in the fabrication of nanostructures as they can form two dimensional patterns with high regularity while being based on bottom up assembly. However, as the films become thinner, new novel behaviors develop that are not found in the bulk (126). In bulk, the equilibrium phase behavior can be described essentially by the interfacial tension between the A and B rich phases, and the entropic stretching energies between the two blocks (127). In a thin film state however, the block copolymer nanodomain formation takes place relative to the surfaces of the film (79). Therefore, the exact orientation with regards to the substrate is controllable depending on the application. For example, cylinders lying parallel to the surface and lamellae standing perpendicular may each be of interest in
the patterning of nanowires (79). On the other hand, upright cylinders and spheres could be of interest for the patterning of hexagonal arrays for the use of data storage (79). While block copolymers easily form these morphologies, it is difficult to control the ordering on a global scale. Many different experimental techniques are available to determine the local and long range structure of polymer thin films (126) including optical (128), ion (129), and electron microscopy (130) (131), neutron (132), and X-ray scattering (129), and various scanning probe microscopies (133).

The typical methods for preparing such block copolymer thin films include dip coating (134), solution casting (135), and spin coating (136). Dip coating and solution casting are two processes that allow self assembly to occur during the casting process. After they are cast, the solvent evaporates slowly which allows for thermodynamic equilibrium to be reached, however the process is very slow. The more commonly used method (and the method being employed in this study) is spin coating. In this method, the polymer is dissolved into a volatile solvent that then is applied to a spinning solid substrate. As the solvent evaporates, the concentration of the solvent at the free surface decreases which leads to the ordering of the block copolymer. The polymer film spreads in this method by centrifugal forces, which leads to a film with low surface roughness as long as the evaporation rate is low. A high volatility solvent has the danger of flow instabilities which could lead to a rough sample (137). The roughness is often critical to the application of these films, as roughness impacts the optical, barrier, and frictional properties (137). The problem arises from solvent-rich films that do not have time to level and heal surface roughnesses created by Marangoni instabilities when the
solvent is rapidly evaporating (137). On the other hand, if the solvent evaporates slowly, Marangoni flow is not experienced and the resulting films are smooth. A basic diagram of the spin coating process is shown here (136):

Figure 36: Scheme of the spin coating process

The final film thickness in this processing technique depends on the spinning velocity, the concentration, the molecular weight of the polymer, the solvent volatility, and the PDI (136).

Many different substrates can be used with the spin coating process such as glass, mica, silicon wafers, salt substrates, or even other polymers. Silicon wafers are commonly used though due to their flatness and industrial importance. As stated previously though, the surfaces have a large effect on the orientation of the polymer morphology. As the solvent evaporates, the polymer becomes less and less mobile. Therefore, it is possible for an ordering front is developed on the air free surface and continues to the substrate (138). A schematic of this process is shown here:
Figure 37: Schematic of solvent evaporation in a diblock copolymer film where the diffusion creates a concentration gradient in the solvent $S$ as the depth $r$ increases resulting in an ordering front. (138)

This method is quite similar to the classical zone refinement which is used to produce large-scale single crystals (139) (140). Kim and Libera designated four zones in order to categorize the volatility and order of thin films on their cylinder forming polystyrene-b-polybutadiene-b- polystyrene triblock copolymer (141). The first zone is fast evaporation (~200 nL/s) and is symbolic for microphase-separated microstructure with no long-range order. The second is intermediate evaporation (~5 nL/s) and it generated hexagonally packed cylinders with the cylinder axis perpendicular to the film plane. The next zone is the slow evaporation regime (~1.5 nL/s) where duplex microstructures of PS cylinders form both vertical and in-plane. Finally the fourth zone, known as very slow
solvent evaporation (~0.2 nL/s), produces a fully in-plane cylinder microstructure. Therefore, as the solvent evaporates slower, the process changes from strictly an ordering front to a solvent annealing process. This method is commonly used by researchers as it is capable of creating consistent and reproducible samples.

As the thickness of the film is decreased, the influence of the interfaces at either film surface becomes more prominent and the surface wetting effects often determine the film properties and structure (142). Generally, the polymeric component with the lowest surface energy will segregate toward the surface (143) and the component with the lowest interfacial energy will be attracted to the substrate (144). It can be imagined then that in a cylindrical block copolymer system, if the matrix material favored the substrate, a parallel morphology would be created. This type of assembly is known as a surface field and is responsible for most parallel lamellar/cylindrical morphologies (145) (32). The surface selectivity blocks can be defined as $\epsilon = \epsilon_a - \epsilon_b$ where $\epsilon_a$ and $\epsilon_b$ represent the interaction energies of the A and B blocks with a surface respectively. A positive value for the surface selectivity indicates that the surface is selective for the B block and negative values for the A block. In both of these cases, the thin films are confined with asymmetric surface selectivity, where one of the blocks is preferred at an interface.

As an example, the orientation of lamellae can vary with the affinity of the different blocks to the interfaces. When both surfaces attract the same block, a film is formed with height equal to $nL_0$. When the two surfaces then attract different blocks, the films thickness initially equals $(n+.5) L_0$. Walton was able to predict that
perpendicular orientations can be stabilized in symmetrically (\( \varepsilon_a = \varepsilon_b \)) confined films where the thickness is incommensurate with the domain spacing (145). This perpendicular orientation works to relieve the unfavorable entropic interactions that are encountered from chain extension and compressions. This orientation is thermodynamically stable when the entropic gain in free energy is greater than the free energy cost of placing both blocks at the surface. If, however, the surface is neutral, then the free energy cost is the lowest and the perpendicular orientation is favored regardless of the thickness (32). An image showing the different possible lamellar morphologies are shown here:
Figure 38: Possible configurations of lamellae in block copolymer films confined at one surface for fixed film thicknesses and arbitrary film thicknesses.

Variances in this line of thought though do exist when other forces dominate (i.e. confinement) the surface force. For non-lamellar systems such as cylinders and sphere forming block copolymers (146) (147), similar behaviors are seen as lamellar. These asymmetric systems form islands and holes where the film thickness does not match the natural thickness given by \( h = \alpha n + \beta \), where \( \alpha \) is the sphere(or cylinder) layer-to-layer distance and \( \beta \) is the thickness of the brush adsorbed on the surfaces(if it exists) (79). As the thicknesses of these films vary then, a competition develops between surface selectivity and confinement. Knoll et al. were able to calculate and verify experimentally...
that a series of phase transitions occur for a cylindrical ABA triblock copolymer at well defined thicknesses (148). Their main findings are shown here (148):

Figure 39: Simulation and experimental data for a cylinder forming ABA triblock copolymer exhibiting a variety of structures based on film thickness (148)

As shown, as the film thicknesses increase the film varies from disorder, to perpendicular cylinder, parallel cylinder, perforated lamellar (a completed different metastable phase), perpendicular cylinder, perpendicular cylinders, and finally parallel cylinders again. Part d of this figure shows the simulation of this work which accurately portrays the phase transformation that occurs with varying film thickness.
Knoll et al. were also then able to simulate that a preference of one type of block at a surface is enough to induce considerable rearrangements near the surface. This idea is well represented in the following image that they produced (148):

![Figure 40: Phase diagram of surface reconstructions of an ABA triblock copolymer film with changing surface selectivities and film heights.](image)

As depicted in this image, for cylindrical morphologies a single thickness/surface selectivity can greatly alter not only the orientation of the sample, but also the morphology itself. This image also describes the idea that thicker films (when in cylindrical/lamellar morphology), greatly prefer a parallel morphology as the
perpendicular phase becomes increasingly more difficult to achieve the required conditions.

It is important to note that the films that are spin coated and imaged directly after casting are not necessarily in the equilibrium morphology. These block copolymers are under the influence of the solvent evaporating out rapidly and it is typical for further steps to be required in order to obtain oriented equilibrium morphologies. Regardless of the precautions taken during the film preparation, it can be difficult to obtain a well ordered morphology. In order to provide this opportunity, the block copolymer must be given additional time for ordering to occur, which can only be done by enhancing the mobility of the sample. This is typically done by two methods: thermal annealing or solvent annealing. This process will allow the films to reach equilibrium and will also eliminate defects in the system (as long as sufficient time is allowed). Thermal annealing is completed by heating the film above the glass transition (T_g) of both blocks and holding it there for a set time period. This allows the chains to become mobile and is driven enthalpically to increase ordering (78) (21). Thermal annealing also has the benefit of removing residual solvent from the system. This process normally is completed in an inert atmosphere or under vacuum to avoid chemical decomposition and to avoid film contamination. This process can run into difficulties with high molecular weight samples as the entangled chains greatly reduce the diffusion/mobility and rearrangement process (149). As an example, Yokoyama et al. found that a high molecular weight block copolymer of PS-b-PVP, even after annealing for 144 hours, was treated for an insufficient time to achieve ordering over a micrometer length scale
(which is far too long to industrial applications) (150). The alternative method then to thermal annealing is solvent annealing. In this method the block copolymer absorbs solvent that is introduced as a vapor to the sample, which then acts as a plasticizer to reduce the glass transition of both blocks below ambient temperature so that mobility is increased. The decision of which solvent to use can alter the final morphology of the system. For example, if one block favors the solvent vapor more, this phase will likely attempt to assemble on the open surface. This approach can lead to a significant time savings and therefore is used often in industrial applications. Cavicchi et al. were able to use this method to align poly(isoprene-b-lactide) cylinder forming block copolymers into nanostructured arrays of hexagonally packed cylinders (151) (152). The morphology of these samples greatly depends on the inputs of the system (temperature, vapor pressure, vapor extraction speed), so quantitative control is typically required on these samples to get reproducible results. It is possible then as films get thicker for the morphology to be completely different at the interface(s) than in the core of the sample due to the surface effects. This mixed morphology is important and characterization must be careful to not overlook this behavior.

Poly(styrene-block-methymethacrylate)

Poly(styrene-block-methymethacrylate) is a highly studied material that is made in an infinite number of different molecular weights. It is a material of interest from an
applications standpoint (37) (38), so it was natural to use it for this study. The basic structure of the materials is as follows:

![Figure 41: PS-b-PMMA structure](image)

It is important to understand the tendencies and properties of this material in the thin film structure before experimentation takes place. The surface tension of polystyrene is 40.7 mN/m and prefers to cover the free air surface of the films because of its lower surface energy (153) (154) (144). In reality, this affinity for PS to the surface is only slightly higher than PMMA, but in the temperature range for this research, PS will have the higher affinity (37). The PMMA then favors the silicon substrate because of the lower wetting energy (153) (154) (142) (144). This lower wetting energy stems from the polarity of the silicon. These interactions are very important in the ordering of PS-b-PMMA, as it was found by Anastasiadis et al. that for a 149 nm thick films, ~62% is comprised of the interface (144). With these inherent properties then, Karim et al. were able to map out the surface morphology diagram to determine at different
thicknesses/annealing conditions what the morphology would be for a specific sample casting method known as flow coating (37). This diagram takes into account surface forces as well as thickness effects:

![Diagram of experimental results showing correlation between annealing temperature and film thickness](image)

**Figure 42:** Plot representing experimental results of correlation between annealing temperature and film thickness

As seen, at 165°C for example, the cylinders can form perpendicular, mixed, or parallel morphology. The purpose of this study is to provide results to show that magnetically aligned particles could be used to help force parallel morphology to turn to perpendicular morphologies. This transformation into a perpendicular microdomain
orientation in thin films is desired (32) (33) (34) (35) (36) as this allows for the microdomain patterns to be used as templates and scaffolds for nanolithographic applications (155) (156). While flow coating will not be used in this study as spin coating studies will only be completed on the affect of magnetic nanoparticles on the PS-b-PMMA system, this diagram will provide for a great reference when further research is conducted.

Block Copolymer Morphology/Orientation Control

Electric Field

While many methods to control the morphological orientation of block copolymers exist including surface fields, solvent annealing, and mechanical shear, only the two methods that have a direct correlation with this project will be discussed in detail. Electric field and magnetic field block copolymer driven orientation are similar in many different aspects, so although electric fields will not be used in this study, direct comparisons can be made with their thermodynamic/kinetic effect on block copolymers. This comparison is important to do as studies based primarily on magnetic fields are lacking required detail. Electric field alignment of block copolymers is a widely studied method that has shown great success in not only the increased ordering of block
copolymers, but also in the ability to alter the alignment direction and even morphology of these materials. This method relies on the difference in the static dielectric constants between the two constituent polymers (157) (158) (159). It has been found that when an electric field is passed through a block copolymer that has this dielectric constant difference, cylindrical microdomains evolve parallel to the applied electric field (160) (161) (162) (163), and lamellar microdomains also orient parallel to the field (164) (158) (159) (165) (162) (166). Amundson et al. were able to describe this difference in terms of the Landau free energy in the system (159). Taking into account that microphase separation causes a spatial modulation of the local composition (thereby affecting the dielectric constants) that causes an increase in the free energy. The following figure represents the response of the energy in the system to the application of an electric field (159):
Figure 43: Landau free energy as a function of the amplitude for a given q. (a) is the case when the system is in the disordered state, (b) is just at the order-disorder transition, and (c) is in the ordered state. When the electric field is applied in the ordered state, the curve (c) changes the shape into that drawn with the broken line (167).

In this figure, curve (a) is representative of the system in the disordered state, the curve (b) is for the system just at the order-disorder transition, and (c) is for the system in the ordered state (167). All of the solid lines represent the system without any external field being applied. As the electric field is applied, the shape of curve (c) changes to the dashed line. This field, as seen in the figure, caused a shift in the two minima to slightly higher values, and also appears to have shifted the minima towards zero (159) (167). This field implies a shift in the order-disorder temperature, which essentially makes the ODT more accessible in the direction parallel to the applied field (167). Gunkel et al. found a similar result using $\chi N$. They found that the application of an external electric
field lowers \( (\chi N)_{ODT} \), which indicates that the electric field favors microphase separation (166). It was found through calculations then for example in a system of PS-b-PMMA, the application of a 400kV/cm electric field causes a decrease in ODT of 2.5K in the direction parallel to the field (166).

Experimental results demonstrating the success of the electric field alignment have been shown through various studies. Amundson et al. successfully showed that lamellar domains align parallel to a strong applied field (158) (168), and Russell et al. showed similar successes with cylindrical domains (165) in the mid-1990’s. The methodology behind this method is that two electrodes (one positive and one negative) are placed on two sides a block copolymer film. An electric field is then generated between them and the block copolymers alter their morphology because of this force. A basic diagram of this system is shown here (165):

![Diagram of an electrode layout with corresponding electric field lines.](image_url)

Figure 44: View of a typical electrode layout with the corresponding E field lines
Within the E field shown in this image, the system between the two dielectrics has its lowest energy when the interface is oriented parallel to this field (165). Images displaying this substantial difference in orientation are shown here by Russell et al. (165):

Figure 45: TEM micrographs of cylindrical-phase diblock copolymer films between the electrodes. (A) is a close up of the region halfway between the electrodes, showing a gradual transition from well-aligned cylinders (left) to random cylinder orientations (right). (B) and (C) are close ups of regions near one of the corners of an electrode with and without an E field, respectively
Image 53A shows in detail a TEM image of a block copolymer sample directly in a region being affected by an electrical field line (left) and the gradual transition to an unaligned behavior with decreasing electric field. Figure 53B and 53C then show the area directly near the corner of an electrode annealed in the presence of an applied E field, and without field respectively. This successful method was scaled-up by Russell et al. in 1998 to a sample of approximately 2 cm² in dimension (157).

Though these initial results showed block copolymers orienting parallel to electric field lines, studies have been completed in order to reverse this trend and orient block copolymers perpendicular (157) (165) to the E fields. For this type of alignment to occur, a deeper understanding must be described as to the effect of an E field on a block copolymer. The orientation of an anisotropic dielectric body in a dielectric media due to an external electric field, $E_0$, occurs because of a depolarization field, $E_p$, that is induced normal to the interface between two dielectric bodies (169) (170). The free energy is then minimized by orienting the dielectric body such that the torque at the interface is zero (170). Within an ordered block copolymer film then, there exists two free energy (per unit volume) minima: $F_\parallel$ and $F_\perp$, which correspond to the parallel and perpendicular orientations respectively (170) (168). The difference of these two values then is given by the following (as an example with poly(isoprene-b-styrene) (168) (162):

$$\Delta F_e = F_\parallel - F_\perp = -E_0^2 \varepsilon_0 \left(\varepsilon_p - \varepsilon_s\right)^2 \frac{2}{(\varepsilon_p + \varepsilon_s)}$$
In this equation, \( \varepsilon_0 \) is the permittivity in vacuum, \( \varepsilon_{PI} \) is the dielectric constant of polyisoprene (PI), and \( \varepsilon_{PS} \) is the dielectric constant of polystyrene (PS). With this equation developed, it can be shown then that when \( \Delta F_c < 0 \), the free-energy well for alignment parallel to the electric field is deeper than the transverse direction (169). Therefore, depending on the dielectric constants, the block copolymer can alter alignment directions when under the influence of an external E field. Elhadj et al. were able to prove this technique to be successful in their 2002 study (169). Their method to do this stemmed from using a second force to trap the system into a shallower minima where cylinders orient perpendicular to the electric field. This secondary factor was to induce a surface field where one of the phases had a higher affinity to the film interface, thereby creating an ordering front from within the material before the electric field was initiated. When the electric field was then activated, the alignment (started by the surface field) was enhanced from an ordered thickness of 500 nm to well over 2500 nm (169). The interfacial energy in E field alignment must be controlled then to avoid a mixed morphology within the sample. Xu et al. found that T junctions develop in block copolymer films where multiple mechanisms are attempting to order the films (171). They found that for complete alignment of symmetric blocks to occur, the interactions between the blocks and the substrate must be balanced (171).

The mechanism by which the alignment of block copolymers by E field is reversed (parallel to perpendicular) has been considered with in-situ studies.
DeRouchey et al. were able to monitor the small angle x-ray scattering measurements of a sample of PS-b-PI to see how the alignment progressed (172). They began with a sample that showed a weak scattering pattern that had lamellae oriented mostly parallel to the substrate surface. When the electric field was applied, just 30 seconds later, it was evident that the overall intensity of the measurements increased, leading to the evidence that stacks of the lamellae had begun to rotate into the direction of the applied field (172). As time progressed, the maxima disappeared in the SAXS measurements, and an isotropic ring appears which represents many small grains of lamellar microdomains oriented with the E field. The longer the field was then applied, a strong meridinal maxima was shown which represents the lamellae oriented perpendicular to the substrate (parallel to the applied field). When this field was removed, the peak intensity decreased within minutes, however the overall orientation was maintained (172). Interestingly then, when the field was subsequently applied again after this break, the orientation was seen to increase once again. This suggested that by cycling the electric field, the block copolymer can circumvent a kinetically trapped state to achieve a higher degree of alignment of the microdomains (172). The mechanism that drives this reversal was first introduced by Onuki et al. (173). They found that undulation instability occurs which leads eventually to a disruption of lamellae misaligned with respect to the electric field. Krausch and co-workers were then able to show that as further orientation develops in solution from a rotation process, intermediate orientations develop (174) (175). This indicates that partial disordering of the copolymer occurs during reorientation (172). This was concluded by
the signification disruption that the original copolymer grains undergo to reduce their size such that domain rotation can occur (172).

A limiting factor in the alignment of block copolymer films with electric fields is due to the large field strengths that must be developed in order to get good orientation. While the field strength needed to provide orientation varies depending on the materials being used (dielectric constants), there typically exists a threshold value of the field strength for alignment to occur. As an example, in order for PS-b-PMMA cylinders to switch the orientation from parallel to perpendicular to the substrate, a threshold field strength in the range of 60-70 kV/cm is needed. This was determined by looking at the average orientation function fitted with an S-shape curve function as seen here (169):

![Figure 46: Average orientation (f) as a function of applied E field. This indicates a threshold field of ~65 kV/cm (dashed line)](image)
For field strengths below this threshold value, \( f \) (average orientation function) is low, indication no orientation. However, when the field strength passes the threshold, the orientation function becomes close to 0.6 (169). In this plot, a saturation at a low value of \( f \approx 0.73 \) exists primarily because of dislocations and disclination defects within the sample (169). A sample then such as PS-b-PI required field strengths of \(~5\-10\) times larger than that required for PS-b-PMMA in order for the microdomains to orient (172). This value however is still below the critical field strength for dielectric breakdown of most polymers (159). As shown in the previous equation, the driving force for alignment is proportional to the square of the product of the electric field and the difference in the dielectric constants. Therefore, from tabulated values for dielectric constants (\( \varepsilon_{PI} = 2.81, \varepsilon_{PS} = 3, \varepsilon_{PMMA} = 5.25 \) as found at 170°C and 10 Hz), \( E_{PS-PI} \approx 12E_{PS-PMMA} \) (172).

As these field strengths get large then, they even have the ability to alter the morphology of the block copolymers. The beginning of this finding occurred when it was discovered that a spherical dielectric material can be deformed into an ellipsoid under the influence of an applied electric field (170). It was then theorized that it should be possible to deform spherical microdomains into ellipsoids, and, for a thin block copolymer with multiple layers of spheres, the ellipsoids can be sufficiently stretched to interconnect to form cylinders (176). This idea was proven to occur at an electric field strength of \(~40 \text{ V/\mu m} \) (176). This required electric field strength was much
lower than the theoretically predicted value of ~70 V/μm, but the difference can be attributed to lithium impurities within the materials from the anionic copolymerization process (176). Though the results did not provide great long range order providing alignment through the film, it was suggested that the microdomains could be improved through cycling on and off of the electric field.

Magnetic Field

The use of electric fields proves to be an extremely beneficial method of driving the orientation of block copolymers into a desired direction; however a crucial problem lies in this method: dielectric breakdown. Essentially as the field strength is inversely related to the distance between the two electrodes, this electric field method is limited to thin films where the electric field strength can be high enough. While this is a problem for electric fields as increasing the field strength too high can lead to dielectric breakdown of polymers, a magnetic field is only limited to the field strength that can be created. Therefore, for magnetic fields, the films do not need to be thin and the current maximum field strength that has been developed is around 35 Teslas (167).

Magnetic fields were first used to control the orientation of block copolymer films in 1998 when a 2.4 Tesla magnetic field was used to align a diblock copolymer comprising both chains of liquid-crystalline polymers (LCP) (167) (177). This type of
alignment works well with LCP as the mesogenic units can be easily aligned with magnetic fields, resulting in microdomain orientation (177). Soon after that Hamley et al. found that they were able to get similar results with LCP-amorphous type diblock copolymers (178). They found that if a 1.8 Tesla field was applied when the LCP made up the cylindrical domain, preferential orientation occurred. However, the magnetic field had to be increased to 9 Teslas in order for PS cylinders to be aligned within a LCP matrix (179). A second study by Hamley found that in reality, 5 Teslas was sufficient to get the PS cylinders to orient within a LCP matrix (180). This type of a material has applications in liquid-crystal displays, as it has been proven by Boamfa et al. that the alignment of a liquid crystal block copolymer is stable even after the field is switched off (181).

A second type of polymer that was found to align well with magnetic fields was crystalline polymers. Within these materials, it was found that the crystallites can be aligned with magnetic fields (182) (183) (184) (185). This occurs because of the anisotropy in the diamagnetic susceptibility of the crystalline lattice (as a consequence of the magnetic torque) (167). Not only have cylindrical domains proven to align by this manner, but lamellar crystalline structures have been oriented using poly-(ethylene oxide)-block-polybutadiene in a 7 Tesla system (186). This is a very specific case for polymers though, and a general method would be beneficial to use for the alignment of all block copolymers.
To this date, there has not been a case where a magnetic field has oriented the microdomains of an amorphous-amorphous type block copolymer without the influence of additives. The main reason that the dielectric difference works for electric field alignment and diamagnetic susceptibility doesn’t work for amorphous materials is that the spatial modulation of the magnetic permeability is trivial compared to the dielectric constants (167). Sakurai et al. attempted to add in small particles (iron-containing chelate compounds) which essentially dope one of the phases into obtaining magnetic properties. Their method consisted of dissolving the particles and block copolymer (polystyrene-block-polyethylenebutylene-block-polystyrene (SEBS)) into a selective solvent so that the molecules would be inhomogeneously distributed (187). This method allowed the particles to accumulate in a phase having a chemical affinity to the solvent. Although the particles did not necessarily have an attraction to either of the block copolymer phases, it would automatically accumulate in the phase having a higher chemical affinity to the solvent. Once the film was cast, the solvent was allowed to evaporate out, consequently leaving a doped phase. As cast, the film was a thermodynamically unstable non-equilibrium lamellar morphology, when the volume fraction should form a cylindrical phase. When the casting occurred then under a 12 Tesla magnetic field, the lamellar microdomains were found to align parallel with the substrate in a much more ordered fashion (187). The films were then annealed at 190°C under a 12 Tesla magnetic field and the film transformed into the equilibrium cylindrical morphology parallel with the magnetic field direction and parallel to the surface (187).
They also did find that the cylinders formed in the same manner without the chelate compounds, although the extent was lesser (187).

Sakurai took this same idea and tried to reorient block copolymer films perpendicular to the surface instead of parallel using the same method stated above (similar to how electric fields can switch the directionality of orientation). Unfortunately though, no homeotropic orientation of the cylinders by the guidance of the magnetic field was attained (167). In that study, it was determined that the effect of the substrate surface (or of the free surface) was a much larger effect to maintain the cylinder parallel orientation than the effect of the magnetic field. To try to overcome this problem, and to build on the knowledge gained from E field alignment that there is an electric threshold that must be passed for alignment to occur, a 30 Tesla magnetic field was applied to the film (167). This study was completed without the chelate compounds, but unfortunately only local reorientation occurred of the cylinders to the perpendicular direction (167). In this case they claim that it is likely that the films were still too thin to overcome the surface forces within the system, as the films were 20 nm to 300 nm thick. Although there was slight reorientation in these films, it is possible (and likely), that the change in ordered direction occurred because the thickness in the film was increasing and not necessarily because the magnetic field was making a larger contribution.

It is reasonable to consider that a similar effect is seen on the order-disorder temperature of a block copolymer film with and without the presence of a magnetic
field as was seen with the decreasing of the ODT with the electric fields. Sakurai takes an extension of the Clapeyron equation to describe the shift of the ODT due to the magnetic field as compared to a quiescent transition temperature (188):

$$\Delta T = \{(\cos^2 \theta - 1/3)\chi_A + (\langle \chi_S \rangle - \chi_i)B^2T_m/(2\mu_0\Delta H)\}$$

Where $T_m$ is the transition temperature in the absence of a magnetic field, $\theta$ is the orientation angle between the principal axis and the field direction, $\chi_A$ is the anisotropy in the diamagnetic susceptibility ($\chi_A = \chi_\parallel - \chi_\perp$), $\langle \chi_S \rangle$ is the average value of the diamagnetic susceptibility in the phase I, $\chi_i$ is the diamagnetic susceptibility in phase II, $B$ is the magnetic flux density, $\mu_0$ is the magnetic permeability of a vacuum, and $\Delta H$ is the enthalpy change associated with the transition. As an example, Sakurai determined through experimentation that a cylinder-forming deuterated polystyrene-block-polybutadiene block copolymer when put in the presence of a 10 Tesla magnetic field had the ODT temperature decrease by 0.15°C (167). The confidence in this solution is relatively low because of the error associated with the accuracy of the temperature control. However, this method still shows great promise since there is no concern about dielectric breakdown or mechanical breakdown, making the magnetic field alignment a very promising method.
Magnetic Nanoparticle/Block Copolymer Blends

Blends of magnetic nanoparticles and block copolymers has shown promise in various nanotechnologies including data storage media \(^{(189)}\) \(^{(190)}\), spin-dependent electron transport devices \(^{(42)}\), and therapeutic or diagnostic medical functions \(^{(43)}\) \(^{(44)}\). These applications however require a uniform distribution of the magnetic nanoparticles into stable single domains. With this goal in mind, many researchers have attempted to use block copolymers as roadmaps for the magnetic nanoparticles to follow by anchoring the particles to a single moiety \(^{(191)}\) \(^{(192)}\) \(^{(193)}\) \(^{(194)}\) \(^{(195)}\) \(^{(196)}\). This would allow for the block copolymer to self-assemble and order the nanoparticles into the microphases of the polymer. Similar methods to this have been conducted with noble nanoparticles \(^{(197)}\) \(^{(198)}\) \(^{(199)}\) \(^{(200)}\) \(^{(201)}\), semiconductor nanoparticles \(^{(202)}\) \(^{(203)}\) \(^{(204)}\), and quantum dots \(^{(205)}\) \(^{(206)}\). As these particles are beyond the scope of this research, only the magnetic nanoparticles will be discussed here.

Difficulties arise with magnetic nanoparticles that make the block copolymer ordering of them difficult. The main problem arises from the magnetic dipole-dipole interactions that exist within the particles. This leads to a poor dispersion of these particles in the copolymer. In addition, as the particles tend to aggregate, phase separation is possible from the polymer matrix that causes disordering of the block copolymer structure. Therefore, care must be taken to ensure the particles do not disrupt the polymer matrix by controlling the nanoparticles size, and the aggregation of
the particles. This can be controlled by using methods such as tethering polymer ligands to increase the minimum distance the particles can interact (and thereby reducing the particle-particle attraction). A secondary problem is that although the particles are intended to simply be ordered by the block copolymer, they have the ability to affect the morphology/orientation of the system. This idea was made clear through work by Composto et al. (45). Their study consisted of a lamellar PS-b-PMMA system doped with PMMA grafted iron oxide nanoparticles at percentages from 0-10%. Naturally, the system is oriented perpendicular to the surface, and turns to parallel as it is annealed to its equilibrium orientation. The addition of the iron oxide nanoparticles however greatly slows the morphological transition to the parallel morphology as seen in the following figure (45):

![Figure 47](image)

Figure 47: Area fraction of perpendicular lamella on the surface as a function of annealing time for 0.1% and 4 wt % of iron oxide nanoparticles. This represents the decreased rate of transition from perpendicular to parallel orientation.
This image shows that even at 1 wt% loading, the transition time is increased. They were also able to show that when the concentration approaches 10%, the nanoparticles aggregate enough to frustrate the assembly of a lamellar structure. As the molecular weight of this brush increases then, the block copolymer eventually begin assembling around the aggregates (45).

Two distinct methods of driving the magnetic nanoparticles to a specific phase are evident within the literature. The first widely used method is to attach ligands onto the magnetic nanoparticle that match the block that they are intended to assemble within. This method successfully works and was proven by Garcia et al. by testing the properties of the film before and after the addition of the particles (207). They were able to prove that while the morphology of the nanocomposite did not change, a different disposition of the lamella was observed. This was shown by an increase of the $T_g$ (stemming from the loss of mobility from the addition of the particles), and an increase in the PS domains from 32 nm to 40-47 nm (as shown by TM-AFM topography) where the nanoparticles segregated (207). This study successfully then showed that magnetic fields originated from the magnetic nanoparticles within the block copolymer. The method of attaching the polymer ligands was proven to work with polystyrene (207) and polymethymethacrylate (45). This approach, while efficient, does not allow high nanoparticle loading and large-area periodic nanostructures are difficult to achieve with
this method (208). Also, the highly grafted nanoparticles with polymer chains do not mix effectively with their linear counterparts (207).

A second method is to put a much shorter ligand onto the nanoparticles (such as oleic acid). This method allows for the blocks of the block copolymer to strongly interact directly with the nanoparticles. Müller-Buschbaum et al. were able to take iron oxide nanoparticles stabilized by oleic acid and selectively segregated them into the PMMA domain of PS-b-PMMA (209). This methodology works specifically well with block copolymer having the moiety of PVP. The PVP chain interacts with metal and metal oxide surfaces, leading magnetic nanoparticles with short ligands to assemble within that phase (208). With this method however, the agglomeration of the nanoparticles must be monitored. The level of agglomeration can be controlled (to an extent) by maintaining a safe ligand molecular weight. When the molecular weight is too high, the particles do not interact with the blocks as much, but when the molecular weight is too low, agglomeration can occur (208). The actual block that the particles are attracted to must be chosen carefully too. For example, iron oxide nanoparticles interact much more strongly with P4VP than with P2VP. This effect likely stems from steric factors and higher chemical interactions with the nitrogen group of the pyridine in P4VP (208).

It has been shown then that these methods work to assemble the magnetic nanoparticles within the block copolymer. However, what if the roles were reversed, and the nanoparticles assembled the block copolymer? This situation has been studied
by Laicer et al. In their study, gold nanorods (d=180nm l=3-6μm) successfully nucleated
the growth of micron-scale, cylindrical-phase domains in solutions of poly(styrene-block-
isoprene) in dibutylphthalate that were cooled below the order-disorder transition
temperature (210). The basic scheme used by Laicer et al. is shown here (211):

![Scheme 1](image)

**Figure 48**: Schematic representing the alignment of block copolymers based on the
orientation of surface attracted additives
Hammond et al. built upon this idea in terms of magnetic nanoparticles to direct the order of block copolymers (55). The system they used consisted of polystyrene-block-poly(2-vinylpyridine) and spindle type hematite (α-Fe₂O₃) particles. These particles were 55 ± 6 nm in diameter and 330 ± 38 nm in length. They found that these particles were weakly ferrimagnetic and have been shown to orient with their major axes perpendicular to an applied magnetic field (212). Films were cast (~500nm) while under the magnetic field, and then solvent annealing (in a neutral solvent) continued for one day under the influence of the magnetic field (55). This process helped to form block copolymer that aligned with the long axis of the particles as seen here (55):

![TEM images of block copolymer/magnetic nanoparticle film cross sections showing the driven alignment of the block copolymer by the nanoparticles](image)

Figure 49: TEM images of block copolymer/magnetic nanoparticle film cross sections showing the driven alignment of the block copolymer by the nanoparticles
The P2VP domain wetted the iron oxide layer as it has been shown to do with oxides (213), metals (214), and semiconductor (215) surfaces. So, overall this method is successfully able to align the orientation of the block copolymer (though modestly) with the long axis of the iron oxide rods. Hammond et al. followed the suggestion of Laicer et al. that the particles should be considerably larger than the block copolymer domains (211).

RESEARCH IDEOLOGY

This project builds on the basis of the work by Laicer et al. (211), Hammond et al. (55), Composto et al. (45), and from Chapter II of this report. A short schematical representation of the proposed methodology for this study is in order to explain the ideology. The overall goal in the future for this project is to be able to directly control the morphological orientation of a block copolymer system through the use of magnetic fields. The current progress made towards this goal will be described in the proceeding sections, but a direct explanation of this approach is needed to understand why these initial steps are taken. It has been described in the introduction, that while electric fields can have a strong influence on block copolymers because of differences in dielectric constants, the magnetic properties of block copolymers are not strong enough
to drive the orientation of the system (at this point). Magnetic nanoparticles however are largely influenced by magnetic fields (as shown in Chapter II), because of dipole-dipole interactions. So, it seems natural that if particles with a direct attraction to one of the block copolymer phases assemble themselves based on a magnetic field, the block copolymer should naturally follow the developed magnetic assemblies. This has been proven to work by Hammond et al. (55). Hammond however used very large particles that have the potential to destroy the packing of the block copolymer system by altering the spacing. Composto et al. then were able to prove that magnetic particles with specific ligands that attract one of the block copolymer phases can easily assemble within the cylindrical domain (45). Therefore, through literature and through Chapter II it has been proven that individual particles can be driven to fit inside one of the block copolymer moieties, that the particles can be assembled into larger complexes whose sizes are based on magnetic field strength, assembly time, and particle interactions, and that larger assemblies can drive the orientation of block copolymer to follow to direction of the assemblies.

The general process for this method will be along the following lines. First, a cylindrical block copolymer system (PS-b-PMMA in this case) will be loaded with a specified concentration of magnetic nanoparticles (PS coated cobalt). This film can be free to self assemble, but if the correct conditions are used, it will develop a cylindrical morphology parallel to the substrate:
As there are cobalt particles in the cylindrical domains, the domain spacing will be slightly different where the particles are:
Once the film has reached its equilibrium morphology, the magnetic field manipulation can take place. In order for the orientation to be switched, the sample must be heated above the glass transition points of both of the block copolymer phases, and must be put into a magnetic field for a substantial enough amount of time for the magnetic particles to arrange as they did in Chapter II. A schematic of this process can be seen here:
As this annealing is occurring, the magnetic nanoparticles are being driven to a mean field line, where they will arrange into “pillars.” Since these particles are attracted to the PS phase, a competition will exist between following the magnetic field, and allowing the surface forces to control the orientation of the block copolymer. If the magnetic field is large enough though, these surface forces can be overcome, and the block copolymer will begin to align with the particles:
Figure 53: Schematic showing particles being attracted to the magnetic flux field lines, which in turn reorient the block copolymer.

Therefore, with this method, the orientation of the block copolymer can be completely switched.

Figure 54: The end result from magnetic field annealing of a block copolymer/magnetic nanoparticle nanocomposite.
EXPERIMENTAL PROCEDURE

Materials and Instrumentation

Poly(styrene-block-methymethacrylate) with molecular weights of 52000 - 142000 (polystyrene cylinders), 33000-33000 (lamellar), and 62000-12000 (polymethymethacrylate spheres) respectively (Polymer Source) and Toluene (Sigma-Aldrich) were used as received. Cobalt nanoparticles (27.5 ± 2.5 nm) with 5000 molecular weight polystyrene ligands were synthesized by Dr. Pyun at The University of Arizona and were used as received. Neodymium magnets (1” diameter x 3” length) were ordered from K&J Magnetics (Jamison, PA).

Experimental Procedure

The cobalt nanoparticles were synthesized using a robust process that prepares nanoparticles with ferromagnetism at room temperature and stable colloidal dispersions in various organic solvents. They were prepared by Pyun et al. using a hierarchical synthetic methodology, in which end-functionalized PS containing amine, or phosphine oxide end-groups were prepared using controlled radical polymerization (56).
These end-functionalized chains were then used in the thermolysis of dicobaltoctacarbonyl (Co$_2$(CO)$_{8}$) to prepare the ferrimagnetic cobalt nanoparticles. The PS surfactants used in this material had a molecular weight of 5000 and a PDI of 1.1. The surfactant passivated the colloidal surface by ligation of chain ends to stabilize the nanoparticles (56). This shell reduces the agglomeration effects of the nanoparticles and enables dispersion of the ferrimagnetic colloids in non polar organic media. These synthesized particles had a diameter of 27.5 ± 2.5 nm with the PS shell composing up 2 nm of that diameter.

The polymeric solution made for casting the films were made by mixing 2% or 7% by weight PS-b-PMMA in toluene with varying degrees of cobalt nanoparticles (0%, <<0.1%, 0.2%, and 1% by weight based on PS-b-PMMA). These solutions were sonicated for 30 minutes to ensure the cobalt particles were not agglomerated, and then were spin coated for 60 seconds at 2000 RPM with an acceleration of 500 RPM/second on to silicon substrates. These films then were put through one of three annealing conditions: no annealing, annealed for 15 or 72 hours without magnetic field at 165°C, and a few select samples were annealed for 15 or 72 hours with magnetic field at 165°C in order for results of the proposed method to be conducted. The magnetic field that was experienced by these samples was on the order of 0.68 Teslas when equilibrated at 165°C, however this measurement may be slightly flawed as it was not taken within a sealed oven. A schematic of the oven annealing process is shown here:
As seen in this image, the magnets are held together by their own attractive force in a north-south arrangement. The sample is placed in the middle of the magnets (using spacers). This type of magnetic orientation led to the following image in the previous study with iron oxide nanoparticles (oleic acid ligands) in a polymerized DDMA matrix:
Figure 56: Optical image from Chapter 2 displaying the assemblies of nanoparticles through the film thickness

The dots in this image represent aligned rods of iron oxide nanoparticles assembled head to tail through the film’s thickness. These films were then imaged using atomic force microscopy (AFM) to see the surface features of the film.

RESULTS AND DISCUSSION

Although, as seen in the background information, studies have been completed proving the ability of magnetic nanoparticles to assemble within block copolymer systems, it is still imperative that our specific system to be tested before further experimentation proceeds. In addition, each system shown through literature has
nanoparticles and block copolymers with specific properties (particle size, particle material, ligand type, ligand molecular weight, block copolymer molecular weight, annealing conditions, etc.), so identifying the behavior of the specific molecules and block copolymers is an important first step. In order for the magnetically driven block copolymer reorientation to be successfully completed, it first must be determined that the addition of the nanoparticles is not detrimental to the natural self assembly of the polymer. Therefore, the performance of these nanocomposites will be described starting with a spherical system.

PS-b-PMMA with molecular weights of 66000 and 15000 respectively were loaded with 27.5 nm cobalt nanoparticles with 5000 molecular weight PS ligands at varying molecular weights to determine if the particles negatively affect the system. In order to get a grasp on that natural ordering of this molecular weight, the system was first spin-coated with no nanoparticles and annealed for 15 hours at 165°C. Atomic force microscopy images of the surface of these two conditions can be seen here (all AFM images in this discussion will be 2 μm x 2 μm and samples all range from 90 nm to 105 nm in thickness):
Figure 57: 66k-15k PS-b-PMMA AFM phase images of as-cast (left) and annealed 15 hours at 165°C (right) conditions

As seen in these images, the as cast image does not show any distinguishable features, while the annealed sample clearly shows the formation of PMMA spheres (white dots). If this sample were to be given further annealing time (or if the annealing temperature was raised), it can be assumed that a hexagonally packed array of PMMA spheres will be formed. The thickness of these films was 95 nm (as-cast) and 91 nm (annealed).

In order to grasp the full spectrum of filling conditions potentially being used in the application of using magnetic nanoparticles to reorient a block copolymer system, particles were loaded into the system at concentrations of <<0.1%, 0.2%, and 1.0%. These percentages are all based on the weight of the block copolymer. Images of the sample as cast and annealed 15 hours at 165°C with a trace (<<0.1%) can be seen here:
Figure 58: AFM phase images of 66k-15k PS-b-PMMA filled with <0.1% cobalt nanoparticles as-cast (left) and annealed 15 hours at 165°C (right)

The initial observations from these images are striking. The as-cast image shows high resemblance to the samples without any particles, while the annealed sample shows a vast improvement in the number of spheres and of the relative packing of the spheres. This image shows great initial results that the addition of the cobalt nanoparticles does not deteriorate the assembly of the block copolymer, but appears to actually help improve/accelerate the assembly process. Results similar to this were seen by Russell et al., where they were able to add salts (some containing cobalt) into a cylindrical block copolymer of PS-b-PEO and get much greater lateral order (216). It is imperative to realize that this is likely only a result at a low fill concentration of the particles, as work
by Composto et al. was able to prove that higher loadings severely slow down the self-assembly process during annealing (45). As the particles in this system prefer the matrix phase (due to the PS coating), they do not appear to be negatively affecting the system at all.

The next concentration of nanoparticles to be discussed is 0.2%. The AFM images of these samples are shown here:

![AFM phase images of 66k-15k PS-b-PMMA filled with 0.2% cobalt nanoparticles as-cast (left) and annealed 15 hours at 165°C (right)](image)

Figure 59: AFM phase images of 66k-15k PS-b-PMMA filled with 0.2% cobalt nanoparticles as-cast (left) and annealed 15 hours at 165°C (right)

The first thing to notice in this image is that the relative color of the spheres changed in the annealed image for this set of experiments. This is purely an artifact of the AFM and
not of the sample itself. As PMMA can be slightly sticky, when the AFM probe taps harder, it can potentially stick to this phase, giving the artificial view that the spherical phase changed hardness, when in fact it still represents PMMA. As seen in these images, while the packing is not as impressive as in the trace filling of the block copolymer, there still does not appear to be any negative influence in the ordering or assembly of the block copolymer system from the cobalt nanoparticles.

The final concentration to be observed is 1.0% and the phase images of the AFM scans for as-cast and annealed 15 hours at 165°C can be seen here:

Figure 60: AFM phase images of 66k-15k PS-b-PMMA filled with 1.0% cobalt nanoparticles as-cast (left) and annealed 15 hours at 165°C (right)
This image shows two distinguishable observations to be discussed. First, it can be seen that the assembly and ordering/packing of this system is once again very good (even better than without particles). Though it is still not a perfectly hexagonally packed system, if given further adequate time or temperature, it can be inferred that the system will successfully form a well packed film. The second important aspect of these images is that these images show for the first time the agglomerations of the cobalt particles (at the surface). This consequence was inevitable, even with the use of the ligands, as the particles inherently are attracted to each other. Therefore, it is expected that as the concentration of the particles increases, the chance the particles will come into contact with each other increases, and thus agglomerations are more probable. In addition to that, the longer the annealing time allowed is, the chance of forming larger agglomerations increases, which in-turn can destroy the morphology of the system as shown by Composto et al. (45).

The next step taken with the 66k-15k PS-b-PMMA was to spin coat thicker samples to see if there is any variation in behaviors. The next set of films are on the order of 150 nm. AFM images of as-cast and annealed 15 hours at 165°C samples with no nanoparticles are shown here:
Figure 61: 150 nm thick AFM images of 66K-15K PS-b-PMMA with no nanoparticles as cast (left) and annealed 15 hours at 165°C (right)

These samples unfortunately contain much more defects, which is a result of the slower spin coating speed used for these samples. Beyond that though, it is evident again (like in the ~100nm thick samples), that the as-cast samples show no general morphological assemblies, and the annealed sample shows the formation of PMMA spheres. Although the packing is not good for the annealed sample, it indeed shows the beginning stages of this morphology. When a trace of cobalt nanoparticles is added into the system, a large change is observed:
Figure 62: 150 nm thick AFM images of 66K-15K PS-b-PMMA with a trace of cobalt nanoparticles as cast (left) and annealed 15 hours at 165°C (right)

These images clearly show that the number of spheres created in the same amount of time as the samples without particles has greatly increased, and the packing also shows vast improvements. Overall, for PS-b-PMMA with molecular weights of 66000 and 15000 respectively, it can be said that the additions of 27.5 nm cobalt nanoparticles up to a concentration of 1% does not negatively influence the assembly of the block copolymer. In fact, it has been shown that the particles actually accelerate/enhance the annealing process.

The next molecular weight of PS-b-PMMA to be studied will be from a balanced molecular weight of 33000-33000. This molecular weight naturally forms a lamellar morphology. The first set of samples were prepared from a 2% solution in toluene and
were spun at 2000 RPM for 1 minute. This combination of conditions formed samples with thicknesses on the order of 75 nm. The following images provide as-cast and annealed (15 hours at 165°C) AFM phase images for samples cast without any nanoparticles:

Figure 63: AFM phase images of 33K-33K PS-b-PMMA with no nanoparticles in the as-cast (left) and annealed at 15 hours at 165°C (right)

The images show that in the as cast condition, no overall morphology is evident, while the annealed samples clearly show lamella with a mixed morphology. The lines that run across the film represent a perpendicular morphology, while the flat areas with no noticeable lamella represent a parallel morphology. This mixed morphology can stem from undulations in the film thickness (parallel morphology prefers a thickness at an
integer of the domain spacing), or from the competition between the two phases attempted to be on the surface (PS only *slightly* prefers the air interface).

In order to determine the effect of cobalt nanoparticles on this lamellar system, initially a trace of particles were added into the solution. The as cast and annealed AFM phase images of these samples are shown here:

![AFM phase images](image)

Figure 64: PS-b-PMMA AFM phase images at a molecular weight of 33k-33k in the as cast (left) and annealed at 165°C for 15 hours (right) conditions

As seen, the images provide almost identical results to the samples created without particles. The as-cast samples show almost no features, while the annealed sample
once again shows a mixed morphology. When, the concentration of the nanoparticles is vastly increased to 1%, the following AFM images develop:

Figure 65: AFM phase images of 33K-33K PS-b-PMMA with 1% cobalt nanoparticles in the as-cast (left) and annealed at 15 hours at 165°C (right)

Although the annealed sample in this case does not show large areas of parallel morphology, it is still slightly mixed, which shows little to no effect of the nanoparticles on the natural self assembly of the 33k-33k PS-b-PMMA films at a thickness of 75 nm.

The final system studied is the most in depth as it provides (what we feel) as the best opportunity for the morphology reorientation to occur. The reasoning behind this thought is that the domain size of the polystyrene phase is large enough that the cobalt
nanoparticles will be able to assemble within that domain. Therefore, if they are able to reassemble following an applied magnetic field, it is possible for the PS phase to follow this rearrangement without critically disrupting the packing of the cylinders. The molecular weight of this PS-b-PMMA material is 52000-142000, respectively, which provides the correct percentages for PS cylinders to develop in a PMMA matrix. As the particles at 27.5 ± 2.5 nm in diameter, they will easily fit within the PS phase. The first set of samples were made in a 2% solution in toluene and spun at 2000 RPM for 1 minute. AFM phase images of the samples without any cobalt nanoparticles with dimensions of 2 μm x 2 μm are shown here:

Figure 66: AFM phase images of PS-b-PMMA with relative molecular weights of 52000 and 142000 in the as-cast (left), annealed 15 hours at 165°C (middle), and annealed 72 hours at 165°C (right) conditions
These films were tested to be on the order of 100 nm thick. The progression of these images is quite interesting, and it starts with the as-cast morphology having a poorly ordered morphology, which however is already well phase separated. It is evident that although the ordering is bad, it appears to be the beginning of a mixed morphology. This early ordering stems from the solvent being pulled out of the film. As toluene is a slightly better solvent for polystyrene than polymethylmethacrylate, the PS is pulled to the air interface as the toluene evaporates. This process continues as seen in the sample annealed for 15 hours. It is quite clear in this image that the surface is primarily PS (dark phase), and this is purely due to toluene being trapped in the middle of the film, which was pulled out during the annealing process. When more time is given, the 72 hour annealed sample shows the equilibrium morphology of this block copolymer. A perpendicular cylindrical morphology is evident (PS cylinders), and although the packing is not well defined at this point, it is likely that a longer annealing process would provide the means for this to occur (as this high molecular weight sample will take much longer to assemble because of the reduced mobility stemming from increased entanglements).

The same progression of the incorporation of nanoparticles was completed for this material as shown in the previous molecular weights. So, the first concentration to be discussed will be simply a trace of particles (<<0.1%). Phase images from the AFM tapping mode of this material under as-cast, annealed for 15 hours at 165°C, and annealed for 72 hours at 165°C are displayed here:
Figure 67: PS-b-PMMA filled with a trace of cobalt nanoparticles AFM phase images with molecular weights of 52k-142k of films with the following conditions: as-cast (left), annealed 15 hours at 165°C (middle), annealed 72 hours at 165°C (right)

This set of images look almost identical to the AFM images taken of the samples without particles, leading to the conclusion that at this low of a concentration (<<0.1%), no effect is seen by the cobalt nanoparticles.

The concentration then can be increased to the level of filling seen in the results of Chapter II, 0.2%. The following images represent the surface morphologies of these 100 nm thick films under the same three annealing conditions:
Figure 68: PS-b-PMMA filled with 0.2% cobalt nanoparticles AFM phase images with molecular weights of 52k-142k of films the following conditions: as-cast (left), annealed 15 hours at 165°C (middle), annealed 72 hours at 165°C (right)

Once again, the images look nearly identical the samples without any particles and the samples with a trace of particles. The final AFM images with a cobalt nanoparticle filling concentration of 1% are shown here:
Figure 69: AFM phase images of PS-b-PMMA with relative molecular weights of 52000 and 142000 filled with 1% cobalt nanoparticles in the as-cast (left), annealed 15 hours at 165°C (middle), and annealed 72 hours at 165°C (right) conditions.

These images again do not show any deterioration of the block copolymer morphology at a filling even up to 1%. This result is very promising then, as it shows that cobalt nanoparticles can be loaded into this specific block copolymer at a concentration up to 1%, be cast in the exact same method as without particles, and not reflect any negative influence on the film.

These films can be made considerably thicker and still show similar morphologies as seen in these images:
Figure 70: 52K-142K PS-b-PMMA filled with 0.2% cobalt nanoparticles AFM phase images of films annealed 15 hours at 165°C at different thicknesses: ~200nm (left), ~600 nm (middle), and ~1μm (right)

This images show great results in that even thick films, where the magnetic nanoparticles have a large space to agglomerate, still do not show any adverse effects by their addition. This is important as a problem plaguing block copolymer films (in the medium thickness range), can have different morphologies in the center of the film as compared to the two interfaces. The method being used in this study could potentially solve this problem then by creating long ordered structures for the block copolymers to follow.

With these results complete representing the ability of the 52000-142000 PS-b-PMMA films to be loaded with cobalt nanoparticles, experiments were continued in this study to determine if the particles can in fact alter the morphology of the system. In order to complete these initial results, samples were annealed in the configuration
shown in Figure 55 for 15 hours to see if the particles can impart any influence. Before results are shown, a brief explanation of the difficulties possible with this process should be made. The first issue that potentially plagued this research is that the formation of the iron oxide strands in Figure 56 was based on a system with very low viscosity (~15 mPa·s) as DDMA is essentially a monomer before curing. This allowed for very high mobility of the particles to organize into the formations seen in the metastable state of Chapter 2. However, in this study, the molecular weight of the system drastically increased to ~194000. This increase would greatly reduce the mobility of the particles. The solution to this problem lies in allowing ample time for the particles to be driven to form their arrangements (15 hours in this study versus 5 minutes in the last study). Enhancing this mobility is the fact that the block copolymer matrix is also in a mobile state to form equilibrium morphologies. There lies a competition in the diffusion of these particles in the system between being attracted to the polystyrene phase and being driven to form dipole-dipole chains. A balance then must exist of the particles working in correlation with the assembly process to produce the images found within this study.

Starting with the samples with no cobalt nanoparticles and the magnets in a north-south orientation perpendicular to the film surface, the following AFM phase images represent samples annealed for 15 hours at 165°C with and without a magnetic field influence:
Figure 71: 52K-142K PS-b-PMMA with no nanoparticles annealed for 15 hours at 165°C without a magnetic field (left) and with a magnetic field (right)

These resulting images show a drastic change made through the influence of the magnetic field. The results seen here are similar to the results found by Yasui et al. (187) in that they found that the application of a magnetic field to the annealing samples worked to help assemble the block copolymer system. What they did not mention, was that this was an accelerated process. It is quite evident that when limiting the amount of annealing time available to a film that is susceptible (although very slightly) to a magnetic field, the magnetic field acts to accelerate the process of formation of individual cylindrical phases. When ample time is given to the annealed samples, such as 72 hours, the films give very similar morphologies:
Figure 72: PS-b-PMMA AFM phase images of samples annealed 72 hours at 165°C without a magnetic field (left) and with a magnetic field (right)

Since the films turn out almost identical, it can be said that the application of the magnetic field merely helps to accelerate the annealing process.

As particles are added into the system, similar results are seen in that the magnetic field still has an “accelerating” behavior which cannot be simply a result of the alignment of the magnetic particles. A system filled with 0.2% cobalt particles reveals the following surface morphologies:
Figure 73: AFM phase images of PS-b-PMMA films filled with 0.2% cobalt nanoparticles that were annealed at 165°C for 15 hours without the presence of a magnetic field (left) and with a magnetic field (right)

These samples again look like the samples without particles, but the morphology still is not negatively affected by any agglomerations that may exist within the film. As the annealing time is extended to 72 hours at 165°C, the following AFM images develop:
Figure 74: PS-b-PMMA AFM phase images of samples annealed for 72 hours at 165°C with 0.2% cobalt nanoparticles annealed without a magnetic field (left) and with a magnetic field (right)

It is quite evident then that through the addition of cobalt nanoparticles and the application of a magnetic field does not negatively influence the morphology of these block copolymer films. It in fact has been shown that the magnetic field works to help accelerate the annealing process. Through the prior discussion in the background information of magnetically controlled block copolymer orientation, this acceleration likely stems from the fact that the magnetic field essentially reduces the order-disorder transition temperature, thereby making the annealing process more mobile and accessible. Magnetic force microscopy was run on these samples to determine if the PS
and PMMA phases do indeed have varying magnetic properties. The MFM phase images are shown here for samples with 0.2% cobalt nanoparticles:

Figure 75: MFM phase images of PS-b-PMMA loaded with 0.2% cobalt nanoparticles annealed for 15 hours at 165°C without a magnetic field (left) and with a magnetic field (right)

It is quite clear then that the samples do have different magnetic properties, which is a possible solution as to why the magnetic field provides the conditions for an accelerated annealing process. Samples filled with a trace of particles and 1% particles showed identical results, proving that the particles can be loaded at a low or high (up to 1%) percentages and still provide this accelerated process.
Upon varying the tapping conditions on the AFM, interesting results were found as to the positioning of the cobalt particles. By tapping harder, the features within the film become more visible in the phase images. Therefore, although the cobalt particles may not be in the surface, their varying hardness within the film represents a different phase. An AFM image representing this idea for PS-b-PMMA with 0.2% cobalt nanoparticles is shown here:

![AFM phase image of PS-b-PMMA loaded with 0.2% nanoparticles annealed for 15 hours at 165°C](image)

Figure 76: AFM phase image of PS-b-PMMA loaded with 0.2% nanoparticles annealed for 15 hours at 165°C
As seen, two new observations can be made from these images. First, it is evident that we can see large agglomerations of the cobalt nanoparticles (represented by the large dark areas). The second observation is that in the middle of (almost) all of the cylindrical PS domains, a lighter colored sport can be seen in the middle of the samples. These lighter spots are likely the PS coated cobalt nanoparticles that have arranged themselves within the PS domains. Therefore, the location of these particles is accounted for.

CONCLUSIONS

The driven orientation of block copolymer systems through the use of magnetic fields has not generated a high level of research as of yet. This project set out to provide a solid analysis of a few different block copolymer systems in order to determine if the loading of magnetic nanoparticles is a viable method to direct this orientation process via magnetic field. The results shown provide the important initial results that cobalt nanoparticles with polystyrene ligands (27.5 ± 2.5 nm) can be successfully loaded into spherical, lamellar, and cylindrical morphologies of polystyrene-block-polymethacrylate at a concentration up to 1% without destroying the natural self-assembly of the block copolymer system. The particles even showed the ability to enhance the annealing process of the spherical system, without the use of any magnetic fields. Upon the application of a magnetic field perpendicular
to the block copolymer substrate, it was evident that the field was able to accelerate the
annealing process for the cylindrical system. This cylindrical system proved to be very
promising in that it did show a positive influence from the magnetic field, it did not have
a negative effect when the particles were added in, and the particles were shown to
assemble within the polystyrene phase. This system shows great promise to
successfully reorient a block copolymer system when the correct annealing time and
conditions are met. Many different aspects still need to be looked into in order for this
method to be completely viable (including exact molecular weights, substrate type,
particle size, casting method, annealing method, and magnetic field strength), however
these initial results show this system to have great promise, and will provide the basis
for further researchers in the future to build upon.
In the future, it is the recommendation of the author that this work to be continued to work towards the goal of being able to directly control the orientation of a block copolymer system through the use of magnetic nanoparticles and magnetic fields. Work in a few specific areas, and foreseeable problems are two subject matters to be addressed here. This first area to be mentioned is the film casting method being used. Spin coating was used in this study, and while it provides consistent flat films, the risk of having trapped solvent in the film and also having residual stresses in the system make that method slightly unattractive. Although spin-coating the samples should lead to the desired film morphology/orientation if the correct conditions and precautions are taken, another method could potentially provide a better way of creating the films. That method is flow coating. As shown in the following image, by controlling the domain size, film thickness, and annealing temperature, the film orientation can directly be predicted (37):
Although flow coating may not reduce the amount of residual solvent in the material, it does provide the means for an alternative method to create consistent films.

The next subject matter that should be researched in the future is the annealing method. While initially it appeared the thermal annealing method described in Figure 55 was the best option, difficulties arise in this in that the magnetic field strength created by the magnets is significantly decreased because of the elevated temperatures. Therefore, stronger magnets, or even electromagnets, would be needed to ideally perform the annealing process. Other options should be looked at to determine the best method for the magnetic field annealing of the block copolymer samples. The first option would simply be to create a small heating chamber, that is thin enough that the sample can fit in, but still allowing the magnets to be on the outside of the chamber.
(thereby keeping the heat away from the magnets). The next method to try would be solvent annealing with a neutral solvent. This neutral solvent would give the benefit of greatly increasing mobility while keeping the system open to any morphological orientation. This is the method that Hammond et al. used in their study (55). The final annealing method that should be considered is cold-zone annealing. This method provides the possibility for a reduced annealing time and has been shown to give good packing of cylindrical morphologies.

There of course are potential downfalls with this method, and although they are not completely detrimental to the plausibility of this research, they could plague the final packing of the block copolymer systems. This problem stems from the fact that when the cobalt particles are added into the block copolymer, the domain spacing is slightly altered where the particles are. This idea is well described by Bockstoller et al. as shown in the following image (217):
This image makes it quite evident the depending on where the particles are, the domain spacing can be greatly changed by $\Delta L$. This change not only effects the phase that it is in, but all of the domains around it. The curve will essentially propagate through the film until enough spacing has occurred so that the curve can be averaged out. A schematic representing this altered spacing in long range is shown here:
Figure 79: Schematic representing the curved domain lines and expanded domain sizes from the addition of particles.

If these expanded domains occur at the surface, the hexagonal packing will evidently be altered by the irregular domains. This could potentially cause the surface to look like this:
Figure 80: Theoretical change in surface block copolymer packing from hexagonal in the absence of particles (left) to irregular (right) because of the expanded domain sizes from the particles.

This problem can even be expanded to the findings by Composto et al., where if the particles are able to agglomerate, the morphology will be completely destroyed (45). These domain spacing problems can be dealt with though if the molecular weight and particle sizes are controlled.
CHAPTER V

REFERENCES


