Determining Solvent Trends and Effects on the Crystallization of Poly(ethylene oxide)-*b*-poly(ε-caprolactone)



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Senior Comprehensive Project

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I hereby recognize and pledge to fulfill my responsibilities, as defined in the Honor Code, and to maintain the integrity of both myself and the College as a whole.

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Abstract

10k-10.3k samples of poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL) were dissolved in various solvents in order to analyze the sequence of crystallization *via* optical microscopy and FTIR. Both evaporation crystallization and solution crystallization methods were utilized in the attempt to achieve efficient single crystals. Solubility parameter appeared to play a large role in the order of crystallization of PEO-*b*-PCL. Specifically, if the solubility parameter is low or closer to that of PCL's, PEO would crystallize first. On the other hand, if the solubility parameter is comparable to PEO's, PCL would crystallize first in sequence. In other words, when the polymer is more soluble in the solvent, it will stay in solution longer and not crystallize out first. These findings can aid in selective crystallization to get final crystal structures with desired properties.

Crystallization of Poly(ethylene oxide)-*b*-poly(ε-caprolactone)

Natasha C. Brigham

Background

Introduction

Within the past decade, biocompatible, amphipathic polymers have gained a lot of attention due to their applications in the biomedical field as well as environmentally friendly components.[1] Specifically, poly(ethylene oxide) and poly(caprolactone) have become relevant for their medical applications, such as bone fracture fixation, sutures, tissue engineering scaffolds, and drug release carriers.[2-6] A combination of these two polymers—or its diblock copolymer, poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL)—has also been studied extensively. Block copolymers have received a lot of attention in different areas of research because of their ability to combine polymers of different structure and properties for an array of practical uses.[7] Depending on their miscibility, the molecules within these copolymers have the ability to self-assemble into a number of ordered morphologies. The structure that is formed will determine the block copolymer's characteristics and control its applicability. Therefore, understanding and controlling the crystallization process is important for applying these molecules to different fields.

Both of the polymers in the PEO-*b*-PCL are semicrystalline, which means that they will crystallize at some point, and therefore, their crystallinity greatly affects their properties. To better comprehend how the crystallization process of PEO-*b*-PCL works, factors that alter the process must be understood first. Research has proven that the crystallization process of this diblock copolymer is sensitive to factors such as thermal history,[8,9] molecular weight[10,11] and the solvent that is used to dissolve the polymer.[12,13] Normally, in a copolymer the temperature at which each block will melt or crystallize causes some structural differences and allows for sequential crystallization to occur. However, in the case of PEO and PCL these temperatures are similar; therefore, this is not an effective method to distinguish the order of crystallization. In

other words, what is called coincident crystallization occurs where it is not probable to distinguish between the crystallization of either block from the other. As such, the above factors have been extensively studied to gain more insight on this process, such as the order of crystallization and the rate at which this occurs for each.

One factor controlled by these parameters is the crystal morphology. Some common morphologies of PEO-*b*-PCL include spherulites, micelles, dendrites, axialites and in some cases, single crystals. The type of crystal depends on the rate of growth and also the distance from equilibrium.[14] Previous research has concluded that this morphology can change to favor the block that is greater in weight fraction (W_f) at a critical value.[10] For example, when W_{PCL} is 0.36 or less, PEO will crystalize first, which results in a confined growth of PCL. Furthermore, Jiang *et al*.[15] used polarized microscopic imaging to show that as temperature increases so do the size of the crystals in PEO-*b*-PCL with unequal molecular weight fractions. Changing the molecular weight will not only effect the temperature at which the copolymer will be able to crystallize, but our research has shown to exhibit a change in the order of crystallization between the PEO and PCL individual blocks. Much research has been dedicated to selective crystallization by controlling the molecular weight and temperature, but little has been done on using solvent to control the crystallization.

Previous research done in our lab on this subject revealed some differences in morphology when using different solvents, however, the images were unclear to which block would have crystallized first.[16] It was taken that the films were probably too thick to see what the actual crystals looked like; it seemed that they were growing on top of one another, convoluting the visible structure. To get a better image of the crystal structure, using less concentrated solutions and also slowing down the available crystallization rate by controlling the temperature at which the films dry might help to achieve this. Controlling the temperature would ultimately allow the crystals to grow slower, rather than the local concentration dictating the rate of crystallization, possibly causing the growth of single crystals rather than more densely packed

crystal morphologies. Depending on the shape, single crystal formation would give insight into which block crystallized first and therefore which solvent either block prefers. PEO has been shown to be shaped more like a square when forming single crystals due to its monoclinic unit cell, and PCL has been shown to be more hexagonal, or shaped with six sides, with an orthorhombic unit cell.[17] The current research aims to continue to gain insight to the overall solvent effects on the crystallization and also the conditions under which each block might crystallize first in 10k-10.3k samples of PEO-*b*-PCL using primarily optical microscopy (POM) and an attenuated total reflectance attachment on the FTIR (ATR-FTIR).

Polymers

Macromolecules are simply defined as molecules with a large number of atoms and therefore, have a high molecular mass.[18] Although these are not synonymous terms, a polymer molecule is a type of macromolecule that is composed of many smaller parts. A polymer then is comprised of many repeating polymer component molecules, or monomers. The number of monomers (*N*) per polymer is known as the degree of polymerization.[18] In addition to polymers, dimers and oligomers also exist. A dimer is comprised of molecules with only two constitutional groups and an oligomer is step in between a dimer and polymer, containing molecules with few to several constitutional units.

A polymer can either be crystalline or amorphous, meaning that it will crystallize at some point, or never will. In other words, the title of amorphous polymers implies that they do not exhibit any crystallization behavior or ordered structures and form a broad group of materials such as glassy, brittle and ductile polymers.[18] Crystalline polymers on the other hand, will form final crystal structures; a variety of which are used in a lot of the materials we use in every day life. The synthesis and overall treatment of these polymers is crucial in their applications. Another important characteristic of crystalline polymers is that, unlike material such as water, polymers do not have an equal transition temperature for which they melt and crystallize.[18] The

temperature at which they melt at is often referred to as T_m and the crystallization temperature is referred to at T_c. Typically, there is not a defined temperature at which the polymer will melt due to the fact that the sample may not be uniform; therefore, the sample may not be completely melted until it is heated well about the T_m, and vice versa for T_c. Some polymers also exhibit a glass transition state (T_g); above this temperature, an amorphous polymer transforms from hard and brittle to soft and malleable.[18]

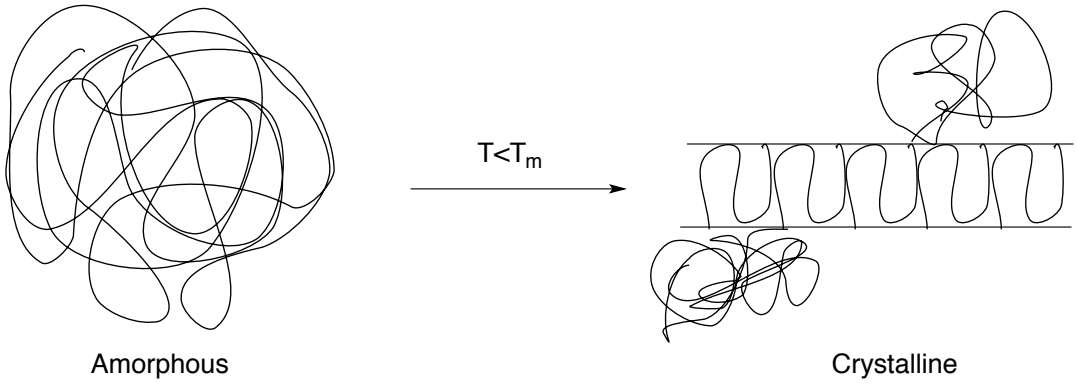
Quantitative measures help define and distinguish one polymer from another. Two ways this is possible involves the degree of polymerization and molecular weight. The degree of polymerization is the number of monomeric units per polymer molecule and is often denoted as "N".[18] Notation includes this as a subscript (i.e. $(polymer)_N$). The other quantitative method involves two distinctions within itself. Specifically, molecular weight can be explained in the weight average molecular weight (M_w) or as the number average molecular weight (M_n).[18] Equations 1 and 2 exhibit how the values can be calculated where N_i is the number of molecules and M_i is the molecular mass of the polymer chain. As the names suggest, M_w is the average size of the chains in the molecule and M_n is based on the average number of monomers per chain. These values are important due to the fact that different samples contain different characteristics. The number average molecular weight is more commonly used and takes into account the masses of all the monomers, divided by the how many are in a chain. These values are often abbreviated. Moreover, if a sample has a M_n value of 10,000 g/mol, it will be expressed as "10k, or 10 thousand" for that polymer.

$$\mathrm{M}_n = \frac{\Sigma \mathrm{N}_i \mathrm{M}_i}{\mathrm{N}_i} \qquad (1)$$

$$\mathrm{M}_w = \frac{\Sigma \mathrm{N}_i \mathrm{M}_i{}^2}{\Sigma \mathrm{N}_i \mathrm{M}_i} \qquad (2)$$

When a crystalline polymer is heated above the T_m, it becomes disordered and is considered to be in the amorphous state. This amorphous-state polymer then can be cooled down below the melting temperature to obtain a more ordered and crystalline structure (Scheme

1). The polymer chains crystallize by folding and forming a sheet, or lamella. The lamella is indicated in Scheme 1 as the two parallel lines, containing the newly folded polymer chains. In the crystalline representation, amorphous material is still attached to the crystalline material. It is depicted this way due to the fact that 100% crystalline polymer materials rarely exist; some portion of the polymer will almost always remain amorphous.[18] The crystallization process is key in the applications of the polymer, however, many other factors play a role in the progression of the final ordered structure.



Scheme 1. Representations of both the amorphous and crystalline states of polymers

Polymers are defined further based on their uniformity. For example, a homopolymer is only comprised of one species of monomer, but a copolymer is comprised of two or more different species of monomers. Furthermore, copolymers that only contain two different types of monomers are called a bimonomer, three types of monomers are distinguished as a terpolymer, and so on.[18] Regardless of the number of different monomers, copolymers are distinguished according to the sequence of the various monomeric units. These different sequences and conformations give rise to statistical, random, alternating, periodic, block, segmented, gradient and graft copolymers.[18] Statistical copolymers sequential composition can be found *via* a statistical method. Random and alternating copolymers are similar and their sequences are described in their name: random copolymers sequence is random in order and alternating

copolymers sequence alternates between each monomer. Periodic copolymers have a certain pattern to them, which repeats throughout the sequence. Block copolymers have an order in which monomers repeat themselves in chunks, or blocks. Segmented copolymers are block copolymers that just have fewer repeated monomers per block. In a gradient copolymer, each end contains primarily either one monomer or the other. Finally, a graft copolymer contains a main chain of one monomer, while the others are connected onto the chain in a branched fashion. These different forms of copolymerization have different degrees of polymerization and molecular weights present; in other words, polymers are polydisperse with regards to these aspects.[18] Thus, because of this non-uniform nature, many different characteristics are attainable in various copolymers.

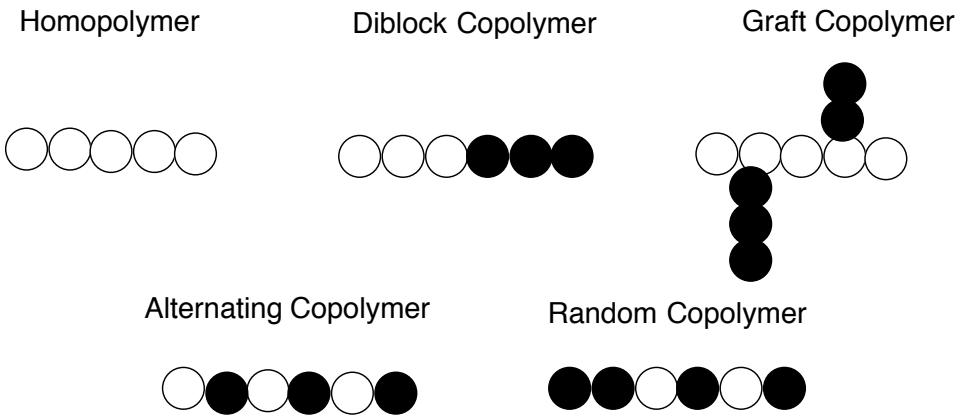


Figure 1. Illustration of a homopolymer and some of the variations of copolymers where the black and white circle are different monomers

Once the nomenclature and different types of polymers are understood, the topic of most current research can be explored: crystallization of polymers. Crystallization, put simply, is the ordering of polymers into micro domains. When the local concentration of polymer is high enough and the conditions are fit, the polymeric crystal will nucleate and begin the growth of the crystal. Multiple factors can effect crystallization, and therefore, the conditions under which crystallization is allowed to occur is of interest to researchers. Different factors that can alter the ultimate crystal structure are thermal history, or crystallization temperature; molecular weight;

concentration of polymer in solutions; the solvent used to dissolve; the atmosphere it is grown in; as well as others.[18] These factors could affect the morphology, orientation of the crystals, thickness of the crystals and even prevent the polymer from crystallizing.

The morphology of a crystal is defined as its macroscopic form and structure.[19] Early work in investigating the morphologies of crystals concluded that crystallization occurs by addition of particles from external fluids, that different crystallization faces may grow including different rates of crystallization, and that the angle between similar faces are always the same.[19] These conclusions were key in the classification of crystals. Moreover, many different shapes of crystals were observed and said to exist, some are shown in Figure 2. These shapes, or habits, aid in characterizing microscopy images of polymers, especially if single crystals are formed.

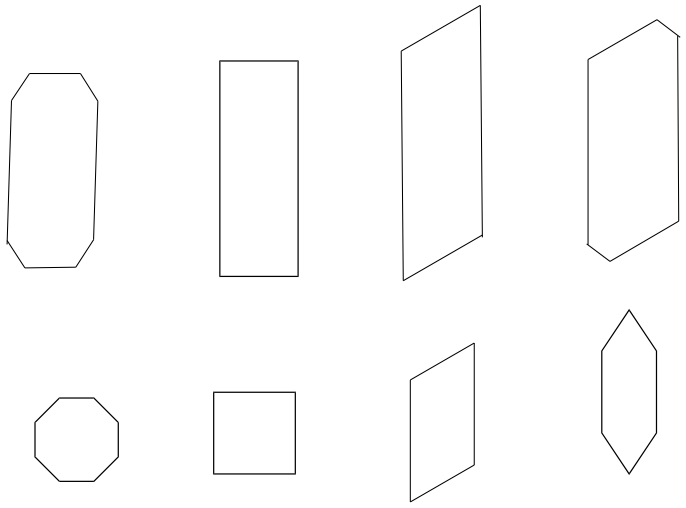


Figure 2. Two-dimensional depictions of different shapes of polymer crystals. The top row are considered to have prismatic habit and the bottom row has isometric.[19]

The most basic type of morphology of a polymer is a single crystal in which one lamellar sheet is present. A lamella is essentially one crystalline layer.[19] Furthermore, single crystal shape can be described in two concepts, the habit and the combination of crystallographic forms. The combination of crystallographic forms refers various combinations of the (100), (010), and (001) faces, but will not be discussed in extent for the purpose of this research. As applied to general crystal structure, the habit is just the general shape of the crystal. Different

habits exist for single crystals as well, such as lamellar, platy, tabular, isometric, prismatic, acicular, needlelike, and fibrillar.[19] Some of these are identified in Figure 3. The various habits of polymeric crystallization are dependent on and characteristic of the conditions. Specifically, lamellar habits are common in crystals that are grown slowly from polymer melts and solutions.[19] Lamellar thickness is also important in this process and has been proven to be a function of temperature and pressure.[19] Lamellar thickness is influenced by the folding of the polymer chains in crystallization and can have an impact on the resulting crystalline structure. Due to the fact that these types of crystals form from only one lamella of the polymer, therefore forming a definitive shape and structure, much can be said about the final assembly and how the conditions may have effected it. Three-dimensional forms of the shapes shown in Figure 2 can occur when forming single crystals.

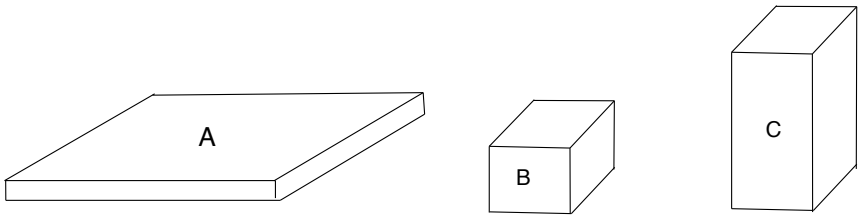


Figure 3. Schematic of (A) lamellar, (B) isometric and (C) prismatic habits for single crystals.

As mentioned briefly before, the folding of the crystalline chains is important to the final structure. Folding can occur in two ways: flat-on and edge-on. Single crystals are crystals that grow in a flat-on manner in one lamellar sheet, in which the habit reveals the identity of the polymer. Flat-on crystals grow in a direction parallel to the surface on which it is growing. A depiction of this growth is shown in Figure 4a. These crystals typically do not polarize light and therefore are fairly easy to tell apart from edge-on crystals when using polarized microscopy. On the other hand, edge-on crystals grow in a manner that is more three-dimensional and in a direction that is perpendicular and parallel to the growth surface (Figure 4b). These crystals are bi-refringent and polarize light in different directions depending on the direction of the chains.

Typically, they are found in morphologies of thicker films. Figure 4 represents what these chains would look like from the side view, however different shapes would be seen from the top view, such as circles, square, spherulites, etc.

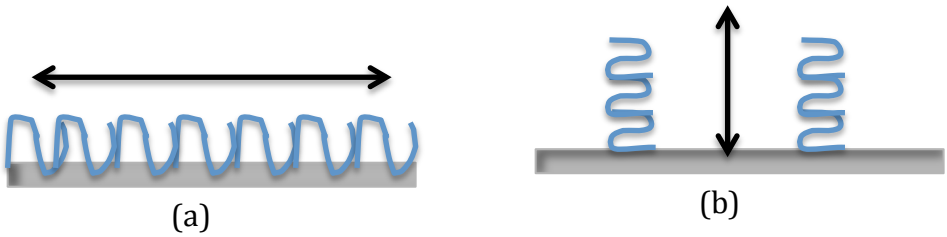


Figure 4. Depictions of crystallization growing in a (a) flat-on and (b) edge-on manner. The blue lines represent the polymer and the grey rectangle represents the surface. The black arrows indicate the directions of growth.

Some other morphologies that are known to form from controlling the crystallization of polymers include spherulites, micelles, and dendrites, examples of which are shown in Figure 5. The type of crystal depends on the rate of growth, if its more kinetically-limited or diffusion-limited, and the distance it is from equilibrium.[14] Kinetically-limited growth is closest to equilibrium and no real driving force exists for crystallization other than the crystals orienting themselves in a manner to allow crystallization. Diffusion-limited crystallization on the other hand involves growth that has a lot of driving forces, and is impacted heavily by environmental factors; this growth is farther from equilibrium. Spherulites consist of the crystal lamella growing concentrically outward from a central nucleation point.[18] These are the most diffusion-limited type of crystals and often make it difficult to decipher how the crystal is growing on a lamellar level due to the densely packed macrostructure. Spherulites can grow edge-on or flat-on crystals depending on various crystallization conditions. Dendrites are similar to spherulites, but instead of looking like a sphere, the crystallized structure extends outward from a central nucleation site in the form of 2D branches.[14] Micelles are a different type of morphology and typically exist in block copolymers when one block wants to stay in solution (corona on the outside), but the other groups together in the center because it does not have high affinity for

the solvent; micelles do not always crystallize in films, but rather form in solutions. Ultimately, what forms in terms of final structure is solely dependent on the type of polymer and the conditions under which crystallization is allowed.

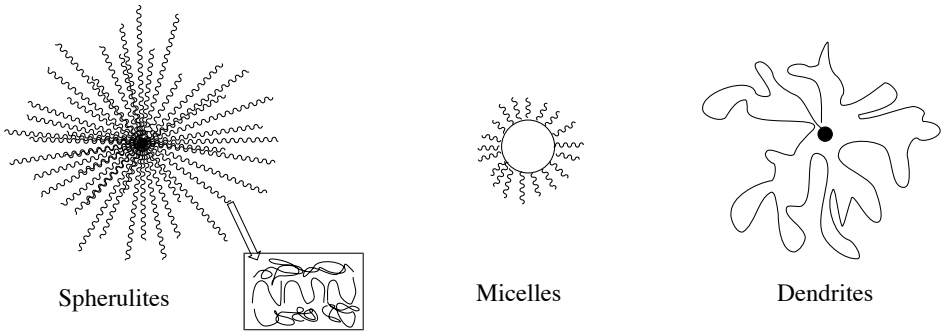


Figure 5. Macromolecular crystal morphologies.

Germane to this research, block copolymers have received much attention due to their ability to combine two different polymers into a new material with shared properties of all the single polymers.[20,21] Block copolymers are macromolecules composed of sequences, or blocks, of chemically distinct repeat units.[22] Moreover, over the last few years, tremendous research efforts have been dedicated to the potential applications of block copolymers in advanced technologies, such as information storage, drug delivery, photonic crystals, etc.[20] Due to their versatility, block copolymers are frequently used for commercial products. Being able to selectively synthesize a block copolymer with a combination of properties brought in from each block is what gives it this resourcefulness and applicability to a wide range of materials.

The number of units a block copolymer contains defines how it gets named (i.e. a block copolymer with two blocks is called a diblock copolymer).[18] Block copolymers can also be distinguished based on molecular weight. Similar to regular polymer naming, a diblock copolymer in which both blocks have a value of M_n=10,000 g/mol would be signified as 10k-10k. Additionally, the polymer names would be separated by the word “block” or *-b-* in the shortened form.

A couple different combinations of block copolymers can occur due to the fact that both crystalline and amorphous polymers exist. Moreover, diblock copolymers can consist of both amorphous blocks (A-A), both crystalline blocks (C-C), or a combination of the two (C-A). The A-A and C-A cases are a bit more complex due to the amorphous polymer aspect; our research focuses on the C-C case. This conformation will be expanded upon here. Both of these blocks are able to crystalize; this process occurs in a separate manner, or in other words polymer "X" will crystallize separate from polymer "Y" and there will be no crystal that is "XY." Comparing this idea to Scheme 1, the crystallized lamella would be one block, and the amorphous part on either side would be the other block. The amorphous part on top would then form it's own lamella on top of the other block's crystal. This is accounted for based on the fact that these two polymers want to demix typically, but cannot because they are connected in the diblock.[18] When these two polymers congregate with their own kind and form domains, it is called microphase separation. Additionally, if one block nucleates and crystallizes first, confined crystallization of the other block may occur, in which the crystals formed are imperfect due to the fact that it must now grow in between the other polymer crystals. Depending on the composition in the diblock, different factors can affect the order of crystallization. Particularly and among other factors, the solvent that is used to dissolve the copolymer has an influence on this due to the potential selectivity of the solvent for one block and not the other.[18] This is especially pertinent for the formation of micelles from diblock copolymers.

Much research is geared towards block copolymers that are amphiphilic, or have both a hydrophobic part and hydrophilic part because of their ability to form spherical micelles from them. Though the current research is focused on thin films, micelles of PEO-*b*-PCL are frequently researched. Specifically, diblock copolymers with these characteristics have been studied as nanoparticle drug delivery systems.[23-26] Micelles for drug delivery are formed on the basis of using a solvent system that forces one polymer into the core of the structure, and the other around the core, or as the corona; the solvent is really the crucial factor. Solvents used to

dissolve polymers can either be distinguished as good, bad, or a theta solvent.[18] The first two speak for themselves, meaning that a good solvent will dissolve the polymer, and the polymer has high affinity for the solvent. A bad solvent is just the opposite of that, and the polymer's interactions with itself are more favorable energetically than with the solvent.[27] Micelles form from a diblock copolymer by using a solvent that is good for one of the polymers, but bad for the other. This solvent selectivity can be also applied to give insight onto the solvent effects on thin films. With regards to the polymer chain, in a good solvent, the polymer spreads out and interacts freely with the solvent molecules, but in a bad solvent, it retracts towards itself due to the fact that it does not want to interact with the solvent. Moreover, in a poor solvent, the solute will likely precipitate due to its high local concentration forced by the solvent; this allows the polymer to avoid unfavorable interactions between the solvent and polymer. These interactions can be visualized in Figure 6. In a theta solvent, there is no energetic preference favoring solvent-solvent interactions compared to solvent-solute interactions.[27] Therefore, the solvent is an important aspect of the crystallization process and depending on the type of solvent can alter how the polymer crystallizes, or arranges itself in solution.

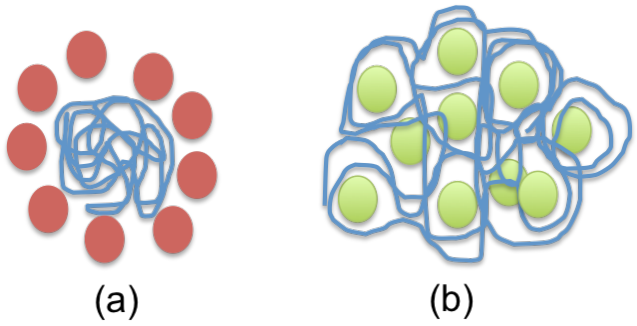


Figure 6. Representation of polymer interactions with a (a) bad solvent and (b) a good solvent. The circles are the solvent molecules and the blue line is the polymer.

Poly(ethylene oxide)-b-poly(ε-caprolactone)

Poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL) is an amphiphilic, biocompatible crystalline-crystalline (C-C) diblock copolymer that has been the focus of much research for biomedical applications, along with its derivatives.[28-33] The hydrophobic block of

PCL combines with hydrophilic PEO to form a structure that has the ability to form micelles in solutions and be used for drug delivery. [34-37] The PEO-*b*-PCL molecule is shown in Figure 7. Although the water solubility characteristic is most relevant for its use, these two polymers have other characteristics as well that are carried into the block copolymer.

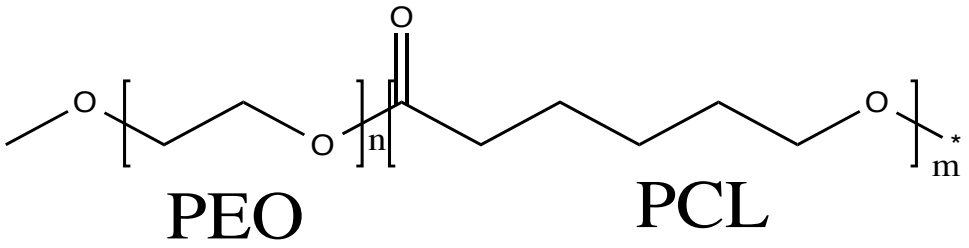


Figure 7. PEO-*b*-PCL diblock copolymer with its respective blocks labeled. The m and n subscripts represent the degree of polymerization.

To better comprehend the crystallization process of PEO-*b*-PCL, factors that alter the process must be first understood. Much research has been dedicated to the effects of molecular weight of each block on PEO-*b*-PCL and similar polymers.[10,11, 17, 38-43] In the diblock copolymer, it has been discovered that when the molecular weight of one block increases and is in greater amount than the other, that block will nucleate and crystallize first, causing the other block to grow in confinement and dictating the characteristics to be more like the polymer that crystallized first. For example, when the weight fraction of PCL (W_{PCL}) is 0.36 or less, PEO will crystalize first, which results in a confined growth of PCL.[10] Conversely, when W_{PCL} is greater than 0.43, then PCL will crystallize first. Not only is this an important factor in the diblock copolymer, but it also changes the crystallization of either block on an individual level. More explicitly, when the molecular weight of one block is increased, the crystallization process is altered due to the fact that the local concentration potentially increasing, making it easier for the polymer to find other chains of the same composition to crystallize.[44] For example, when 5k-5k diblocks are being analyzed versus 10k-10.3k, the order of crystallization has the potential to switch, and depending on which block crystallizes first, the final crystal structure can be controlled.[45, 46]

Another factor that has been extensively studied for the purpose of changing the crystallization of diblock copolymers is temperature: crystallization or melting. Most CC diblock copolymers have a large difference in T_m, which helps distinguish between crystallization of each block in analysis.[47-50] In the case of PEO and PCL, their melting and crystallization temperatures are very close and therefore, coincident crystallization occurs, making it difficult to distinguish what block is crystallizing at a given time. The temperatures at which melting and crystallization are allowed to occur, however, has been proven to have an effect on the crystalline structure.[8,9,51,52] Moreover, at higher crystallization temperatures, the diameter and size of PEO-*b*-PCL spherulites are larger due to the slower rate of crystallization at heightened temperatures. This information can be generalized to when temperatures are higher, crystallization is slower and the process becomes more kinetically controlled instead of being controlled by diffusion.[14]

Another factor that is not as well known, but still impacts crystallization is the use of solvent and the method at which crystals are grown from a solvent solution.[12,13, 51] *Via* the good/bad solvent cognitive, one might realize that many different crystalline structures could be possible. As stated previously, through addition of a solvent system of water, for example, followed by addition of a solvent that is bad for PEO, but good for PCL, micelles are likely to form containing a PEO core. However, when PEO-*b*-PCL is dissolved in one solvent that is good for PCL, but bad for PEO, such as amyl acetate, PCL wants to stay in solution but PEO does not, and therefore, has been shown to precipitate out of solution to form single crystals.[17] This is commonly known as solution crystallization. Hamley[53] further describes this: “If the solvent is selective for the crystalline block, it can swell the crystalline lamella” making this block not easy to crystallize. In contrast if the solvent is not selective for the crystallized block, then it will precipitate out of solution. In CC copolymers, where both can crystallize, the order can be controlled using this idea.

Depending on what shape the crystal forms, the block that had less energetically favorable interactions with the solvent can be deduced because PEO and PCL form different habits. Relevant solvent parameters that may have an effect on crystallization are shown in Table 1. The results in specific solvents may lead to gaining insight onto which factor effects PEO-*b*-PCL crystallization prominently. Namely, there may be a trend in crystallization that follows the solvent's dielectric constant, vapor pressure, or solubility parameter. PEO is known to form single crystals in the shape of squares due to it's monoclinic unit cell.[17,54-58] Previous studies of PCL have clearly showed the preference for forming six-sided single crystals with an orthorhombic unit cell under a wide array of conditions both in the homopolymer and the diblock copolymer.[17, 59-67] If a square crystal results from a specific solvent, then that solvent was likely a good solvent for PCL and therefore PCL crystals swelled while PEO separated from the solvent and nucleated first. Depending on the film thickness and molecular weight of each block, these crystals could be subject to change and contain defects. However, one conclusion from forming single crystals is that solvent can be used to effectively grow them. Along side this theory, the atmosphere that crystals are growing in can also alter what crystal structure is formed.[68-70]

The goal of the current research is to achieve single crystal formation through solvent evaporation and solution crystallization methods in order to determine which block crystallizes first in specific solvents, depending on the shape and structure of the resulting single crystal. Ultimately, the intended outcome is to be able to organize the order of crystallization with a trend in either of the solvent factors found in Table 1. A method under which consistent single crystal formation occurs will be developed. In the case of single crystal formation, the order of crystallization can be determined and therefore solvent-polymer interactions can be suggested. Optical microscopy (OM) with polarizing (POM) abilities and Fourier-Transform infrared spectroscopy with an attenuated total reflectance (ATR-FTIR) attachment will be used in majority to analyze the characteristics of the crystals formed. Dissolution tests of the

homopolymers in each solvent were also be utilized to apply back to the diblock copolymers to confirm which block would crash out of solution first.

Solvent	Dielectric Constant	Solubility Parameter ($[cal/cm^3]^{1/2}$)	Vapor Pressure (kPa)
Acetone	21.01	9.82	30.8
Amyl Acetate	4.79	8.41	0.6
Methyl Ethyl Ketone	18.56	9.29	12.6
Chloroform	4.81	9.29	26.2
Dichloromethane	8.93	9.92	58.2
Diethyl Ether	4.27	7.72	71.7
Ethanol	25.3	12.92	7.87
Ethyl Acetate	6.1	8.9	12.6
Ethyl Formate	8.57	9.58	32.3
Hexyl Alcohol	13	10.7	0.11
THF	7.52	9.48	21.6
Toluene	2.38	8.9	3.79

Table 1. Relevant solvent characteristics for polymer crystallization. Values for the listed solvents are from references 71 and 72.

Experimental

Materials

10,000 g/mol-10,300 g/mol (10k-10.3k) samples of poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL) were purchased from Advanced Polymer Materials Inc. 9,500 g/mol (9.5k) and 30,000 g/mol (30k) samples of poly(ε-caprolactone) (PCL) homopolymer, and 32,000 g/mol (32k) samples of poly(ethylene oxide) (PEO) homopolymer were purchased from Polymer Source Inc. and used as received. 10,000 g/mol (10k) PEO homopolymer was synthesized at the University of Akron by Christopher Nardi and used as prepared. Solvents were purchased from EMD Chemicals and Fischer Chemicals (acetone, amyl acetate, chloroform, ethyl acetate, ethyl formate, methyl ethyl ketone, *n*-hexanol and toluene).

Preparing Solutions and Films

Solutions were prepared starting with concentrations of 1% by weight of 10k-10.3k PEO-*b*-PCL in chloroform, acetone, and toluene. These concentrations were subsequently decreased to 0.5%, 0.1%, 0.05%, and finally, 0.01% in an attempt to achieve single crystal formation *via* evaporation. Some solutions required minimal heat in order to get the solid to completely dissolve. Using a micropipette, samples were cast onto glass slides in 10 µL amounts at room temperature and also in an oven to slow down the crystallization rate where the temperatures at which the films were dried were manipulated. Films prepared in the oven were left to dry for a week at the set temperature.

Preparing Solutions and Solution Crystallization

Samples of 10k-10.3k PEO-*b*-PCL were prepared at either 0.01% or 1% by weight in amyl acetate, ethyl acetate, ethyl formate, methyl ethyl ketone, or *n*-hexanol. All solutions were first heated to get the samples to dissolve, then left to sit at room temperature until a precipitate formed. If a precipitate was not formed, solutions were placed in the fridge to force precipitation. When a precipitate formed, this indicated that the sample crystallized in solution and was then taken to the optical microscope (OM) for analysis.

Measurements

Optical Microscopy

A Leica DM2700P optical microscope (OM) with polarizing capabilities (POM) was used to analyze all the prepared samples. Magnifications available for use were 5x, 10x and 50x. The shape, size, and overall assembly of the final crystalline structure were analyzed. In the case of single crystals, the shape of the formed structure allowed for characterization based off of previous literature.[17]

Attentuated Total Reflectance-FTIR

1% solutions of 10k-10.3k PEO-*b*-PCL in acetone, chloroform, toluene, ethyl acetate, ethyl formate, or methyl ethyl ketone were placed onto the smart iTR attachment of a Nicolet

6700 FT-IR (ATR-FTIR) in 25 µL amounts, and spectra were taken in 10 second intervals to monitor the sequence of crystallization of PEO-*b*-PCL for each solvent. The resolution and number of scans were set to 16 and the data spacing was 1.928 cm^{-1}. Once the solvent was completely evaporated and both blocks crystallized, data collection ceased. The peaks used to monitor PEO crystallization were appearances of peaks at 842 and 1063 cm^{-1}. For PCL crystyallization, the appearance of peaks at 731 and 1041 cm^{-1} and also a shift in the peak at 1735 cm^{-1} (amorphous PCL) to 1725 cm^{-1} (crystalline PCL) were monitored. The series of peaks which occurred first determined the order of crystallization in the diblock.

Preliminary Results

Single Crystal Formation in Films

Single crystals that form from the diblock copolymer would give us insight into which block crystallized first and from the structure, would tell us more about the solvent affinity and how this affects the crystallization process. Single crystal formation was the goal of the current research, in order to easily conclude which block crystallized first. Furthermore, getting single crystals might allow us to organize the results based on a specific solvent parameter, as mentioned earlier. 1% by weight samples produced crystals that were spherulitic all over the film in most solvents. Although spherulites strongly allude to crystalline structure, it does not tell enough about the assembly level of the copolymer and how those crystals are forming. Specifically, when the film is too thick, one cannot accurately depict or decipher which block crystallizes first. To obtain a better image of how the crystal is forming, concentration was decreased in order to promote single crystal-like growth in thin films. When the sample was left long enough in the oven, and/or at low enough concentrations, single crystal formation was observable under OM. Based off of the geometry present; the block that crystallized first can be suggested.

Chloroform, acetone and toluene are all solvents that dissolve the polymer at room temperature; therefore getting solution crystallization to occur with these solvents is not in the

realm of the available technology for this research. With that known, evaporation or film crystallization is the more practical technique to form single crystals.

To obtain a good representation of what each respective block should look like, solutions of the homopolymers, PEO and PCL, were prepared using 0.05% by weight of polymer in various solvents. Solutions were cast and placed in the oven for about a week. Optical microscope images using 50x magnification for crystals grown from chloroform can be observed in Figure 8. Figure 8a reveals a prolate spheroid shape that was taken to suggest what PCL single crystals can be expected to look like. This habit may be subject to change depending on solvent effects. Figure 8b shows single crystals of PEO in chloroform, which are too small to make any definitive conclusions on shape. Comparing the two images, PCL seems to form more definite and larger crystals. This could be a possible indication of chloroform being a more prominent solvent for PCL crystallization and crystal formation. Figure 8 was used as an idea of what the crystals of the diblock may look like, depending on which block nucleates first in chloroform as well as a basis of what PEO or PCL crystallizing first may look like in the other solvents. The homopolymer samples in acetone, toluene, ethyl acetate, ethyl formate, and methyl ethyl ketone were viewed under the optical microscope as needed.

Single crystal formation of the 10k-10.3k copolymer was not present until decreasing the concentration to 0.1%, however the only solvent that exhibited the ability to form these at this concentration was chloroform. From the elongated hexagonal shape, shown in Figure 9, PCL was concluded to have crystallized first in chloroform. Further, the 0.05% solution in chloroform also formed PCL single crystals (Figure 9b). These results suggest that PCL nucleated first and dictated the crystalline habit; PEO then grew in confinement on the top and bottom surfaces if at all. Figure 9b also exhibits that when concentration is decreased, the crystals appeared to be thinnerand fewer rings formed around the crystal.

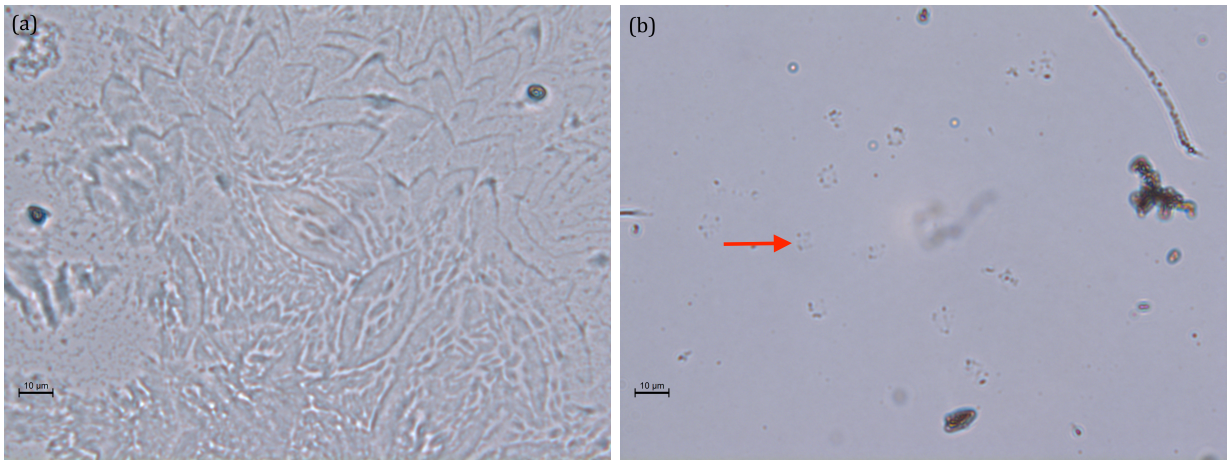


Figure 8. OM images of (a) 9.5k PCL homopolymer and (b) 10k PEO homopolymer in chloroform with the crystals indicated with a red arrow (0.05% by weight, each). The scale bar represents 10 μm.

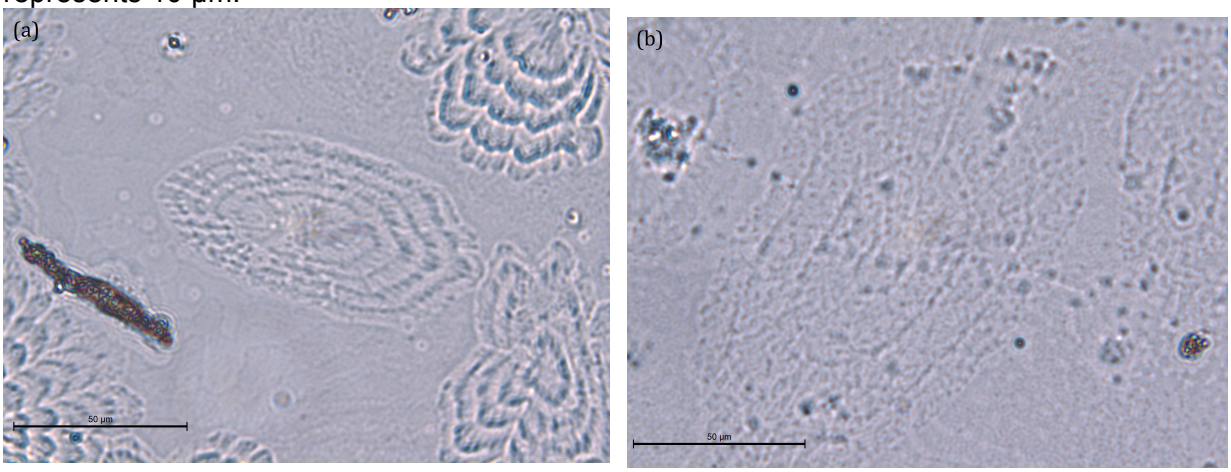


Figure 9. OM images of crystalline structures formed in (a) 0.1% and (b) 0.05% 10k-10.3k PEO-*b*-PCL samples in chloroform solutions cast onto glass. The scale bar represents 50 μm.

When dissolved in solvents other than chloroform, no single crystal formation was observed until the concentration was decreased to 0.01%. The images for crystals grown from 0.01% acetone are shown in Figure 10. These more prominently rhombic shapes were taken to be PCL single crystals as well, due to the fact that they provided crystal angles that were not 90 degrees at the ends. This order of crystallization was confirmed using ATR-FTIR.[16] 1% by weight solutions of 10k-10.3k PEO-*b*-PCL in acetone exhibited that PCL crystallized first *via* this method as well.[16] This suggests that PEO has a higher affinity for acetone, and therefore PCL crystallization is more frequent and perfected in this solvent.

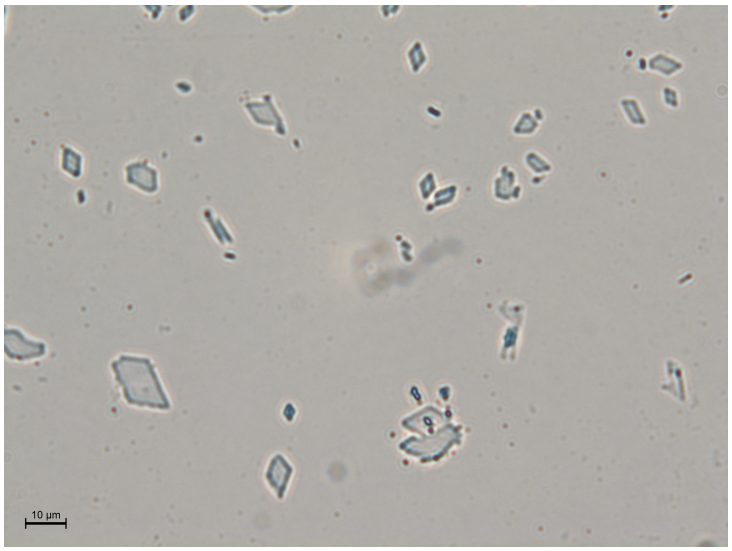


Figure 10. OM image of the crystalline structure from 0.01% PEO-*b*-PCL (10k-10.3k) acetone casted film. The bar indicated 10 µm.

Samples of copolymer dissolved in toluene did not provide sufficient single crystals for analysis at this point. Figure 11 shows typical results. These samples may have to be left in the oven longer due to the possibility that the single crystals may take longer to grow to a point that they can be clearly viewed or prepared using more advanced technology not available to this research. Another possibility is that they simply will not form single crystals or will not form ones large enough for viewing. This is likely due to the factor that PEO is known to crystallize quicker than PCL, leaving crystal structures to grow imperfectly. Moreover, PEO has been seen to crystalize first in toluene.[16] Therefore, it is theorized that when spherulites or undefined structures are observed in films from one solvent under the same conditions as another solvent that produced hexagonal single crystals, PEO nucleated first and dictated the structure. As mentioned, PEO has been perceived to have a faster rate of crystallization than PCL once it nucleates, which may drive it to be a more diffusion-limited process when crystallizing.

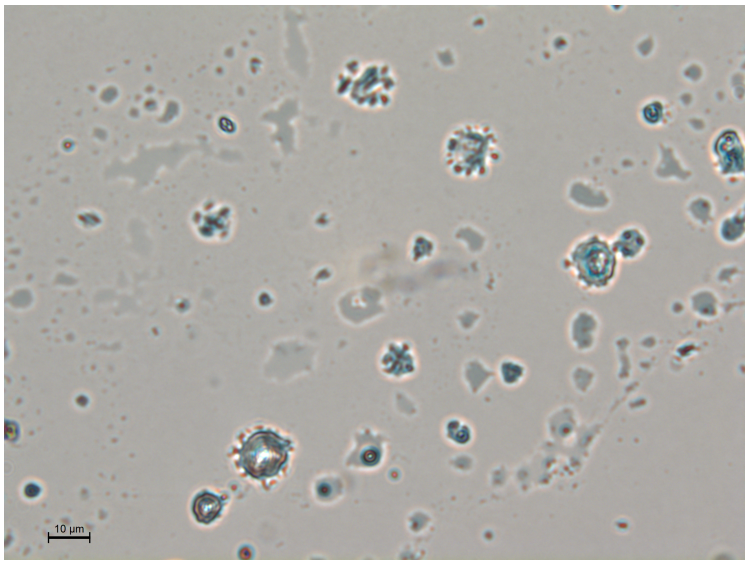


Figure 11. OM image of structures of 10k-10.3k PEO-*b*-PCL (0.01% by weight) that formed when cast in toluene. The bar represents 10 µm.

In order to gain more information about the effects of PEO-*b*-PCL when dissolved in toluene, work with the homopolymer was done. When preparing the samples, it was noted that the PEO homopolymers (10k and 32k) did not dissolve at room temperature in toluene while PCL did. This observation suggests that PEO would be the first block to crash out of solution and crystallize due to the decreased affinity for the solvent suggested by the lack of dissolution. OM images of PEO and PCL homopolymer crystallization in toluene are shown in Figure 12. Similar to what was formed in acetone, the PCL homopolymer dissolved in toluene created crystals that were rhombic in shape. This not only shows what kind of single crystals PCL forms in toluene, but also helps to confirm that the structures formed in acetone were likely from PCL-dictated crystallization.

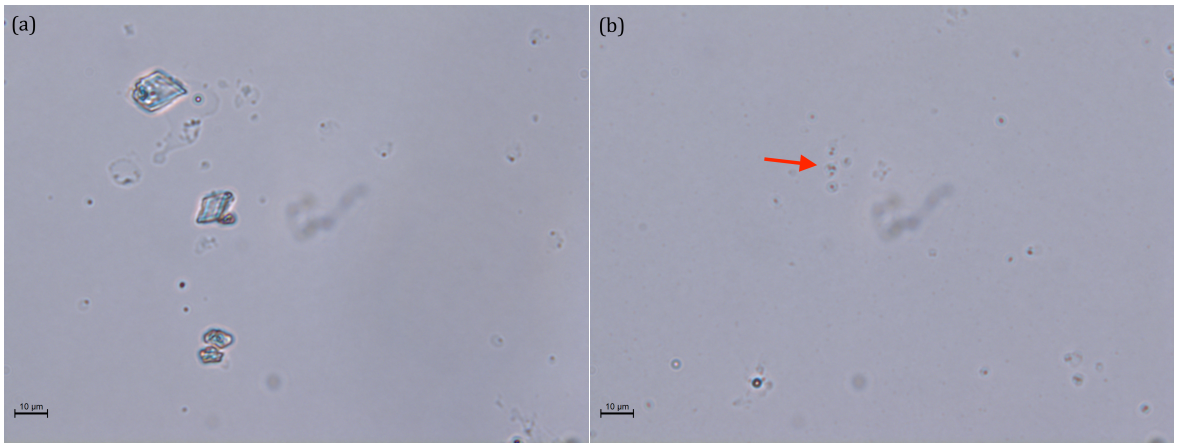


Figure 12. OM images of the crystallization of the homopolymers dissolved in toluene, (a) 9.5k PCL and (b) 10k PEO. The scale bar represents 10 µm.

To confirm the microscopy results, all the samples were also analyzed *via* the ATR-FTIR to track which block crystallized first based on the occurrence of the set of peaks known to indicate PEO and PCL crystallization. Solutions in each room temperature solvent, acetone, chloroform, and toluene, were placed onto the ATR-FTIR attachment in 25 µL aliquots. Spectra of the sample then were taken as the solvent evaporated to determine which block crystallized first. All the solvent spectra are shown in Figure 13 and are plotted against the melt for comparison. Figure 13a shows crystallization peaks that appear for PEO and PCL, indicated by the purple and orange arrows, respectively. Appearance of the PCL crystallization peaks first is evident in samples of acetone and chloroform, confirming the previous conclusions from the OM images. In this case, it can also be noted that PEO has not yet begun to crystallize by the lack of true peaks at 842 and 1063 cm^{-1}. For toluene, though the PEO crystallization peak is obvious in Figure 13a at 842 cm^{-1}, it also looks like there is a PCL peak formed at 731 cm^{-1}. For clarity, Figure 13b shows that PCL had not yet begun to crystallize based on the peak being centered at 1735 cm^{-1} and it matching up fairly well with the amorphous PCL peak indicated by the melt. The apparent peak at 731 cm^{-1} is likely due to residual toluene, as PCL is clearly amorphous based on Figure 13b. It was also confirmed that with multiple melts, the 731 cm^{-1} peak diminishes, proving the characterization of this peak as a solvent peak.

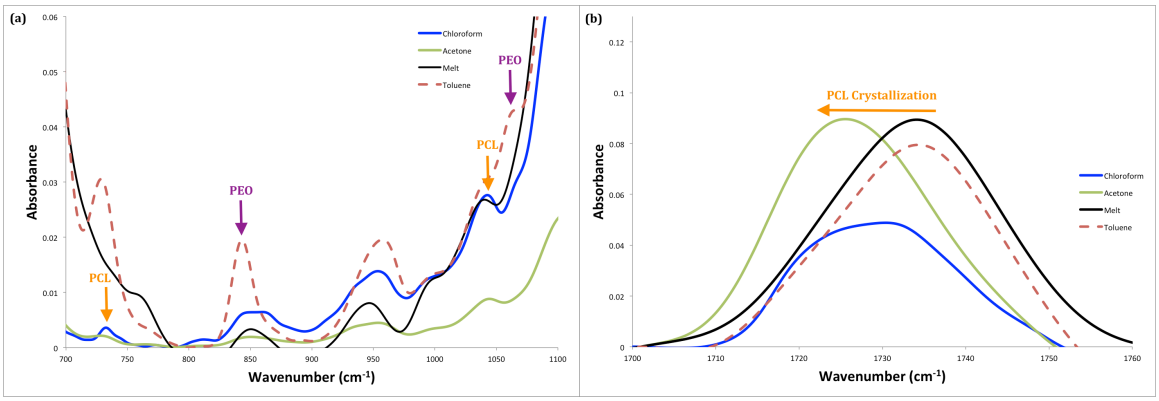


Figure 13. ATR-FTIR spectra of the relevant peaks used for analysis of 10k-10.3k PEO-*b*-PCL dissolved in the room temperature solvents, acetone, chloroform, and toluene compared to the melt. Selected spectra include from (a) 700 to 1100 cm^{-1} and (b) 1700 cm^{-1} to 1760 cm^{-1}.

To get a better idea of the solvent effects on crystallization sequence in PEO-*b*-PCL, different solvents that are similar to acetone, chloroform, and toluene were used in experimentation to see if they yielded comparable or clearer results. Specifically, amyl acetate, ethyl acetate, ethyl formate, methyl ethyl ketone and hexyl alcohol were used for analysis due to their resemblances in solvent traits as the room temperature solvents as well as their availability at our facilities. Additionally, in light of the fact that some of the new solvents do not dissolve the polymer at room temperature, a different method of crystallization was tried: solution crystallization. With a stronger representation of which block crystallizes first with solution crystallization, the solvent trend in crystallization sequence can be better concluded.

Single Crystal Formation from Solution Crystallization

Solution crystallization has been proven in the literature to produce clear single crystals of either PEO or PCL, unlike the evaporation method used for the room temperature solvents.[17] Using different solvents gives the possibility for solution crystallization and the capability of learning more into the specific solvent effects on crystallization of equal molecular weight diblocks of PEO-*b*-PCL (i.e. whether it is mainly a solubility parameter, dielectric constant, or vapor pressure effect). Based on the fact that these solvents do not dissolve the polymer

sample at room temperature, amyl acetate, ethyl acetate, ethyl formate, methyl ethyl ketone, and hexyl alcohol were used to induce crystallization of either block in solution.

Specific to the research done by Van Horn *et al.*[17] using solution crystallization, amyl acetate and hexyl alcohol were used to replicate the work using our 10k-10.3k PEO-*b*-PCL samples. In their research, they found that amyl acetate and hexyl alcohol formed PCL and PEO single crystals in solution, respectively for a 13k-9k sample. To get a clear representation of what the final structure of PCL and PEO crystals look like in the OM, 10k-10.3k samples in these solvents were prepared at a lower temperature. Solutions were left in the oven for a week to perfect crystal formation. The resulting crystals are shown in Figure 14. The results confirmed those of the literature; PEO formed definite squares (Figure 14b) and PCL formed a six-sided shape with angles not equal to 90 degrees (Figure 14a). Additionally, these images reveal that crystals may overlap each other in clumps, which might make further samples more difficult to analyze. The crystals in both the previous figures and Figure 14 will be continually used for comparison to determine which block dominated crystallization in other solvents. These results show that the order of crystallization can be manipulated by using different solvents, which lead to conducting trials in other solvents.

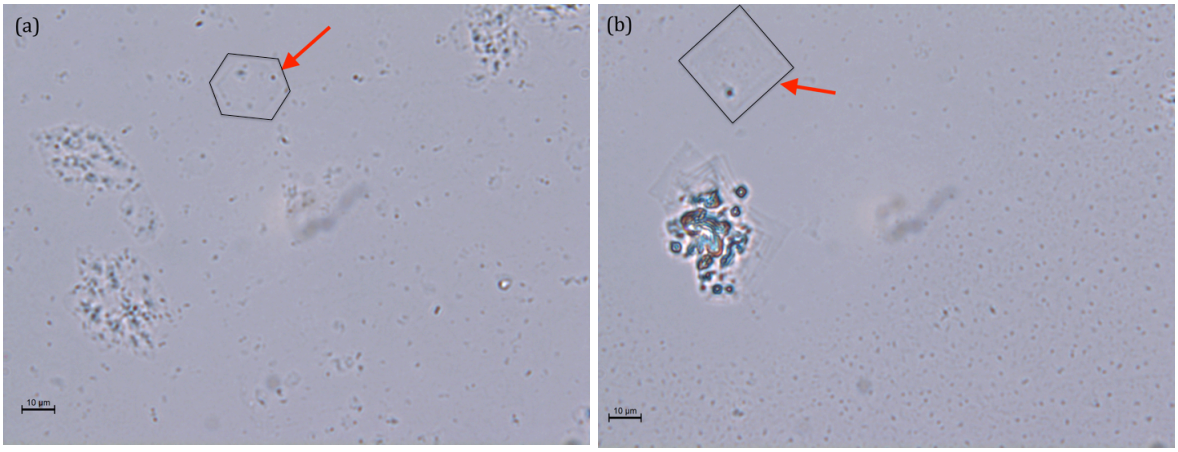


Figure 14. OM images of (a) PCL single crystals grown in hexyl alcohol and (b) PEO single crystals grown in amyl acetate solutions indicated by the red arrows and lines were added to aid in visualization. The bar represents 10 µm. Both solutions were 0.01% by weight of 10k-10.3k PEO-*b*-PCL.

After preparing the 10k-10.3k PEO-*b*-PCL samples in ethyl acetate, it was noted that the solution turned cloudy after it was left at room temperature for a day. The OM image of 1% 10k-10.3k PEO-*b*-PCL in ethyl acetate after the precipitate formed is shown in Figure 15. The image was taken with a 50x magnification and appears to contain crystals that are shaped like squares. These results indicated that PEO crashed out and crystallized in solution, as this habit of single crystal is typical of PEO. At lower concentrations, no conclusive crystals could be seen. This could be a matter of the crystals being too small for the magnification available. It should be noted that increasing the concentration may not always work for forming single crystals due to the fact that the process requires a balance finding what works for slow enough crystallization; increasing the concentration will speed up the rate of crystallization, therefore making the process more diffusion-limited. Regardless, this suggests that ethyl acetate preferentially interacts with PCL in solution and that PEO interactions with this solvent are less favorable.

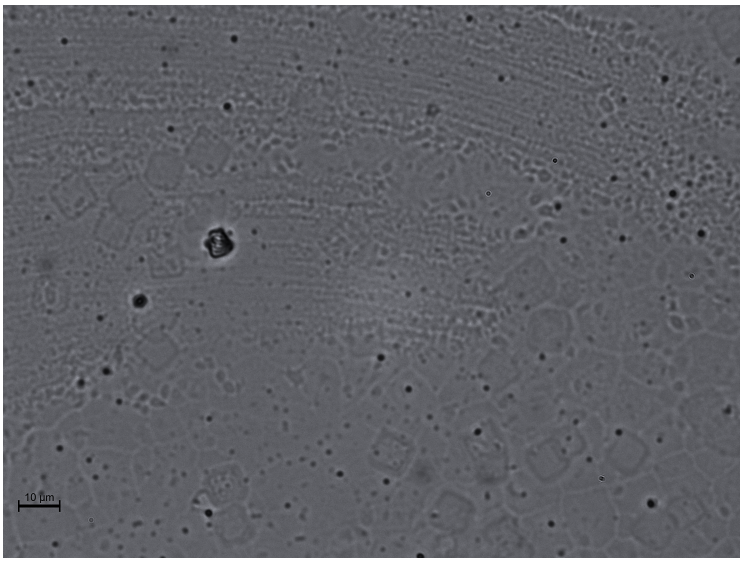


Figure 15. OM image of PEO single crystals grown in solution from 1% 10k-10.3k PEO-*b*-PCL dissolved in ethyl acetate. The scale bar represents 10 µm and the image was taken with a 50x magnification.

In order to confirm that the precipitate was PEO, a dissolution test was done on the homopolymers, 10k PEO and 9.5k PCL, in ethyl acetate. In testing dissolution, both

homopolymers needed to be heated up in order for the sample to dissolve. While the solution of 9.5k PCL stayed clear, a precipitate was formed with the solution of 10k PEO after sitting at room temperature. This confirms that PCL will likely stay in solution and PEO will crash out and crystallize first. Moreover, this proposes that what was seen in the diblock precipitate was more likely PEO than PCL.

The same methods were used for ethyl formate as were ethyl acetate to determine the order in which the diblock crystallizes. When dissolved in ethyl formate, a precipitate formed when the solution was cooled in the fridge, indicating solution crystallization at lower temperatures. Moreover, the OM images revealed single crystals that appeared to be hexagonal in shape (Figure 16). Given this data, PCL was presumed to have crystallized first as suggested by comparison of typical PCL single crystal geometry to Figure 16. This also advocates that ethyl formate favors interactions with PEO over PCL, allowing PCL to crash out of solution first and crystallize. To further this conclusion, 1% solutions of 10k-10.3k PEO-*b*-PCL in ethyl formate were analyzed using the ATR and dissolution test.

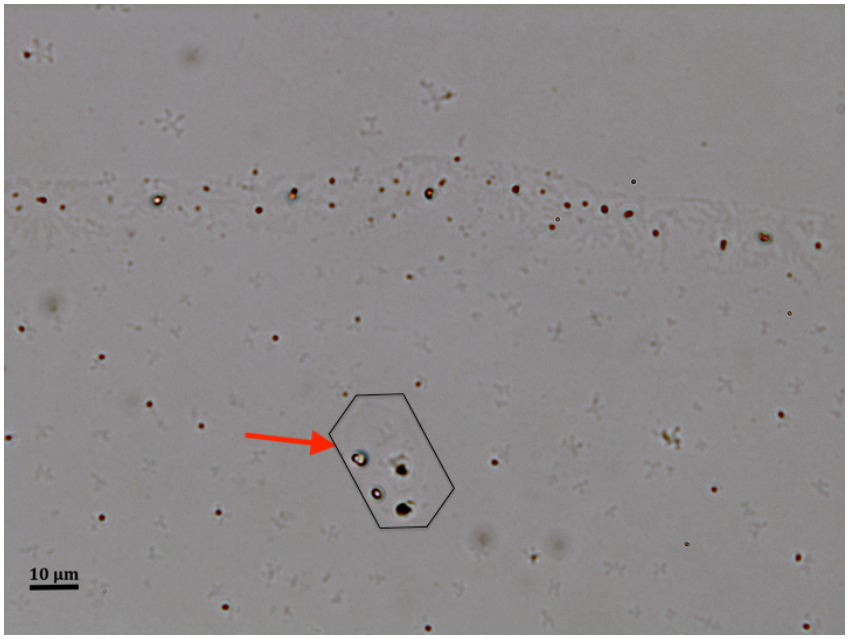


Figure 16. OM images of crystals grown from 10k-10.3k PEO-*b*-PCL dissolved in ethyl formate (0.01% by weight) indicated by the red arrow and outlined for clarity. The scale bar represents 10 µm.

Samples of the 9.5k PCL and 10k PEO in ethyl formate had to be heated up first to get the solid to dissolve. After heating, a dissolution test of the homopolymers revealed that PCL crashed out of solution, but PEO did not after being placed at a lower temperature. After returning to room temperature, the PCL homopolymer solutions eventually became clear once again. Getting the PCL to crash out of solution, but not the PEO is a signal that PCL does not preferentially interact with ethyl formate and that the interactions of PEO and the solvent are more favorable.

10k-10.3k PEO-*b*-PCL samples dissolved in methyl ethyl ketone required heat to get the solvents to dissolve, but did not crash out of solution after being cooled to room temperature. However, after cooling below room temperature, the solution precipitated. The OM image of the precipitate formed is shown in Figure 17. It does not appear that this solvent yielded proficient single crystals for determining which block crystallization first. Instead, undefined crystals formed, which do not yield an exact square or hexagon geometry. To determine which block was more favorable to crystallize first, further experimentation with dissolution tests and ATR analysis was completed.

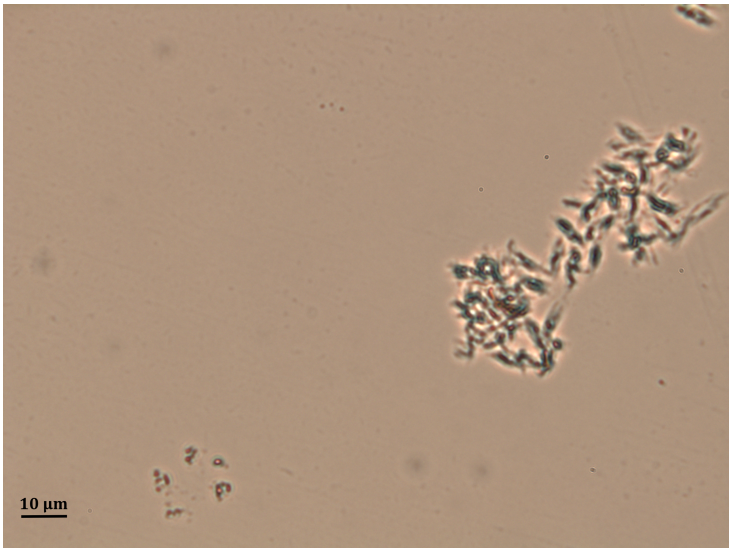


Figure 17. OM image of 10k-10.3k PEO-*b*-PCL crystals formed in methyl ethyl ketone. The scale bar represents 10 µm and the image was taken at 50x magnification.

A dissolution test of the homopolymers, 10k PEO and 9.5k PCL in methyl ethyl ketone revealed that, after being placed in the fridge, both solutions formed a precipitate. Seemingly, these results would suggest that methyl ethyl ketone does not have preference of which block it interacts with compared to the other. In other words, the solvent-polymer interactions are equally favorable for both PEO and PCL in this solvent. With that said, methyl ethyl ketone acts like a theta solvent for both PEO and PCL. To shed more light onto if there is a slight favoring of one block, the solutions might be able to be monitored closer to see which solution precipitates first. Instead, FTIR analysis was conducted.

To further confirm the sequence of PEO crystallizing before PCL in the diblock copolymer, 1% films of 10k-10.3k PEO-*b*-PCL in ethyl acetate, ethyl formate, and methyl ethyl ketone were monitored using the ATR-FTIR. Spectra were taken, as the solvent was cast and every 10 seconds until the solvent was completely evaporated. Peaks at 842 cm^{-1} and 1063 cm^{-1} were watched for PEO crystallization and 731 cm^{-1} and 1041 cm^{-1} for PCL crystallization (Figure 18a). For PCL crystallization, the peak shift from 1735 cm^{-1} (amorphous PCL) to 1725 cm^{-1} (crystalline PCL) was monitored (Figure 18b). These peaks are also pointed out with arrows in orange (PEO) and purple (PCL). From these graphs, it can be noted that the peaks that indicate PEO crystallization occur before any shift or peak appears for PCL crystallization, therefore ATR further confirms that in ethyl acetate, PEO crystallizes first. Additionally, for both ethyl formate and methyl ethyl ketone, the opposite appears to occur, in which peaks for PCL crystallization appear first in sequence, indicating that PCL crystallizes first in these solvents. Though this confirms the OM and dissolution results for ethyl formate, it does not exactly confirm methyl ethyl ketone, but suggests that there might be a slight affinity for polymer-solvent interactions with PEO over PCL in solution. Additionally, PCL crystallized first from the melt in this solvent. It was found that when this happened after just one melt, PCL was typically first to crystallize first in the solvent due to the fact that all of the solvent might not be evaporated, therefore solvent effects are still present.

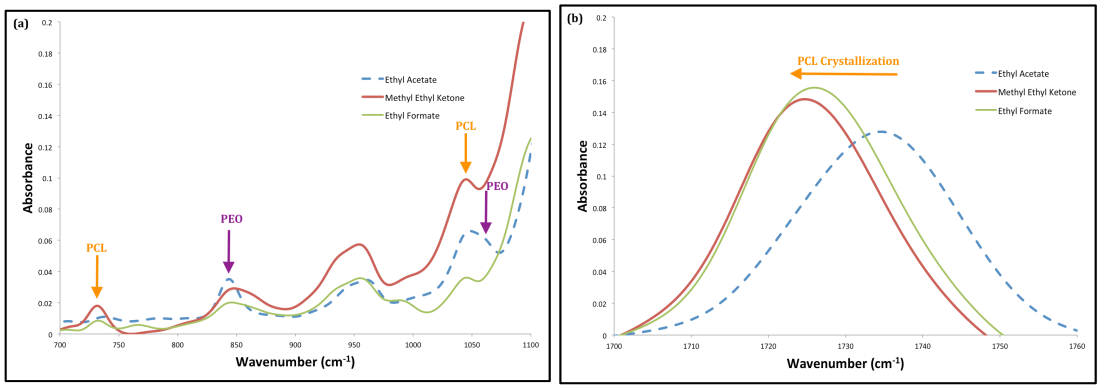


Figure 18. FTIR spectra of 10k-10.3k PEO-*b*-PCL dissolved in ethyl acetate (blue dashed), ethyl formate (green solid) and methyl ethyl ketone (red solid) from (a) 700 to 1100 cm^{-1} and (b) 1700 to 1760. The dashed line represents that PEO crystallization first. Specific peaks for block crystallization are pointed out in orange (PEO) and purple (PCL).

After compiling the results of crystallization order in each solvent to the trends of solvent characteristics (dielectric constant, solubility parameter, and vapor pressure), solubility parameter appeared to be best fit to explain the solvent-polymer interactions and which factor plays the most significant role. Results from solvents that were not within the confines of this research have been obtained from research done previously in our lab to create a better trend table.[16] A summary of the trends is shown in Table 2. Vapor pressure seemed to have an impact on crystallization in extreme measures; if the solvent evaporated very fast, PCL was more likely to crystallize first, while if the solvent was slow to evaporate, the crystallization was more driven by solvent interactions. This is why solvents with vapor pressures that are not too high or low were used. Vapor pressure did not provide any true trends when listing results. However, solvents that have a solubility parameter closer to each respective block (PEO=10.03 $[cal/cm^3]^{1/2}$ and PCL=9.73 $[cal/cm^3]^{1/2}$)[73] were more favorable to interact with that block and therefore will stay in solution and crystallize second. Because the values are very close for the solubility parameters of PEO and PCL, it could be that only with a low solubility parameter solvent that PEO will crystallize before PCL. Once solvent effects were eliminated, it was proven that PCL always crystallized first from the melt.[74] This suggests that for 10k-10.3k PEO-*b*-PCL, PCL is the preferential block to crystallize, but using solvent solubility parameters, PEO-*b*-PCL

can be selectively crystallized to get PEO to nucleate first. It should be noted that tetrahydofuran (THF) typically promotes PCL crystallization first sequentially, but has been shown to stick to the polymer and be slow to evaporate out of the film. As such, clear results were more difficult to obtain. Based on these results, one might be able to predict the crystallization order based on the solubility parameter of the solvent for future experimentation.

From Table 2, it can be noted that the solubility parameters of chloroform and methyl ethyl ketone are very close. Due to this and to the fact that their values are on the border of PEO or PCL crystallization, it was suggested that in the correct conditions, PEO could be crystallized first. Again, these two solvents can be considered to behave more like theta solvents for PEO and PCL because of this ability to get either to crystallize first in the copolymer.

Solvent	Solubility Parameter ($[cal/cm^3]^{1/2}$)	Sequence of Crystallization
Diethyl Ether	7.72	PEO first
Amyl Acetate	8.41	PEO first
Ethyl Acetate	8.9	PEO first
Toluene	8.9	PEO first
Chloroform	9.29	PCL first
Methyl Ethyl Ketone	9.29	PCL first
THF	9.48	PCL first
Ethyl Formate	9.58	PCL first
Acetone	9.82	PCL first
Dichloromethane	9.92	PCL first
Hexyl Alcohol	10.7	PCL first
Ethanol	12.92	PCL first

Table 2. Proposed trends of solvent effects on the crystallization of PEO-*b*-PCL (10k-10.3k), listed in order of increasing solubility parameter. The solvents used this semester are in italics. Respective solubility parameters for PEO and PCL are 10.03 $[cal/cm^3]^{1/2}$ and 9.73 $[cal/cm^3]^{1/2}$ (from reference 73).

Conclusions and Future Work

Using the symmetric diblock copolymer poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL), solvent effects and trends were concluded *via* single crystal formation, FTIR analysis and dissolution testing. Proximity of the solubility parameter of the solvent to the

polymer's solubility parameter played a significant role in their affinity for one another. Namely, amyl acetate, ethyl acetate and toluene were solvents that promoted PEO-first crystallization, while the other solvents promoted PCL first. Vapor pressure also may play a role, but only in extreme cases; this was deemed to not be the primary factor that affects the crystallization order.

Future work should expand upon different and more controlled methods as well as introducing new solvents that fit within the parameters of Table 2 (i.e. similar solubility parameters). Now that the order of crystallization can be controlled, other factors of crystallization can be studied, such as biodegradability, kinetics, and other crystallization characteristics. If PCL crystallized first, the film should degrade more because PCL is more biodegradable than PEO. Films in different solvents (i.e. one solvent that promotes PEO crystallization first and another that promotes PEO) can be tested for their biodegrability, or other factors can be used to alter this process using the same solvent. Another study that can be elaborated on would involve crystallization kinetics. In our previous research with isothermal crystallization of PEO-*b*-PCL, we noticed different rates of crystallization appear when either block crystallizes first. When PEO nucleated first, two rates of crystallization were noticed in the diblock: PEO growing alone, and PCL growing alone in confinement of the PEO crystals. But when PCL nucleated first, there were three: PCL growing first, then PEO growing inbetween PCL crystals, and PEO out growing it's confinement in the PCL crystals. Knowing some influences that causes PEO to crystallize first, these kinetics can be further studied to better understand the crystallization of PEO-*b*-PCL. This work as a whole aids in achieving more selectivity over crystallization of PEO-*b*-PCL using an uncommonly researched factor.

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