A comparison of drop-cast and spin-cast films of poly(ethylene oxide)-*b*-poly(ε-caprolactone) using Fourier Transform Infrared spectroscopy



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Senior Comprehensive Project

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Submitted to the Allegheny College Department of Chemistry in partial fulfillment of the requirements for a degree of Bachelor of Science

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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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William de Montmollin

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Abstract

PEO-*b*-PCL thin films were made from chloroform and THF solutions using two different casting methods—drop-casting and spin-casting. FTIR spectroscopy was used to determine crystalline content for each block. The films were analyzed by comparing as-cast films to their recrystallized from melt films in order to investigate the effect of casting method on the relative crystallinity of each polymer and the crystal directionality in the thin films. However, film recrystallization was inconsistent, and most of the films could not be reliably compared. Chloroform films of both casting methods showed suppressed PEO crystallinity in the recrystallized from melt films and much lower crystallinity overall. None of the spin-cast chloroform films recrystallized, while most of drop-cast ones did. Spin-cast THF films were found to have more crystal axes oriented perpendicular to the IR beam than the drop-cast films.

Introduction

Understanding the diverse variables controlling block copolymer crystallization is essential for influencing its material properties, such as optical/mechanical properties and biodegradability.[1] This study attempts to compare the effect of two different methods of thin film (< 1 μm) casting, drop-casting and spin-casting, on the relative crystallinity of the blocks of the diblock copolymer poly(ethylene oxide)-*b*-poly(ε-caprolactone) (PEO-*b*-PCL), as well as its crystal orientations. Thin films were made with both casting methods and analyzed using Fourier Transform Infrared spectroscopy (FTIR). PEO-*b*-PCL is an important biomedical polymer because of its amphilicity, biocompatibility, and biodegradability.[2] This study will begin with a short review of what polymers are, how they crystallize, and factors which affect that process, then, the two different film casting methods will be discussed.

Polymers

A polymer is a long chain molecule composed of many repeating molecular units, called monomers. They have many widespread uses, and it is nearly impossible to go a day without coming into contact with a polymer of some kind. The size of a polymer is related to its molecular weight. Polymer synthesis always leads to a distribution of different length polymer chains, so the average molecular weight is most often reported in two different ways, the number average molecular weight (M_n) and the weight average molecular weight (M_w).[3] M_n is defined by equation 1.

$$M_n = \frac{W}{N} \quad (1)$$

where W is the sum of the molecular weights of every different length polymer chain in a sample and N is the total number of moles. M_w is defined by equation 2.

$$M_w = \sum w_x M_x \quad (2)$$

where w_x is the weight fraction of polymer chain x (the ratio of the chain mass x to the total mass) and M_x is its molar mass. The ratio of M_w over M_n is called the polydispersity index (PDI) and is a measure of the molecular weight distribution. A PDI of 1 means that all of the polymer chains have the exact same molecular weight and length.

Diblock Copolymers

Polymers can be composed of one or more types of monomers. Those that are composed of only one kind of monomer are called homopolymers, while those composed of two or more kinds of monomers are called copolymers. The material properties of copolymers often combine those of their constituent monomers, so their use and study is widespread. There are many types of copolymers, but this study is concerned with diblock copolymers, which consist of chains, or blocks, of two different polymers that have been chemically linked together. The polymers in the two blocks in PEO-*b*-PCL are the poly(ethylene oxide) (PEO) and poly(ε-caprolactone) (PCL) whose molecular structures are shown in Figure 1, where *n* is the number of repeating units that would compose the polymer.

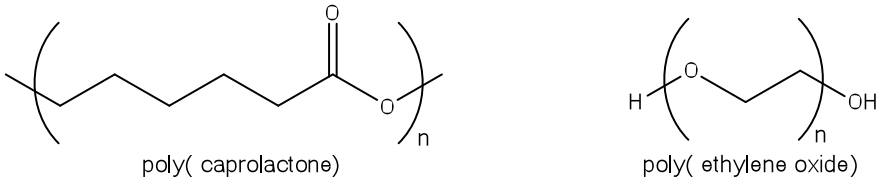


Figure 1. Molecular structures of PEO and PCL, where *n* is the number of repeating units.

PCL is a hydrophobic biodegradable polymer with low toxicity to humans that has numerous applications in the medical field, including wound dressings, contraceptive devices, and tissue scaffolding.[4] It is crystallizable because of its small nonisomeric shape. PEO has many of the same characteristics as PCL, including low toxicity and crystallizability, but it is more hydrophilic because of its ester group.[5] The combination of the two monomers make the copolymer amphiphilic and leads to micelle structures in solvents that interact more strongly with one monomer than the other.[2] This is an important trait for medical applications, such as drug delivery systems that incorporate a hydrophobic drug into the polymeric micelle.

Amorphous and Crystalline Phases and Polymer Crystallization

Polymers are found in two phases: a disordered amorphous phase and an ordered crystalline phase, both shown in Figure 2. The amorphous phase is a disordered mass of polymer chains in which the chains are capable of a large range of motion and are often tangled together in entropically favored bundles that resemble tangled cords. The crystalline phase consists of rigid and ordered structures of folded polymer chains called lamellae.

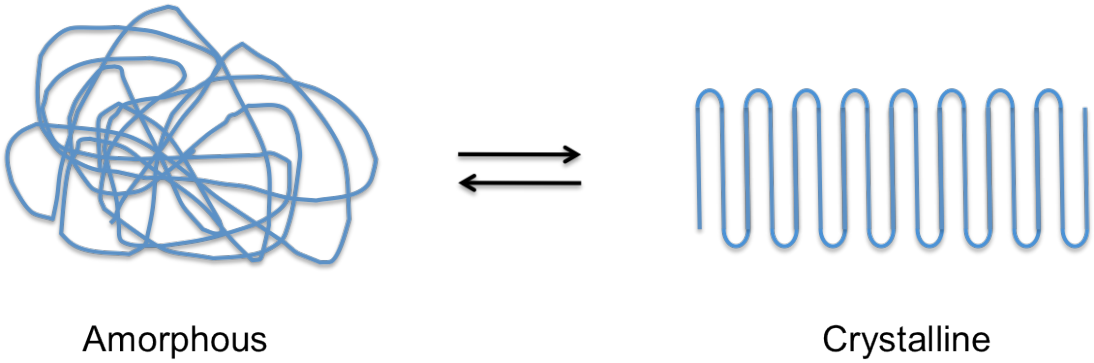


Figure 2. Polymer Phases

Polymers are usually entirely amorphous due to the kinetic difficulty of folding such large, tangled molecules. Only polymers with certain molecular structures like straight chains and small side groups (such as PEO and PCL) are capable of crystallization. However, 100% crystallinity in a polymer has never been achieved. Even polymers with crystallinity of 98 and 99% still have small amorphous regions at the folds of the lamellae.

The first and most widely used model of polymer crystallization is the Hoffman-Lauritzen model.[6] Also known as nucleation theory, this model begins with the precipitation of a crystalline polymer from an amorphous solution. Growth occurs as more amorphous phase overcomes an activation barrier and crystallizes on the face of the already precipitated phase.

In thin films, polymer nucleation and growth can occur on the surface on which the film is cast, known as the substrate surface. Lamellae grow in two orientations: edge-on and flat on, in which the chain axes (the normal vector of the crystal) are parallel and perpendicular to the substrate, respectively. They are illustrated in Figure 3, where *b* and *c* represent the growth face of the crystal for flat-on and edge-on, respectively, and *a* represents the substrate surface. Lamellar

crystals grow to maximize crystallinity, and the type of lamellar growth that occurs in a film depends on its thickness. Edge-on growth requires more vertical space and therefore favors thicker films. Flat-on growth is closer to the substrate, so it takes place in thinner films where the vertical space is diminished.

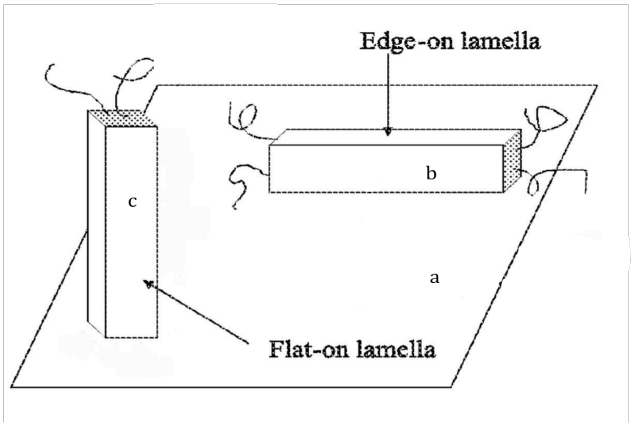


Figure 3. Edge-on and flat-on lamellar growth, where *a* represents the substrate; *b* and *c* represent growth faces. Adapted from Chan 2005.[7]

Some Factors that Affect PEO-*b*-PCL Crystallization

Solvent

Whether or not a polymer will dissolve in a solvent is determined by the favorability of the solvent-polymer interactions compared to the polymer-polymer interactions. If a solvent is good, the polymer will expand in order to increase polymer-solvent interaction, and the radius of gyration, which is proportional to the room mean square distance from the polymer's center of mass to every monomer, will increase. In a poor solvent, the polymer will collapse to limit polymer-solvent interaction and increase polymer-polymer interaction, thus causing the radius of gyration to decrease. Theta solvents are solvents in which neither polymer-polymer interactions nor polymer-solvent interactions are more favorable than the other, so

the polymer assumes the most energetically favorable shape via random motion, called its ideal chain.

In thin films of PEO-*b*-PCL created by drop-casting or spin-casting at room temperature, the crystallization process occurs as the solvent evaporates from the substrate. As the solvent leaves, the polymer precipitates out and begins to nucleate on the substrate surface. In diblock copolymers, one of the variables that affects the crystallization of one block over the other is their respective interactions with the solvent. When both blocks have similar crystallization temperatures (like PEO-*b*-PCL), if one block interacts more strongly with the solvent than the other, then it will remain in solution longer and therefore crystallize later than the other block.[8-9] However, this does not necessarily reflect the final composition of the copolymer crystals. The block that crystallizes second may still dominate in the final crystal structure depending on the growth rates of both blocks. If the crystallization rate of the second block is faster than the first, then it may still end up as the major crystalline phase.

Block Length

Previous research has shown that the length of each block (measured by molecular weight) in PEO-*b*-PCL influences which block crystallizes first. Using Differential Scanning Calorimetry (DSC) and Polarized Optical Microscopy (POM), He *et al.*[10-11] showed that the larger block crystallized first in films made from chloroform solvents and dictated the morphology of the crystals. Crystals from polymers with larger PEO blocks resembled pure PEO crystals, and those from polymers with larger PCL blocks resembled pure PCL crystals. With increasingly

larger PCL blocks, PEO still crystallized when its weight fraction was as low as 14%. Below that, only PCL crystallized. In PEO-*b*-PCL crystals with equal block lengths, the PCL was shown to crystallize before PEO.[12-13] However, the PEO growth was much faster than the PCL growth and quickly overtook it. Since the PCL began crystallizing first, the PEO growth began in the interlamellar regions between the PCL crystals and spread outward. The resulting crystal contained inner portions with higher concentrations of PCL crystals than PEO crystals and outer portions with higher concentrations of PEO than PCL. The exact mechanism for this crystallization process is still being investigated.

Spin-casting

Spin-casting is a method of making thin films that involves spinning a polymer solution on a substrate that results in a solute film.[14] The polymer solution is deposited on the substrate while it is not moving, and then it is quickly accelerated to a high angular velocity. Figure 4 shows a schematic of the spin-casting process. The two main pathways of solution removal are shown: evaporation and radial liquid flow, also called ejection. Due to the high angular velocity, most of the polymer solution is ejected immediately, and the evaporation of the rest of solvent results in a uniform film.

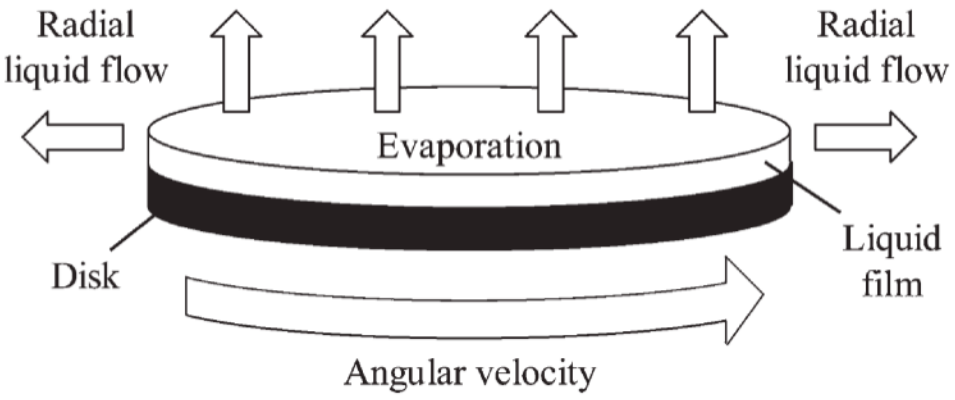


Figure 4. The spin-casting process. Adapted from Norrman *et al*.[9]

The thickness of these films is generally controlled by both the solution concentration and the angular velocity. The choice of solvent is also important. Solvents that have favorable solvent-polymer interactions, known as good solvents, were shown to produce more uniform polymer films.[15] Among good solvents, only those with low volatility produced uniform films. Wong *et al.*[16] compared spin-cast films of poly (3-hexylthiophene) to those that were drop-cast and inkjet printed using spectroscopic techniques. They found that the spin-cast film were the least crystalline, and that their crystals were the most anisotropic, meaning that the their normal vector, or crystal axis, was the most oriented. They attributed this observation to the spin-cast films being locked in a highly non-equilibrium state as a result of the fast casting process.

Drop-Casting

Drop-casting is a simpler method of film making that involves applying a solution to a substrate and allowing the solvent to evaporate and deposit a polymer film.[17] Drop-cast films are rougher than spin-coated ones because the evaporation of the solvent leaves terraced polymer layers compared to the homogenous spin-cast

ones.[18] These terraces have been attributed to the evaporating solvent creating dimples in the height of the polymer solution that lead to a ringed pattern of polymer commonly referred to as coffee stains.[19] Solvents effects have a greater influence on the polymer crystallization in drop-casting compared to spin-casting because the solvent evaporates much more slowly and has more time to interact with the polymer.

Analysis Techniques

FTIR. FTIR measures molecular motions, such as the vibrations of chemical bonds in a molecule, caused by the absorbance of infrared light. Commonly used to identify functional groups, FTIR also is useful for polymer physical chemistry because it can shed light on the crystallinity of a sample, crystal orientation, and the expression of one block over another in crystalline copolymers.

With PEO-*b*-PCL, the relative crystallinity of PEO to PCL is determined by the ratio of the absorbance of the PEO band at 842 cm^{-1} to the PCL band at 732 cm^{-1}, both of which are attributed to CH_2 rocking.[20-21] These bands are used because they correspond to specifically crystalline vibrations and will not appear if the film does not crystallize. It is important to note that their ratio only expresses the relative amounts of PEO to PCL and is not related to exact amounts of either crystal. To determine crystal orientation, the PCL bands used are 1295 and 1193 cm^{-1}, and the PEO bands are 1343 and 962 cm^{-1}.[22-24] These bands all correspond to molecular vibrations parallel to the chain axis of the polymer: 1295 cm^{-1} is C-O and C-C stretching; 1193 cm^{-1} is OC-O stretching; 1343 cm^{-1} is CH_2 wagging; and 962 cm^{-1} is CH_2 rocking and stretching.

Experimental Methods

Polymer Solution Preparation

Both 1% and 5% by weight polymer solutions were made by dissolving PEO-*b*-PCL in chloroform, methylene chloride, tetrahydrofuran (THF), or toluene. THF and toluene solutions were lightly heated to fully dissolve the polymer. The copolymer was purchased from Polymer Source Inc. (Montréal, QC) and had an average molecular weight of 5000 g/mol for each block and a PDI of 1.25. Equal block lengths were used to minimize the effect of molecular weight on the results.

Film Preparation

Drop-casting. Thin films were made by evaporating 10 drops of the desired 1% solutions on a KBr salt plate at room temperature. The plates were left in a desiccator at room temperature for at least one hour before analysis to allow crystallization to reach completion. Later films were made by applying 20 μL of solution using a micropipette, rather than 10 drops, in order to more precisely control the amount of polymer on each plate. Films that were melted were placed in a convection oven at 95 ˚C for 15 minutes and then placed in a dessicator for at least one hour at room temperature to allow recrystallization to reach completion.

Spin-casting. Thin films were made by applying 10 drops of the desired 5% solution onto a KBr salt plate and spinning it at 2040 ± 20 rpm for 30 seconds on an INTRAS Scientific Spin-Caster at room temperature. Later films were made by applying 100 μL of solution using a micropipette, rather than 10 drops, in order to more precisely control the amount of polymer on each plate. Films that were melted were placed in a convection oven at 95 ˚C for 15 minutes and removed to a

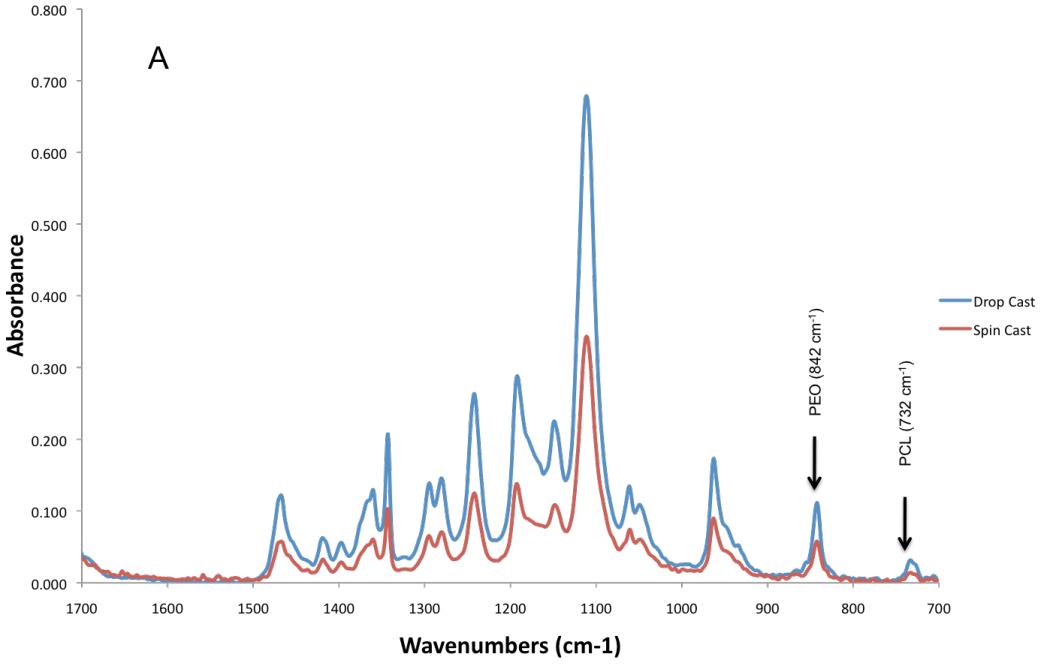
dessicator to crystallize at room temperature for at least one hour to allow recrystallization to reach completion. The 5% solutions were used because the spin-casting process requires a more concentrated polymer solution in order to deposit enough polymer for an FTIR signal due to solution loss from ejection.

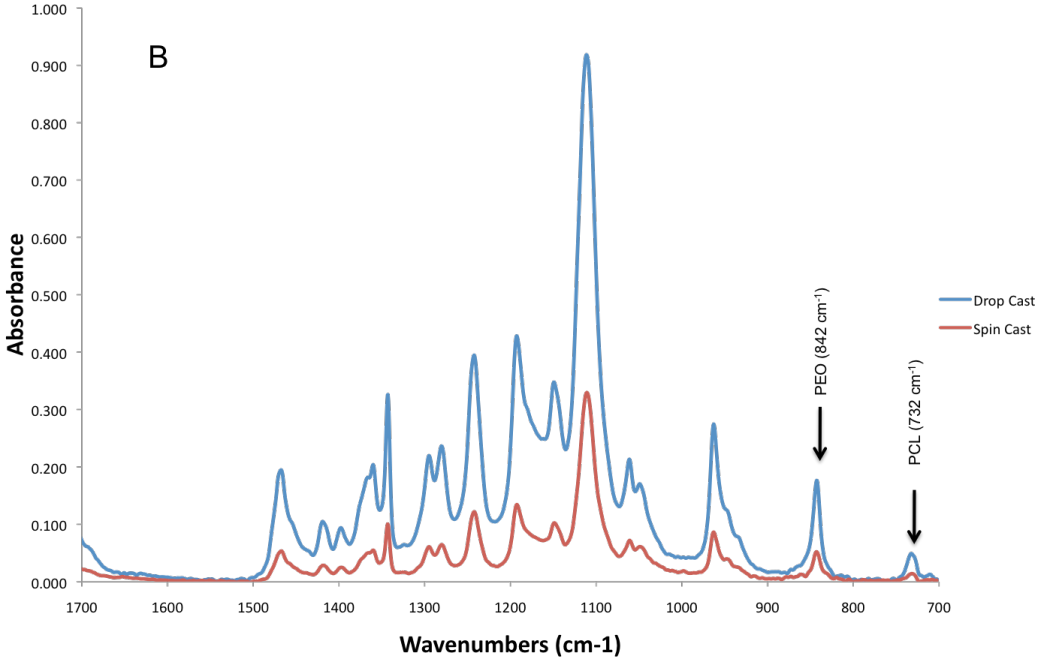
FTIR Spectroscopy

The films were analyzed using a Thermo Scientific Nicolet iS10 FTIR spectrometer. Spectra were recorded in absorbance mode between 400-4000 cm^{-1} with 16 scans and a resolution of 4 cm^{-1}. Three spectra of each plate were taken to determine film uniformity. The averaged spectra were created by averaging the spectra of 3 different films.

Results and Discussion

Drop-cast and spin-cast films from chloroform, methylene chloride and THF solutions were made and analyzed with FTIR. Drop-cast toluene films were made, but their spin-cast counterparts were not, because the copolymer would not dissolve in the 5% solution. Figure 5a shows representative spectra of drop-cast and spin-cast films from chloroform solutions; Figure 5b shows representative spectra of films from methylene chloride; and Figure 5c shows representative spectra of films from THF. In order to highlight the bands of interest, the spectral region is shown from 700 to 1700 cm^{-1}.


A
Absorbance
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
1700
1600
1500
1400
1300
1200
1100
1000
900
800
700
Wavenumbers (cm-1)
PEO (842 cm-1)
PCL (732 cm-1)
Drop Cast
Spin Cast


B
Absorbance
1.000
0.900
0.800
0.700
0.600
0.500
0.400
0.300
0.200
0.100
0.000
1700
1600
1500
1400
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Drop Cast
Spin Cast

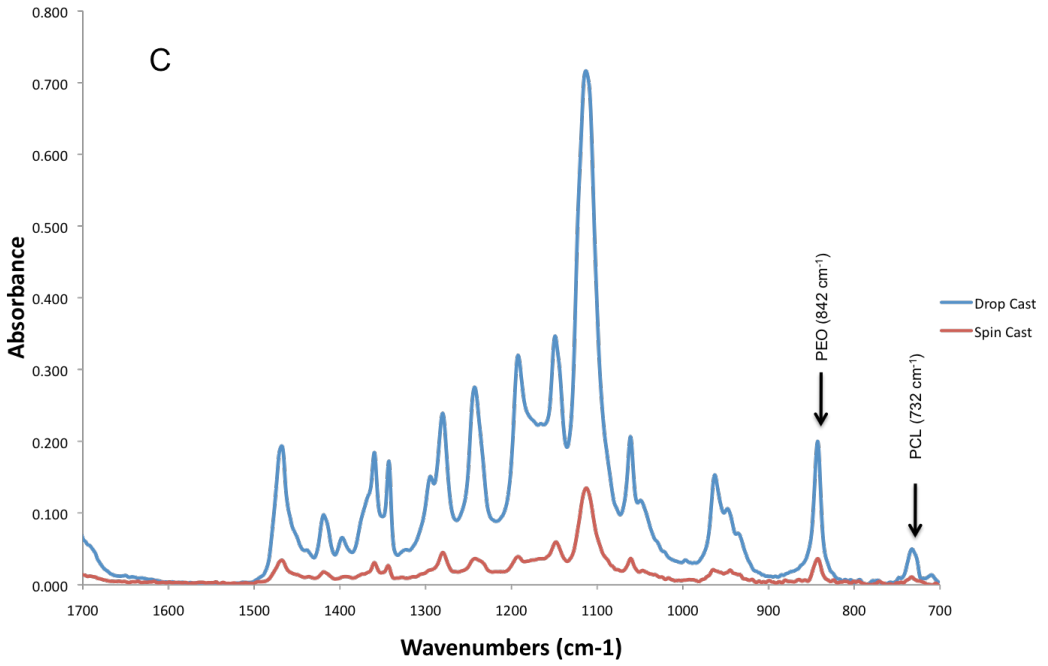


Figure 5. Representative FTIR spectra of drop cast and spin cast films from (A) chloroform, (B) methylene chloride, and (C) THF solutions in the spectral region between 700 and 1700 cm^{-1}.

Immediately evident is the much lower absorption of the spin-cast films across all solvents, with THF being markedly smaller than the others. The difference in signal is most likely because of the loss of polymer material during the spin-coating process due to solvent ejection. A smaller mass in the film would result in less absorption. Even with 5 times more material in the spin-casting solutions, there was still less material on the substrate than was the case for drop-cast films. This large difference in absorption between the two casting methods makes qualitative analysis of the spectra difficult, but it appears that the same bands are in each spectrum, suggesting that both films have crystallized.

Table 1 shows the relative crystallinity ratios of the films made with the 10 drop casting method. This ratio was calculated by finding the absorbance ratio of

the PEO band at 842 cm^{-1} to the PCL band at 732 cm^{-1} (highlighted in the above Figures). All ratios are an average of 3 trials except THF, which are an average of 2.

Table 1. Relative crystallinity of drop-cast and spin-cast films by solvent.

Solvent	A_{842}/A_{732} in drop-cast films	A_{842}/A_{732} in spin-cast films
Chloroform	3.27 ± 0.15	3.88 ± 0.58
Methylene Chloride	3.43 ± 0.22	3.66 ± 0.67
THF	4.09 ± 0.13	3.31 ± 0.55
Toluene	3.00 ± 0.40	No data

As can be seen, the relative crystallinities of the chloroform and methylene chloride drop-cast films are lower on average than the spin-cast films, but there is a large overlap based on standard deviation. Conversely, the drop-cast THF relative crystallinity is higher on average than the spin-cast, but they are very close within standard deviation. These overlaps could be a result of poor control over the casting method leading to erratic films. Also, the standard deviations of the spin-cast films are higher than those of the drop-cast, suggesting that the spin-cast films were more dissimilar to one another than the drop-cast films.

In order to determine what effect spin-casting had on the films, spin-cast chloroform films were analyzed by IR before and after melting and recrystallization. The films were melted because recrystallization from the melt should be the same for every film, assuming that they have same amount of polymer deposited. Melting also removes casting and solvent effects from the film, thus making it a normalizing casting process. If the casting method has any effect on the crystallization process, then comparing the cast spectra to its recrystallized counterpart should reveal it.

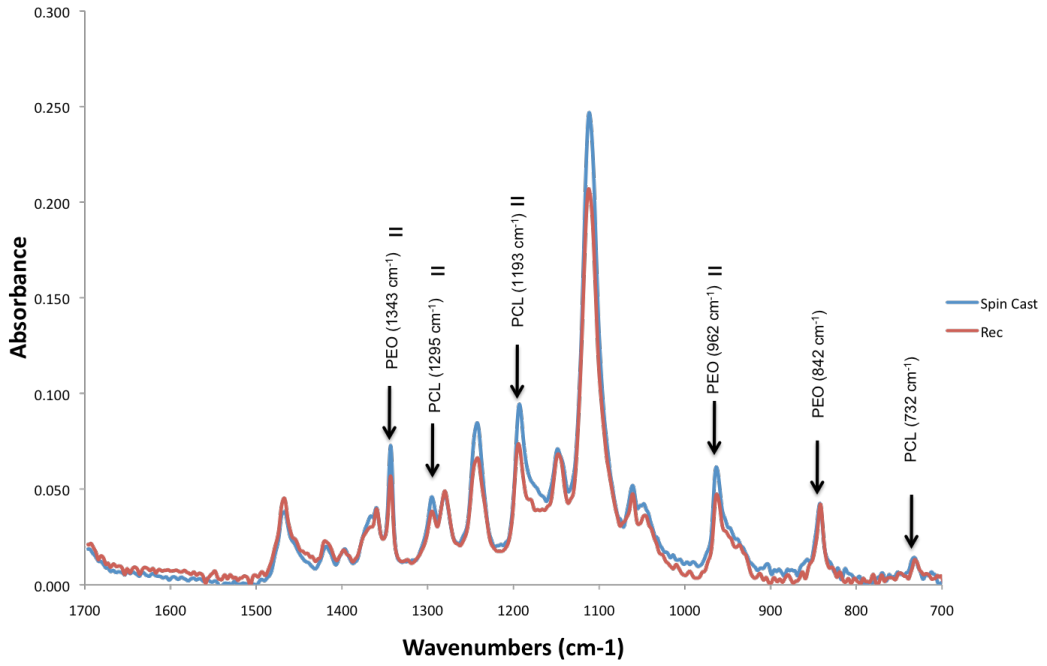


Figure 6. Representative FTIR spectra of a spin-cast chloroform film and its rec film. An = indicates that the band is associated with a crystal vibration parallel to the chain axis.

Figure 6 shows representative spectra of a spin-cast chloroform film along with its recrystallized spectra (referred to as rec). There was almost no difference in relative crystallinity ratios (A_{842}/A_{732}) of the cast and the rec films: 2.94 ± 0.52 for the spin-cast films and 3.06 ± 0.58 for the rec films. However, the intensity of several bands appeared to increase. The highlighted bands at 1343, 1295, 1193, and 962 cm^{-1} all correspond to molecular vibrations that are parallel to the crystal chain axis.[22-24] Only molecular vibrations that are perpendicular to the IR beam appear in an IR spectra, so an increase in the absorption for these bands indicates that more chain axes of both polymers are perpendicular to the IR beam. This is evidence that the casting method may influence the orientation of the crystals.

Both film-casting methodologies were changed in order to minimize the variability of the plates and standardize the amount of polymer on each. The polymer solutions were applied to the plates using a micropipette: 20 μL for drop-casting, and 100 μL for spin-casting. Micropipetting was chosen because it is more precise than counting drops. Higher solution volumes were tested for spin-casting, but they did not appear to be significantly different from 100 μL. Their spectra are show in Figure 7. Using 100 μL also deposited similar amounts of polymer material on the spin-cast films as were on the 20 μL drop-cast films (as can be seen later) so it was used for the new casting method. Slowing the RPM of the spin-caster was also tested and the spectra are shown in Figure 8. Once again, variation was not significant so the RPM value of 2040 was not changed.

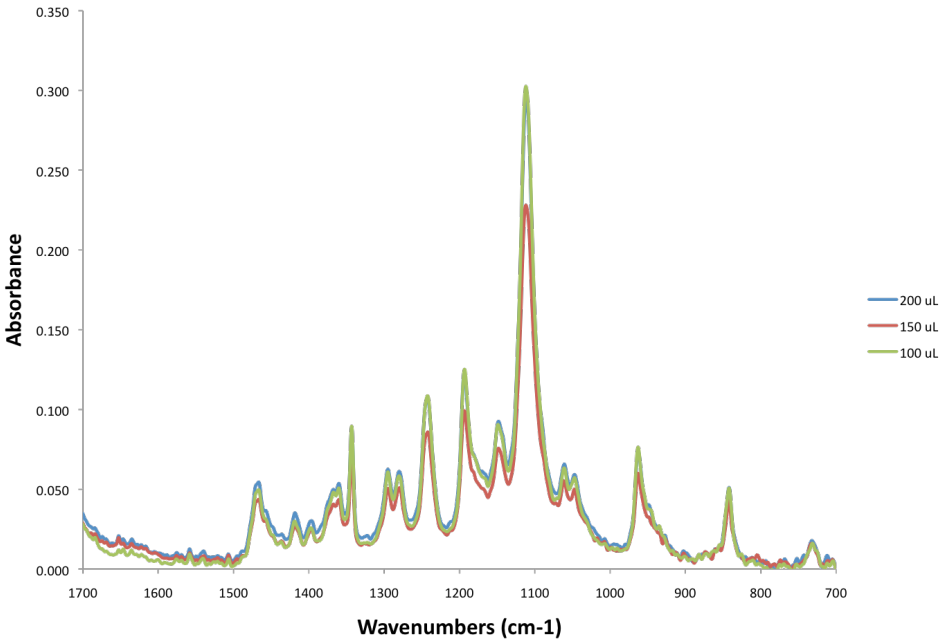


Figure 7. FTIR spectra of spin cast films from chloroform solutions with varying initial solution volume in the spectral region between 700 and 1700 cm^{-1}.

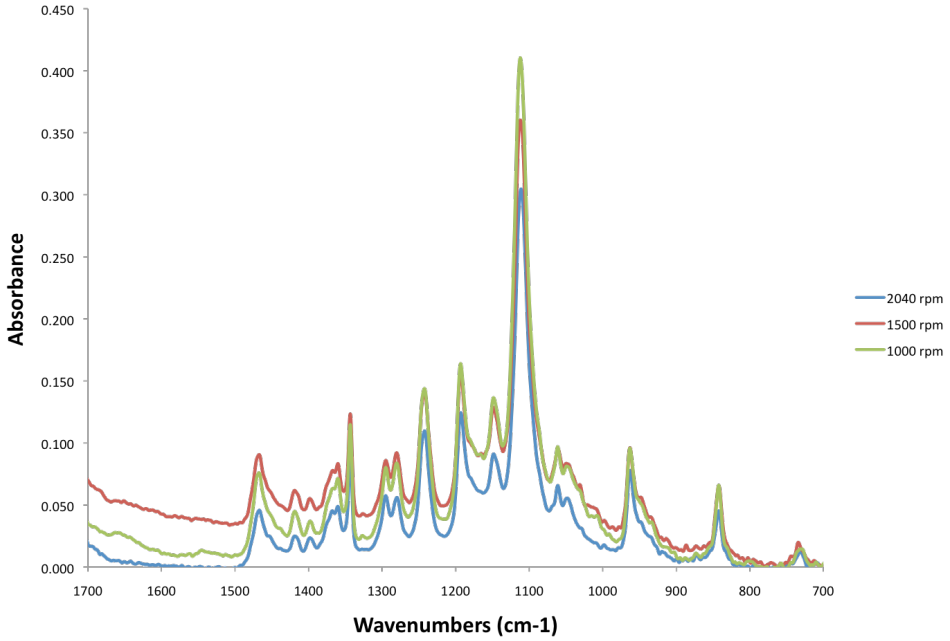


Figure 8. FTIR spectra of spin cast films at varying RPMs from chloroform solutions in the spectral region between 700 and 1700 cm^{-1}.

Using these more precise methods, drop-cast and spin-cast films were made from chloroform and THF solutions and their cast and rec spectra were compared to one another. Films from methylene chloride solutions were not made because of its similarity to chloroform as a solvent. As mentioned earlier, the cast and recrystallized melts should have the same mass so comparing them should reveal the effects of the casting method. Figure 9A shows the averaged spectra of drop-cast chloroform films and their rec counterparts, and Figure 9B shows those of the spin-cast chloroform and their rec counterparts. All of the spectra are averages of 3 films, except for the drop-cast chloroform, which is an average of 5 films.

A total of 7 drop-cast chloroform films were made, but only 5 recrystallized from the melt. The other 2 films, while not entirely amorphous, were much less crystalline. The averaged spectra of these two non-crystalline rec films appear as a

purple line in Figure 9A, and the average of the 5 crystalline rec films is in red. Since more films recrystallized than did not, the averaged spectra of the cast films excludes the 2 that did not recrystallize from the melt.

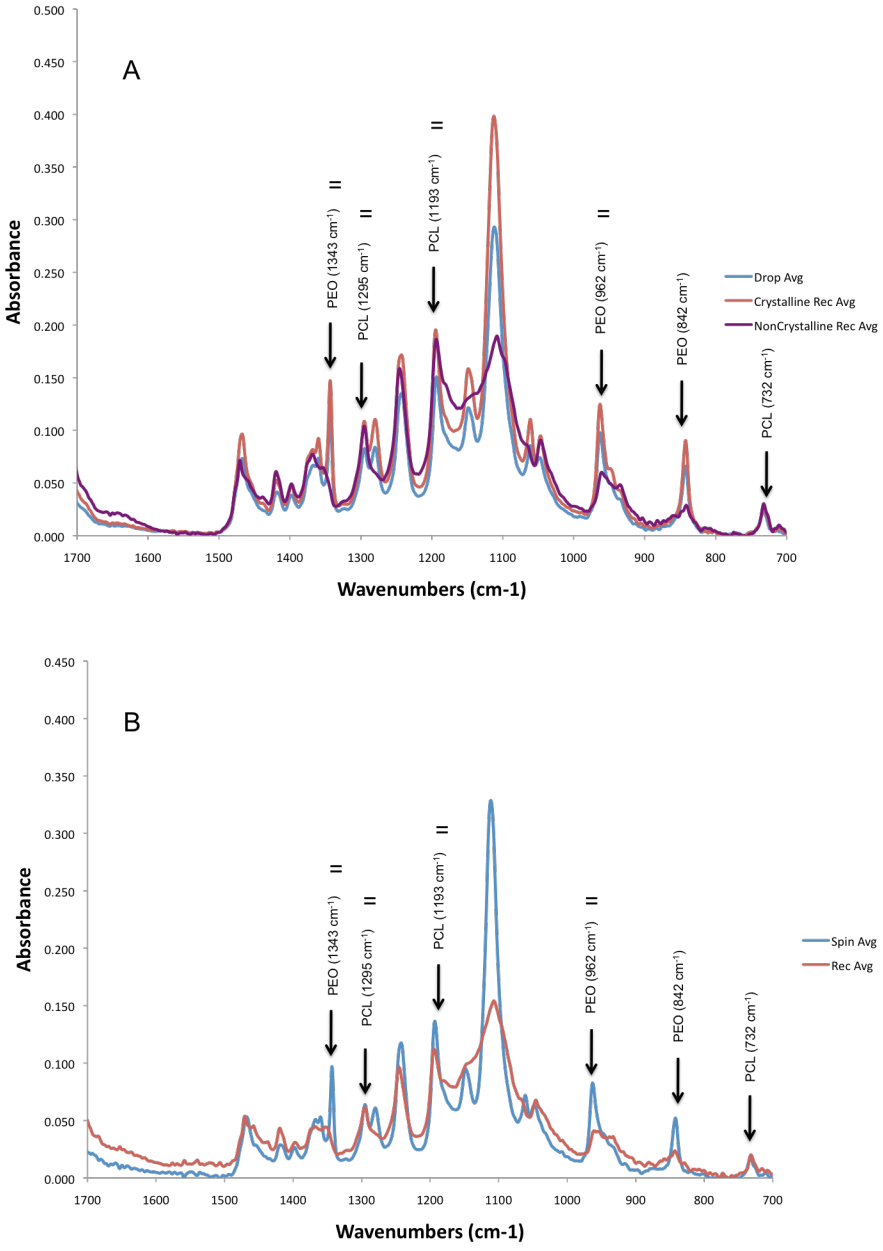


Figure 9. Averaged FTIR spectra of (A) drop-cast and (B) spin-cast chloroform films and their crystalline and non-crystalline rec films and in the spectral region between 700 and 1700 cm^{-1}. An = indicates that the band is associated with a crystal vibration parallel to the chain axis.

When comparing the drop-cast chloroform films that did recrystallize to their rec films (Figure 9A), it is evident that the cast films' bands are smaller than those of the rec films. Contrastingly, the spin-cast bands are larger when compared to their rec films (Figure 9B), but that is because their rec films are much less crystalline. Of the 3 spin-cast chloroform films, none of them recrystallized from the melt. The averaged spin-cast rec films in Figure 9B and the averaged non-crystalline drop-cast rec films in Figure 9A both have broader bands than their crystalline counterparts, indicating they are more amorphous. They are also missing or have greatly reduced crystalline PEO bands (1343, 962, and 842 cm^{-1}), but maintain visible yet diminished crystalline PCL bands. This difference suggests that PEO crystallization was suppressed more than that of PCL.

The reason that films made with both casting methods did not recrystallize from melt is not known. The fact that it happened to both the spin-cast and drop-cast films suggests that it may be related to solvent effects. Furthermore, the majority of the drop-cast chloroform films did recrystallize, while none of the spin-cast films did, suggesting that spin-casting might also influence the mechanism by which nucleation has been suppressed. However, the melting process should ideally have erased both the solvent and casting effects from the plate, so it cannot be said which is the true culprit. Further research must be done to investigate this phenomenon.

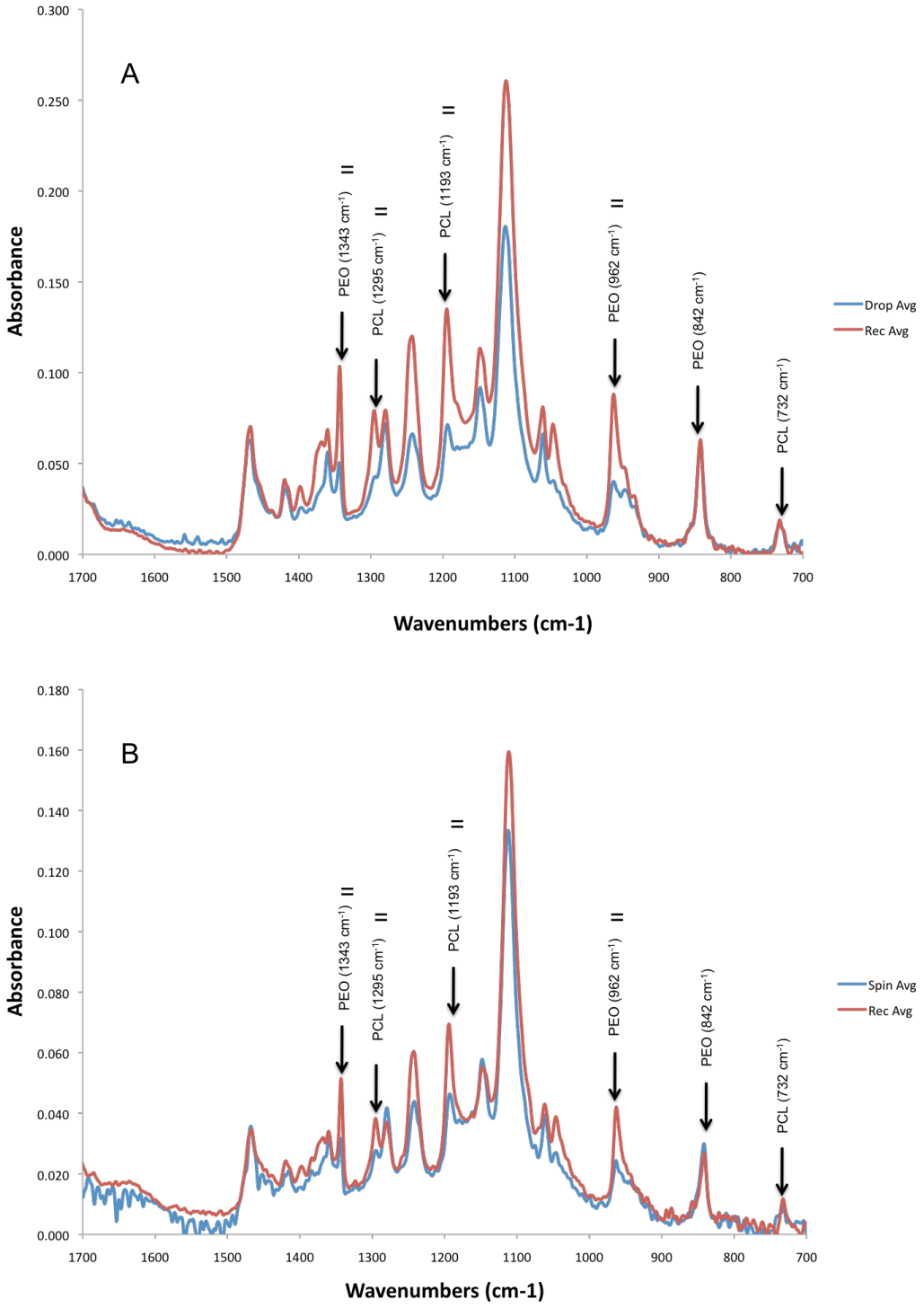


Figure 10. Averaged FTIR spectra of (A) drop-cast and (B) spin-cast THF films and their rec films in the spectral region between 700 and 1700 cm^{-1}. An = indicates that the band is associated with a crystal vibration parallel to the chain axis.

Figure 10A shows the averaged spectra of the drop-cast THF films and their rec films, and Figure 10B shows those of the spin-cast THF films and their rec films. In Figure 10B, the baseline from 1500 to 1700 cm^{-1} has a weak signal-to-noise ratio, but the spectra were still used because it is not in the region of interest. In THF's case, all of the melted films of both casting methods recrystallized. Like the drop-cast chloroform films that recrystallized, the averaged THF rec films have larger bands than their as-cast counterparts. Spin-cast films of both solvents appear to more closely resemble their rec films than the drop-cast films and their maximum absorption is lower.

To be able to compare films made with different casting methods, the amount of polymer material must be roughly the same in each film. If the amount of material is the same, then the melts should be the same. In order to confirm that they are the same, the rec films of both casting methods were compared to one another. Figure 11A shows a comparison of the chloroforms rec films, and Figure 11B shows a comparison of the THF rec films. The bands have been normalized at the 1733 cm^{-1} peak so only a qualitative analysis is possible. This band is associated with PCL carbonyl stretching and was chosen because it appeared to vary the least between films. The spectral region has been expanded to 2000 cm^{-1} to incorporate it.

The averaged spin rec spectrum of the chloroform is clearly different from the drop rec spectrum because it did not recrystallize so comparisons between the two casting methods in chloroform are tenuous. With THF, the averaged spin rec spectrum and the averaged drop rec spectrum resemble one another so comparisons between the two casting methods are more meaningful.

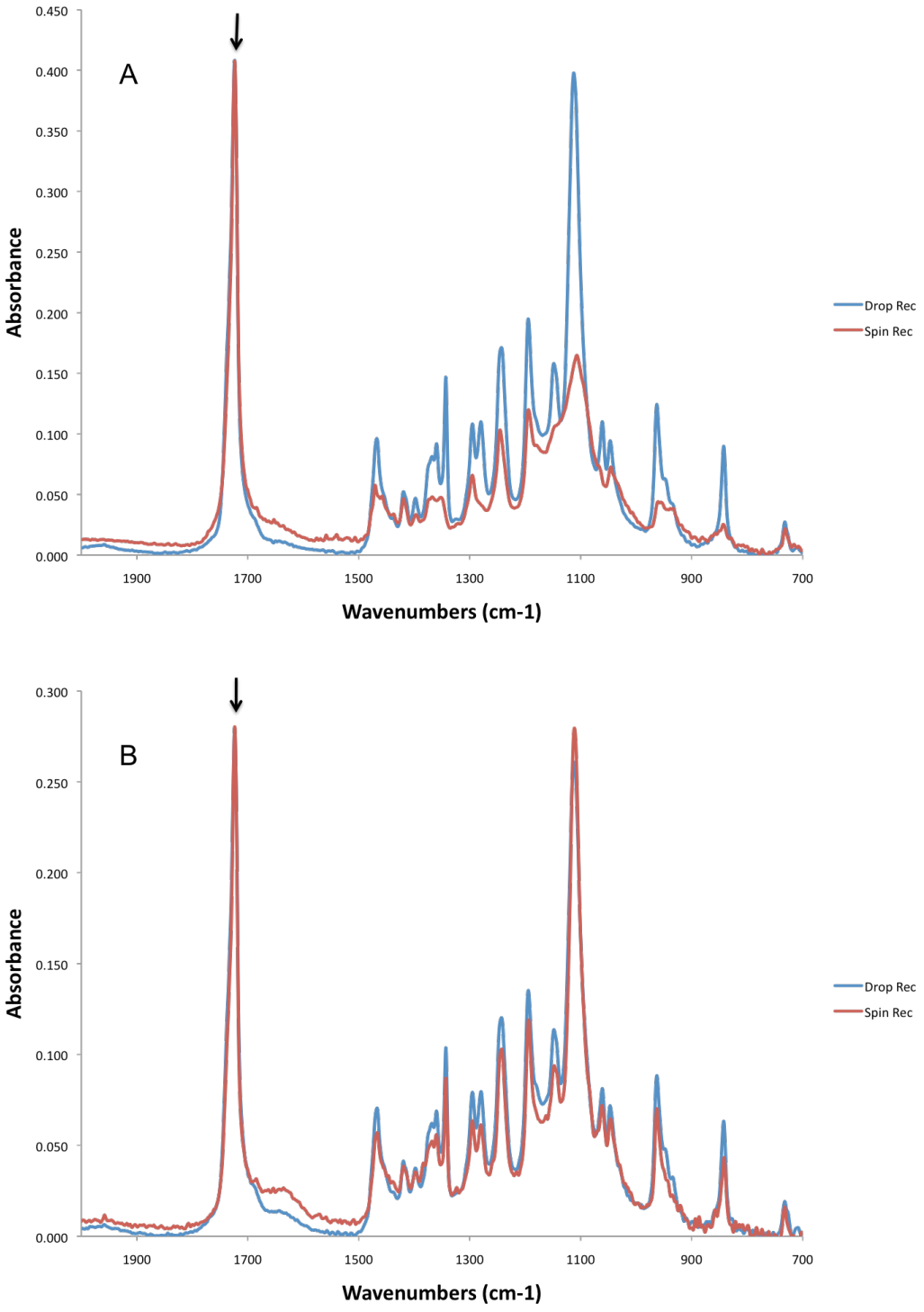


Figure 11. Averaged FTIR spectra of the (A) chloroform and (B) THF rec films normalized at the indicated band in the spectral region between 700 and 2000 cm^{-1}.

The ratios of absorbencies of the bands at 1343, 1295, 1193, and 962 cm^{-1} of the as-cast films to the rec films were calculated in order to determine the effect of the casting method on crystal orientation. These bands were chosen because they are associated with vibrations parallel to the crystal axis.[22-24] Their increase or decrease indicates more or less crystal axes perpendicular to the IR in the films and could be related to crystals growing edge-on. Their averages are shown in Table 2. The average relative crystallinities (A_{842}/A_{732}) were also calculated and are shown in Table 3.

Table 2. Average cast to melt ratios of the listed peaks by casting method and solvent. The X indicates that the band did not reappear in the melt.

Solvent	Casting Method	As-Cast/Rec at 1343 cm-1	As-Cast/Rec at 1295 cm-1	As-Cast/Rec at 1193 cm-1	As-Cast/Rec at 962 cm-1
Chloroform	Spin	X	1.1 ± 0.08	1.22 ± 0.10	2.05 ± 0.20
	Drop	0.81 ± 0.17	0.81 ± 0.17	0.80 ± 0.17	0.81 ± 0.15
THF	Spin	0.66 ± 0.18	0.77 ± 0.11	0.69 ± 0.14	0.61 ± 0.14
	Drop	0.49 ± 0.05	0.54 ± 0.04	0.53 ± 0.04	0.49 ± 0.05

Table 3. Average relative crystallinity by casting method and solvent.

Solvent	Casting Method	A_{842}/A_{732} in Cast Film	A_{842}/A_{732} in Rec Film
Chloroform	Spin	2.96 ± 0.20	1.18 ± 0.21
	Drop	3.15 ± 0.30	3.42 ± 0.44
THF	Spin	2.82 ± 0.19	2.22 ± 0.04
	Drop	3.50 ± 0.33	3.23 ± 0.28

As stated earlier, comparisons between the spin-cast and drop-cast chloroform films are tenuous because their rec films are not the same. However, one can observe the suppressed PEO crystallization of the spin-cast films that was seen in Figures 9A and 9B in two ways. First, of the two band ratios associated with PEO, 1343 and 962 cm^{-1}, the former could not be measured because the band had disappeared in the recrystallized film, and the latter has a remarkably high cast-to-rec ratio because it was almost non-existent. Second, the relative PEO crystallinity of

the recrystallized film is much lower than the others, meaning that there is less crystalline PEO in the spin rec film.

The spin-cast THF films and the drop-cast THF films can be compared because their melts were similar. As can be seen, the cast-to-rec ratios of the spin-cast THF films are higher on average than the drop-cast THF cast-to-rec ratios. The higher ratios suggest that there are more crystals axes perpendicular to the IR in the spin-cast films. This might be attributed to the radial force of the spin-caster aligning crystals parallel to the surface, which nucleates as edge-on orientation. In edge-on orientation, vibrations parallel to the chain-axis are perpendicular to the IR beam so more parallel vibrations implies more edge-on crystals. The relative crystallinity of the spin rec film is lower than the drop rec film, which could be result of the being recrystallized at different times. Comparisons between were still made between the two because their rec spectra were similar as seen in Figure 11B.

The spin-cast THF films also had lower relative PEO crystallinity than the drop-cast films. Previous research had shown that THF interacts more strongly with PEO than PCL and therefore suppresses its crystallization because it remains in solvent longer than PCL.[25] However, this study has found that the drop-cast THF films have higher relative PEO crystallinity than the drop-cast chloroform films. Chloroform is a neutral solvent for both polymers, so THF actually appears to be inhibiting PCL. If this is the case, than the lower relative PEO crystallinity in the spin-cast films could be attributed to a reduction in solvent effect from the casting process.

Conclusion

Overall, this study is the first step in developing a promising method for comparing the two methods of thin film making in question using FTIR, but several obstacles still need to be overcome before it is reliable. Differences in crystallinity make direct comparisons between plates cast by the two methods difficult with FTIR. By comparing them to a neutral film that should be the same for both—the recrystallized from melt film—it becomes possible to make indirect comparisons between the two. However, this approach is only valid when the recrystallized from melt films are the same for both methods. In order for them to be the same, they must have the same amount of polymer, the same film thickness, and they must be recrystallized under the same conditions.

Using this method, spin-cast THF films were found to have slightly higher bands associated with parallel crystal vibrations than the drop-cast THF films, suggesting that there are more edge-on crystals in the spin-cast films. However, it was not possible to compare the spin-cast chloroform films to the drop-cast chloroform films because they did not recrystallize from melt in the same way. The spin-cast chloroform rec films had suppressed PEO crystallinity and were much less crystalline overall. Most of the drop-cast chloroform films recrystallized from melt, but two were more like the spin-cast rec films. The cause for this phenomenon is not known and further research must be done to understand it.

In order for this indirect comparison method to be reliable, the casting methods must result in films with the same amount of copolymer and the same film thickness. To this end the casting methods were adapted to be more precise.

Micropipettes were used to deposit solution on the film instead of counting drops and experiments were performed to determine the ideal RPM and solution amount for spin-cast films. However, these methods still resulted in variations like the non-crystalline films discussed above. Future research could be done to more thoroughly explore the variables that affect the amount of copolymer in each film for the different casting methods in order to better control them. In addition, various microscopic and diffraction techniques such as SEM, AFM, optical microscopy, and x-ray diffraction could be used in support of FTIR to develop a better picture of the two casting methods and how they affect crystallization.

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