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Microwave-Assisted Ring-Opening Polymerization of Poly(ϵ-caprolactone)

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MICROWAVE-ASSISTED RING-OPENING POLYMERIZATION OF POLY(ϵ-CAPROLACTONE)

A Thesis

by

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ABSTRACT

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Poly(ϵ-caprolactone) (PCL) is a biodegradable polyester notorious by its promising properties and applications in the biomedical field. In this work, microwave-assisted ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL) was performed. Stannous octoate [$Sn(Oct)_2$] was used as catalyst with and without an alcohol initiator. The different initiators tested were glycerol, diethylene glycol (DEG) and poly(ethylene) glycol (PEG). Aiming to establish reaction parameters, the influence of different reaction times, temperatures, and monomer:initiator:catalyst ratios were examined. It was observed that the reaction was obtained and high molecular weight PCL was achieved successfully without an initiator. However, mixed results were obtained using an initiator. Products were characterized using FTIR, Raman, and NMR; molecular weight of products was determined by GPC. Crystallization and thermal properties were characterized by XRD, DSC and TGA. The high molecular weight PCL obtained was used to produce fibers via electrospinning. Tensile strength of fibers was examined, observing good mechanical properties.

DEDICATION

This thesis and all my academic achievements are dedicated, with all my love and gratitude, to my friends and specially my family. Thanks to all of you, I am the woman I am today and have been able to reach this special moment in my life. First, I dedicate this work to my dear friends, Ariana, Cristina and Daniela. Even though, we have known each other since high school, I feel that we have been together forever. Thanks for your friendship, acceptance and all those special moments when we laugh uncontrollably remembering our high school adventures. To Lorena and Karen. I consider you my sisters. Thanks for all your support, I do really listen to you and consider all your words. I know that I do not talk that much, but thank you for listening when I do talk. I deeply thank my grandparents and relatives, especially mi tio Tavin and mis tias Lupita and Juany. And the ones who are not here anymore, mi tio Jorge, mis abuelitas Eva and Jovita, and mi abuelito Aurelio. It is heartbreaking that you cannot enjoy this moment with me, but I know that wherever you are, you are proud of me and I will forever feel your blessings. To my sister, Annette. Thank you for letting me be me around you and for staying with me even when I am not the most enjoyable person to be around. You are my rock and the person I trust the most. Without you everything will be so dull and boring. I hope that this set a good example for you because I just want the best for you my little sis. And finally, I dedicate all this work to my parents, Aracely and Jaime, I would not be here without you. Thank you for never stop believing in me. Words cannot describe the love and gratitude I feel for you.

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CHAPTER I

INTRODUCTION

Poly(ϵ-Caprolactone)

Poly(ϵ-caprolactone) (PCL) is an attractive and useful polyester that has gained tremendous notoriety over the years thanks to its promising properties and commercial availability. PCL is a non-toxic, biodegradable and biocompatible polymer[1-5]. In addition, its high hydrophobicity, its thermal properties such as low glass transition temperature (-60°C) plus low melting point (60°C),[1] and its good mechanical properties like elastic behavior, make of PCL an important material in biomedical and pharmaceutical applications, like tissue engineering, drug delivery implants and bone graft substitutes.[2]

Much of PCL interest has come from its suitable application in biodegradable materials. PCL is approved by the Food and Drug Administration (FDA) for its use in human body in the mentioned applications.[2,3] PCL materials were discovered to completely degrade by bacterial and fungal enzymes. In addition to the expected degradation by esterases, it was also noticed the tendency of the enzymatic degradation by lipase enzymes.[4]

PCL degradability within the body is due to the chemical tendency of ester bonds toward hydrolysis, which is autocatalyzed by the carbonyl end groups on the polymer chains. However, the number of carbon atoms in the chain, the hydrophobicity of the monomer, the crystallinity of the sample, the molecular weight and the glass transition temperature are factors that greatly affect the rate of the ester bonds hydrolysis.[4,5] During the biodegradation process, there is not a

significant change in the mechanical properties of PCL in the first 6 months, and after this period, there is a gradual decay in the strength and stiffness until it is completely metabolized in a period of 2 years.[5] This aspect makes the selection of PCL for use as tissue scaffold reasonable. However, long term toxicities from the acidic hydrolysis byproducts released during the process, which are responsible of inflammatory responses, have not been thoroughly analyzed as the degradation process is difficult and costly to study;[4] especially, if it is taken in consideration that full degradation of PCL implants can take a number of years in comparison with the few months for full degradation that polyglycolide (PGA) (2-3 months) or poly(lactic-co-glycolic acid) (PLGA) (1-6 months) take, which are polymers also extensively studied for biomedical purposes.

Regardless of the reservations on the long-term fate of PCL as biomaterial, another important characteristic of PCL could be used to address this degradation problem and enhanced its mechanical properties, its high miscibility with a wide range of other polymers for effective blending. To further improve the PCL properties, copolymers of PCL have been investigated. For example, attention has been put in the combination of PCL elasticity and the faster degradation of polyglycolides or polycarbonates.[4] For applications that encounter problems in PCL hydrophobicity and high crystallinity, hydrophilic polymers like poly(ethylene) glycol (PEG) have been blended with PCL. PEG helps to accelerates the hydrolysis of the ester bond present in PCL, forming block copolymers with an amphiphilic character.[2]

Also, PCL diols, which are based on di-functional initiators containing two terminal hydroxy groups have been investigated. They are highly crystalline and miscible with other polymers and they can be used as prepolymers to produce different block copolymers. Production of PCL with different physical and chemical properties can be obtained using diethylene glycol (DEG), triethylene glycol (TEG), 2-propanol, 1,4-butandiol, PEG 600, PEG 1000 and 10000,

tetraethylene glycol (TetEg).[2] Nonetheless, the major obstacles that these alcohol-initiated polymerizations find are the byproducts and residual starting materials that can be present in the final product affecting its properties. It is noted that in most of the publications, a fully characterization of PCL diols is missing since the identification and quantitative determination of these impurities is a complex task.[2]

Ring-Opening Polymerization

PCL is a saturated aliphatic linear polyester consisting of hexanoate repeat units.[4] PCL is commercially synthesized by polycondensation of hydroxy-carboxylic acids or by ring-opening polymerization (ROP) of ϵ-caprolactone (ϵ-CL), a cyclic monomer containing a polar carbonyl group (Figure 1). Even though polycondensation is less expensive, it is difficult to produce a high molecular weight polymer with low dispersity; therefore, ROP has become by far the most standard method for the synthesis of PCL[6].

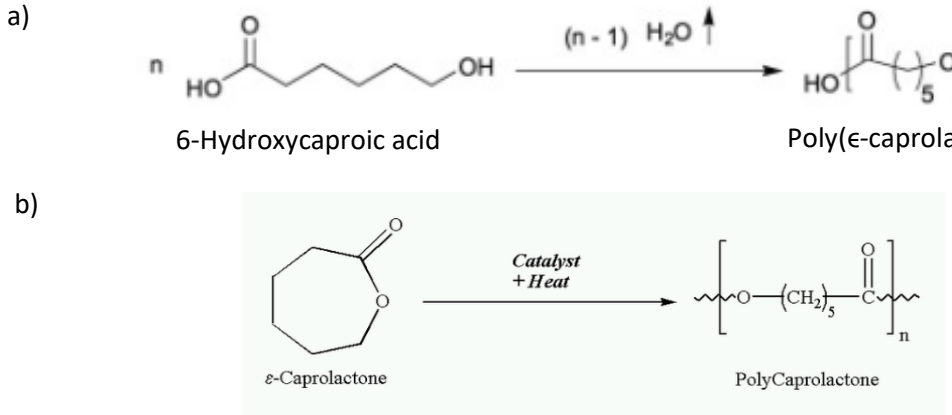


Figure 1: Schematic Representation of the Polymerization of Poly(ϵ-Caprolactone) by (a) Polycondensation and (b) ROP [4,15]

ROP of PCL is similar to the ROP of common lactones and dilactones. PCL is formed when ϵ-CL is reacted with a catalyst or initiator. Figure 1 (b) presents the reaction pathway for the ROP of ϵ-CL. The ring-opening reaction can be carried-out in bulk, solution, emulsion or dispersion[6]. Depending on the initiator/catalyst, ROP proceeds following three different mechanisms: cationic, anionic or coordination-insertion. However, only with anionic and coordination-insertion ring opening polymerization, high molecular weight polyesters have been obtained[7].

Many organometallic compounds, such as metal alkoxides and carboxylates have been studied in order to have a better control of the reaction. Since the reactions catalyzed by metal complexes are highly specific, polymers with a specific structure can be produced by the careful selection of the metal and ligands. The covalent metal alkoxides and carboxylates with free p or d orbitals reacts as coordination initiators/catalysts with the ability to produce stereoregular polymers of high molecular mass and low dispersity; therefore, the most widely used initiators/catalysts are aluminum and tin alkoxides and carboxylates[7]. Although, it is important to emphasize that carboxylates are weaker nucleophiles than alkoxides, thus, metal carboxylates are usually used with an active hydrogen compound as co-initiator[7].

Tin (II) 2-ethylhexanoate, most commonly known as stannous octoate [$Sn(Oct)_2$] is an important initiator or catalyst for the production and research of biodegradable polyesters.[13] $Sn(Oct)_2$ is approved by the FDA as a food additive, and it is used as catalyst since it is very effective and versatile, it has a low cost, and is soluble in common organic solvents and lactones.[8,11]

In the literature, the mechanism of the ROP with $Sn(Oct)_2$ as catalyst has been widely discussed. Although, there have been disputes and several mechanisms have been proposed over

the years, two basics mechanisms have been accepted[8]: the directly catalytic or activated monomer type (Figure 2, a), where the purpose of the catalyst is the activation of the monomer by coordinating with its carbonyl oxygen; and the monomer-insertion type (Figure 2, b), where the catalyst acts as co-initiator in conjunction with hydroxy impurities, which could be either intentional or unintentional added.

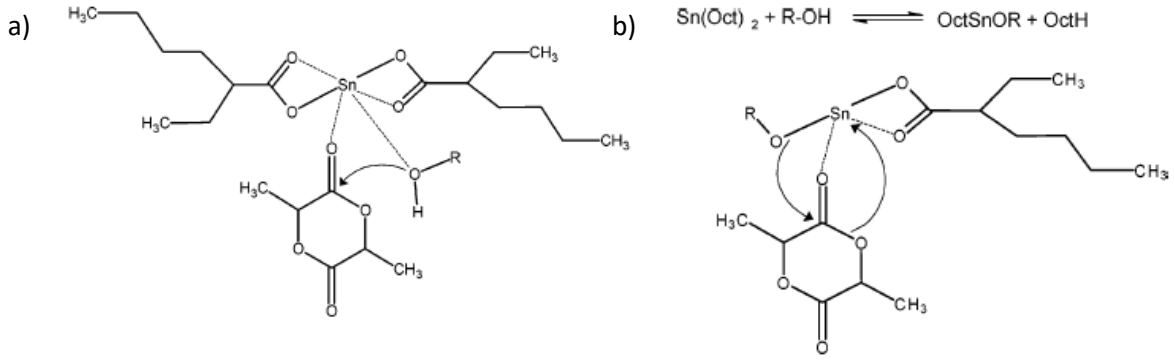


Figure 2: Main ROP Mechanism Proposals with $Sn(Oct)_2$ as Catalyst, a) Directly Catalytic or Activated Monomer Type and b) Monomer-Insertion Type[7]

In the activated monomer mechanism, the monomer is activated by coordinating with the catalyst. The coordination of the exocyclic oxygen of the monomer to the metal of the catalyst, makes the carbonyl carbon of the monomer more susceptible for a nucleophilic attack. Therefore, the reaction proceeds by the nucleophilic attack of an alcohol, which is followed by a rearrangement of electrons for the insertion of the monomer into the metal-oxygen bond. (Figure 3). During propagation, both monomer and alcohol are coordinated to the $Sn(Oct)_2$ complex. A hydroxyl end group formed during hydrolysis terminates the reaction.[7]

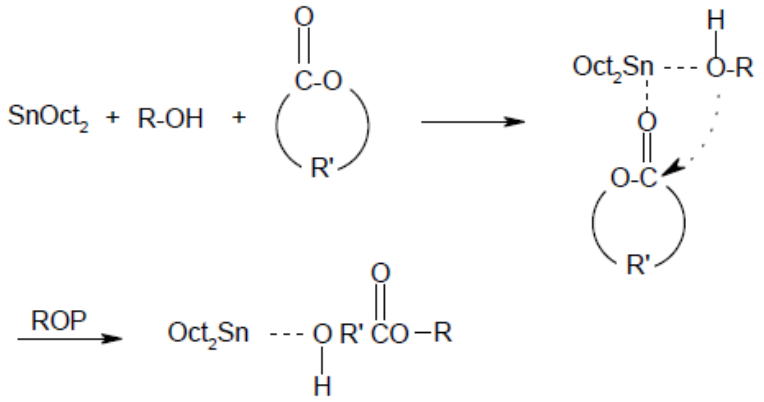


Figure 3: Activated Monomer Mechanism for the ROP of Lactones[6,7]

In 1998, Penczek et al.[8] proposed the alternative mechanism suggesting that in the presence of a purposely added alcohol or any other protic impurity present in the polymerization medium[6], $Sn(Oct)_2$ acts as a co-initiator. As it can be seen in Figure 4, before the beginning of the polymerization, the alcohol reacts with $Sn(Oct)_2$ producing a stannous alkoxide active specie and a free 2-ethylhexanoic acid. The stannous alkoxide complex produced is the real initiator of the polymerization. Then, the alkoxide coordinates to the carbonyl of the monomer to continue with the reaction. Following this step, the now nucleophilic alkoxide adds onto the electrophilic ester function. The reaction proceeds via acyl-oxygen bond cleavage, which opens the ring and forms a new alkoxide, the propagating specie[6]. During the propagation, the growing chain remains attached to the metal through the alkoxide bond. The formation of a hydroxyl end-group by hydrolysis terminates the reaction.

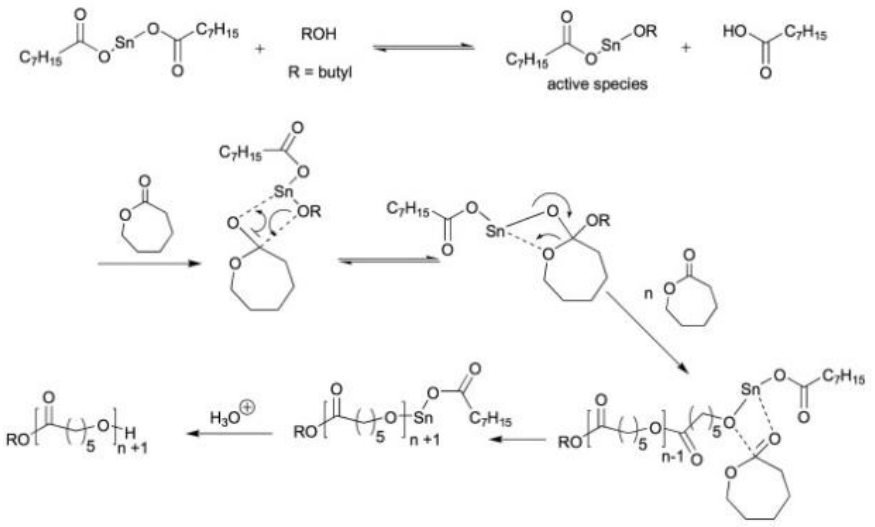


Figure 4: Monomer-Insertion Mechanism for the ROP of ϵ-CL[4]

In addition, as supporting evidence of this mechanism, an increase in the rate of ROP by adding butanol to $Sn(Oct)_2$ and octanoic acid to tin (II) butoxide was observed. MALDI-TOF experiments were used to detect the presence of tin alkoxides in the reactions. As well, Kricheldorf and coworkers[8] published mechanistic work dealing with the interaction of a variety of alcohols and ester/alcohols with $Sn(Oct)_2$, and how the strength of the catalyst-alcohol interaction could affect each structure.

Nevertheless, it is well known that the use of organometallic initiators/catalysts at high temperatures or at long reaction times can lead to a loss of control of the polymerization and influence transesterification reactions in the ROP of lactones and lactides. Alkoxides tend to react with the ester function of the monomer; however, it can also react with the ester functions present along the polyester chain producing both inter- and intramolecular transesterification reactions.[6, 7]

In the case of intramolecular transesterification reactions or back-biting (Figure 5), the alkoxide, the propagating specie, reacts with a carbonyl within the same polymer chain generating a rearrangement of atoms and a random break in the chain. As result, free shortened chains and cyclic oligomers are produced. This type of reaction leads to a decrease of the molar mass and an increase in the polydispersity of the polymer. On the other hand, a reshuffle in the length of the polymer chain is produced by intermolecular transesterification reactions (Figure 6). In this type of reaction, the alkoxide reacts with a carbonyl within a different polymer chain, leading to an increase in the polydispersity index of the polyester.[6,7]

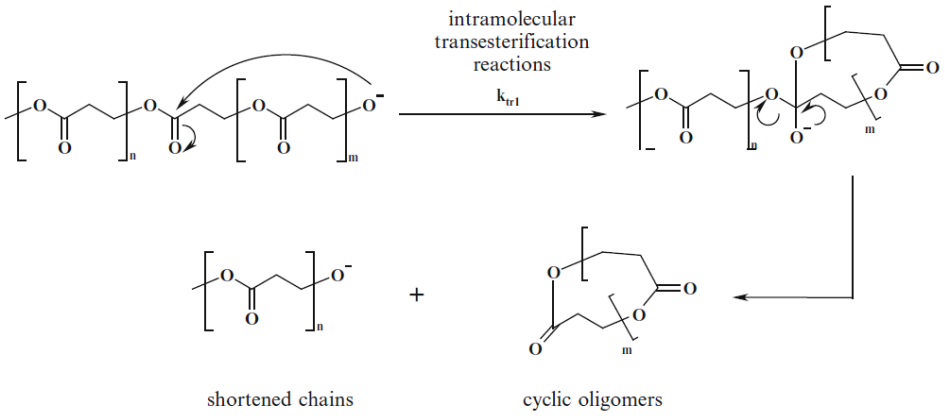


Figure 5: Intramolecular Transesterification Reactions[6]

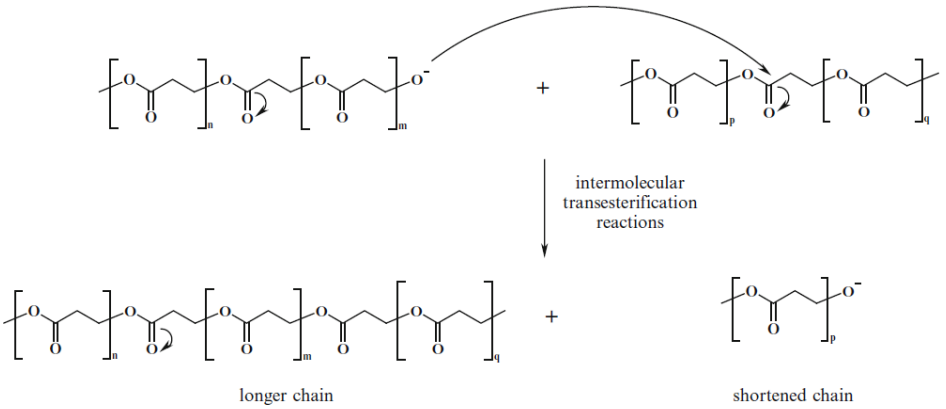


Figure 6: Intermolecular Transesterification Reactions[6]

To disfavor transesterification reactions, the reactivity of the initiator/catalyst needs to be decreased; this way, the initiator/catalyst will react with the more reactive esters groups of the cyclic ester and not with the less reactive ester groups present along the chains. Steric and electronic effects can be used to decrease the reactivity of the initiator/catalyst; for this, hindered ligands are normally used to have a better control of the polymerization. It is known that the metal plays a critical role for the relative reactivity of the different metal alkoxide initiators/catalysts. The following order of reactivity has been reported: $Bu_2Sn(OR)_2$ > $Bu_3Sn(OR)_2$ > $Ti(OR)_4$ > $Zn(OR)_2$ >$Al(OR)_3$. As well, the different parameters that could affect the transesterification reactions are temperature and time of the reaction, the configuration of the lactone, and the concentration and type of catalyst/initiator.[7]

Over the years, many researchers have dedicated their time investigating the parameters that disfavor the transesterification reactions and improve ROP. Kowalski et al.[9] investigated the kinetics of the polymerization of ϵ-CL utilizing $Sn(Oct)_2$ in tetrahydrofuran at 80°C. The kinetic data and structural studies (obtained by dilatometry and MALDI-ToF mass spectrometry respectively) suggested that the $Sn(Oct)_2$ initiated polymerization takes place by an active-chain end mechanism with tin(II) alkoxides as active centers. These studies backups the monomer-insertion type mechanism suggested by Penczek and which was explained before. The possibility of the an activated-monomer mechanism involving a nucleophilic attack of an OH-group was ruled-out since the results showed that the actual initiator is a stannous alkoxide active specie, which is formed when $Sn(Oct)_2$ reacts with ROH. ROH is the compound containing the hydroxyl group like water or an alcohol present in the polymerization mixture.[9,11] Storey and Taylor[14] investigated the bulk polymerization of ϵ-CL at 120°C using ethylene glycol as initiator and various concentration of $Sn(Oct)_2$ as catalyst. Results obtained by GPC showed that the molecular

weight of the product was determined by the [ϵ-CL]/[ethylene glycol] ratio; the concentration of $Sn(Oct)_2$ did not affect the molecular weight. On the other hand, when no ethylene glycol was added to the polymerization mixture, molecular weights were higher but decreased as the concentration of $Sn(Oct)_2$ was increased. Barakat et al.[10,11] used zinc alkoxides as initiators for living ROP of ϵ-CL under mild conditions in toluene, obtaining PCL with narrow molar mass distribution. It was discovered that zinc halides were effective initiators and by adjusting the monomer/initiator ratio, molar mass of PCL could be perfectly controlled.

Other investigations used alternative catalysts; however, as explained before, tin octoate is the most widely catalyst used for the ROP of lactones. Even thought, $Sn(Oct)_2$ is accepted by the FDA, its main limitation is the toxicity of the metal, which hindrance the use of the polymer produced for biomedical purposes. Most of tin compounds are cytotoxic, meaning that they are toxic to animals, microbes and fungi. Also, it is worth noting that the complete removal of tin compounds from the product is almost impossible making questionable its used in biomedical applications since a low level of impurities is required for the employment of PCL or any other polymer. Less toxic metals such as magnesium and calcium alkoxides have been investigated in order to replace tin and aluminum alkoxides as initiators/catalysts and overcome this drawback.[12,13]

Microwave-Assisted Ring-Opening Polymerization

In recent years, ROP has been modified to have a better control of the mechanism and to produce more complex polymeric structures. As mentioned before, achieving an efficient and rapid ROP of ϵ-CL has become a specific target in which several studies have focused. However,

mixed results have been obtained because of most of the catalytic mechanisms or species investigated have not regulatory clearance for industrial exploitation or they are not available commercially.[15]

Industrial production of synthetic polymeric biomaterials is characterized by limited reproducibility. Therefore, focus has changed to synthesis techniques, such as microwave heating, which is a novel approach needed in order to get reproducibility, scalability and cost-viability. In the 90s, thanks to the extensive expertise gained in the organic synthesis field, microwave radiation became a powerful and new tool for organic synthesis. The success that this technology has had in this area has inspired its use in polymerization reactions. Since then, the use of microwave irradiation as an alternative heat source has become popular.[1]

Dielectric heating plays a critical role in microwave heating. Microwave irradiation heats the molecules directly through the interaction between the microwave energy and molecular dipole moments of the starting materials. Molecules that exhibit a permanent dipole moment will generate heat by the rotation, friction and collision of the molecules resulting from its alignment to the applied microwave electromagnetic field (Figure 7).[17,19] In the specific case of ϵ-CL, it is a liquid containing a polar carbonyl group and with a tan δ value of 0.35. Considering that tan δ values between 0.1 and 0.5 indicate a moderate ability to absorb microwaves, leading to an effective dielectric heating by the absorption of microwaves.[1] Therefore, it can be concluded that microwave assisted ROP of ϵ-CL could be efficient and fast.

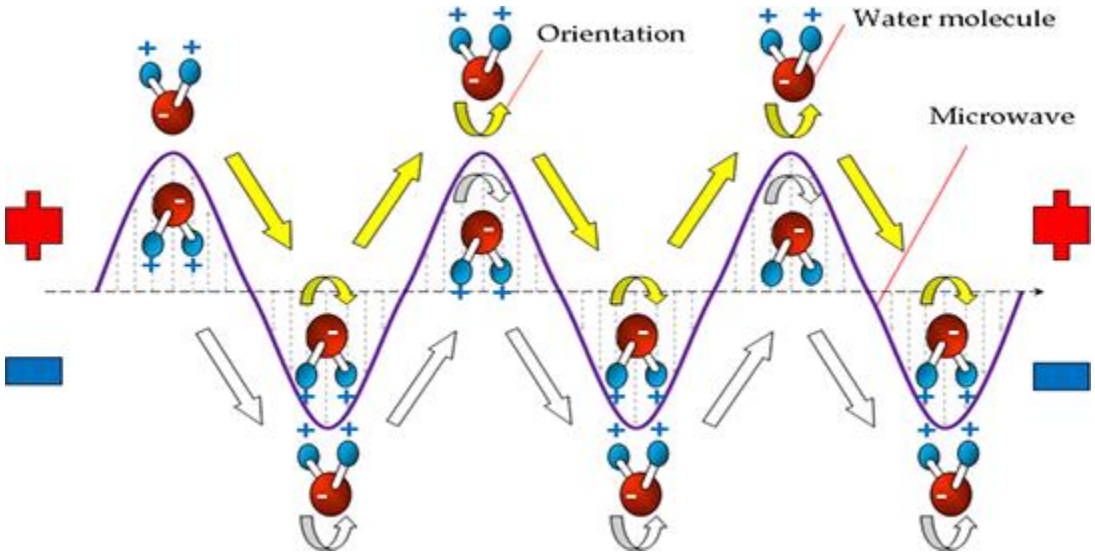


Figure 7: Microwave Heating Mechanism: Water Molecules Are Oriented when Exposed to Microwave[21]

In addition, non-thermal microwave effects due to the heating of polar intermediates have been also observed. These effects result from the way polar components of the reaction seems more reactive by the absorption of microwave irradiation, leading to carry-out reactions that cannot be done using thermal heating.[17]

Many difficulties of conventional synthesis can be successfully overcome by microwave heating. In difference of conventional heating, microwave irradiation provides an effective, selective, and fast synthetic method for polymerization processes. Microwave radiation advantages over conventional heating includes: 1) enhancement of radiation rates, which leads to shorter reaction times; 2) an increase of reaction temperatures and homogenous heating of the whole volume of the reaction mixture, which lead to higher purity and higher yields since there is a limited formation of by-products; and 3) high transfer energy per unit of time, high molecular weight products, great conversion percentages, and easy scale-up.[16-20]

In many of the cases previously mentioned (Kowalski, Storey and Taylor, Barakat), ROP took over 10 hours to be completed by conventional heating. However, it has been demonstrated that the use of microwave irradiation can reduce the polymerization time drastically, from 10 hours to only 5-30 minutes. In addition to the process acceleration, there is also the possibility of synthesis without using any or just very little quantity of solvent. This characteristic also brings an economic and environmental advantage like energy saving and accelerated product development.[16]

The use of closed-pressurized reaction vials permits an increase in the reaction temperatures, which lead to the enhancement of the reaction rates.[17] These closed vials also simplify product isolation by replacing high boiling point solvents with ones with low boiling point. The direct heating with microwave irradiation leads to homogenous heating, which removes local overheating at the vials walls, and as explained before, this results in the reduction of side reactions, cleaner products and higher yields.[16,17]

For most of biomedical applications, features such as molecular weight and molecular weight distribution play a critical role in the performance of the polymeric material. Recent studies have found that with microwave heating, there can be a better control of the molecular weight. Mallon and Ray[19,20] showed that microwave energy could induce small increases in the molecular weights of poly(ethylene terephthalate) and nylon-6,6 via solid-state reactions. However, they associate this effect with a microwave-enhanced diffusion rate of the polymers.

Yu and Liu[17] investigated the effect microwave radiation on a benzoic acid initiated polymerization of ϵ-CL. Using closed ampules and a domestic microwave oven, the parameters studied were microwave power, monomer to initiator ratio and temperature of polymerization.

Their studies demonstrated that the use of microwave heating favors chain growth in the initial stage which limits the number of polymer chains, resulting in high molecular weight polymers.

Ritter and coworkers[17] investigated the synthesis of ϵ-CL using a $Sn(Oct)_2$ catalyzed ROP under microwave irradiation. This investigation allowed a rapid optimization of the polymerization conditions. Fang et al.[17,19] also used a microwave oven for the polymerization of ϵ-CL using $Sn(Oct)_2$ as catalyst. The results demonstrated that high products yield and molecular weights can be obtained at much faster rate than thermal processes. Normally, PCL is thermally polymerized at 120-140°C in a period of 16-18 hours obtaining yields of 92-99% and molecular weight of 44 kg/mol. Fang´s results displayed the efficiency and rapidity of the microwave synthesis by obtaining this same yield and molecular weights of 86 kg/mol in just 2 hours and at a temperature of 150°C.

Current Thesis Goals

Independent of catalyst/initiator systems or the type of microwave reactor used, the majority of authors claim to have observed ROP rate enhancement of ϵ-CL by using microwave irradiation heating in comparison to conventional heating. Also, investigations have found that PCL can be synthesized under microwave irradiation without any solvent or metal catalyst, just using nontoxic acids and alcohols initiators. Nevertheless, it is common the use of $Sn(Oct)_2$ as catalyst for bulk microwave-assisted ROP of ϵ-CL in the presence of an alcohol initiator.

Taking all these in consideration, this investigation will be designed to explore microwave-assisted ring-opening polymerization of ϵ-CL using $Sn(Oct)_2$ as catalyst. As well, the effect that alcohol initiators could have in this same polymerization will be investigated. The

main purpose will be achieving basic reaction parameters to produce high molecular weight PCL that can be used to produce nanofibers via electrospinning which then can be employed in biomedical fields. It has been found that PCL could mimic the mechanical properties of ligaments, such as the Anterior Cruciate Ligament. Therefore, the creation of reconstruction scaffolds is possible using this biocompatible polymer.

CHAPTER II

METHODOLOGY

Starting Materials

ε-caprolactone (ϵ-CL) (monomer 99%) was purchased from Acros Organics. Stannous octoate [$Sn(Oct)_2$] was purchased from Nusil and stored in a refrigerator. Polyethylene glycol (PEG), diethylene glycol (DEG) and glycerol, used as initiators, were acquired from Fisher Scientific and Acros Organics, respectively. The solvents, dichloromethane, chloroform, dimethylformamide and tetrahydrofuran were all purchased from Acros Organics. Hexane was kept in a freezer and was purchased from Sigma-Aldrich. All chemicals were used without further purification.

Microwave Equipment and Set Up

The apparatus used for the polymerization was an Anton Paar Monowave 400, in which reaction temperature and reaction time are set up as desired. The microwave reactor was calibrated by a representative of Anton Paar. It has 850 W of output power; however, the irradiation power that the equipment uses for each reaction is controlled by the temperature. This means that once the temperature and time of the reaction are programmed, the set temperature is maintained throughout the entire set time by an irradiation power pulse in "on/off" cycles. The

temperature of the polymerization was recorded using an IR laser built into the microwave reactor. The air pressure for the microwave reactor was always kept at 5.5 torr.

Microwave-Assisted Ring-Opening Polymerization

A mixture of ϵ-caprolactone (0.02 mol) and catalyst (0.00002 mol) or ϵ-caprolactone (0.02 mol), initiator (0.0005 mol) and catalyst (0.00002) was poured in a 10-ml reaction tube with a stirring bar and purged for 10 min. with Argon gas to evacuate moisture and oxygen. The vessels used were specifically designed for the Anton Parr monowave microwave reactors, the tube mentioned is the G10 model, with a min. and max. filling volume of 3-mL and 6-mL respectively. The vessel containing the mixture was placed inside the reactor and irradiated at a pointed temperature for a predetermined period of time. The reaction conditions used are listed in Tables 1, 2, 3, 10, 11 and 12 located in CHAPTER III-RESULTS AND DISCUSSION.

Polymer Extraction

After the reaction was completed, the crude product was dissolved in dichloromethane (0.5 mL), and for the alcohol initiated PCL, chloroform (0.5 mL). The dissolved PCL was then precipitated by cold hexane (5 mL). The solution containing the PCL was placed in the freezer for at least 24 hours. Finally, the precipitate was filtered out and placed in a 20-mL scintillation vial, and dried in a Isotemp Vacuum Oven Model 280A at 40 °C under 20 in. Hg.

Characterization

Fourier Transform Infrared (FTIR) Spectroscopy

Infrared Spectroscopy was done with a Bruker ALPHA Platinum ATR single reflection diamond ATR and OPUS software with the resolution set to 4 cm^{-1}, scans set to 256, and background scans set to 128. The frequency range used was 3500-400 cm^{-1}.

Raman Spectroscopy

The sample was crushed into a fine powder and then tested on a glass slide. Raman Spectroscopy was done with the utilization of a Bruker Optics Senterra Raman microscope and OPUS software with the resolution set to 3-5 cm^{-1}, integration time set to 50, and spectral range from 1200ab,80-1530 & 1507- 2635.

Nuclear Magnetic Resonance (NMR)

Nuclear Magnetic Resonance was done with a Bruker 600 MHz FT-NMR in tubes Kimble borosilicate glass thrift N-51A 5mm NMR tubes. The number of scans were set to 16 and the chemical shift range used was 0-10 ppm. The solvent used was Chloroform-D1 (MagniSolv).

Molecular Weight Analysis

Gel Permeation Chromatography (GPC)

Nine PCL samples were dissolved in tetrahydrofuran (THF). 5 mg of sample was dissolved in 5-ml of THF at a temperature of 40°C using a PL-SP 260 VS sample preparation system and transferred to a 2-ml vial. The equipment used was a GPC 1260 Infinity with a Refractive Index (RI) detector. Separation was performed using a PLgel 5um MIXED-C (300 x

7.5 mm) column. Samples were injected at a volume of 50 µL and eluted through the system at a flow rate of 1 mL/min.

Crystallization and Thermal Behavior

X-Ray Diffraction (XRD)

The sample was crushed into a fine powder and then tested on a glass slide XRD, and carried out in a Bruker D8 instrument, using Cu Kα radiation (40 Ma, 40 KV). The scanning range was 10-40° at a scanning speed of 2°/min.

Differential Scanning Calorimetry (DSC) and Thermogravimetric Analysis (TGA)

DSC and TGA thermograms were obtained simultaneously using a TA Instruments SDT Q600 analyzer. The experiments were performed using a small amount of sample (mg) starting from room temperature and heating up to 600°C at 10°C/min under a nitrogen atmosphere with nitrogen flow of 100 ml/min. Universal Analysis software was used to indicate melt peak temperature, melt onset temperature and enthalpy of melting from the melting endothermic peak obtained in the thermogram.

Fiber Formation

Electrospinning was performed using polymer produced in the first part of this work, the PCL synthesized using just the monomer and catalyst. This PCL was used because its preliminary solution viscosities indicated a relative high molecular weight.

Electrospinning

Electrospinning was performed with a custom made rotating mandrel machine at atmospheric conditions and room temperature. The high voltage power supply was a standard model series ES purchased from Gamma High Voltage Research. The positive of the power supply was set at +12kV and the negative at -12kV. The positive end was connected to the spinneret, a 22-gauge needle, and the negative end grounded to the collector which was an aluminum can. The positive charge induced on the spinneret allowed for the fibers to be attracted towards the grounded collector. The contents inside of the 10-mL glass syringe consisted of 6mL of a 15% wt/vol PCL solution in 1:1 (DMF/THF). The syringe was then placed on an automated KDS 210 pump and programmed to dispense at a flow rate of 0.2 mL/min.

Tensile Strength Testing

The tensile strength and percent elongation of the electrospun fiber were evaluated using an INSTRON® tensile tester 5943 with a 25 N maximum load cell under a crosshead speed of 10 mm/min. The samples utilized for mechanical characterization were cut using a die that shaped the electrospun materials into a “dog-bone” shape. The die cut the samples with a 2.75 mm width at their narrowest point and a gauge length of 7.5 mm. A Fractional Digital Caliper was used to measure the thickness of each dog-bone shaped sample. A minimum of 10 samples were used to tests the tensile behavior of the polymer and the average values were recorded. Data from tensile strength was then replotted using origin software.

CHAPTER III

RESULTS AND DISCUSSION

Ring-Opening Polymerization of ϵ-CL was performed in a microwave reactor. In this study, $Sn(Oct)_2$ was used as catalyst with and without an alcohol initiator. The initiators tested were glycerol, diethylene glycol (DEG) and polyethylene glycol (PEG). Experimental conditions (reaction time, reaction temperature and monomer to catalyst, and monomer to initiator to catalyst ratios) used are summarized in Tables 1, 2 and 3 for the glycerol, DEG and PEG initiated polymerization respectively and in Tables 10, 11 and 12 for the polymerization without an initiator. The product obtained was confirmed as PCL using FTIR, Raman Spectroscopy and NMR.

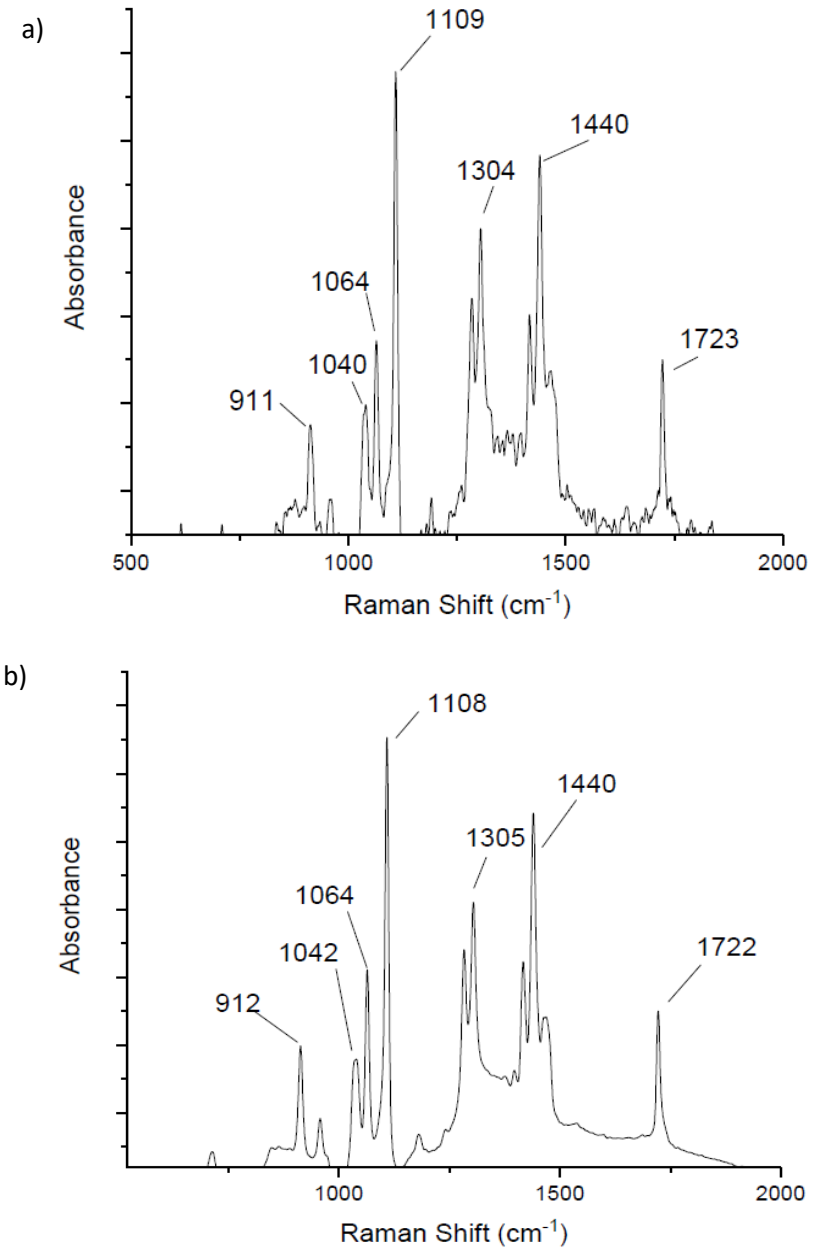
Microwave-Assisted ROP of ϵ-CL Using $Sn(Oct)_2$ as Catalyst with an Alcohol Initiator

Following as reference the research done by Fang[19] and Gotelli[1], different alcohols were used as initiators for the polymerization of PCL. The conditions used for the reactions using glycerol, DEG and PEG are listed in Tables 1, 2 and 3 respectively. The amount of initiator used was decided using as reference the work done by Yu and Liu.[36] In order to save time and resources, all the products obtained underwent simple visual testing of viscosity. Higher viscosity is correlated with higher molecular weight, and therefore higher probability to form fibers. However, mixed results were observed. The products obtained were characterized using Raman

spectroscopy. In the case of the product obtained using DEG as initiator, NMR and FTIR were also used since it was the one that showed higher viscosity.

Characterization

Raman



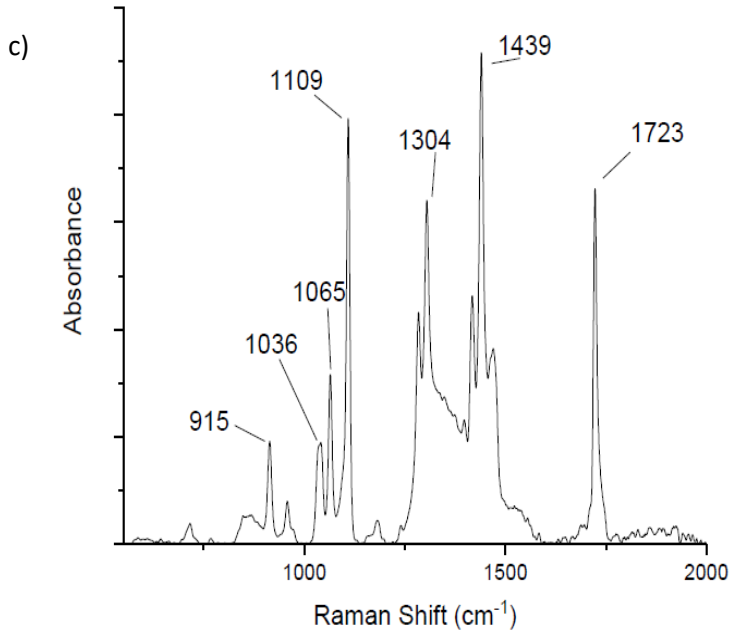


Figure 8: Raman Spectra of PCL Using a) Glycerol (2 Hours, 150°C, 1000:250:1), b) PEG (2 Hours, 150°C, 1000:250:1) and c) DEG as Initiator (3 Hours, 150°C, 1000:250:1)

The Raman spectra for the products showed in Figure 8 confirms the expected vibrations for PCL. The CH_2 movements that signify twist and bend are in the 1284-1309 cm^{-1} region and 1417-1442 cm^{-1} region respectively. C=O stretch regions of the spectrum correspond to peaks in spectra at wavenumbers 1723-1725 cm^{-1}. The skeletal stretch region consist of primarily C-COO stretches and correspond to region 850 - 965 cm^{-1}. Other C-C stretch regions were correlated to regions with wavenumber between 1030 -1106 cm^{-1}.[23]

FTIR

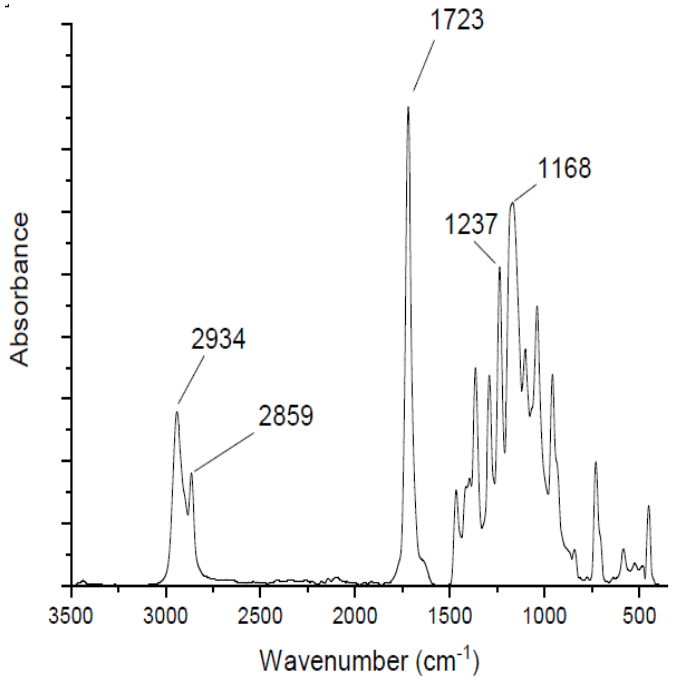


Figure 9: FTIR Spectrum of PCL Using DEG as Initiator (3 Hours, 150°C, 1000:250:1)

The IR spectrum of the product produced with DEG as initiator showed characteristic absorption of PCL. FTIR spectrum is shown in Figure 9. It is easy to identify the strong band produced by carbonyl stretching around 1723 cm^{-1}. The peaks at 2934 cm^{-1} and 2859 cm^{-1} are due to asymmetric CH_2 stretching and symmetric CH_2 stretching respectively. The peaks around 1000-1300 cm^{-1} indicate C-O and C-C stretching, illustrating the backbone of the molecule.[22]

NMR

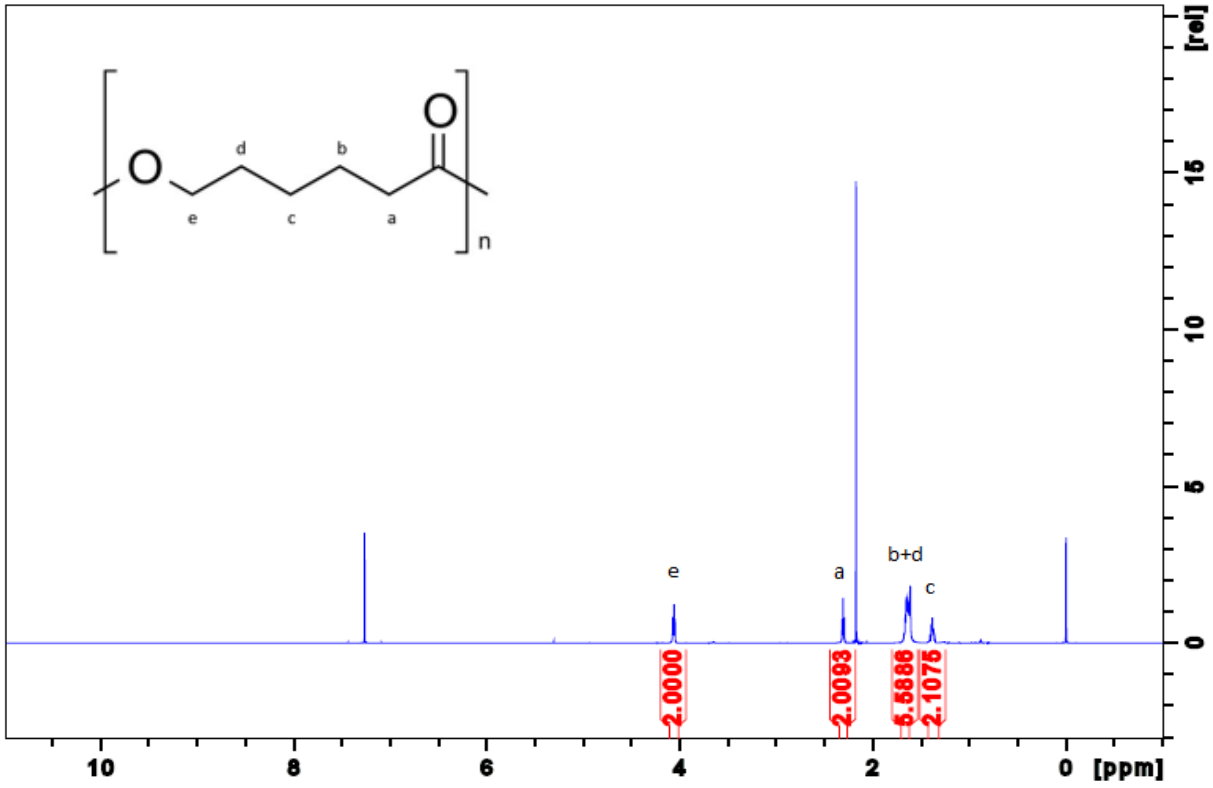


Figure 10: NMR Spectrum of PCL Using DEG as Initiator (3 Hours, 150°C, 1000:250:1)

The NMR showed in Figure 10 confirms the molecular structure of the synthesized PCL. In the NMR spectrum, the peaks that represent the hydrogens in the 5 carbons at the repeating sub-unit of the PCL are identifiable. The hydrogens from the α carbon resonate at 2.3 ppm. The hydrogens from the β carbon resonate at 1.7 ppm. The hydrogens from the γ carbon resonate at 1.4ppm. The hydrogens from the σ carbon resonate at 1.7 ppm. The hydrogens from the ε carbon resonate at 4 ppm.[24] However, a strong peak around 2.2 ppm is shown in the spectrum, this peak must be due to contamination from acetone, which was used to clean the NMR tubes.[25]

Glycerol

Polymerization of PCL using glycerol as initiator and $Sn(Oct)_2$ as catalyst is represented in Figure 11. As mentioned before, the conditions used for this reaction are listed in Table 1. It was noticed that after the polymer extraction stage, the polymeric material produced was not solid, instead a viscous liquid was obtained. As it can be seen in Figure 11, the low molecular weight polymer obtained with the glycerol can be explained by branching, since it is tri-functional compound and polymerization can initiate at any of its three -OH groups

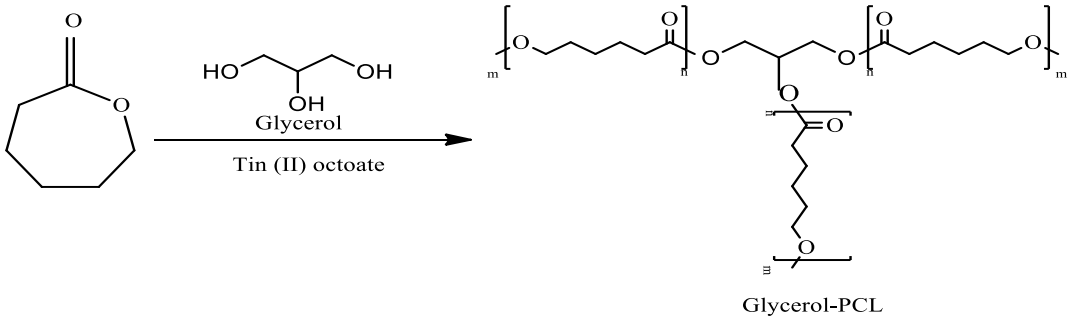


Figure 11: Polymerization of PCL Using Glycerol as Initiator and $Sn(Oct)_2$ as Catalyst

Time (hrs)	**Monomer: Initiator: Catalyst**	**Temperature (°C)**
2	1000:250:1	150
2	1000:250:1	170
4	1000:250:1	150
4	1000:250:1	170

Table 1: Parameters Examined Using Glycerol as Initiator

PEG

Figure 12 represents the polymerization of PCL using PEG as initiator and $Sn(Oct)_2$ as catalyst. Table 2 lists the conditions used for this polymerization. As with glycerol, it was observed that after the polymer extraction stage, the polymeric material produced was not solid, instead a viscous liquid was obtained. In contrast to glycerol, PEG will produce a linear polymer (Figure 12); and if the high molecular weight of PEG (380-420 g/mol) is taken in consideration, higher molecular weights were expected.

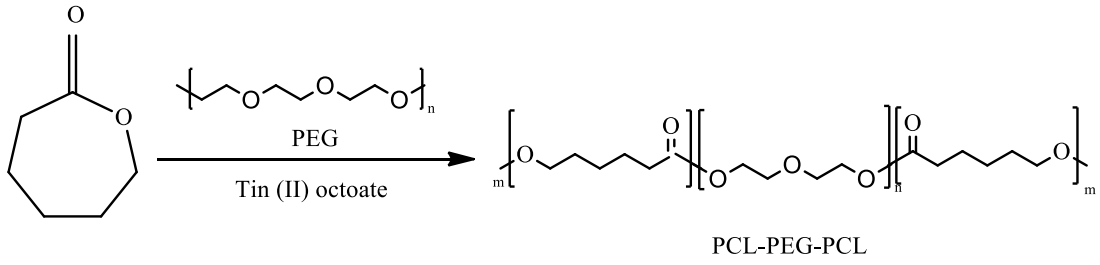


Figure 12: Polymerization of PCL Using PEG as Initiator and $Sn(Oct)_2$ as Catalyst

Time (hrs)	Monomer: Initiator: Catalyst	Temperature (°C)
2	1000:250:1	150
2	1000:250:1	170
4	1000:250:1	150
4	1000:250:1	170

Table 2: Parameters Examined Using PEG as Initiator

DEG

DEG initiated polymerization of PCL using $Sn(Oct)_2$ as catalyst is represented in Figure 13. Table 3 shows the conditions tested using this initiator. A difference was noticed using DEG, since the product obtained was a solid or a solid with texture of wax. As with PEG, DEG has a high molecular weight (106.12 g/mol) and will produce a linear polymer; therefore, high molecular weights were expected. However, it was difficult to see a pattern in the results. According to these observations and after confirming that the product obtained was PCL by characterization, the investigation was continued using DEG as initiator.

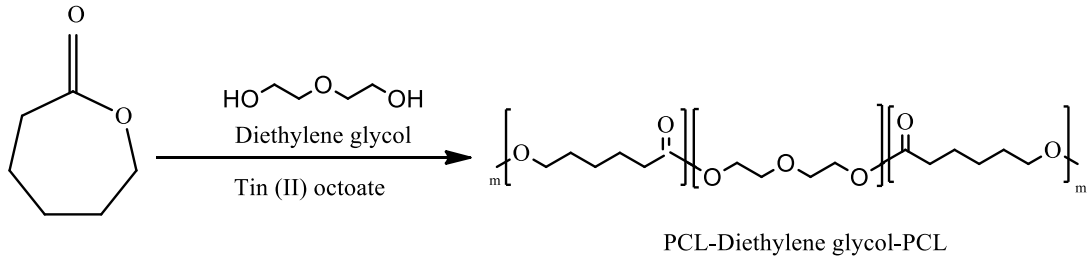


Figure 13: Polymerization of PCL Using DEG as Initiator and $Sn(Oct)_2$ as Catalyst

Time (hrs)	**Monomer: Initiator: Catalyst**	**Temperature (°C)**
2	1000:250:1	150
2	1000:250:1	170
4	1000:250:1	150
4	1000:250:1	170

Table 3: Parameters Examined Using DEG as Initiator

In Table 4, the effect of time was investigated. The temperature was kept at 150°C for all these reactions since, at this temperature, a solid product with higher viscosity was observed. After the extraction process, a solid PCL was only obtained at 2 hours, while at 3 and 4 hours, a liquid PCL was the product. In addition, the PCL produced at 3 and 4 hours presented a slightly yellow color. These observations suggest that irradiation times longer than 2 hours lead to a decrease of the molecular weight and thermal degradation upon microwave exposure. Therefore, it is reasonable to assume that after 2 hours of microwave irradiation, almost all the monomer has been consumed, which decreases the probability of new ester bond formation and increase the probability of transesterification reactions[7]. As result, it was concluded that the ideal reaction time was 2 hours.

Further, it should be noted that the state of the PCL obtained at 3 and 4 hours at a temperature of 150°C with a monomer to initiator to catalyst ratio of 1000:250:1, changed from liquid to solid after more tests were made. This observation could suggest that the polymerization continued even after the product was treated. Thus, this changed our first assumption and open the possibility of an incomplete monomer conversion during the polymerization. However, since the product was purified, it is expected a complete elimination of ϵ-CL residues.

Therefore, a plausible explanation for this unexpected slow monomer conversion could be the formation of the true initiator of the reaction, stannous alkoxide, via monomer-insertion mechanism proposed by Penczek. A stannous alkoxide complex produced from the reaction of the $Sn(Oct)_2$ and the alcohol initiator is the real initiator of the polymerization. This initiator ring-opens the monomer via coordination-insertion forming the first chain component of the polymerization, which then continue to ring-open the remaining monomer until the consumption of the monomer. Literature evidence suggests that diols initiators slow down the initiation

process because they interact strongly with $Sn(Oct)_2$, acting as a bidentate ligand[15]. Therefore, a slow formation of the real initiator complex contributes to a slow rate in the formation of the first chain component and further to a slow initiation process. Therefore, it can be inferred that more time is needed for the polymerization process to be completed.

Reaction time (hrs)	**ε-CL: initiator:catalyst**	**Temperature (ºC)**
2	1000:250:1	150
3	1000:250:1	150
4	1000:250:1	150

Table 4: Using DEG as Initiator, Effect of Reaction Time

The effect of the temperature was tested next, with the parameters listed in Table 5. At this stage, problems with reproducibility were observed. The reaction at 150°C for 2 hours, same conditions as the one listed in Table 9, produced a liquid PCL. This reaction was reproduced several more times with this same last result. The product obtained at 160°C was solid, while the PCL produced at 170°C was liquid. As well, both products presented a yellowish color which, as explained before, could indicate thermal degradation or an incomplete monomer conversion. However, after further testing, these products changed from liquid state to solid indicating a continuation of the reaction. These observations question the previous assumptions and lead to consider that monomer conversion happens at a slower rate than expected.

Reaction time (hrs)	ε-CL: initiator:catalyst	Temperature (°C)
2	1000:250:1	150
2	1000:250:1	160
2	1000:250:1	170

Table 5: Using DEG as Initiator, Effect of Reaction Temperature

Furthermore, Tables 6, 7 and 8 list the additional testing that was done in the PCL obtained using DEG as initiator at the different reaction times and reaction temperatures. This was done in an effort to find how the molecular weight is affected by these conditions. However, the results were inconclusive and no pattern was found.

	Solid at:			
	Room Temp.	Fridge (-16°C)	Room Temp. (After fridge)	Color
150 °C	No	Yes	No	Clear
160 °C	Yes	Yes	Yes	Clear/Yellow
170 °C	No	Yes	Yes	Clear/Yellow

Table 6: Effect of Reaction Temperature on Molecular Weight, at 2 Hours with DEG as Initiator

	Solid at:			
	Room Temp.	Fridge (-16°C)	Room Temp. (After fridge)	Color
150 °C	No	Yes	Yes	Clear/Yellow
160 °C	No	Yes	Yes	Clear/Yellow
170 °C	No	Yes	No	Clear/Yellow

Table 7: Effect of Reaction Temperature on Molecular Weight, at 3 Hours with DEG as Initiator

	Solid at:			
	Room Temp.	Fridge (-16°C)	Room Temp. (After fridge)	Color
150 °C	No	Yes	Yes	Clear/Yellow
160 °C	No	Yes	No	Clear/Yellow
170 °C	Yes	Yes	Yes	Yellow

Table 8: Effect of Reaction Temperature on Molecular Weight, at 4 Hours with DEG as Initiator

Finally, a last parameter was tested, the monomer to initiator to catalyst ratio. The conditions are listed in Table 9. The amount of initiator, DEG, was decreased a factor of ten and running the reactions at 150°C for 2 and 3 hours. The PCL obtained was a white solid with a slightly higher viscosity than the one observed for the previously mentioned cases. Comparing both products, the viscosity of the product at 3 hours seemed slightly better. Therefore, a reaction at 150°C for 3 hours reducing the initiator by another factor of ten was performed. The resultant PCL was liquid but a change was observed after 5-7 days, it went from liquid to solid and when the solid was dissolved, the viscosity was similar to the one observed at the previous reaction. Again, implying that the polymerization continued after a few days. This is another clear

indication that the monomer was converted more slowly. Therefore, it is suggested that to obtain complete monomer depletion, longer irradiation time is also necessary when less initiator is used.[36]

Time (hrs)	Monomer: Initiator: Catalyst	Temperature (°C)
2	1000:25:1	150
3	1000:25:1	150
3	1000:2.5:1	150

Table 9: Effect of Monomer to Initiator to Catalyst Ratio, Using DEG as Initiator

In summary, the low viscosity obtained in the PCL produced using different initiators is correlated to a low molecular weight. This could indicate that polymer chains of lower molecular weight are produced because, in a very short time frame, many initiations are occurring.[19] Nevertheless, the final PCL obtained still displayed the properties of pure PCL since low molecular weight bifunctional and trifunctional initiators in small amounts were used. No further investigation was done with these PCLs since high molecular weight is needed for the production of fibers.

Microwave-Assisted ROP of ϵ-CL Using $Sn(Oct)_2$ as Catalyst Without an Alcohol Initiator

The polymerization of PCL using $Sn(Oct)_2$ as catalyst is illustrated in Figure 14. As mentioned before, the different reaction conditions investigated are listed in Tables 10, 11 and 12.

These polymerization conditions were set using as reference a study conducted by Fang and associates.[19] This investigation concluded that high molecular weight PCL could be produced using a microwave reactor under conditions of 150°C for 2 hours, with and without a diol initiator. However, some changes needed to be done since the microwave reactor used in Fang´s research was not the same model and had different characteristics as the Anton Paar microwave used for this work. At the beginning, to save time and resources, all the products obtained underwent simple visual testing. At the stage of polymer purification where the viscosity of the dissolved product was visually examined, as explained before, higher viscosity is correlated with higher molecular weight, and therefore higher probability to form fibers. The polymer produced was characterized using Raman, FTIR and NMR. The results from the characterization confirmed that ε-CL had been successfully polymerized into PCL.

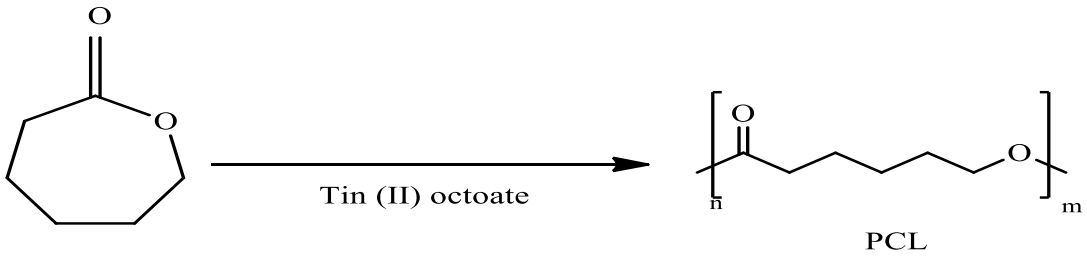


Figure 14: Polymerization of ϵ-Caprolactone Using $Sn(Oct)_2$ as Catalyst

Characterization

FTIR

The IR spectrum of the product produced showed characteristic absorption of PCL. The FTIR spectrum is shown in Figure 15. The strong band produced by carbonyl stretching can be seen around 1723 cm^{-1}. Asymmetric CH_2 stretching and symmetric CH_2 stretching is represented

by the peaks at 2949 cm^{-1} and 2865 cm^{-1} in the spectra respectively. Illustrating the backbone of the molecule, the peaks around 1000-1300 cm^{-1} indicate C-O and C-C stretching.[22]

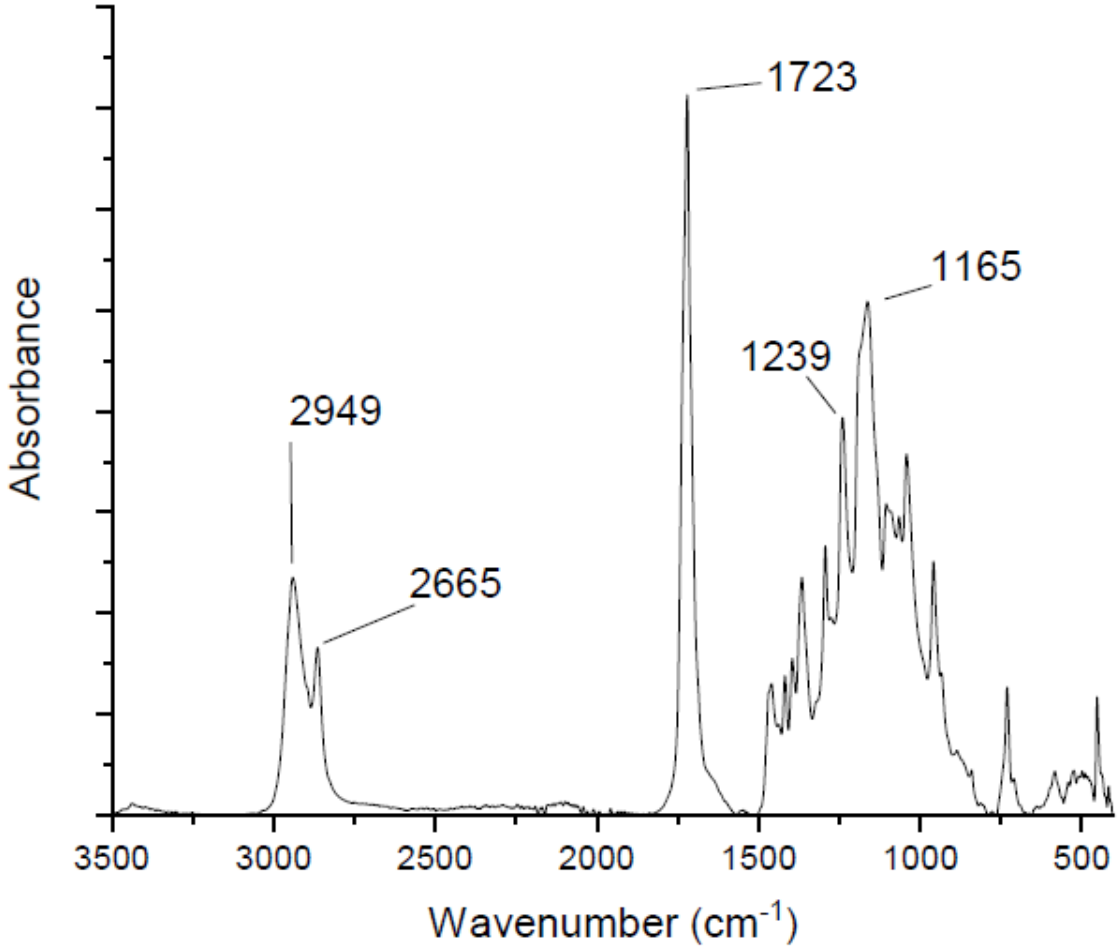


Figure 15: FTIR Spectrum of PCL Using $Sn(Oct)_2$ as Catalyst Without an Alcohol Initiator (3 Hours, 150°C, 1000:1)

Raman

The Raman spectrum for the product showed in Figure 16 confirms the findings in the FTIR spectrum. The peaks in the 1284-1309 cm^{-1} region and 1417-1442 cm^{-1} region represent the twist and bend CH_2 movements respectively. C=O stretch regions of the spectrum correspond to peaks in the 1723-1725 cm^{-1} region. 850 - 965 cm^{-1} region corresponds to the skeletal stretch region consisting of primarily C-COO stretches. Other C-C stretch regions correspond to peaks located between 1030 -1106 cm^{-1}.[23]

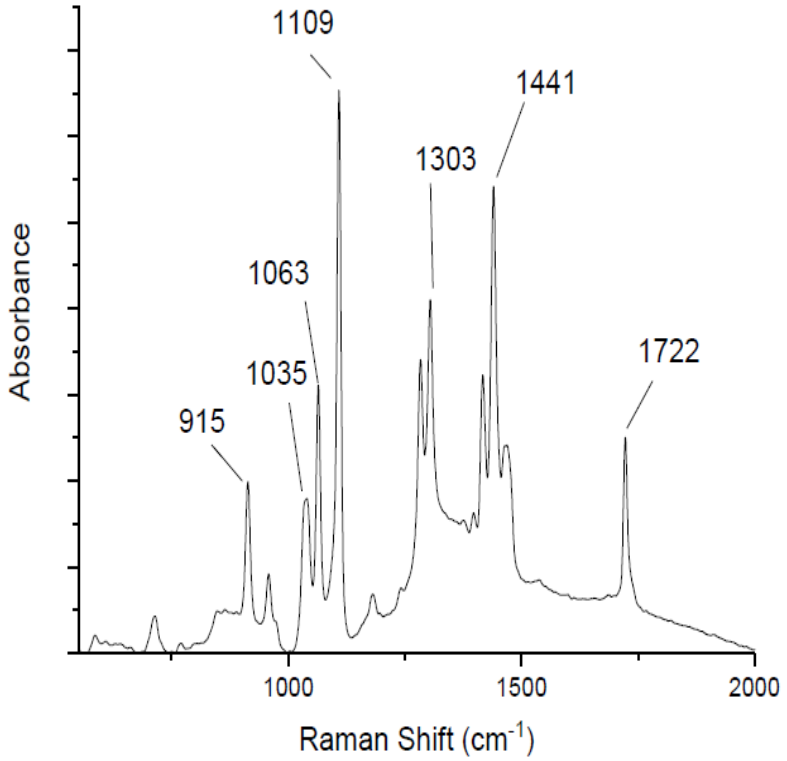


Figure 16: Raman Spectrum of PCL Using $Sn(Oct)_2$ as Catalyst Without an Alcohol Initiator (3 Hours, 150°C, 1000:1)

NMR

The NMR showed in Figure 17 confirms the molecular structure of the synthesized PCL. In the NMR spectrum is easy to identify the peaks corresponding to the hydrogens attached to the 5 carbons of the repeating sub-unit of PCL. The hydrogens from the α carbon resonate at 2.5 ppm. The hydrogens from the β carbon resonate at 1.6 ppm. The hydrogens from the γ carbon resonate at 1.4ppm. The hydrogens from the σ carbon resonate at 1.7 ppm. The hydrogens from the ε carbon resonate at 4.1 ppm.[24]

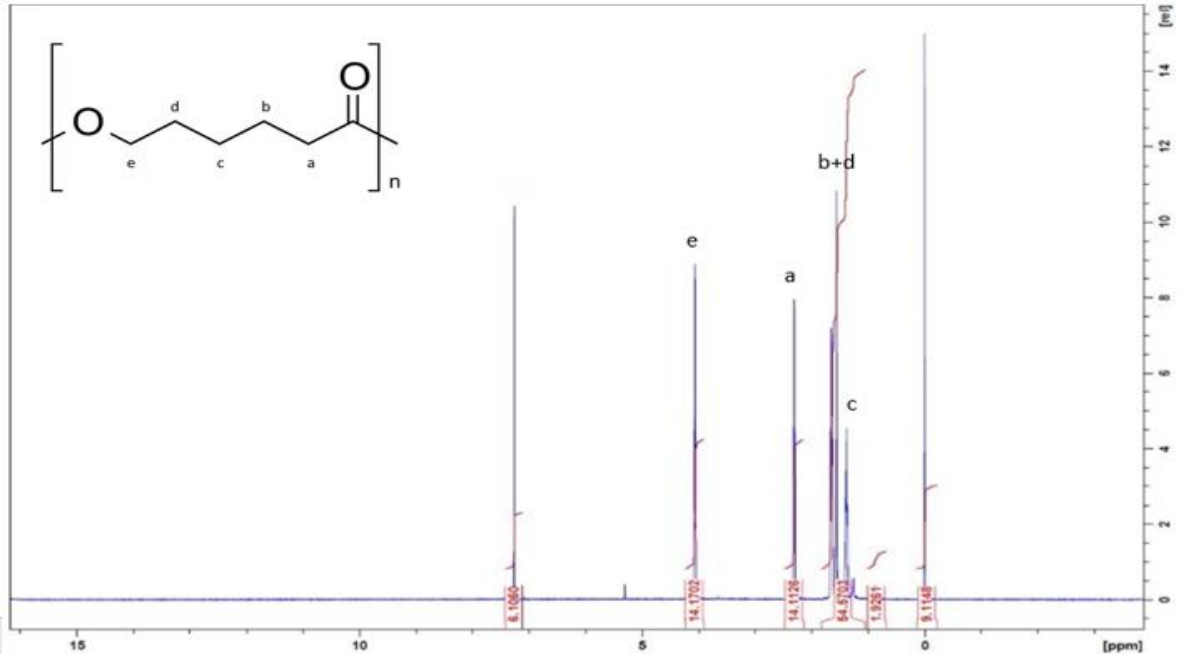


Figure 17: NMR spectrum of PCL Using $Sn(Oct)_2$ as Catalyst Without an Alcohol Initiator (3 Hours, 150°C, 1000:1)

Effect of Reaction Time

As it can be noted, in Table 10, the effect of time was examined. The results yielded a noticeable change in viscosity as the reaction time increased. It is also worth noting that the obtained PCL was more viscous than the one produced using any of the alcohol initiators tested. At 1 hour, the produced PCL was not very viscous; however, at 2, 3 and 4 hours higher viscosities were observed with 3 and 4 being slightly more viscous than the others. Nevertheless, the PCL produced at 4 hours presented a slightly yellowish color, which indicated thermal degradation. As explained before, the polymerization of PCL with an alcohol initiator showed a slow monomer conversion thanks to the reaction of $Sn(Oct)_2$ with the alcohol leading to the production of an alkoxide, the real initiator. Although, no initiator is used in these polymerizations, any hydroxy impurity present in the reaction mixture can react with $Sn(Oct)_2$. Thus, it is reasonable to assume that at 3 and 4 hours higher viscosities are obtained because almost all monomer has reacted. However, after 3 hours of reaction, the probability of forming new ester bonds decreases and chain scission of the long polymer chain starts to occur. This explains the change in the properties in the polymer at 4 hours. Therefore, the selected time for the next reactions was 3 hours.

Reaction time (hrs)	**ε-CL: catalyst**	**Temperature (ºC)**
1	1000:1	150
2	1000:1	150
3	1000:1	150
4	1000:1	150

Table 10: Effect of Reaction Time

Effect of Reaction Temperature

Table 11 shows the effect of the reaction temperature. The results obtained indicated that: as the reaction temperature increased, thermal degradation was more and more noticeable. As in the previous trial, the presence of a yellow color in the product indicated a thermal degradation occurring during the synthesis at high temperatures. It was observed that as the temperature increased, the tone of the yellow color increased. Therefore, it can be assumed that higher temperatures accelerated the polymerization process and after 3 hours all the monomer had been consumed. The depletion of the monomer leads to a breaking of the backbone of the polymer chain, producing fragments of different molecular weights. This explains the change in the color and the slightly viscous product. As a result, it was concluded that 150°C was the ideal temperature for the reaction.

Reaction time (hrs)	**ε-CL: catalyst**	**Temperature (ºC)**
3	1000:1	150
3	1000:1	160
3	1000:1	170
3	1000:1	180

Table 11: Effect of Reaction Temperature

Effect of Monomer to Catalyst Ratio

Another parameter evaluated was the monomer to catalyst ratio, as seen in Table 12. Extremely low viscosities were observed when large amount of catalyst was present in the

polymerization process, in this case in the 10:1 and 100:1 monomer to catalyst ratio. Therefore, it can be assumed that at high concentration of catalyst, higher conversion rates are found, leading to high molecular weights. In contrast, using a 10000:1 monomer to catalyst ratio, no polymerization was observed, indicating that there were not enough catalyst molecules present in the reaction. In summary, the conditions evaluated indicated that the ideal parameters to produce high molecular weight PCL (based on high viscosity) without any indication of oxidation were 150°C for 3 hours with a 1000:1 monomer to catalyst ratio.

Reaction time (hrs)	**ε-CL: catalyst**	**Temperature (ºC)**
3	10000:1	150
3	1000:1	150
3	100:1	150
3	10:1	150

Table 12: Effect of Monomer to Catalyst Ratio

GPC

To determine the molecular weight of the PCL produced, Gel Permeation Chromatography was used. The nine different PCL samples analyzed (from different reaction conditions) are listed in Table 13, numbers reported by the GPC are listed in Table 14 and the chromatogram obtained from this data is showed in Figure 18. The results confirmed most of our observations. Samples “PCL 1”, “PCL 2”, PCL 3”, and “PCL 4” are for the effect of time. At constant temperature of 150°C, the molecular weight (Mw) increased with reaction time,

reaching its peak at 3 hours (35910 g/mol), and then lowering again at 4 hours (17900 g/mol). This same trend is noted with the polydispersity, there is an increase in the polydispersity index number with reaction time, reaching its highest point at 3 hours and lowering again at 4 hours. Sample "PCL 3" (3 hours, 1000:1, 150°C) showed the highest polydispersity of all the samples with 2.12. This indicates a broader Mw distribution, which could be attributed to the slow monomer conversion explained before. At longer reaction times, the polymerization proceeds, more monomers react and chains grow longer, decreasing the polydispersity because the relative length differences between the chain decreases.[37] Samples "PCL 5", "PCL 6" and "PCL 7" are for the effect of temperature on molecular weight at constant reaction time. These samples showed the highest molecular weight, 62900, 54000 and 36500 g/mol. These molecular weights were obtained at 3 hours, using a 1000:1 monomer to catalyst ratio and a temperature of 160°C, 170°C and 180° respectively. However, as it was mentioned before, as the temperature increased, a yellowish color was presented in the samples suggesting thermal degradation. The polydispersity numbers for this samples were slightly lower than the one observed in the "PCL 3" sample (3 hours, 1000:1 monomer to catalyst ration, 150°C). Again, this could be an effect of the monomer conversion. As explained before, the increase in temperature leads to an acceleration of the polymerization process; thus, monomer is converted faster and the chains grow longer decreasing the polydispersity. In the case of samples "PCL 8" and "PCL 9", as the amount of catalyst increased, the molecular weight decreased and the polydispersity decreased. Therefore, the results obtained with the GPC analysis complied with the observations mentioned before, the ideal parameters to produce high molecular weight PCL without any indication of degradation were 3 hours, 150°C and 1000:1 monomer to catalyst ratio.

	Time (hrs)	monomer:catalyst ratio	Temperature (°C)
PCL 1	1	1000:1	150
PCL 2	2	1000:1	150
PCL 3	3	1000:1	150
PCL 4	4	1000:1	150
PCL 5	3	1000:1	160
PCL 6	3	1000:1	170
PCL 7	3	1000:1	180
PCL 8	3	100:1	150
PCL 9	3	10:1	150

Table 13: PCL Samples Analyzed Using GPC

	PCL 1	PCL 2	PCL 3	PCL 4	PCL 5	PCL 6	PCL 7	PCL 8	PCL9	
Mn	8500	12900	17000	10400	32900	28500	18600	15300	6650	g/mol
Mw	12250	23700	35910	17900	62900	54000	36500	28500	10000	g/mol
Mz	17200	38600	71500	27900	10700	91000	61100	46200	14200	g/mol
Mv	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	0.000	g/mol
D	1.44	1.84	2.12	1.72	1.92	1.90	1.97	1.86	1.51	

Table 14: Molecular Weight of PCL Samples Analyzed Using GPC

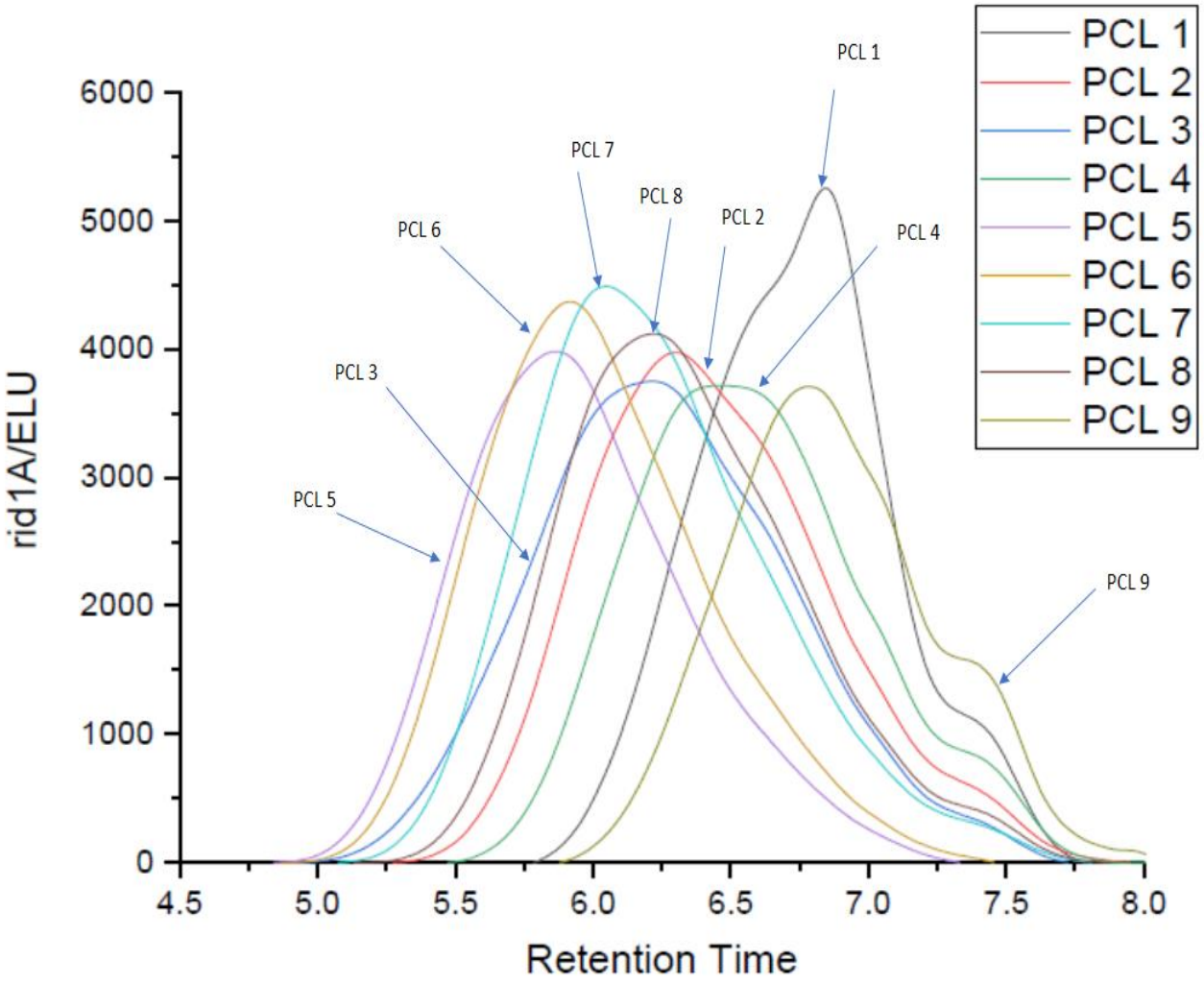


Figure 18: Chromatogram of the Nine Different PCL Samples

XRD

Figure 19 shows the XRD spectrum of the PCL obtained using the ideal parameters set before (3 hours, 150°C, 1000:1) displaying its crystalline peaks. PCL is a semi-crystalline material which exhibits highly ordered folding chain characteristics represented by three crystalline peaks. The obtained spectrum displays the three strong reflections at the angles (2θ) 21.6°, 22.3° and

23.8°, corresponding to the (110), (111) and (200) crystallographic planes of the orthorhombic crystal structure.[26-31]

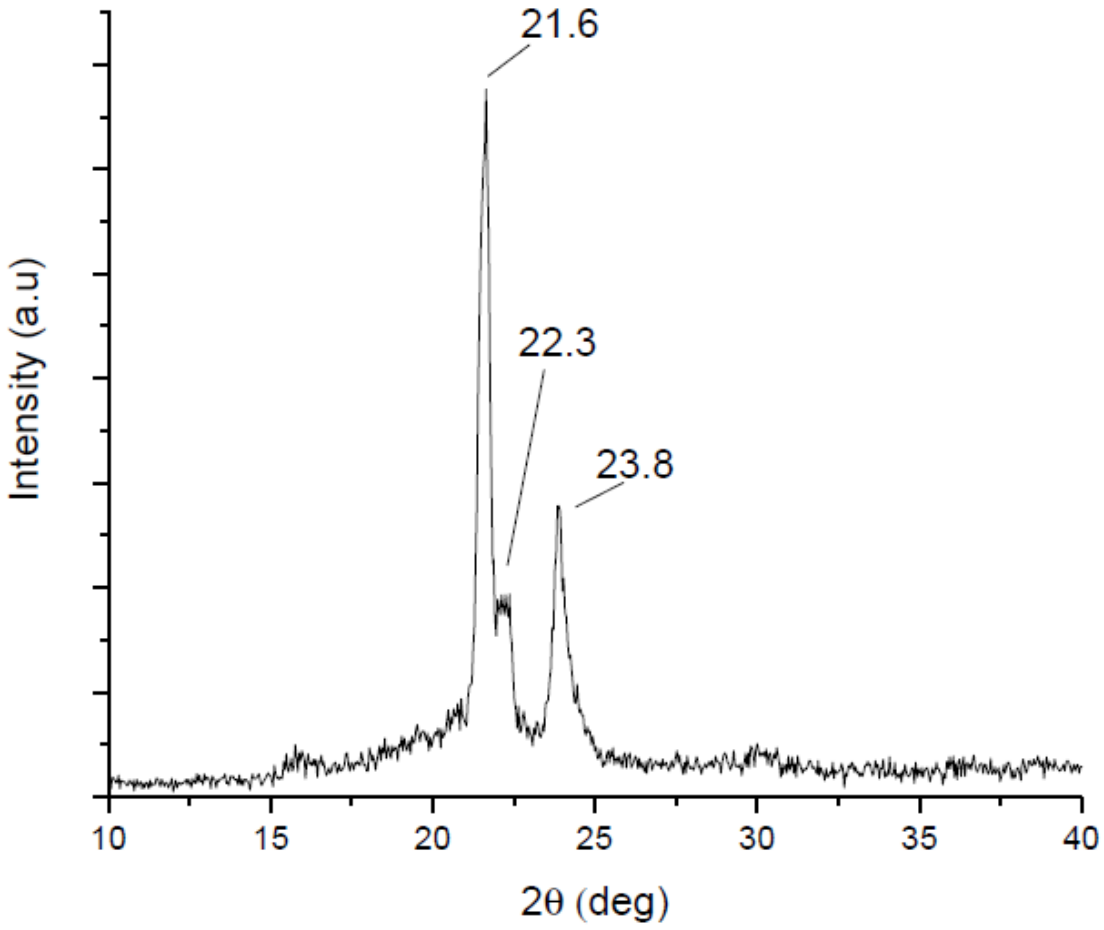


Figure 19: X-Ray Diffraction Scan of PCL Obtained at 150°C for 3 Hours with a 1000:1 Ratio

TGA

Thermal degradation of the PCL produced was analyzed using TGA. Figure 21 displays the TGA curve for the PCL sample obtained using the ideal parameters set: 3 hours, 1000:1 monomer to catalyst ratio and 150°C. It can be seen that the PCL sample started to lose weight

(about 1-2%) between 50-70°C due to moisture evaporation[28], then it stabilizes up to ~250°C. A major weight loss is observed in the range 368.88-421.98°C. This indicates great thermal stability, and its capability to endure high temperatures without degradation.[28,30] A closer examination of Figure 22, the DTGA curves highlights the presence of a two-step thermal degradation. The first step is found around 300-350°, where 20% mass percent is loss. This first step indicates that ester pyrolysis reactions cause the break of the polyester chains. The second step is found around 380-430°C. In this main degradation step, 90% percent of mass is loss and leads to the formation of the monomer, ϵ-caprolactone. The monomer is produced via unzipping or chain-end scission depolymerization process (Figure 20).[38]

As well, it can be seen in Figure 22 both TGA and DSC curves superimposed. After the defined melting peak indicated previously in the DSC curve, the post-melt baseline changes slope as the sample begins decomposition. The DSC endothermic broad peaks at 346.28°C and 404.29°C corresponds to the TGA temperature around which decomposition started and the temperature around 50 weight percent of the sample was left respectively.

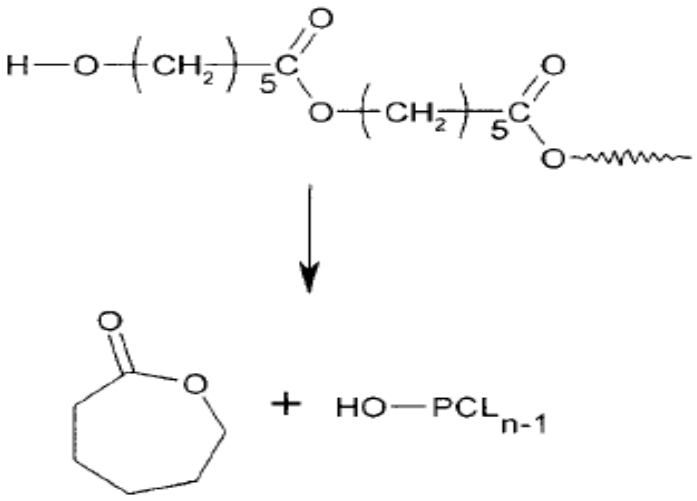


Figure 20: Depolymerization of PCL Chains via an Unzipping Mechanism[38]

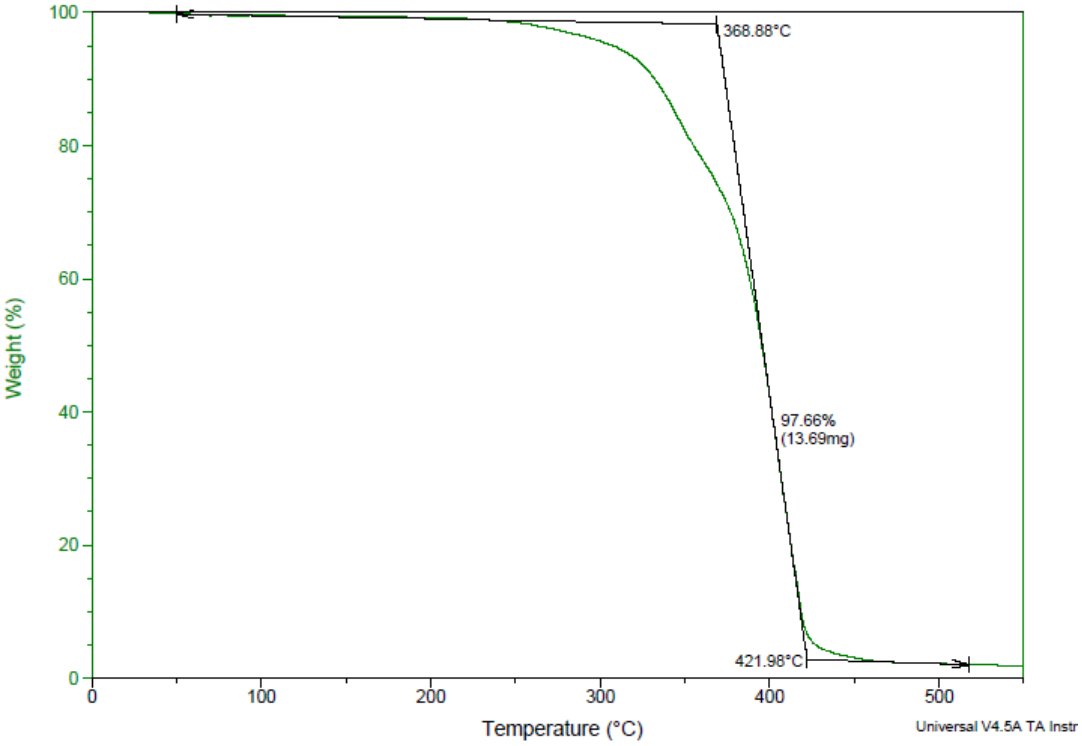


Figure 21: TGA Thermogram of the PCL Produced at 150°C for 3 Hours Using 1000:1 Ratio

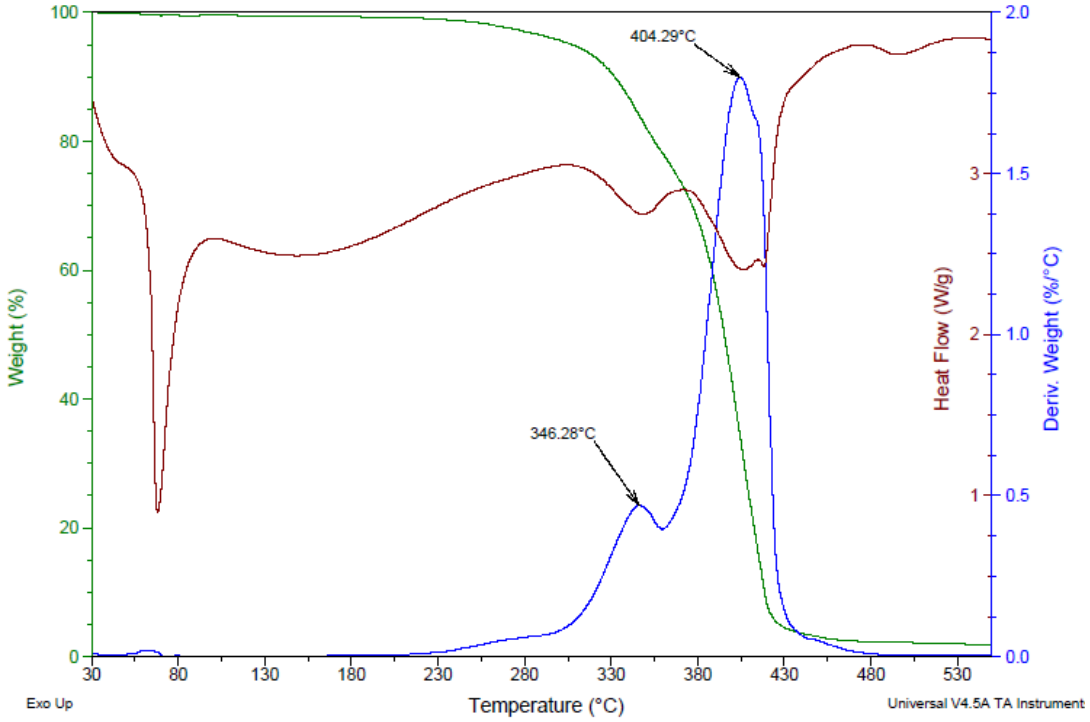


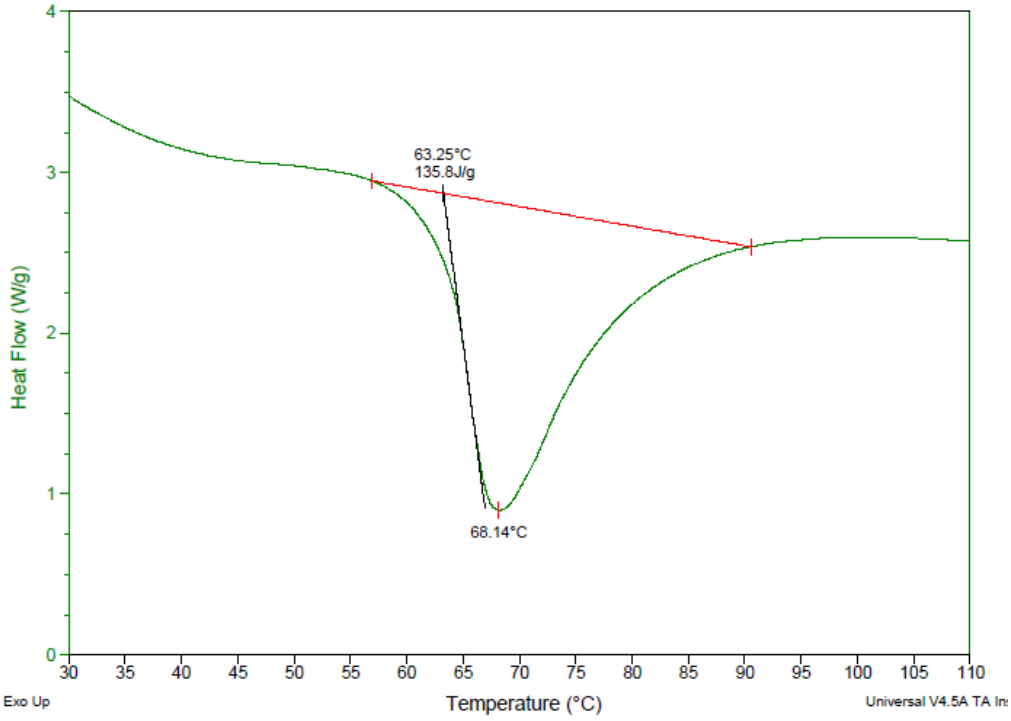
Figure 22: DSC and TGA Curves

DSC

The thermal properties and the crystalline nature of the PCL produced at 150°C for 3 hours with 1000:1 ratio were studied by DSC. The resultant DSC thermogram is showed in Figure 23. Semi-crystalline polymers such as PCL, exhibit three thermal transitions, the glass transition at -60°C, a peak around ~25°C corresponding to exothermic crystallization, and one corresponding to melting endothermic at ~60°C.[30] These first two temperatures are not indicated in Figure 23, the melting temperature was obtained at the peak of the melting endotherm (68.14°C), while the enthalpy of melting was obtained from the area under the peak (135.8 J/g) and the melt onset temperature (63.25°C) is also indicated. The degree of crystallinity was calculated using the following equation:

$$\text{Degree of crystallinity} = \frac{\Delta H_f}{\Delta H_{f\,100\%}}\ 100\% \qquad (27)$$

where ΔH_f is the enthalpy of melting and $\Delta H_{f\,100\%}$ is the enthalpy of melting for a fully crystalline polymer. Although there is a broad interval of values reported for the melting enthalpy of pure PCL 100% crystalline, the most commonly used is 139.5 J/g.[5,22,32] Therefore, the degree of crystallinity calculated for the PCL sample was 97.35%, indicating a nearly 100% crystalline material. The typical ranges for semi-crystalline polymers are 10 and 80%, and PCL specifically can reach 69%.[33] Higher values are normally obtained in materials containing small molecules and low molecular weight (due to chain folding).[4] It is known that the physical, thermal and mechanical properties of PCL or any other polymer are influenced by the degree of crystallinity and molecular weight;[5,33,34] normally, high crystallinity indicates a strong but brittle material.[35]



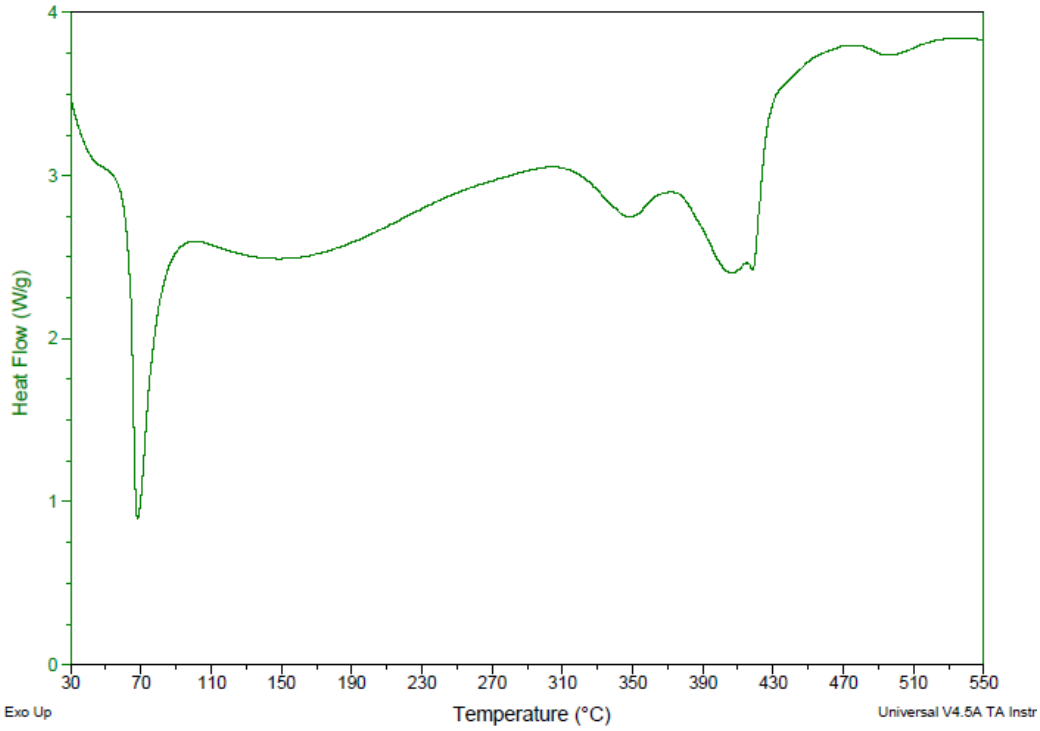


Figure 23: DSC Heating Curve Showing Melting Point of PCL Sample (3 Hours, 150°C, 1000:1)

Tensile Strength

Figure 24 shows the electrospun sheet used to conduct the tensile strength test. Prior to the electrospinning, a 15% wt/vol solution of PCL dissolved in 1:1 (DMF:THF) had a sufficient viscosity for electrospinning applications. Figure 25 exhibits the tensile strength and the tensile strain (extension) of the PCL fibers, and Table 15 demonstrates the maximum of those values. Upon examination, the fibers elongated over a 50 % extension rate with tensile strain exceeding over 10 MPa. The curves are steep showing a tensile modulus over 50 MPa. This illustrate a material with a high tensile strength and with a high resistance to deformation. The results show that the PCL fibers are strong and tough; as well, they show have characteristics similar to flexible plastics due to the gradual curves, high modulus, high tensile strength and long elongation. These great mechanical properties expressed by the fibers could be due to the high degree of crystallinity calculated previously for the PCL produced. These results sharply contrast with work done in the past utilizing PCL commercially available at our laboratory. Figure 26 shows the strain-stress curves of the commercial PCL and Table 16 presents the maximum values. The fibers produced via electrospinning with this PCL have high tensile strain with little tensile stress, giving very steep curves in the graph. The curves exhibit a strong but not tough material, which also exhibits characteristic of a flexible plastic with a moderate strength and large elongation. Therefore, the microwave synthesized PCL have more potential for the application in biomedical scaffolds, however still require further investigation.

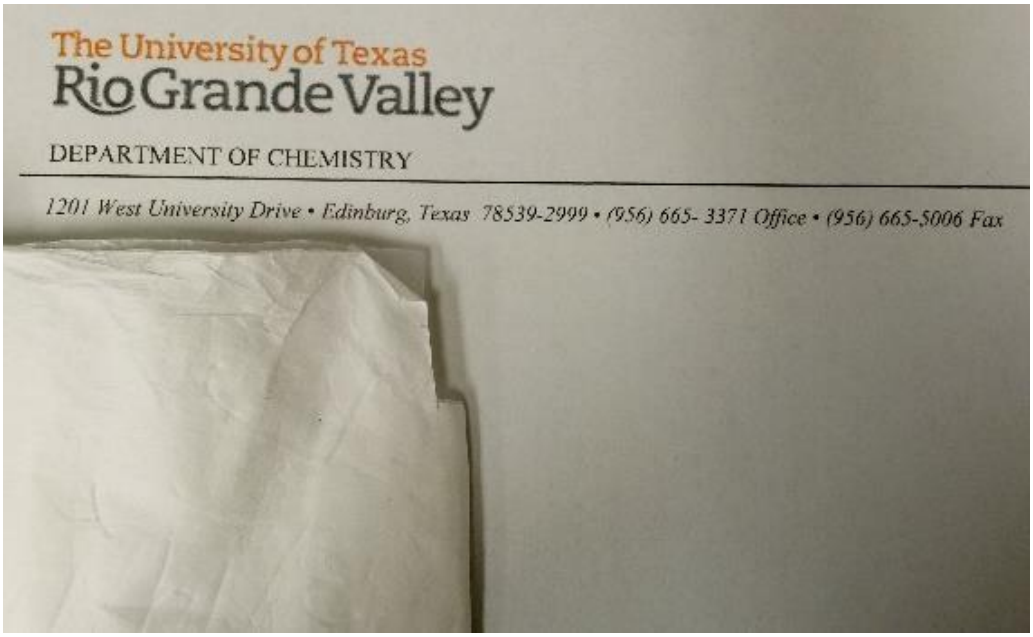


Figure 24: Electrospun Sample of PCL

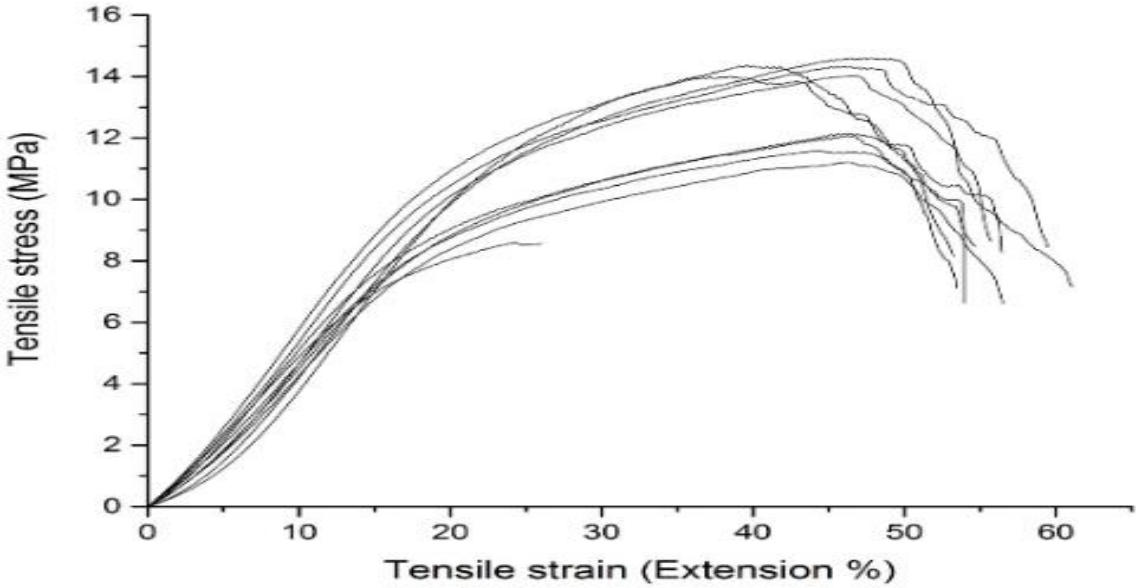


Figure 25: Tensile Strength Test of PCL, Conditions 3 Hours, 150°C, 1000:1. All Samples Were Taken from Same Electrospun Sheet (Figure 23)

Trial	Tensile Stress at Maximun (MPa)	Tensile Strain at Maximum (Extension %)	Modulus (Automatic Young´s)
1	12.13938	61.08	55.2849
2	14.36606	54.666	65.7431
3	14.00255	52.88	66.55623
4	14.01409	56.402	64.19208
5	12.08047	53.433	59.2063
6	8.53465	55.38	53.49634
7	11.58141	53.936	53.31016
8	11.21278	55.48	53.89354
9	14.32369	59.448	64.48264
10	14.61092	55.72601	61.80256
Mean	12.6866	55.943101	59.99678
SD	1.943557	2.600806383	5.17824

Table 15: Tensile Strength Tests Maximum Values

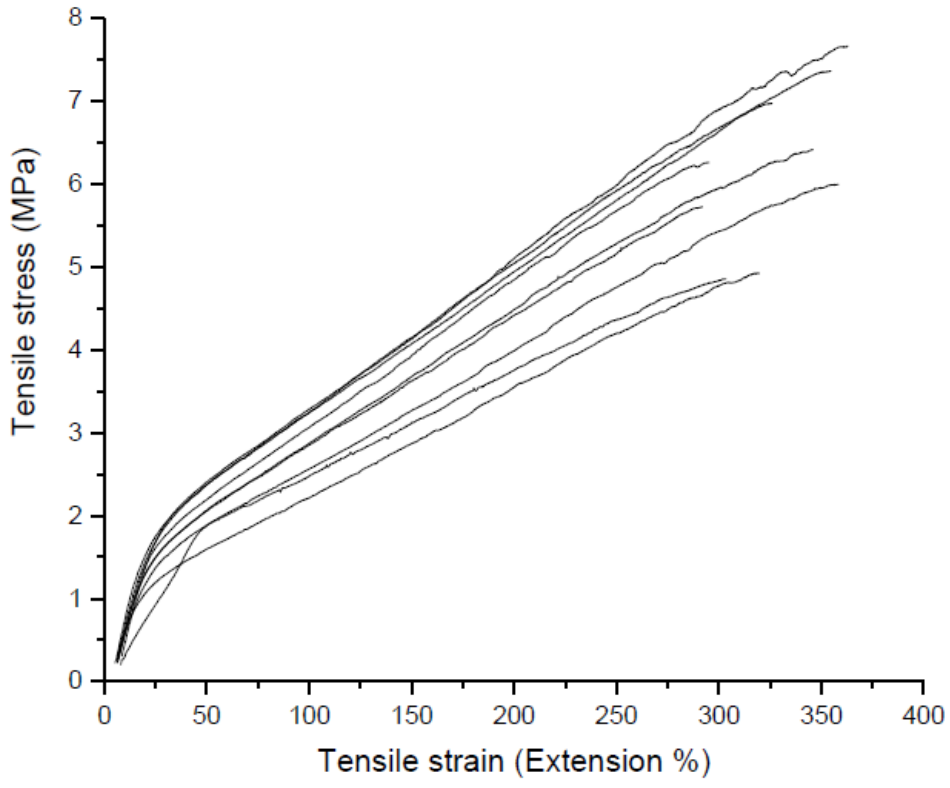


Figure 26: Tensile Strength Test of Commercial PCL

Trial	Tensile Stress at Maximum (MPa)	Tensile Strain at Maximum (Extension %)	Modulus (Automatic Young´s)
1	4.85922	303.32301	4.32628
2	5.72905	291.97602	8.09187
3	6.41975	345.82901	7.73357
4	5.99818	358.34501	6.83436
5	6.97875	325.90704	9.35186
6	7.36842	354.58703	8.32294
7	6.26461	295.13199	9.2567
8	7.66913	362.92801	8.73485
9	4.93031	319.59002	5.99704
Mean	6.24638	328.624127	7.62771889
SD	0.98966114	27.8929175	1.64886268

Table 16: Tensile Strength Tests Maximum Values of Commercial PCL

CHAPTER IV

CONCLUSIONS

The Ring-Opening Polymerization of ϵ-caprolactone under microwave irradiation was successfully performed using $Sn(Oct)_2$ as catalyst. PCL polymers with molecular weights as high as 62900 g/mol were produced. Also, PCL displayed high thermal stability and a high degree of crystallinity. The influence of reaction time, reaction temperature and monomer to catalyst ratio on the molecular weight of the polymer was examined and key parameters were successfully established. High molecular weight PCL without any signal of oxidation was obtained at 150°C for 3 hours using a 1000:1 monomer to catalyst ratio.

The high molecular weight PCL was further treated, leading to the formation of fibers via electrospinning. The PCL fibers formed showed excellent mechanical properties, such as a 50% extension rate, tensile strains over 10 MPa and modulus over 50 MPa. Considering all these characteristics, it can be concluded that the PCL produced using a microwave reactor is a promising candidate for biomedical applications.

On the other hand, mixed results were obtained when the polymerization of ϵ-CL was initiated by an alcohol in the present of $Sn(Oct)_2$ as catalyst. First of all, the PCL polymers obtained using glycerol, diethylene glycol and polyethylene glycol as initiators have a low molecular weight based on viscosity analysis. In order to continue with the investigation and explore the different parameters that could have some influence in the molecular weight of the polymer, DEG was stated as the best initiator.

However, it was difficult to set optimum conditions for this polymerization. Any pattern was recognized when reaction time, reaction temperature and monomer to initiator to catalyst ratio were tested. Indeed, problems with reproducibility were encountered. The PCL produced using DEG as initiator at 150°C for 3 hours with a 1000:25:1 monomer to initiator to catalyst was the best polymeric material having in consideration all the circumstances mentioned before. No further studies are considered for the PCL produced using an alcohol initiator.

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BIOGRAPHICAL SKETCH

Nancy Obregon was born in McAllen, Texas on February 9, 1992. She grew up in Reynosa, Tamaulipas, where she had most of her academic formation. She graduated from Jose de Escandon High School in Reynosa on 2010, and continued her education at the University of Texas Pan American (UTPA). She started working with Dr. Macossay on various joint projects that included the use of centrifugal spinning to produce PCL fibers. This research was published as an article in a scientific journal. On May 2015, she received her Bachelor´s Degree in Chemistry from UTPA. That same year, Nancy returned to the now University of Texas Rio Grande Valley (UTRGV) to obtain her Master´s Degree in Chemistry. Nancy worked as a Graduate Teaching Assistant for the organic chemistry laboratories during the completion of her Master´s Degree. She obtained her Master´s Degree in Chemistry from UTRGV on December 2017.

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