Synthesis of Polylactide with Varying Molecular Weight and Aliphatic Content:

Effect on Moisture Sorption

A Thesis

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Dedications

To my family
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Abstract

Synthesis of Polylactide with Varying Molecular Weight and Aliphatic Content: Effect on Moisture Sorption
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Advisor: Dr. Richard A. Cairncross
Dr. Giuseppe R. Palmese

Polylactide (PLA) is a bio-based, biodegradable polymer which is derived from lactic acid and has numerous potential applications, some of which are limited by its moisture barrier and thermal properties. Prior studies have been inconsistent about how moisture sorption in PLA varies with crystallinity and molecular weight.

This research is a systematic study of how moisture sorption in PLA depends on molecular weight and aliphatic content via end group modification. PLA with varying aliphatic content is achieved by initiating ring opening polymerization of L-lactide with different long chain aliphatic alcohols. Molecular weight was controlled by varying the ratio of L-lactide monomer to alcohol (C16 Palmityl, C10 Decyl, C4 Butyl) initiator and triethylaluminum was used as a catalyst for precise control over molecular weight.

PLA with different molecular weights and with varying end groups were synthesized and characterized by GPC, DSC, and NMR. Moisture sorption in PLA was measured with a quartz crystal microbalance (QCM). QCM experiments revealed
that both molecular weight and aliphatic content contribute to sorption properties of PLA.
1 Introduction

1.1 Motivation

Most common polymeric materials are produced from non-renewable fossil resources. Waste of polymeric material from incineration contributes to atmospheric carbon dioxide and the United States Environmental Protection Agency estimates that nearly 25% of the municipal landfill space is occupied by plastics. This concern is even more severe in Europe and Japan where landfill space is less available than in the United States. Many widely used plastic materials like polystyrene and poly(vinyl chloride) are made from toxic monomers. There is need to use eco-friendly methods in producing renewable commodity plastics that do not include harmful compounds in their manufacture.

Polylactide or polylactic acid (PLA) has numerous advantages over other polymers such as it is produced from renewable resources, it consumes quantities of carbon dioxide during production, it is recyclable and compostable, and its physical and mechanical properties can be altered though the manipulation of PLA architecture. Studies have shown that it is economically feasible to use PLA as a packaging material. Medical studies have shown that the amount of lactic acid that transfers from packaging material to food is lower than the level of lactic acid used in common food ingredients.\[1\]
1.2 Bio-Based and Biodegradable Polymers

*Bio-based* and *biodegradable* are terms that describe independent characteristics of polymers. Degradable plastics as defined by the American Society for Testing of Materials (ASTM) and the International Standards Organization (ISO) are those which can go through a significant change in the chemical structure under specific environmental conditions.[2] Biodegradable plastics go through the process of degradation with the help of naturally occurring microorganisms such as bacteria, fungi, and algae.

Because polylactide is a bio-based and biodegradable polymer it has numerous advantages over traditional polymers, such as: less waste, lower toxicity, reduction in greenhouse gases, reduction in fossil fuel consumption, and a secure supply chain. However, there still are certain features which limit the commercialization of PLA: thermal instability, moisture permeation, high cost, processing conditions and inefficient technology. Some frequently used bio-based polymers are given in Table 1.1.

Plant based biodegradable polymers start their lifecycle as renewable resources, generally in the form of starch and cellulose. The main purpose of these polymers is to convert them to end products which can be used by consumers and then they be disposed into bio waste collection and further composted. This whole process will finally leave behind by-products like CO₂ and H₂O.
### Table 1.1: Structure of widespread bio-based polymers

<table>
<thead>
<tr>
<th>Polymer</th>
<th>Structure</th>
</tr>
</thead>
<tbody>
<tr>
<td>Polyglycolide (PGA)</td>
<td><img src="image" alt="PGA structure" /></td>
</tr>
<tr>
<td>L-Polylactide (PLA)</td>
<td><img src="image" alt="PLA structure" /></td>
</tr>
<tr>
<td>Poly(hydroxybutyrate) (PHB)</td>
<td><img src="image" alt="PHB structure" /></td>
</tr>
<tr>
<td>Poly(ethylene glycol) (PEG)</td>
<td><img src="image" alt="PEG structure" /></td>
</tr>
</tbody>
</table>

#### 1.3 Introduction to PLA

Polylactide (PLA) is a bio-based, biodegradable polymer which can be produced from renewable sources such as corn and sugarcane and has found numerous applications in the medical and pharmaceutical fields. Some large scale
manufacturers are beginning to favor PLA because it is renewable, conserves energy, and degrades easily. Figure 1.1 shows a closed life cycle of the PLA.[3,4]

The properties of PLA, such as melting point, crystallinity, and mechanical strength are affected by the polymer architecture and its molecular weight. PLA has glass transition temperature \((T_g)\) in the range of 50 to 80 °C while the melting temperature \((T_m)\) ranges from 130 to 180 °C. Copolymerization of lactide with other monomers like glycolide or caprolactone can significantly enhance the properties and broaden the use of polylactide.[5-7]

![Figure 1.1: PLA cycle showing its renewability](image)
1.3.1 Advantages / Disadvantages of PLA

PLA has numerous advantages over other polymers such as: (1) produced from renewable resources, (2) considerable energy savings, (3) to recycle back to lactic acid which is a non toxic and naturally occurring metabolite through hydrolysis or alcoholysis, (4) uses quantities of carbon dioxide while its manufacture, (5) compostable, (6) improvement of farm economics, (7) decline of landfill volumes, (8) and physical and mechanical properties can be tailored through the modification of its architecture.[1,8]

The commercialization of PLA has been hindered mainly from three factors: (1) high cost in comparison to other polymers because of its immature technology, (2) moisture sorption properties, and (3) need for modified processing conditions. The primary petroleum based polymers which are derived from alkenes or aromatic monomers are non-polar while PLA is fairly polar, thus increasing degradability but also reducing their water resistance property. When the polymer is used in packaging it can have negative impact on the product inside. Also, when the polymer is used to make a water bottle, water seeps out of the bottle thus decreasing the amount of water inside.[9]

1.3.2 Architecture, Characteristics and Properties of PLA

Due to the chiral nature of lactic acid, polylactides exist in distinct forms, which are poly(L-lactide), poly (D-lactide), and poly(DL-lactide) as shown in Figure
1.2. Polymerization of L-lactide (m.p.96°C) gives poly(L-lactide) and polymerization of D-lactide (m.p.96°C) gives poly(D-lactide). Poly(L-lactide) and poly(D-lactide) have identical properties except for stereochemistry. However, racemic (50% D- and 50% L-Lactide) mixture gives poly (DL-lactide), which is an amorphous polymer. In addition, PLA can be produced with varying fractions of L & D lactide.
Figure 1.2: Architecture of PLA based on its chirality

Crystallinity, degree of chain orientation, spherulite size and crystalline thickness are important molecular characteristics of PLA polymers, as well as other polymers. The physical properties of PLA polymers depend on all these molecular characteristics.

Enantiomeric purity of the lactic acid stereocopolymers is an important feature that influences the physical properties of polylactide. The high D- or L-lactide copolymers and homopolymers poly(D-lactide) or poly(L-lactide) have regular structures and form a crystalline phase. PLA of high molecular weight is either amorphous or semicrystalline at room temperature depending on the amounts of L, D and meso-lactide in the polymer and on thermal history. Totally amorphous and semi-crystalline PLA can be produced. PLA resins having more than 93% of L-lactic acid
are semicrystalline while PLA with 50–93% L-lactic acid is strictly amorphous. The imperfections in the crystalline structure are produced by the presence of both meso- and D-lactide which reduce the percent crystallinity.[10,11]

For amorphous PLA, glass transition temperature ($T_g$) is an important parameter as dramatic changes in polymer chain mobility occur at or above $T_g$. For the prediction of PLA behavior in semicrystalline PLA, both the $T_g$ and melting temperature ($T_m$) are important physical parameters. The proportion of different lactides influences glass transition temperature. The commercial applications of amorphous polylactide are based on the temperature at which the PLA will be used. Properties of amorphous PLA depend on how far below $T_g$ the article is used or stored.[10,11]

For semicrystalline polylactide, the melting temperature depends on the stereochemistry and the processing conditions of the polymer. Figure 1.3 shows temperature ranges corresponding to properties of semicrystalline PLA having high molecular weight. The crystalline melting temperature ($T_m$) of PLA is affected by the presence of mesolactide in the structure and results in depression of the melting temperature. PLA made of 100% L-lactide has a melting temperature of 175°C. For semicrystalline PLA, the transition between brittle and ductile fracture is indicated by $T_g$. The maximum obtainable melting point of stereochemically pure polylactide (either L- or D-) is around 180 °C. Addition of D-lactide to the polymer structure causes reduction in the melting temperature between 130°C to 160°C.[10,12]
Figure 1.3: Metastable states of high molecular weight semicrystalline Polylactide, adapted from Witzke [10]

1.4 Previous Studies and Research Objective

Many studies have been done on the thermal, mechanical, physical and barrier properties of PLA. One of the major hindrances in the competitiveness in the marketplace of PLA are its moisture barrier and thermal properties compared to other conventional synthetic polymers. The major application areas of PLA are cups, packaging, bottles, food service applications and many other biomedical applications. Many of the products are commercially available in the market. The importance of moisture transport has become a critical property in the commercialization of water bottles. In Figure 1.4, it is seen that if the PLA water bottle is kept in a warehouse for a period of months, buckling occurs due to loss of water. Figure 1.5 shows the loss of water to be 1 g water/week when the bottle was stored at ambient conditions for several months.
Figure 1.4: Buckling of commercial PLA water bottle due to water loss after storage in warehouse for several months
Figure 1.5: Mass loss for PLA water bottle stored at ambient conditions, the bottle loses about 1 g water/week [Prof. Cairncross Observation]

This research project is part of large collaborative project between the University of Minnesota and Drexel University funded by the USDA. The goal of this project is to synthesize and study modified PLA with improved moisture barrier properties through chemical modification, copolymerization and composites while retaining or enhancing its thermal, mechanical, and optical properties.
Copolymerization is done by collaborators Hillmyer et al. in the chemistry department and degradability of modified PLA samples is studied by Ramaswamy et al. in bio-based products department at the University of Minnesota.

The objective of this thesis is a systematic study of how moisture sorption in PLA depends on molecular weight and aliphatic content via end group modification. PLA with varying aliphatic content was achieved by initiating ring opening polymerization of L-lactide with different long chain aliphatic fatty alcohols. Also, PLA with Benzyl end was synthesized to get better insight about the effect of change in end group on moisture sorption properties. Molecular weight was controlled by varying the ratio of L-lactide monomer to alcohol (C16 Palmityl, C10 Decyl, C4 Butyl, Benzyl) initiator and triethylaluminum was used as a catalyst because of the better control over molecular weight.

PLA with different molecular weight and with varying end groups have been synthesized and characterized by GPC, DSC, and NMR. Moisture sorption in PLA was measured with quartz crystal microbalance (QCM).

1.5 Direct and Indirect Outcomes of Thesis

This thesis investigates the prospective methods of making PLA more hydrophobic and improving its sorption properties. The desired impact of the thesis is to replace petroleum-based plastic with PLA in commodity applications. Modification of PLA is done through chemical and physical means in order to produce a polymer
that is equivalent or better in physical and thermal properties, biodegradability, and moisture sorption properties in comparison to conventional plastics derived from non-renewable sources of energy. Plastic production has been roughly doubling every decade over last forty years, making environmental issues like energy sustainability and carbon dioxide emission troublesome. The advancement and commercialization of PLA with enhanced moisture properties will help in the reduction of fossil fuel consumption. Also, its direct influence would be less waste, reduction in greenhouse gases, and secure supply chain.
2 Background

2.1 Synthesis Methods of PLA

2.1.1 Polycondensation

PLA can be synthesized primarily by two methods: polycondensation of lactic acid and by ring opening polymerization of lactide. Polycondensation leads to the formation of a polymer by the linking of molecules of a monomer and the releasing of water, or a similar simple substance, as shown in Figure 2.1. The major disadvantage of this synthesis technique is that it does not produce high molecular weight PLA due to its complication in removing impurity and water. Other drawbacks of these techniques are the need for large reactor, evaporation, solvent recovery and increased racemization.[67]

\[
\text{CH}_3\text{H}\ddot{\text{O}}\text{CH} - \text{C}^\dddot{\text{H}}\text{OH} + \text{CH}_3\text{H}\ddot{\text{O}}\text{CH} - \text{C}^\dddot{\text{H}}\text{OH} \leftrightarrow \text{CH}_3\text{H}\ddot{\text{O}}\text{CH} - \text{C}^\dddot{\text{H}}\text{OH} \cdots \text{H}_2\text{O}
\]

Figure 2.1: Polycondensation reaction of lactic acid to give polylactic acid

2.1.2 Ring-Opening Polymerization

Ring-opening polymerization (ROP) is an addition polymerization where the terminal end of a polymer acts as a reactive center and cyclic monomers join to form
a larger polymer chain. In case of polylactide, alkoxide of some metal having d-orbitals like aluminum and tin are considered to be good initiators for ring opening polymerization (ROP) of lactide.[13]

In Anionic ROP, the carbonyl group of the lactide goes through nucleophillic reaction followed by cleavage of the acyl-oxygen (O=\text{C–O}) bond. This results in an alkoxide end group which can propagate further as shown in Figure 2.2.[13]

Fig. 2.2 Anionic ROP mechanism for PLA [13]

Primary alkoxides like potassium methoxide can give well-defined polymers with negligible racemization, transesterification, or termination. Jedlinski et al. has shown that less than 5% racemization is seen when starting with pure L-lactide.[14,15]

Different anionic initiators for lactide polymerization had been extensively studied. Kricheldorf et al. has shown that initiators with higher nucleophilicity are required to initiate lactide and weaker bases such as zinc stearate, potassium
phenoxide, and potassium benzoate initiate only at higher temperatures (120°C). Initiations at high temperature are in bulk but accompanied by racemization and other side reaction which are obstacle to propagation.[16-19] Normal butyl lithium, secondary butyl lithium or tertiary butyl lithium or potassium tert-butoxide initiate the polymerization reaction rapidly at low temperature but are deprotonation reagents. So deprotonation of lactide takes place and thus results in racemization, inconsistent polymerization and low molecular weights.[20-22] Lithium initiators have some issues regarding toxicity but utilizing sodium or potassium metal ions results in less toxic and biocompatible polymers.[13]

Stannous octoate or tin(II) bis-2-ethylhexanoic acid is the catalyst which has been researched thoroughly in the past and is generally used for bulk polymerization for lactide because of its solubility in lactide, catalytic activity and racemization of the polymer has low rate. This catalyst promises good reaction rate, conversion of greater than 90%, low levels of racemization, that is less than 1% and providing higher molecular weight polymer.[23,24]

There are different mechanisms suggested in case of stannous octoate and one of them is coordination-insertion as shown in the Figure 2.3. It is now an accepted fact that true initiator is stannous alkoxide which is formed in reaction 1 and 2 shown below. If water coexists with the alcohol/stannous octoate initiating system then it converts tin(II) alkoxide into dormant hydroxyl end capped chains and stannous hydroxides which are less reactive than stannous alkoxide. This decreases
concentration of active propagating species and thus resulting in slower polymerization.[25]

\[
\text{Sn(Oct)}_2 + \text{ROH} \rightleftharpoons \text{Oct-Sn-OR} + \text{Oct-H} \quad (1)
\]

\[
\text{Oct-Sn-OR} + \text{ROH} \rightleftharpoons \text{Sn} (\text{OR})_2 + \text{Oct-H} \quad (2)
\]

Figure 2.3: Generalized coordination–insertion mechanism of lactide to PLA; R = growing polymer chain.[23,24]

Aluminum alkoxides like Al trialkoxide [Al(OR)₃] and dialkyl Al alkoxides are also used widely as initiators. They reduce transesterification reaction and control over ring opening polymerization reaction. Aluminum alkoxide can be prepared by the reaction of alcohol and trialkyl aluminum. As there are varieties of alcohols available, this results in having a large choice for the structure of the alpha end group. In non-polar solvents like benzene or toluene, aluminum alkoxide tend to self-associate. For example Al(O-\text{-}i\text{-}C_3\text{H}_7)_3 in benzene or toluene exists as an equilibrium mixture of trimeric and tetrameric. Also the average number of active alkoxide
available are not three but one.[26,27] In this thesis, diethylaluminum ethoxide and triethylaluminum were used as catalysts for synthesis of PLA. The latter gave better control over molecular weight.

2.2 Copolymers of PLA

Polylactide has been copolymerized with a number of different monomers including other lactone monomers like glycolide and caprolactone. For instance, there are two ways to prepare block copolymer of polycaprolactone and polylactide. First, a sequential addition of the required monomer on the living growing chain end of the first monomer. This method produces diblock copolymers of PCL-PLLA or PCL-PDLA. However it is not possible to synthesize triblock copolymer with this because the polylactide end chain can not initiate the caprolactone. Second, a prepolymer with hydroxyl end group can be developed and then the second monomer can be added in the presence of a catalyst.[28,29]

The properties of PLA can be considerably improved and broadened when lactide is copolymerized with other monomers. Development of both block and random copolymers containing PLA has been done, and PLA block copolymers containing low glass transition temperature segments are notably tougher than the naturally brittle homopolymer. PLA can be toughened by a block co-polymer approach like PLA diblock co-polymers containing polyisoprene (PI) since PI is a
low $T_g$ amorphous polymer that has been used to strengthen conventionally brittle polymers such as polystyrene.[30]

Copolymerization of PLA has been extensively studied but the effect of copolymer content on the moisture sorption properties of polymer has not been explored much. Preparing copolymers to reduce permeation of water through the film is being done by collaborators in the Hillmyer group in the chemistry department at the University of Minnesota. If they prepare a copolymer of polylactide with some polymer that is more hydrophobic like polyethene or polyisoprene then it may result in copolymer with enhanced moisture sorption properties.

**2.3 Composites**

Recently, polymer/layered silicate nanocomposites have made a significant impact because of its impressive enhancement of mechanical, optical, thermal, and physicochemical properties than pure polymer or micro- and macro composites.[31,32] These improvements in properties also include increased strength, decreased gas permeability, and heat resistance. Nanocomposites with organically modified layered silicates have been developed from a number of polymers with varying degrees of polarity and the chain rigidity like polystyrene, poly(ethylene oxide), poly(methacrylates), and many others.[33,36] Nature of the polymer, type, packing density, and the size of the organic modifiers on the silicate surface are the
characteristics of a polymer matrix and the OMLS tell us that if their mixture would be exfoliated of intercalated nanocomposite.[37]

Intercalation of polymer chains in silicate galleries is generally done by two ways. First is by inserting the desired monomer in the silicate galleries followed by polymerization. The second way is by inserting polymer chains in to the silicate galleries from the solution or the melt.[38-41] Vaia et al.[41] were the first to demonstrate the possibility of direct melt intercalation, and this method is the mainstream method for preparing intercalated polymer/layered silicate nanocomposites as it is suitable for industrial use.[42,43] This whole process includes the annealing and mixture of polymer and OMLS above the softening temperature of the polymer. During annealing, the polymer chains from the melted bulk diffuse in to the galleries of silicate galleries. The degree of penetration of these polymer chains in to the OMLS galleries decides the structure of nanocomposites which ranges from intercalated to exfoliate. Intercalated nanocomposites are well ordered with an alternating polymer and silicate layer with a repeating distance of few nanometers. While disordered structures which is a result of extensive polymer penetration are exfoliated nanocomposites.[44,45]

Preparation of polylactide with layered silicates nanocomposites has been successfully done by melt extrusion of organically modified montmorillonite and polylactide.[46,56] These nanocomposites have shown remarkable improvement in properties of the material than PLA matrices without clay.
3 Experimental Procedures: Synthesis of PLA

3.1 Introduction

This section covers experimental procedures used during the synthesis of PLA. Section 3.2 discusses the materials used, the synthesis of PLA, the procedure to recrystallize L-lactide, and the glove box. Sections 3.3 and 3.4 discuss the various characterization instruments for polymer and its reaction mechanism respectively.

3.2 Experiment

3.2.1 Overview of Synthesis Technique

The basic steps involved in the synthesis of PLA were as follows:

- Recrystallized L-lactide with ethyl acetate.
- Brought moisture level in the glove box to less than 20 PPM.
- Took L-lactide, catalyst, initiator, solvent, stirrer, Teflon stopper inside glove box.
- Measured quantities required for the polymerization reaction.
- Sealed the reaction vessel and took it out of the glove box.
- Placed the reaction vessel in 70°C oil bath for 40 hours.
- After 40 hours, dissolved the content of reaction vessel in chloroform.
- Precipitated PLA in methanol followed by vacuum filtration.
- Dried PLA at 100°C overnight under reduced pressure.
- Obtained dry PLA.
3.2.2 Recrystallization of L-lactide

Ethyl acetate (450-500ml) was taken in a 500 ml three neck round bottom flask and heated to boiling by raising the temperature of the oil bath to 77°C (boiling point of ethyl acetate). L-lactide (100gm) was taken in a 500ml beaker with a magnetic stirrer. When ethyl acetate began to reflux, it was added slowly and carefully with the help of pipette to the monomer beaker with a stirrer and on a hot plate (around 70°C). The purpose of this was to dissolve L-lactide in the minimum amount of solvent. Around 450 ml ethyl acetate was used to fully dissolve L-lactide. The dissolved monomer was removed from heat and allowed to cool at ambient temperature. The equilibrated monomer solution was placed in to the refrigerator (0°C) for one hour. Subsequently, it was taken out and the resulting crystals in the beaker were scrapped with a spatula into a filter funnel and vacuum filtered. The lactide monomer crystals were dried overnight in the vacuum oven. \(^1\)H NMR analysis was done on recrystallized L-lactide to confirm the absence of a water and ethyl acetate.

3.2.3 Glove Box

The glove box HE-493 (Vacuum/Atmosphere DRI-LAB) as shown in Figure 3.1 provided a working area of inert atmosphere nearly free of moisture. The materials like triethylaluminum (pyrophoric), initiators, and L-lactide used in our synthesis reaction were handled inside the glove box. Nitrogen gas was used as the
principal inert gas. Helium, argon, or any combination of these gases could also be used. There was HE-493 DRI TRAIN (purifier) attached to it where nitrogen gas was continuously cycled through a purifier which removed moisture from any source, such as: diffusion through the rubber gloves in the glove box, insertion of contaminated parts into the glove box, and use of makeup gas which is not completely free of moisture. The PC-1 Pedatrol was used for pressure control of a glove box. Because a Dri-Lab is a hermetically sealed system, slight changes in pressure, caused by volume or temperature changes, will readily affect the gloves by forcing them out or drawing them in. Also, there was a moisture analyzer which kept track of moisture content inside the glove box.

Some synthesis experiments were done when the moisture level inside the glove box was greater than 700 PPM. The molecular weight of those samples came out to be higher than expected (~260K vs. 85K anticipated and ~240 vs. 50K anticipated) and polydispersity was greater than 2. Reasons of high molecular weight may be due to exposure of the initiator (diethylaluminum ethoxide) to moisture and thus destroying some of the initiator in the beginning. Moisture was detrimental to our synthesis reactions.

The overall moisture level during operation of the glove box was brought down to less than 20 PPM from 2200 PPM. It took six months for the moisture level to be achieved and maintained by following methods: (1) Purged the glove box numerous times with dry nitrogen; (2) Regenerated purifier (HE-493 DRI TRAIN)
with a mixture of 3.5% H\textsubscript{2} and 96.5% N\textsubscript{2} gas several times to get rid of moisture absorbed by its molecular sieves; and (3) Continuously recycled nitrogen gas through a purifier ((HE-493 DRI TRAIN)) which removed moisture from any source of glove box (HE-493 DRI-LAB).

![Figure 3.1: Setup of the glove box](image)

**3.2.4 Synthesis of PLA**

Inside the glove box (moisture level < 20 PPM), the following things were put inside the reaction vessel: recrystallized lactide, triethylaluminum in toluene (1.9 M), anhydrous toluene (99.8%), stirrer, and desired initiator. Then the flask was sealed
with a Teflon stopper under nitrogen atmosphere which prevented the whole reaction from being exposed to moisture. Further, the reaction vessel was taken out from the glove box and kept in an oil bath at 70°C for 40 hours. Subsequently, the viscous solution was removed from the oil bath and dissolved in chloroform. Then, the polymer solution was precipitated in cold methanol. The resultant white spongy precipitate was vacuum-filtered and dried in the oven at 100°C overnight under reduced pressure (about 0.5mm Hg). Figure 3.2 shows the schematic of synthesis of PLA.
Figure 3.2: Schematic of synthesis of PLA

Recrystallized L-lactide +
Toluene + Initiator +
Catalyst + Reaction Vessel
Teflon Stopper + Stirrer

Taken Inside Glove Box

Reaction Vessel Sealed

Glove Box

After 40 hours
Equilibrate at Room Temperature

70°C + 250 RPM (Stirring)

Reaction Vessel Taken Out

Spent CHCl₃ & MeOH with catalyst and unreacted monomer

Dissolved in Chloroform

Precipitated in Methanol

Vacuum Filtered

PLA Dried in Vacuum Oven

After Overnight

PLA Obtained
3.2.5 Reaction Mechanism

Reaction mechanism as shown in Figure 3.3 was followed by all the initiators taken in our study. One end group of PLA changed based on the initiators use. For example, benzyl alcohol gave benzyl end while palmityl alcohol resulted in palmityl end.

Figure 3.3: Reaction mechanism of synthesization of PLA with palmityl alcohol
3.3 Materials

All chemicals were bought from Sigma-Aldrich. (3S)-cis-3,6-Dimethyl-1,4-dioxane-2,5-dione or L-lactide (98%) was our monomer which was purified by recrystallization from anhydrous ethyl acetate (99.8%). Palmityl alcohol, decyl alcohol, butyl alcohol (anhydrous, 99.8%), benzyl alcohol (anhydrous, 99.8%) and water were used as initiators. Triethylaluminum in toluene (1.9M) was used as a catalyst because of the better control over molecular weight. Anhydrous toluene (99.8%) was used as a solvent. All the monomers, initiators (except water), solvents and catalysts were stored under a dry nitrogen atmosphere in a glove box. Chloroform and methanol were used to finally precipitate the polymer out. Figure 3.4 shows the chemical structure of these materials.

Palmityl Alcohol

Decyl Alcohol
3.4 Characterization Techniques

3.4.1 Gel Permeation Chromatography (GPC)

GPC was utilized to find out the molecular weight and molecular weight distribution. A Waters® 515 GPC was used with two 30 cm-long, 7.5 mm-diameter, 5 \( \mu \)m styrene-divinyl benzene columns in series (PL gel, Polymer Laboratories, Amherst MA; 50 Å pore-size and mixed-C as the first and second columns respectively). The columns were equilibrated and run at 30°C using THF as the elution solvent at a flow rate of 1 ml/minute. A two-channel UV detector and a refractive index detector were used to analyze data based on polystyrene standards. In general 4 to 6 mg samples were used in 2 ml of THF for complete dissolution.
3.4.2 Differential Scanning Calorimeter (DSC)

The glass transition temperature, $T_g$, and the melting temperature, $T_m$, of the polymers synthesized was obtained by differential scanning calorimetry (DSC, TA Instruments Q2000) based on the second heating scan of 5°C/min. Samples ranged in weight from 5 to 12 mg and were placed in sealed aluminum pans; at least 3 scans per samples were taken.

3.4.3 Hydrogen Nuclear Magnetic Resonance ($^1$H NMR)

Varian 500 MHz $^1$H NMR in chemistry department (Drexel University) was used by the help of Ms. Radisic Dunja to confirm the structure of polymer prepared. Solvent used was d-chloroform and temperature 25°C. The number of scans taken was between 8 to 64 with a recycle delay of five seconds.
4 Review of Moisture Permeation

4.1 Diffusion Models

Fickian diffusion is the simplest form of transport of sorbate into substrate where concentration gradient is the driving force for the transport phenomena. Fick’s First Law states that:

\[ J_{s,x} = -D \frac{\partial C_s}{\partial x} \]  \hspace{1cm} (4.1)

Where, diffusion flux \( J_{s,x} \) whose unit is mole time\(^{-1}\) area\(^{-1}\) is directly proportional to the concentration gradient of the substance in the diffusing medium. The proportionality constant is the mutual diffusion coefficient of the substance and the medium. The variation of diffusion coefficient is due to several factors, particularly through the plasticization of the polymer chains due to effect of moisture sorption.[47]

Fick’s law does not always give exact description of the diffusion behavior within polymers. One factor that can cause such an inconsistency is the relaxation behavior of the polymer chains parallel with the diffusion. Several academicians argue that deviation from Fickian behavior must be considered for systems where polymer relaxation happens at a much slower pace than the diffusion of the penetrant. Also, if the polymer chains are inflexible, like in the case where temperature is lower than glass transition temperature of polymers, correction factor must be taken in to
account to study systems effectively for the obstruction that the chains cause to the solute.[48] Vrentas proposed an another decisive factor for the applicability of Fick’s laws, bringing in the idea of a diffusion Deborah number to relate the characteristic times of relaxation of polymer chains and diffusion to each other. The material can be estimated as an elastic solid at large values of the diffusion Deborah number, where polymer relaxation is much slower than the rate of diffusion, and a Fickian approximation give reasonable precision. Similarly, for low values of the diffusion Deborah number, the material behaves as a viscous liquid. Based on this view, non-Fickian diffusion exists between these two extreme conditions, where neither route can be assumed to be insignificant with respect to the other.[49]

Deviation from Fick’s law in a system can be articulated in a system’s diffusion kinetics in various ways. In Fickian diffusion, the mass uptake from the bulk vapor phase to the surface of the solid substrate is at the start proportional to the square root of time elapsed, eventually equilibrating to some value of mass uptake. A few systems have shown two different time regimes of sorption, where the graph of mass vs. the square root of time does not come to some constant equilibrium or saturation value but continue to extend through a non-Fickian region, until it reaches a next saturation level. Berens et.al. theorized that mass uptake in the sorption pattern depends on two factors, first is Fickian diffusion and second is due to polymer relaxation over time which increases free volume, thus allowing extra moisture to penetrate through the polymer past its original saturation value.[50] A sorption
system in which the mass vs. square root of time curve gives sigmoidal shape was observed by Long and Richman, where mass uptake rate reaches to a maximum value before leveling off to some saturation value. De Wilde et. al. recognized that the sigmoidal shape can also be pursued by a second non-Fickian stage originated from polymer relaxation similar to simple Fickian sorption. The sigmoidal shape can be explained by a variable surface concentration model.[51] Case II sorption is an additional class of sorption which was observed by Crank et.al., Petropoulos et.al. and others.[52,53] This sorption pattern shows a Fickian induction period followed by linear kinetics due to swelling induced by a sharp diffusion front of constant velocity. Westing explained that the induction period is because of the initial entry of water molecules inside the pre-existing pores which do not perturb the polymer structure. Here, although these pores are filled up, the interaction among the water molecule and the polymer chains causes the material to swell and hence changes its rate of mass uptake.[54]

4.2 Techniques of Determining Mass Uptake

The moisture sorption in-to polymer films has been done various times in different types of studies. There are many ways to record the amount of water transferred from the bulk atmosphere in-to the polymer. The majority of these methods include gravimetric means in determining the advancement of this process. One of the techniques is dynamic vapor sorption (DVS) analysis. In this technique,
working with very small sizes combined together with a dynamic flow of required vapor significantly reduces time to measure moisture sorption isotherms from weeks or months to hours or days. Another set of method utilizes relationship connecting frequency change of an oscillator and its mass load like quartz crystal microbalance (QCM). Moisture sorption in the polymer causes changes in the interaction between the atoms within polymer that can be calculated through a multiple ways of spectroscopic ways including FTIR, NIR, NMR.[55-58]

4.3 Moisture Transport in PLA

The initial study on the permeability of water in PLA was done by Siprsky et al. in the late 1990s. To study this, polymer films were molded into bags and they were filled with molecular sieves and then sealed. As a result, the gravimetric measurement of the mass raised would give values for the permeability. The series of individual films were used to determine the solubility of water in to the polymer, and the pairs of values were compared to generate a diffusion coefficient. For systems at lower temperatures, the solubility of water was larger in polymers, since the partial pressure of water in the atmosphere is a strongly increasing function with temperature than the equilibrium water uptake. While crystallinity was expected to give less mass uptake of water in the polymer because of the organized polymer chains hindering the penetration of water, nothing happened as predicted. This indicated the presence of clustering of water in the film which delivers water-polymer interaction trivial
relative to cohesive water interaction. Alternatively, diffusion coefficients were seen to be powerfully increasing functions with respect to temperature.[48]

Sharp et al. compared the water uptake of poly(DL-lactide) and a 50:50 copolymer of PLA with glycolic acid by means of QCM, relative humidity was controlled within the sample chamber by using saturated salt solution. It was revealed that the solubility of water in a homopolymer is considerably higher than the copolymer, and that, with an increase in average molecular weight, there is a slightly higher sorption in the polymer. One probable justification for this result is that a PLA with a higher molecular weight has a lower proportion of hydrophilic end group to hydrophobic chain units. Nevertheless, this justification is contradicted by Cairncross’ finding that change in the end groups of the polymer does not have an effect on the sorption properties. Sharp also witnessed that increase in vapor activity causes an enhancement in the initial rate of sorption, but on the other hand, also causes an increase in the time desired to reach equilibrium. This is interesting in terms of DSC studies which showed a decrease in glass transition temperature of the polymer film with an increase in the moisture sorption due to plasticization, which should increase the rate of diffusion through the film, thus reducing the decrease in the sorption rate over time. While, kinetic measurements demonstrated major negative deviations from the Fickian behavior, representing that rate limiting step of the process is the swelling kinetics, and that the rate of diffusion is nominal.[59]
Yoon compared solubility of water and diffusion coefficient in PLA to their values in various other polymers. While in the other polymers, crystallinity had a major impact on the sorption and diffusion properties, no such relationship was found in PLA, which supported Siparsky’s findings. Interestingly, polyhydroxybutyrate (PHB), which is more hydrophobic than PLA, showed a crystallinity effect, thus questioning the explanation of PLA and its non-effect of crystallinity through water cluster mode of transport through the film.
5 Experimental Procedures: Moisture Sorption of PLA

5.1 Introduction

This chapter includes the experimental procedure adopted during the moisture sorption study of the PLA synthesized. Section 5.2 contains sample preparation methods, section 5.3 incorporates discussion of film thickness and mass measurements, and sections 5.4 and 5.5 comprise of instrument setup and experimental setup respectively.

5.2 Sample Preparation

5.2.1 Sample Solution

Sample solutions were prepared by dissolving the synthesized PLA in chloroform. Here, chloroform is used as a solvent because the polymer is soluble in it. The solution was heated in a sealed vial at low temperature (~ 40°C) and stirred overnight to speed up the dissolution. The caps of the solution’s vials were tightly sealed with parafilm to prevent any evaporation of chloroform. Avoiding solvent evaporation is important because loss of any solvent will change the concentration of the solution. Once the prepared solutions are completely clear and uniform, they can be further coated on to the quartz crystals.
5.2.2 Quartz Crystal

The usual preparation for quartz crystals used for QCM applications is AT-cut, where the crystals are cut into slices at a 35°10’ angle from the vertical axis and of few hundred microns thickness. The benefit of this type of geometry is that it gives steady oscillation. The crystal goes through thickness shear mode (TSM) oscillation, which generates motion lateral to the surface with lateral amplitude on the order of 1-2 nm.

Earlier, when the QCM was initially developed, natural quartz was harvested, chosen for its quality and finally cut in the lab. But, today most of the crystals are grown using seed crystals in the lab. The seed crystals act as an anchoring point for the growth of crystal; promoting growth in two directions and restraining growth in another. The crystals, AT or SC used in majority applications run in the thickness shear mode at a frequency in the 1-30 MHz range.

The resonance frequency of acoustic resonators depends on pressure, temperature, and bending stress. Temperature frequency coupling can be reduced by using special crystal cuts. A commonly used temperature-compensated cut of quartz is the AT-cut. These types of crystal are singularly rotated Y-axis cuts where the top and the bottom half of the crystal move in reverse directions during oscillation. The AT-cut crystal is easily manufactured. But, it has limitations at high and low temperature because it is easily disturbed by internal stresses due to temperature gradients in these temperature extremes in comparison to room temperature. These
internal stress points create unwanted frequency shifts in crystal, thus decreasing its precision. Stress-compensated (SC) crystals minimize the frequency changes due to temperature gradient because they have a doubly-rotated cut (quartz crystals cut on an angle relative to two of the three crystallographic axes). However, they have more difficult manufacturing process and thus they are more expensive and are not extensively commercially available.\[60\]

In this study mass detectors used were 5MHz, AT-cut quartz crystal microbalances, having thickness of 0.33 mm, and diameter of 2.45 cm. The electrodes on both sides of the crystal consisted of a 15 nm layer of chromium, upon which a gold electrode of 160 nm thickness was vacuum deposited. The electrode on the top, which is 1.29 cm in diameter, serves as an active surface of the QCM, while the smaller electrode of 0.66 cm diameter at the bottom completes the electric circuit.

**5.2.3 Crystal Coating**

The major decisive factors of a good coating are: completely dry, homogeneous, and of uniform thickness throughout the crystal surface. Once the sample solution is prepared, the quartz crystals are cleaned to get rid of any deposit from prior experiments. It is important to know the history of the crystal to clean the crystal. It is often adequate to dip the crystal for 4-5 minutes in a solvent which is known to dissolve the earlier-coated polymer. If normal solvents are unsuccessful then a piranha solution can be used, which is 1:3 volume ratios of hydrogen peroxide
and sulfuric acid. It is used for cleaning organic residues off substrates, as this mixture is a strong oxidizer that removes most organic matter, and it hydroxylates most surfaces making them extremely hydrophilic.[12] Care must be taken while using piranha solution, because it is explosive and mixing the solution is exothermic. Once the crystals are clean and dry, it is weighed by gravimetric balance and their resonant frequency is measured with the help of quartz crystal microbalance probe.

If the surface of the film is non-uniform then Sauerbrey equation which relates change in mass and change in frequency as a linear function will not hold true because of effects related to the pattern of the polymer which is on the electrode.[62] There are two common methods for creating uniform polymer films on QCM crystals: spin coating and drop coating. Drop coating is the easiest method: a sample of coating solution is applied to the quartz crystal by micropipette, it spreads by gravity and the solvent is allowed to evaporate. Drop coating often leads to unacceptable coating due to the non-uniformity by the side of edges.

For samples in this thesis research, crystals were coated through spin coating. In spin coating, an excess amount of solution is placed on the top of the crystal, which is then rotated at high speed so as to spread the solution by centrifugal force. As the spinner rotates, the solvent spreads towards the edge of the crystal and excess solution falls of the substrate with the drying of the solution on top of the crystal occurring simultaneously. The outcome is a solid film which is not completely dry. The thickness of the film depends on the viscosity of the solution used and viscosity
depends on the polymer taken and its concentration in preparing the solution. In some situations, the films produced from spin coating are not as transparent as expected, and they come out to be translucent even when the liquid solution used was clear. The cause of this is considered due to formation of small bubbles. It is supposed that condensation of water vapor on the surface of the film from the atmosphere is the result of these bubbles. The problem of this translucency can be avoided by either spin coating the crystal in dry atmosphere or raising the temperature of the solution before applying it on the crystal.

5.2.4 Crystal Drying

When the spin coating of the samples is done, the next step is to completely remove the solvent to get a fully-dried polymer film. Residual solvent in the film can affect diffusion and sorption properties of the water on the film. Furthermore, traces of any solvent left will lead to the inconsistency of sorption results of polymer due to evaporation of solvent, thus producing mass changes over the period of experimental runs. Air drying of the polymer films can be done but it can be time consuming and complete evaporation of the residual solvent is not assured. In our case, drying in an oven is done as it is more efficient method.
5.2.5 Summary for Successful Coating

In this thesis, conditions for successful coating were as follows:

- Prepared 250 µg/µl concentration solution (750 mg of PLA in 3 ml of Chloroform).
- Stirred solution in sealed vial at 40°C for 12 hours.
- Cleaned QCM crystal & mounted on spin coater.
- Deposited ~ 1 ml of solution on crystal.
- Spinned at 3000 rpm for 60 seconds.
- Dried in ambient condition for one hour and then placed inside 70°C oven for 12 hours.

5.3 Film Thickness and Mass Measurement

Once the polymer film of the crystal was dried, the mass and thickness were measured with the quartz crystal microbalance probe. Resonant frequency by a QCM probe and weight by gravimetric balance of the bare and coated crystal were noted. By taking the difference of coated crystal mass and bare crystal mass, the gravimetric mass of the film was calculated. Though, for calculating the mass of film, the resonant frequency of the bare crystal was subtracted from the coated crystal. The resulting change in frequency gave mass of the film by the known Sauerbrey equation (5.2) which is relationship of change in frequency and mass. This method for calculating mass of film was preferred over gravimetric method. Since, the mass of
the film directly over the electrodes is more important, as sorption only in this region has an effect on the resonant oscillation frequency.

Once the mass of the film was known, the thickness of the film was determined by the relation:

$$\frac{m}{A} \rho = \ell$$

(5.1)

Here, m is mass of the polymer film calculated through the Sauerbrey equation. A is the area of crystal, \( \rho \) is the density of polymer and \( \ell \) is the thickness of the polymer film. The only unknown variable is \( \ell \), thus we can determine the thickness of the film. In perfect coating the mass calculated through the Sauerbrey equation should be equivalent to the calculated gravimetric mass of the polymer. If the mass calculated through the Sauerbrey equation is less than the gravimetric mass. Then, it may be due to the enhanced thickness around the border of the crystal which will decrease the mass density of the polymer over the electrode in comparison to the total crystal.

5.4 Instruments Used

5.4.1 Spin Coater

A SCS1G3P-12 (Cookson Electronics Equipment) spin coater was used for coating the polymer film. It is a method used to apply uniform thin films to quartz crystal. Coating was done at 3000 rpm for 60 seconds. Here, excess amount of
solution is placed on the top of the crystal, which is then rotated at high speed so as to spread the solution by centrifugal force.

5.4.2 QCM

The quartz crystal microbalance is a device that measures changes in mass through variations in the oscillation frequency of a quartz crystal from its resonance frequency. So, in our study, it is used to determine the effect of relative humidity on sorption phenomena within polymer films. QCM is a highly mass sensitive measuring device which can determine as low as 1 ng/cm². The piezoelectric effect discovered by Pierre and Jacques Curie in 1880 is the mechanism which is involved in mass sensing in QCM. Here, an applied, alternating electric field induces oscillations inside the crystal. The gold electrodes are vacuum-deposited on the quartz crystal detector. There is a smaller electrode at the bottom whereas the top part has a larger electrode. An alternating electric potential is applied to the two electrodes that causes electrodes to oscillate at a rate which decays while moving outward from the center. The function of the phase lock oscillator is to examine the crystal current using an internal oscillator and adjust its frequency to the point where crystal voltage is in phase with the current. This point is known as resonant frequency, where the crystal current is directly proportional to the crystal’s conductance.[61]
The absorption of mass onto the quartz crystals surface causes the change in mass, which is proportional to change in frequency, $\Delta f$, as stated by Sauerbrey equation [62]:

$$\Delta f = \frac{-2f_0^2 \Delta m}{\sqrt{\rho_q c_q} A}$$  \hspace{1cm} (5.2)

Where $\Delta m$ is the mass change over the piezoelectric active area (A), $f_0$ is the bare crystal’s resonant frequency, $\rho_q$ is the density (2.65 g/cm$^3$) of quartz, and $c_q$ is the elastic constant (2.95 X 10$^{11}$ dyn/cm$^2$) of quartz. After simplifying the above expression, the equation becomes:

$$\frac{\Delta m}{A} = -C\Delta f$$  \hspace{1cm} (5.3)

where C is a constant whose value is 56.6 ng cm$^{-2}$ Hz$^{-1}$ for an AT-cut crystal with resonant frequency 5MHz, this constant depends on the properties and intrinsic properties of the quartz slab. This equation demonstrates that an increase in mass due to liquid sorption causes decline of the frequency of the crystal.
5.5 Experimental Set Up

5.5.1 Schematic of Experiment

A schematic of the experiment used to study the sorption properties by QCM probe is shown in Figure 5.1.

![Schematic of experimental set-up](image)

Figure 5.1: Schematic of experimental set-up

Our setup consisted of a nitrogen gas cylinder, mass flow controllers, valve, humidifier, QCM probe, incubator, and humidity meter. Mass flow controllers were used to vary the ratio of dry and wet stream of nitrogen to get the desired moisture
level. The valve was to bypass the system with mixture of wet + dry stream (Position A) or completely dry stream (Position B). The humidifier transformed dry stream to wet stream of N₂. The temperature of the system was controlled by the incubator based on our requirements. The QCM probe was to detect the mass change of the polymer film due to variation in moisture content by measuring the difference between the registered frequencies. The humidity meter was downstream and revealed the most closely water vapor pressure or relative humidity in the system.

The stream of nitrogen left the cylinder at a pressure of 35 psi and then it was passed through two mass flow controllers with a rate of 10 sccm (standard cubic centimeters per minute) from each. Opening of valve’s position A gave 10 sccm of dry stream + 10 sccm of wet stream and opening of valve’s position B gave 20 sccm of dry stream. The polymer film was dried by opening valve’s position B and measured the frequency when the polymer film was dried and equilibrated (negligible change in relative humidity and frequency with time). Further, we opened the valve’s position A which increased the moisture content or relative humidity of the system. Subsequently, we noted the frequency at some humidity once the system came in equilibrium. The difference in the frequency gave the mass uptake of water by polymer film. The experiment was repeated several times by opening the valve’s position A and B or sorption and desorption respectively to get picture of sorption isotherm. Relative humidity could also be varied by changing the temperature of the incubator or by varying the ratio of wet and dry stream with mass flow controller.
5.5.2 Gas Humidifier

An early design utilized a solvent bubbler for the gas humidification and redesign of it replaced it with Nafion tubing passing through a pool of water as shown in Figure 5.2. The advantage of using the Nafion humidifier over the bubbler is a decrease of the possibility of aspirating liquid water into the gas conduit. In this thesis, 15 cm length of Nafion tubing was used. Nafion was discovered by DuPont and is a sulfonated tetrafluoroethylene copolymer. It is the first of a class of synthetic polymers having ionic properties. The sulfonic acid groups which are spread through the fluorocarbon matrix act as ionic channels which bind to water molecules in a reversible hydration reaction. The water molecules pass through these channels to the interior part of the tubing, where water evaporates and becomes the part of the flowing gas stream. Gas becomes saturated with water vapor as it passes through the tubing at the temperature of the humidifier. Analysis confirmed that configuration of the Nafion tubing is sufficient to fully saturate the gas stream as relative humidity of the existing stream did not reduce with the increase of flow rate.[65,66]
Figure 5.2: Humidifier showing Nafion tube immersed in water
6 Results and Discussion: Synthesis Experiments

6.1 Overview of Synthesis Experiments

PLA was synthesized by ring-opening polymerization of L-lactide with various alcohols and water as initiator. Triethylaluminum was used as a catalyst because of the better control over molecular weight. An experimental overview of experiments is shown in Table 6.1.

Table 6.1 Experimental overview: Synthesis of PLA

<table>
<thead>
<tr>
<th>S.No.</th>
<th>Initiator</th>
<th>Molecular Weight (gm/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P</td>
<td>Palmityl Alcohol</td>
<td>3000, 4000, 6000, 10000, 20000, 21000</td>
</tr>
<tr>
<td>D</td>
<td>Decyl Alcohol</td>
<td>6000, 10000</td>
</tr>
<tr>
<td>B</td>
<td>Butyl Alcohol</td>
<td>4000, 10000</td>
</tr>
<tr>
<td>Φ</td>
<td>Benzyl Alcohol</td>
<td>6000, 10000, 20000</td>
</tr>
<tr>
<td>W</td>
<td>Water</td>
<td>*4000₁, *4000₂, 6000</td>
</tr>
</tbody>
</table>

Molecular weight = Number average molecular weight

* 4000₁ & 4000₂ are the anticipated molecular weight of PLA with water as initiator which were synthesized by different techniques.
A variety of alcohols were used as initiators like Palmityl (C16), Decyl (C10), Butyl (C4) and Benzyl (C6H5) alcohols. One end group of PLA changed based on the initiators used, taking benzyl alcohol and not Palmityl alcohol gives benzyl end instead of Palmityl end. The use of alcohol initiators and Triethylaluminum as catalyst produced PLA with molecular weight as lower as 4000 and having good polydispersity (<1.5) index.

Synthesis of PLA with water as an initiator did not give good results. Here, water was directly added to the monomer as was previously done with other initiators. A reaction was run to prepare PLA with molecular weight 4000\textsubscript{1} and 6000 but the polymer did not precipitate in methanol. This was due to formation of oligomers and a very low molecular weight polymer which were probably formed due to transesterification (exchanging the alkoxy group of an ester compound with another alcohol) reactions. To better control water concentration, toluene was saturated with water and then a known volume of it was added to L-lactide in the reaction vessel so as to give the desired amount of water to initiate the reaction. Synthesis of PLA of molecular weight 4000\textsubscript{2} was done using this technique. But, this method also did not yield any polymer. Probably, a low molecular polymer was formed which remain dissolved in methanol.
6.2 Controlling Molecular Weight & GPC Analysis

Molecular weight was controlled by varying the ratio of L-lactide monomer to Alcohol (C16 Palmityl, C10 Decyl, C4 Butyl, C6H5 Benzyl) as shown in Table 6.2 and the plot denoted by Figure 6.1. Polydispersity (PDI) index is the ratio of weight average molecular weight to the number average molecular weight. DP is the average degree of polymerization of the PLA. GPC analysis of all the PLA samples synthesized is attached in Appendix A.
Table 6.2 GPC analysis of PLA synthesized:

<table>
<thead>
<tr>
<th>S.No</th>
<th>Ant. Wt.</th>
<th>Exp. Wt.</th>
<th>PDI</th>
<th>Theoretical DP</th>
<th>Experimental DP</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3K</td>
<td>1000 ~ 3000</td>
<td>1.26</td>
<td>6.9</td>
<td>20.5</td>
<td></td>
</tr>
<tr>
<td>P4K</td>
<td>3000 ~4000</td>
<td>1.22</td>
<td>20.4</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td>P6K</td>
<td>5000 ~6000</td>
<td>1.20</td>
<td>34.7</td>
<td>40.5</td>
<td></td>
</tr>
<tr>
<td>P10K</td>
<td>10000 ~10000</td>
<td>1.31</td>
<td>69.4</td>
<td>70.8</td>
<td></td>
</tr>
<tr>
<td>P20K</td>
<td>20000 ~20000</td>
<td>1.33</td>
<td>138.7</td>
<td>140.7</td>
<td></td>
</tr>
<tr>
<td>P21K</td>
<td>30000 ~21000</td>
<td>1.36</td>
<td>208.1</td>
<td>147.6</td>
<td></td>
</tr>
<tr>
<td>D6K</td>
<td>6000 ~ 6000</td>
<td>1.20</td>
<td>41.6</td>
<td>42.3</td>
<td></td>
</tr>
<tr>
<td>D10K</td>
<td>10000 ~10000</td>
<td>1.32</td>
<td>69.4</td>
<td>70.5</td>
<td></td>
</tr>
<tr>
<td>B4K</td>
<td>5000 ~ 4000</td>
<td>1.18</td>
<td>34.7</td>
<td>27.3</td>
<td></td>
</tr>
<tr>
<td>B10K</td>
<td>10000 ~10000</td>
<td>1.30</td>
<td>69.4</td>
<td>68.4</td>
<td></td>
</tr>
<tr>
<td>Ф6K</td>
<td>5000 ~6000</td>
<td>1.20</td>
<td>34.7</td>
<td>42.5</td>
<td></td>
</tr>
<tr>
<td>Ф10K</td>
<td>10000 ~10000</td>
<td>1.33</td>
<td>69.4</td>
<td>70.9</td>
<td></td>
</tr>
<tr>
<td>Ф20K</td>
<td>20000 ~20000</td>
<td>1.51</td>
<td>138.8</td>
<td>140.8</td>
<td></td>
</tr>
</tbody>
</table>

Ant. Wt = anticipated or expected molecular weight

(gm/mole, Number average molecular weight)

Exp. Wt = experimental molecular weight

(gm/mole, Number average molecular weight)

Theoretical DP = theoretical average degree of polymerization

Experimental DP = experimental average degree of polymerization

PDI = polydispersity index
Figure: 6.1 Plot of Table 6.2

Theoretical DP =>

Average degree of polymerization = mole ratio (monomer/initiator)
The blue triangle shows theoretical DP in the graph as shown in Figure 6.1 and was calculated assuming that all the alcohol groups participated in L-lactide initiation and all monomer was consumed. The experimental DP coincided well with the theoretical DP. This showed that the above assumption were convincing under the polymerization conditions. This results indicated that alcohols used were true initiators for lactide polymerization and triethylaluminum acted as a catalyst. Furthermore, the low PDI (<1.5) represented minimal transesterification.

6.3 $^1$H NMR Analysis

Palmityl, decyl, butyl, and benzyl end groups were confirmed by Varian 500 MHz $^1$H NMR analysis of the PLA samples. As seen in Figure 6.2, P10K is shown, and the number average molecular weight was calculated to be 10,605 by comparing ‘a’ and ‘c1’ peak’s area, which is close to what was obtained through GPC (10,200). Similarly, comparison of molecular weight of B10K, D10K, and $\Phi$10K samples through $^1$H NMR and GPC was done, given in Table 6.3. $^1$H NMR analysis of PLA with decyl (D), butyl (B), and benzyl (\Phi) ends is given in Appendix B and it showed that molecular weight calculated by $^1$H NMR was comparable to GPC molecular weight.
Table 6.3: Molecular weight by $^1$H NMR analysis:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>GPC MWt. (g/mole)</th>
<th>$^1$H NMR MWt. (g/mole)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P10K</td>
<td>10200</td>
<td>10605</td>
</tr>
<tr>
<td>D10K</td>
<td>10151</td>
<td>9309</td>
</tr>
<tr>
<td>B10K</td>
<td>9853</td>
<td>9055</td>
</tr>
<tr>
<td>Ф10K</td>
<td>10213</td>
<td>9120</td>
</tr>
</tbody>
</table>

GPC MWt. = number average molecular weight (g/mole)

$^1$H NMR MWt. = number average molecular weight (g/mole)
The percentage conversion of monomer to polymer was done by taking out a crude sample (before dissolving reaction content in chloroform) from our reaction vessel after 40 hours of polymerization reaction. $^1$H NMR of the crude sample in d-chloroform gave the amount of lactide converted into polylactide. From the $^1$H NMR we get Figure 6.3 and integration of the peaks tells us that ratio of methine protons of lactide to PLA is 1:6.42 whereas methyl protons is 1:5.54. We can say that conversion of lactide to polylactide for this experiment lies in the range of 84 to 87%
Figure 6.3: $^1$H NMR spectrum of crude sample showing ratio of lactide and Polylactide
6.4 DSC Analysis

Thermal behavior, that is, glass transition temperature ($T_g$) and melting temperature ($T_m$) of the PLA synthesized were analysed with DSC. $T_g$ and $T_m$ of PLA with Palmityl, Decyl, Butyl, and Benzyl end is shown in Table 6.4. It is observed that when molecular weight increases, the $T_g$ and $T_m$ of PLA increases simultaneously. This fits with the existing concept of polymers that when molecular weight increases, chain entanglement increases and therefore $T_g$ & $T_m$ increases.

The results for PLA with same molecular weight but with different end groups show that there is not significant difference between $T_g$ & $T_m$. This is likely due to highest weight fraction of end group is ~7.5%, that is, in PLA with Palmityl end with molecular weight 3,000 and this fraction is not high enough to show the thermal behavior changes with different end groups.

The percentage crystallinity ($X_c$) of the samples was calculated by the following equation[67,68]:

\[
\% X_c = \left( \frac{\Delta H_m}{93} \right) \times 100
\]

(6.1)

where $\Delta H_m$ is the melting enthalpy and 93 (J/g) the melting enthalpy of totally crystallized PLA. $\Delta H_m$ was calculated from the first heating (5°C/min) cycle of DSC.

Percentage crystallinity varied from 44% to 73% as shown in Table 6.4 and increased
with molecular weight except sample P3K. The increase in the crystallinity may be due to the reduction in end group defect, because of the decrease in the percentage volume of end group at higher molecular weight.

Table 6.4: DSC analysis of PLA synthesized:

<table>
<thead>
<tr>
<th>S.No.</th>
<th>$T_g$ ($^\circ$ C)</th>
<th>$T_m$ ($^\circ$ C)</th>
<th>$\Delta H_m$ (J/g)</th>
<th>% $X_c$</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3K</td>
<td>31</td>
<td>132</td>
<td>68.2</td>
<td>~ 73</td>
</tr>
<tr>
<td>P4K</td>
<td>38</td>
<td>147</td>
<td>52.4</td>
<td>~ 56</td>
</tr>
<tr>
<td>P6K</td>
<td>49</td>
<td>153</td>
<td>54.6</td>
<td>~ 59</td>
</tr>
<tr>
<td>P10K</td>
<td>56</td>
<td>164</td>
<td>56.1</td>
<td>~ 60</td>
</tr>
<tr>
<td>P20K</td>
<td>59</td>
<td>166</td>
<td>68.3</td>
<td>~ 73</td>
</tr>
<tr>
<td>D6K</td>
<td>50</td>
<td>155</td>
<td>50.1</td>
<td>~ 54</td>
</tr>
<tr>
<td>D10K</td>
<td>55</td>
<td>164</td>
<td>56.6</td>
<td>~ 61</td>
</tr>
<tr>
<td>B4K</td>
<td>37</td>
<td>144</td>
<td>52.7</td>
<td>~ 57</td>
</tr>
<tr>
<td>B10K</td>
<td>53</td>
<td>162</td>
<td>59.9</td>
<td>~ 64</td>
</tr>
<tr>
<td>Ф6K</td>
<td>48</td>
<td>152</td>
<td>41.0</td>
<td>~ 44</td>
</tr>
<tr>
<td>Ф10K</td>
<td>54</td>
<td>160</td>
<td>45.3</td>
<td>~ 49</td>
</tr>
<tr>
<td>Ф20K</td>
<td>62</td>
<td>168</td>
<td>66.4</td>
<td>~ 71</td>
</tr>
</tbody>
</table>
PLA samples with different degree of polymerization (N) gave different glass transition temperature ($T_g$). In 1950, Fox and Flory founded the dependence of degree of polymerization on glass transition temperature by equation:

$$T_g(N) = T_g(\infty) - C/N$$  \hspace{1cm} (6.1)

Where $T_g(\infty)$ is glass transition temperature for infinity molecular weight and C is a constant.[63]

In Figure 6.4, the glass transition temperature versus reciprocal of degree of polymerization of all the samples is plotted. The glass temperature data was fitted to equation 6.1 by linear regression.

We get, $T_g(\infty) = 338.78 \, ^{\circ}K$ and $C = 741.1$

![Figure 6.4: The glass transition temperature versus reciprocal N](image)
7 Results and Discussion: Sorption Experiments

7.1 Overview of Sorption Experiments

Sorption experiments were run on the synthesized modified PLA samples. Ten different PLA samples were chosen for sorption experiments (listed in Table 7.1). For each sample, three replicas of crystal were prepared and at least three sorption/desorption experiments were performed.

Film thickness of the samples is listed in Table 7.1. Thickness was determined as previously described in section 5.3. Thickness of all the samples varies from 4.5 to 5.3 µm except F20K. Thickness of F20K is ~6.9 µm, which is considerably higher than other samples and may be due to its high molecular weight.

Each polymer film sorption experiment lasted 12 hours and had three sorption/desorption cycles. WVP (water vapor partial pressure) and corresponding frequency was recorded every two hours. Prior experiments measuring water vapor pressure showed that two hours were sufficient for the polymer to equilibrate in the sorption and desorption cycles, as shown in Appendix C. Ambient temperature in all the runs was maintained at 21.9°C in an incubator.
Table 7.1: Samples and thickness of films prepared:

<table>
<thead>
<tr>
<th>Sample</th>
<th>Thickness of Films Prepared (µm)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P4K (Palmityl 4000)</td>
<td>4.5, 4.5, 4.6</td>
</tr>
<tr>
<td>P6K (Palmityl 6000)</td>
<td>4.6, 4.7, 4.9</td>
</tr>
<tr>
<td>P10 (Palmityl 10000)</td>
<td>4.9, 5.1, 5.3</td>
</tr>
<tr>
<td>D6K (Decyl 6000)</td>
<td>4.8, 4.8, 4.9</td>
</tr>
<tr>
<td>D10K (Decyl 10000)</td>
<td>4.7, 4.8, 4.8</td>
</tr>
<tr>
<td>B4K (Butyl 4000)</td>
<td>4.5, 4.6, 4.6</td>
</tr>
<tr>
<td>B10K (Butyl 10000)</td>
<td>4.8, 4.9, 4.9</td>
</tr>
<tr>
<td>Ф6K (Benzyl 6000)</td>
<td>4.9, 4.9, 5.0</td>
</tr>
<tr>
<td>Ф10K (Benzyl 10000)</td>
<td>5.1, 5.2, 5.2</td>
</tr>
<tr>
<td>Ф20K (Benzyl 20000)</td>
<td>6.8, 6.9, 6.9</td>
</tr>
</tbody>
</table>
7.2 Analysis / Discussion

7.2.1 Summary of Sorption Results

Sorption isotherms with multiple points of samples P6K and P10K were measured as shown in Figure 7.1. These isotherms explain that since they are linear, only two points are necessary to capture key behavior. An example of P4K (Palmityl 4000) is shown in Figure 7.2. Y-axis represents ratio of mass of water uptake (absorbed by polymer film) and mass of the film deposited on quartz crystal as determined by sauerbrey equation 5.2. X-axis represents the relative humidity which was controlled by the wet and dry streams of Nitrogen into the QCM probe. Slope 1, 2, and 3 are the slopes obtained by running three different runs (different coated crystal) and each run with three different cycles. So, the Figure has 18 points total. The average slope is 79.3E-06, with error ±2.6E-06 at 95% confidence level. The unit of slope is gH2O/(gPLA*relative humidity). Similar graphs of all the samples are attached in Appendix D.
Figure 7.1: Sorption isotherm of P10K and P6K

Figure 7.2: Sorption isotherm of P4K
A summary of all sorption results is shown in Figure 7.3, where mass uptake by the polymer film is considered to be zero corresponding to the lowest (1.3% or 1.4%) relative humidity possible. Each sorption isotherm is shown by its mean slope.

Figure 7.3: Sorption isotherms of all samples
To better analyze the relative mass uptake by different samples, the slopes of all samples are compared as shown in Figure 7.4. The horizontal axis represents the slope of the sorption isotherms and the vertical axis shows 10 samples taken in our study. The average slope of each samples is listed in the graph and error with 95% confidence level marked. Comparing slopes of sorption isotherms of different samples tells the distinction in mass uptake of water by different samples. The larger slope suggests that amount of water absorbed by that sample is more than the sample with lower slope.

The statistical analysis to determine the differences in the mean slopes of all 10 samples was performed. It was found that all means are different based on the statistical test, one-way analysis of variance (ANOVA). This analysis is a way to test the equality of sample means of two or more data sets at a time.
Figure 7.4: Summary of slope of sorption isotherm result
7.2.2 Comparison of P4K, P6K, P10K

One-way ANOVA statistical analysis showed that the differences in the sample means of P4K, P6K, and P10K was statistically significant at 95% confidence level, shown in Figure 7.5.

![Figure 7.5: Comparison of slopes of sorption isotherms of P4K, P6K, and P10K](image)

As molecular weight decreases, aliphatic content at the end group increases from ~2.3% (P10K) to ~5.7% (P4K) by mass. There is a decrease in mass uptake of water from P10K to P6K but it again increases if the molecular weight is decreased further. Possibly, molecular weight and aliphatic content both contributed towards sorption properties. Where, increase in aliphatic content (hydrophobic end group) of
end group reduced mass uptake of water but simultaneously enhanced water uptake due to decrease in molecular weight.

### 7.2.3 Comparison of P10K, D10K, and B10K; P6K and D6K

Comparing samples with the same molecular weight and varying aliphatic content gave better insight about the affect of end groups on sorption properties. One-way ANOVA statistical test was performed to compare the sample means of the following groups: (P10K, D10K, B10K) and (P6K, D6K). It was found that the differences in the sample means was statistically significant at 95% confidence level, shown in Figure 7.6 and Figure 7.7.

In the Figure 7.4, with an increase in mass percentage of aliphatic content from 0.6% (B10K) to 1.4% (D10K) and then finally to 2.3% (P10K), there was consistent decrease in mass upatake of water (slope is decreasing).
Figure 7.6: Comparison of slopes of sorption isotherms of P10K, D10K, and B10K

The same thing was observed in Figure 7.7 When mass percentage of aliphatic content of the end group was increased from 2.4% (D6K) to 3.8% (P6K), there was decrease in mass uptake of water by the sample. In both the cases, increase in hydrophobic content resulted in better sorption properties of the samples.

Figure 7.7: Comparison of slopes of sorption isotherms of D6K and P6K
7.2.4 Comparison of Aromatic End Group with Aliphatic End Group

At first, samples \( \Phi_{20K}, \Phi_{10K}, \) and \( \Phi_{6K} \) were compared, where \( \Phi_{20K} \) and \( \Phi_{10K} \) were not statistically different, so they could not be compared. Though, \( \Phi_{6K} \) was statistically different than \( \Phi_{20K} \) and \( \Phi_{10K} \) as shown in Figure 7.2. When slopes were compared, mass uptake of water in \( \Phi_{6K} \) was found to be less than \( \Phi_{20K} \) and \( \Phi_{10K} \). More samples were needed to draw any conclusion based on aromatic end content.

Samples \( \Phi_{6K}, \Phi_{6K}, \) and \( \Phi_{6K} \) were compared and the amount of mass uptake of water was highest in \( \Phi_{6K} \). Similarly, \( \Phi_{10K}, \Phi_{10K}, \) and \( \Phi_{10K} \) were compared, again mass uptake of water in \( \Phi_{10K} \) was highest. This comparison showed that the aromatic end content (Benzyl end) had the highest mass uptake of water when compared to any aliphatic end content sample of the same molecular weight.

7.2.5 Analysis of B4K & P4K

Mass uptake of water in B4K was highest among all the samples studied. As shown by Figure 7.4. It had a slope of 120.3 ± 1 (Appendix D). The mass uptake of water was second highest among aliphatic end content end group samples. High mass uptake of water in B4K and P4K could be due to the low molecular weight of the samples. Whereas, mass uptake of water of B4K is higher than P4K. This could be
due to the higher aliphatic end group content of P4K than B4K, which reduces its mass uptake of water.

The glass transition temperatures ($T_g$) of B4K and P4K are $37^\circ$C and $38^\circ$C, respectively, which is close to the temperature at which moisture sorption studies were done ($21.9^\circ$C). The properties of the polymer change near $T_g$ which may result in unusual behavior of the mass uptake of B4K and P4K.
8 Conclusions

The overall goal of this thesis was synthesis of polylactide with varying molecular weight and aliphatic content and its effect on moisture sorption. PLA with varying aliphatic content was achieved by initiating ring-opening polymerization of an L-lactide with different long chain aliphatic fatty ((C16 Palmityl, C10 Decyl, C4 Butyl) alcohols. PLA with Benzyl ends of different molecular weight were also synthesized to compare sorption properties of aliphatic and aromatic end groups. A summary of all the experiments is given in Table 8.1.

Initial synthesis experiments produced PLA of higher molecular weight than expected (~260K vs. 85K anticipated and ~240K vs. 50K anticipated) with a polydispersity index greater than two due to high moisture level inside the glove box (>700 PPM). The moisture level in the glove box changed slowly; after ~6 months the moisture level dropped to 20 PPM and remained steady for the rest of the experiments. Also, the polymerization catalyst was changed to triethylaluminum from diethylaluminum ethoxide because of the better control over molecular weight.

GPC results showed that the experimental DP coincided well with the theoretical DP. These results indicated that alcohols used were true initiators for lactide polymerization and triethylaluminum acted as catalyst. Furthermore, the low PDI (<1.5) showed minimal transesterification. PLA synthesized with palmityl, decyl, butyl, and benzyl end groups were confirmed by $^1$H NMR. The percentage conversion of L-lactide to PLA came out to be $\geq 85\%$ as determined from some crude samples.
during synthesis experiments. DSC analysis showed, when molecular weight increased then \( T_g \) and \( T_m \) of PLA increased simultaneously which fits with the existing concept. The results for PLA with same molecular weight but with different end group showed that there is no significant variation in \( T_g \) and \( T_m \) of the samples. This is likely due to the highest weight fraction of end group was \( \sim 7.5\% \), that is, in PLA with palmityl end with molecular weight 3,000 and this fraction was not high enough to show the thermal behavior changes with different end groups.

Moisture sorption of the samples synthesized indicated that the aliphatic content of the end group contributed towards sorption properties. With the increase in mass percentage of aliphatic content from 0.6\% (B10K) to 1.4\% (D10K) and then finally to 2.3\% (P10K), there was a consistent decrease in mass uptake of water. Similarly, when mass percentage of aliphatic content of the end group was increased from 2.4\% (D6K) to 3.8\% (P6K), there was a decrease in mass uptake of water by the sample. Also, mass uptake of water of B4K (~1.5\% aliphatic content) is higher than P4K (~5.7\% aliphatic content). This study confirmed our hypothesis that with the increase in aliphatic content of the end group there is decrease in the mass uptake of water.

Varying molecular weight of the PLA backbone also affected the sorption characteristics. D6K (2.4\% aliphatic content) and D10K (1.4\% aliphatic content) films did not have statistically different mass uptake of water. According to aliphatic content percent, sorption in D6K should be less but it was not. Similarly, P6K (3.8\%
aliphatic content) and P4K (5.7% aliphatic content) were compared and the mass uptake of water was more in P4K which contradicts aliphatic content hypothesis. So, this indicated that the increase in molecular weight decreased the mass uptake of water.

It can be concluded that molecular weight and aliphatic content both contribute towards sorption properties of the PLA synthesized. Where the decrease in aliphatic content (hydrophobic) of end group caused increase in the mass uptake of water; and increase in molecular led to decrease in mass uptake of water.
Table 8.1 Summary of the experiments (GPC, DSC, QCM):

<table>
<thead>
<tr>
<th>S.No</th>
<th>Experimental Weight (g/mole)</th>
<th>PDI</th>
<th>Aliphatic Content (%)</th>
<th>$T_g$ (°C)</th>
<th>$T_m$ (°C)</th>
<th>%age Crystallinity</th>
<th>Slope Sorption Isotherm (S)</th>
</tr>
</thead>
<tbody>
<tr>
<td>P3K</td>
<td>~3000</td>
<td>1.2</td>
<td>~7.5%</td>
<td>31</td>
<td>132</td>
<td>~73</td>
<td>___</td>
</tr>
<tr>
<td>P4K</td>
<td>~4000</td>
<td>1.2</td>
<td>~5.7%</td>
<td>38</td>
<td>147</td>
<td>~56</td>
<td>79.3 ± 2.6</td>
</tr>
<tr>
<td>P6K</td>
<td>~6000</td>
<td>1.2</td>
<td>~3.8%</td>
<td>49</td>
<td>153</td>
<td>~59</td>
<td>59.0 ± 2.92</td>
</tr>
<tr>
<td>P10</td>
<td>~10000</td>
<td>1.3</td>
<td>~2.3%</td>
<td>56</td>
<td>164</td>
<td>~60</td>
<td>63.7 ± 2.6</td>
</tr>
<tr>
<td>P20</td>
<td>~20000</td>
<td>1.3</td>
<td>~1.1%</td>
<td>59</td>
<td>166</td>
<td>~73</td>
<td>___</td>
</tr>
<tr>
<td>P21</td>
<td>~21000</td>
<td>1.3</td>
<td>~1.1%</td>
<td>59</td>
<td>169</td>
<td>~72</td>
<td>___</td>
</tr>
<tr>
<td>D6K</td>
<td>~6000</td>
<td>1.2</td>
<td>~2.4%</td>
<td>50</td>
<td>155</td>
<td>~54</td>
<td>69.3 ± 0.6</td>
</tr>
<tr>
<td>D10</td>
<td>~10000</td>
<td>1.3</td>
<td>~1.4%</td>
<td>55</td>
<td>164</td>
<td>~61</td>
<td>71.0 ± 1.7</td>
</tr>
<tr>
<td>B4K</td>
<td>~4000</td>
<td>1.1</td>
<td>~1.5%</td>
<td>37</td>
<td>144</td>
<td>~57</td>
<td>120.3 ± 1</td>
</tr>
<tr>
<td>B10</td>
<td>~10000</td>
<td>1.0</td>
<td>~0.6%</td>
<td>53</td>
<td>162</td>
<td>~64</td>
<td>74.3 ± 1</td>
</tr>
<tr>
<td>Ф6K</td>
<td>~6000</td>
<td>1.2</td>
<td>___</td>
<td>48</td>
<td>152</td>
<td>~44</td>
<td>77.7 ± 1</td>
</tr>
<tr>
<td>Ф10</td>
<td>~10000</td>
<td>1.3</td>
<td>___</td>
<td>54</td>
<td>160</td>
<td>~49</td>
<td>81.7 ± 1</td>
</tr>
<tr>
<td>Ф20</td>
<td>~20000</td>
<td>1.5</td>
<td>___</td>
<td>62</td>
<td>168</td>
<td>~71</td>
<td>81.3 ± 2.6</td>
</tr>
</tbody>
</table>

Experimental weight = number average molecular weight (g/mole), PDI = polydispersity index, aliphatic content = mass percentage of aliphatic end group, $T_g$ = glass transition temperature, $T_m$ = melting temperature, %age crystallinity = percentage crystallinity of the samples synthesized, S = slope of sorption isotherm (Higher slope means more sorption of water by the polymer film sample) [gH2O/(gPLA* relative humidity)]
Appendix A: GPC analysis

Figure A.1: Molecular weight distribution of P3K

Figure A.2: Molecular weight distribution of P4K
Figure A.3: Molecular weight distribution of P6K

Figure A.4: Molecular weight distribution of P10K
Figure A.5: Molecular weight distribution of P20K

Figure A.6: Molecular weight distribution of P21K
Figure A.7: Molecular weight distribution of D6K

![Molecular weight distribution of D6K](image)

- $M_n = 6100$
- $M_w = 7319$
- $PDI = 1.20$

Figure A.8: Molecular weight distribution of D10K

![Molecular weight distribution of D10K](image)

- $M_n = 10151$
- $M_w = 13399$
- $PDI = 1.32$
Figure A.9: Molecular weight distribution of B4K

Figure A.10: Molecular weight distribution of B10K
Figure A.11: Molecular weight distribution of Φ6K

Mn = 6121
Mw = 7345
PDI = 1.20

Figure A.12: Molecular weight distribution of Φ10K

Mn = 10213
Mw = 13583
PDI = 1.33
**Figure A.13:** Molecular weight distribution of Φ20K

**Figure A.14:** GPC calibration curve
Appendix B: $^1$H NMR plots

Expected Molecular Weight = 10000

$^1$H NMR Molecular Weight = 9309

(By comparing peak’s area of a & c1)

Figure B.1: $^1$H NMR analysis of D10K
Figure B.2: $^1$H NMR analysis of B10K
Figure B.3: $^1$H NMR analysis of Φ10K
Appendix C: WVP (water vapor partial pressure) Vs time plots

Figure C.1: Sorption cycle B10K, equilibrating in 2 hours

Figure C.2: Desorption cycle of B10K, equilibrating in 2 hours
Figure C.3: Sorption cycle D6K, equilibrating in 2 hours

Figure C.4: Desorption cycle D6K, equilibrating in 2 hours
Figure C.5: Sorption cycle P4K, equilibrating in 2 hours

Figure C.6: Desorption cycle P4K, equilibrating in 2 hours
Appendix D: Graphs of sorption isotherms

Figure D.1: Sorption isotherm of P6K

Figure D.2: Sorption isotherm of P10K
Figure D.3: Sorption isotherm of D6K

Mean Slope = \((69.3 \pm 0.6) \times 10^{-6}\)

Slope 1 = 69E-06
Slope 2 = 69E-06
Slope 3 = 70E-06

Figure D.4: Sorption isotherm of D10K

Mean Slope = \((71 \pm 1.7) \times 10^{-6}\)

Slope 1 = 70E-06
Slope 2 = 72E-06
Slope 3 = 71E-06
Figure D.5: Sorption isotherm of B4K

Figure D.6: Sorption isotherm of B10K
Figure D.7: Sorption isotherm of $\Phi_{6K}$

Figure D.8: Sorption isotherm of $\Phi_{10K}$
Figure D.9: Sorption isotherm of Φ20K
References


[60] A. Ballato, T. J. Lukaszek, and E. P. Eernisse, 26, 163 (1979)