KINETIC STUDIES ON POLYMERIZATION OF POLY(LACTIC ACID) USING SUITABLE CATALYST

Thesis submitted
in fulfillment of the requirement
for the award
of

Doctor of Philosophy

By

PARAMJIT KAUR
(Regd. No. 90601001)

Department of Chemical Engineering
Thapar University, Patiala
(Formerly, known as Thapar Institute of Engineering & Technology)
Patiala-147004, Punjab, India. URL: www.thapar.edu

December, 2011

GURU TEG BAHADHUR SIMRIYE GHAR

NAU NIDH AAVE DHAYE

CERTIFICATE

This is to certify that the thesis entitled **"Kinetic Studies on Polymerization of Poly(Lactic Acid) using Suitable Catalyst"** which is being submitted by Ms. Paramjit Kaur in fulfillment of the degree **DOCTOR OF PHILOSOPHY,** in Chemical Engineering, Thapar University, Patiala is a record of the candidate's own work carried out by her under our supervision and guidance. The matter embodied in this thesis has not been submitted in part or full to any other university or institution for the award of any degree.

Rajeev Mehta

(Dr. Rajeev Mehta)
(Supervisor)
Associate Professor & Head

Department of Chemical Engineering
Thapar University
Patiala -147004

SNUpadhyay

(Dr. S.N. Upadhyay)
(Supervisor)
Professor

Department of Chemical Engg. & Tech.
Institute of Technology
Banaras Hindu University
Varanasi - 221005

PREFACE

This research work was carried out by the author under the guidance of Dr. Rajeev Mehta, Associate Professor & Head, Department of Chemical Engineering, Thapar University, Patiala, Punjab, India and Dr. S.N. Upadhyay, Professor, Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi, India.

Several research papers were published out of this research work. The list of international journals/international conferences in which the research papers find place is given below:

Publications/Communication in International Journals

1. **Paramjit Kaur,** R. Mehta, D. Berek, S.N. Upadhyay, 2011. "Synthesis of Polylactide: Effect of Dispersion of the Initiator", *Journal of Macromolecular Science, Part A: Pure and Applied Chemistry*, A48 (10), 840-845.
2. **Paramjit Kaur,** R. Mehta, S.N. Upadhyay, 2011. "Role of important Parameters in Ring-opening polymerization of Polylactide", *Journal of Polymer Engineering,* 31(2-3), 243–249.
3. **Paramjit Kaur,** R. Mehta, D. Berek, S.N. Upadhyay, 2011. "Comparison in Kinetics Parameters of Ring-Opening Polymerization of poly (lactic acid) using Stannous Octoate with/without Triphenylphosphine as an Initiator", *Journal of Polymer-Plastics Technology and Engineering*, (submitted vide ID LPTE-2011-1358).
4. **Paramjit Kaur,** R. Mehta, D. Berek, S.N. Upadhyay, 2011. "Synthesis of Polylactide under Inert Atmosphere and Vacuum", *Macromolecular Symposia* (accepted).

Presented at International/National Conferences

1. **Paramjit Kaur,** Rajeev Mehta, S.N. Upadhyay, "*Polymers in Medical Applications*", Punjab Science Congress, Patiala, February 7-9, 2008.
2. Rajeev Mehta, **Paramjit Kaur,** S.N. Upadhyay, "*Synthesis of Poly (lactic acid) by Ring-Opening Polymerization*", Polychar 16 – World forum for advanced materials, Lucknow, February 17-21, 2008.
3. **Paramjit Kaur,** Rajeev Mehta, S.N. Upadhyay, "*Role of Biodegradable Polymers for the Environment in Green Chemistry*", National symposium on green chemistry, Thapar University, February 5-6, 2009.
4. **Paramjit Kaur,** Rajeev Mehta, S.N. Upadhyay, "*Role of Important Parameters in Ring-opening polymerization of Polylactide*", Second International Conference on Polymer Processing and Characterization (ICPPC – 2010), Kerala, January 15-17, 2010.
5. **Paramjit Kaur,** Rajeev Mehta, D. Berek, S.N. Upadhyay, "*Dibutyltindimethoxide and Stannous Octoate initiators with Triphenylphosphine for the synthesis of Poly (lactic acid) by ring - opening polymerization*", International Conference on Polymer Science and Engineering: Emerging Dimensions (PSE-2010), University institute of Chemical Engineering and Technology, Punjab University, Chandigarh, November 26-27, 2010.
6. **Paramjit Kaur,** Rajeev Mehta, D. Berek, S.N. Upadhyay, "*Synthesis of Polylactide under Inert Atmosphere and Vacuum*", International Conference POLYCHAR 19 – World Forum on Advanced Materials, March 20-24, 2011, Kathmandu, Nepal. I was awarded with **Gold Medal** for **"Diploma of Distinction for Best Student Presentations".**

ACKNOWLEDGEMENTS

I am highly grateful to the authorities of Thapar University, Patiala for providing this opportunity to carry out the present research work. Words are often less to revels one's deep regards. First and foremost I offer my sincerest gratitude to my supervisors, Dr. Rajeev Mehta, Associate Professor & Head, Department of Chemical Engineering, Thapar University, Patiala and Dr. S.N. Upadhyay, Professor, Department of Chemical Engineering and Technology, Institute of Technology, Banaras Hindu University, Varanasi for their valuable insight, continues guidance, encouragement, support, immense knowledge and made it possible for me to complete this thesis.

I owe my sincere thanks to Dr. Abhijeet Mukherjee (Director, Thapar University, Patiala) for providing support and facilitation. I am also grateful to Dr. K.K. Raina (Deputy Director, Thapar University, Patiala), for his encouragement and support. I am also thankful to Dr. P.K. Bajpai (Dean, Research and Sponsored Projects, Thapar University, Patiala) who helped me in tying all the loose ends. It is a pleasure to thank Dr. D. Gangacharyulu (Professor, Department of Chemical Engineering, Thapar University, Patiala) for his continuous encouragement.

I owe sincere and earnest thankfulness to Dr. Susheel Mittal, Dr. Satnam Singh, Dr. Haripada Bhunia and Dr. (Mrs.) Sanghamitra Barman who made this thesis possible. I am grateful to Mr. Sandeep Sharma and Mr. Ranpreet Singh of Thapar University, Patiala for providing all the possible assistance and cooperation. I would like to thank Er. Rakesh Bajaj (Chairman) and Dr. R. Sharma (Director), College of Engineering and Management, Kapurthala for providing their cooperation and support.

vi

With deep sense of gratitude I express my sincere thanks to Prof. Dusan Berek, Polymer Institute of the Slovak Academy of Sciences, Slovakia for his advice and willingness to share his bright thoughts with me, which was very fruitful for shaping up my ideas and research.

In my daily work, I have been blessed with a friendly and cheerful group of fellow students so I cannot forget to express appreciation to my friends Ms. Harkirat Sandhu, Ms. Navneet Chahal, Ms. Harmanjit Kaur, Ms. Mandeep Kaur, Ms. Pankil Singla, and Ms. Shilpa Narang for their cooperation, encouragement and company during the moments of respite. I am heartily thankful to the all the faculty members and staff of Chemical Engineering Department, Thapar University, Patiala for their cooperation and encouragement.

Special thanks to my Father, Mr. Prem Singh, Mother, Mrs. Manjit Kaur, Mr. Davinder Singh, Mr. Rajinder Singh, Mrs. Rashmi, Ms. Priya and other family members for supporting me throughout all my studies. I pride myself in having words for everything, but they truly shut me up when it comes down to describing how much I love them and appreciate the efforts they have put into giving me the life. I would like to say special thanks to Waheguru for not letting me down at the time of crisis and showing me the silver lining in the dark clouds.

Lastly, I offer my regards and blessings to all of those who supported me in any respect during the completion of the thesis.

(PARAMJIT KAUR)

ABSTRACT

Biodegradable polymer materials are of great interest because these are used in packaging, agriculture, medicine and other areas. Poly (lactic acid), PLA is one of the most promising biodegradable polymers (biopolymers) and has been the subject of abundant study over the last decade.

This thesis embodies the subject matter resulting out of this study. The entire work is arranged in five chapters. A brief introduction, historical background and the applications of biodegradable polymers (plastics) are described first. The importance of lactic acid, monomer used in the synthesis of polylactide, is also discussed. A brief account of physical characteristics and advantages and disadvantages of PLA is presented. Ring-opening polymerization technique is more useful for the production of high molecular weight PLA than polycondensation, which yield low molecular weight of PLA. For an estimation of kinetic parameters, mathematical modeling of the ring-opening polymerization is also described.

Both the methods for the synthesis of PLA from lactide are described and out of these the ring-opening polymerization method has been chosen for the present work because it gives higher molecular weight of PLA. Three major reaction mechanisms: cationic, anionic, and coordination-insertion are discussed. However, high molecular weight polyesters have only been obtained by using anionic or coordination-insertion ring-opening polymerization. Studies on the effects of different parameters: polymerization temperature, polymerization time, monomer/initiator ratio, nature of the initiator, amount of water or other impurities etc. which affect the polymerization of lactide are reviewed. Determination of kinetic rate constants by modeling and simulation and polymerization mechanism is also discussed. Relevant literature for the determination of intrinsic viscosity by using Ubbelohde viscometer (Mark-Houwink equation) is also reviewed.

Ring-opening polymerization has been studied wherein the starting monomer is L- lactide. The importance of recrystallization of monomer in synthesis of PLA is also explained. To carry out ring-opening polymerization of lactide, the experimental set-up was housed in a fume hood. Some polymerization reactions were carried out under dry nitrogen atmosphere and some reactions were carried out under vacuum only. Synthesis of polylactide under inert atmosphere and vacuum are briefly explained. Viscometry method, for the determination of intrinsic viscosity of synthesized PLA samples, is described.

Synthesis of PLA has been carried out under two different environments, an inert atmosphere and vacuum. Mark-Houwink parameters have been determined for intrinsic viscosity and average molecular weight. Synthesis of polylactide was carried out by using various initiators like stannous octoate, dibutyltindimethoxide, zinc stearate and one co-initiator, triphenylphosphine. These initiators were chosen because all of them have bulky groups attached to the metal atom which would provide the steric hindrance around metal atom during polymerization reaction. There would be possibility of the large polymer chains to be produced during reaction due to the bulky groups attached to metal atom. Zinc stearate is used in a large scale in chemical industries. Dispersion of initiator in monomer with a solvent (diethylether) was found to be a very important factor during polymerization. If the dispersion of initiator is not proper, one may get pockets of less as well as more number of initiator molecules (and also more number of growing polymer chains). The poor dispersion has been related with the bimodality or multimodality observed in the SEC chromatogram of the product so formed. With proper dispersion, bimodality or, multimodality in the SEC chromatogram of the product was reduced to single or unimodal peak. It has been reported in the literature that triphenylphosphine (as co-initiator) helps in increasing the molar mass of polylactide. The molecular weight of polylactide obtained in the present study using stannous octoate was upto thousands but when triphenylphophine was used as co-initiator, molecular weight increased from thousand to lakhs.

High molecular weight PLA has been obtained only in case of stannous octoate and stannous octoate/triphenylphosphine. While in the case of dibutyltindimethoxide and dibutyltindimethoxide/triphenylphosphine, low molecular weight of polylactide up to a few thousands has been obtained because these initiators are known to be effective transesterification catalysts and also known to cause 'back-biting' degradation. Zinc stearate (initiator) gave lower molecular weight PLA than stannous octoate but higher than dibutyltindimethoxide because it is a weaker base, require higher nucleophilicity to initiate lactide and that too only at higher temperatures. Some experiments were also performed with zinc stearate at 180 °C, but degradation took place at this temperature. Anionic ring-opening polymerization mechanisms of synthesized polylactide with various initiators have been proposed.

A simple and reliable model has been presented for the polymerization of lactide to PLA. The model enables numerical solution of rate equations for initiation, propagation, and termination steps. It is easily extendable to more complex polymerization mechanisms. The simulation can be done in conjunction with the experimental data to yield individual rate constants. It is possible to obtain unique values for various rate constants using M_n versus time and polydispersity data. Accurate rate constants can be predicted using appropriate and reproducible rate data. This methodology offers greater opportunity for capturing high, non-equilibrium polymer yield through appropriately timed termination of the polymerization reaction.

A comparison of polymerization kinetics (polymerization carried out under two different environments: nitrogen atmosphere, vacuum) has been done when the initiator used is stannous octoate with and without triphenylphosphine. It is interesting that the propagation rate constant, k_p, is same for both the initiators. This means that the polymer chain once initiated will grow at the same rate in both cases (also, there is an assumption in the analysis that the propagation rate constant is independent of the chain length). The initiation rate constant, k_o, is comparatively very less for pure stannous octoate initiator (nitrogen atmosphere). This would also explain the high experimental values of PD (implying a very broad molecular weight distribution). The growing polymer chains will start and terminate at different time leading to a broad MWD. In contrast, for stannous octoate with triphenylphosphine initiator, the experimental PD is very less which would be a desirable attribute of this system. For the vacuum atmosphere polymerizations, k_o, is identical for both stannous octoate and stannous octoate/triphenylphosphine. Thus, it is possible that the nitrogen atmosphere provided in the reaction kettle somehow decrease the rate constant. The termination rate constant, k_t, for pure stannous octoate initiator is about 2.6 times that for stannous octoate with triphenylphosphine initiator. This could be the major reason for the difference in the average molecule weights achieved in PLA synthesis in the two cases. In case of vacuum, k_t, is same for both.

TABLE OF CONTENTS

LIST OF FIGURES

LIST OF TABLES

LIST OF SYMBOLS

Symbol	**Description**
CNF	Cellulose Nanofiber
^{13}C NMR	Carbon Nuclear Magnetic Resonance Spectroscopy
DPAT	Diphenylammonium Triflate
DP_n	Number-average degree of polymerization (dimensionless)
DP_w	Weight-average degree of polymerization (dimensionless)
DMTA	Dynamic-Mechanical Thermal Analysis
DSC	Differential Scanning Calorimetry
FTIR	Fourier Transform Infra Red
^{1}H NMR	Proton Nuclear Magnetic Resonance Spectroscopy
IR	Infra Red Spectroscopy
I	Initiator
$[I_o]$	Initial initiator concentration (mol/l)
j	Number of repeat units in the polymer (dimensionless)
k_j	Propagation rate constant for the j^{th} propagation step on a chain (l/mol.min)
k_o	Initiation rate constant (l/mol.min)
k_p	Propagation rate constant (l/mol.min)
k_t	Termination rate constant corresponding to termination by transfer to monomer (l/mol.min)
k_{tc}	Termination rate constant corresponding to termination by transfer to water (l/mol.min)
k_{tp}	Termination rate constant corresponding to termination by transfer to polymer (l/mol.min)
k_{ts}	Termination rate constant corresponding to unimolecular termination (first order relative to active species) and intramolecular termination (min^{-1})
M	Monomer
MeOTf	Methyl triflate

Symbol	Description
M_n	Number-average molecular weight
$[M_o]$	Initial monomer concentration (mol/l)
M_v	Viscosity-average molecular weight
M_w	Weight-average molecular weight
M_w/M_n	Polydispersity (dimensionless)
MWD	Molecular Weight Distribution
m_j	Weight of *j*-mer (gm)
N_j	Number of moles of polymer of *j* units (dimensionless)
NMR	Nuclear Magnetic Resonance Spectroscopy
NPCC	Nano-Sized Precipitated Calcium Carbonate
n	A large integer (dimensionless)
PDLA	Poly (D- lactide)
PLLA	Poly (L- lactide)
PDLLA	Poly (DL- lactide)
PGA	Poly (glycolic acid)
PET	Polyethylene Terephthalate
PLA	Poly (lactic acid)
PVC	Poly (vinyl chloride)
P_1	Activated polymer of one unit
P_j	Activated polymer of chain length *j*
ppm	Parts per million
ROP	Ring-opening Polymerization
s	Number of chain(s) initiated by an initiator molecule (dimensionless)
SEC	Size Exclusion Chromatography
SEM	Scanning Electron Microscopy
TPP	Triphenylphosphine
TGA	Thermo Gravimetric Analysis
T_c	Crystallization Temperature
T_m	Melting Temperature
TEC	Transesterification Coefficient
TEM	Transmission Electron Microscopy

Symbol	**Description**
WAXD	Wide-Angle X-Ray Diffraction
w	Weight of all the molecules in a polymer sample (gm)
w_j	Weight-fraction of molecules whose weight is m_j (dimensionless)
χ_c	Degree of Crystallinity
τ	Time variable (dimensionless)
η_{rel}	Relative Viscosity
η_{sp}	Specific Viscosity
η_{red}	Reduced Viscosity
η_{inh}	Inherent Viscosity
$[\eta]$	Intrinsic Viscosity

CHAPTER - 1

INTRODUCTION

CHAPTER 1 INTRODUCTION

1.1 Background

Polymers form the backbone of plastic materials and are continually being employed in an expanding range of areas. Polymeric materials are solid and non-metallic compounds of high molecular weights. Plastics are polymeric materials, a material built up from long repeating chains of molecules. During the Second World War, plastics such as nylon and polyethylene were used as a replacement for other materials because the early plastics were not completely chemically stable. However, advances in plastic technology since then, have shown that plastics are a very important and reliable class of materials for product design. Biodegradable polymeric materials are of great interest because these are used in packaging, agriculture, medicine and other areas. Bioplastics are an increasingly well known alternative to petroleum based plastics. They are derived from biological sources instead of petroleum based feed stock. A number of biological materials may be incorporated into biodegradable polymeric materials, with the most common being starch and fiber extracted from various types of plants.

The decade of the 1950s saw the introduction of polypropylene and polycarbonate that, along with nylon, came to form the nucleus of a sub-group in the plastics family known as the "engineering thermoplastics." Their outstanding impact strength and dimensional stability enabled them to compete directly and favorably with metals in many applications. During, 1960s and 1970s several new plastics were introduced, most notable were thermoplastic polyesters with outstanding resistance to gas permeation that made them applicable for use in packaging. During this period, another sub-group of the plastics family called "high temperature plastics," also started to emerge which includes the polyimide, polyamide-imides, aromatic polyesters, polyphenylene sulfide and polyether sulfone. These materials were designed to meet the demanding thermal needs of aerospace and aircraft applications.

The durability of plastics, under both aerobic and anaerobic conditions, contributes to growing waste and waste disposal problems. Even improving recycling rates for many types of plastics have not kept up with increase in overall plastics consumption and in some cases recycling yields new problems associated with concentration of contaminants through the recycling process (Vink *et* al., 2003).

Poly(lactic acid), PLA is quite an old polymeric material, discovered in the 1890s, but it has only now found a universal route to market in the form of bio-degradable packaging. In 1932, Wallace Carothers, a Dupont scientist, produced a low molecular weight product by heating lactic acid under vacuum. Due to high costs, the focus since then has been mainly on the manufacture of medical grade sutures, implants and films for controlled drug release applications. Until the 1960s, researchers struggled to get high molecular weight polylactide and later found methods to produce high molecular weight polymer which was still relatively expensive to make.

As of Jun 2010, NatureWorks was the primary producer of PLA (bioplastic) in the United States. Other companies involved in PLA manufacturing are PURAC Biomaterials (Netherlands) and several Chinese manufacturers. Galactic and Petrochemicals operate a joint-venture, Futerro, that is developing a second generation of polylactic acid product. This project includes the building of a PLA pilot plant of 1500 tons/year in Belgium. In 2008, 5000 tons per year of lactides and PLA were produced. Since 2009, Purac has developed a unique business model by starting production of lactides (D and L), the monomers for PLA production, in their Spanish production plant with a capacity of several thousands of tons. First commercial plant at Synbra (NL) for the production of Biofoam (EPLA) was installed in 2010, while in the year of 2011, 75,000 tons per year lactide monomers plant at their production site in Thailand (Rayong Province). Purac has developed the technology to polymerize these lactides with Sulzer, a Swiss engineering company. Purac collaborates with various PLA production partners to develop production scale and new markets for PLA. Due to the availability of D- lactide, Purac partners will be able to use stereo-complex technologies to produce new PLA grades with heat-stability up-to 180 °C, enabling use in higher value application areas. In a tripartite collaboration between Purac, Sulzer and Synbra solutions were developed to allow Synbra to start production of PLA and subsequently E-PLA, an attractive biodegradable and/or bio-based alternative to EPS-foam in a variety of application areas (http://en.wikipedia.org/wiki/Polylactic_acid).

The cost of production of the monomer (lactic acid) has been a deterrent to widespread development of the polymer. Recently, there have been advances in fermentation of glucose, which turns the glucose into lactic acid. This has dramatically lowered the cost of producing lactic acid and significantly increased the interest in the polymer. Cargill, Inc. was one of the first companies to develop polylactic acid polymers. Cargill began researching PLA production technology in 1987, and began production in pilot plants in 1992. In 1997, after a 15 month joint investigation, Cargill formed a joint venture with Dow Chemical

Company, Inc., creating Cargill Dow Polymers LLC (CDP). The joint venture was dedicated to further commercializing PLA polymers (Harper, 2000) and they formally launched Nature Works TM PLA technology in 2001. Construction was recently completed on a large-scale PLA manufacturing facility in Blair, Nebraska. The Nebraska facility will be capable of producing up to 300 million pounds (140,000 metric tons) of PLA per year, using 40,000 bushels of corn per day (http://cargilldow.com/release.asp?id=92).

Total capacity of lactide in China already comes to over 200,000 t/a. Meanwhile, there are four major polylactide, PLA manufacturers in China as of May 2011, all of them are expanding capacity to 10,000 t/a, among which two will launch their new production lines at the end of 2011. It can be predicted that China will become a large production base of lactic acid and PLA worldwide in the future (http://pdf.marketpublishers.com/785/benchmarking_of_lactic_acid_and_polylactic_acid_in_china.pdf).

The economic benefits include an estimated $2 billion/yr of net income that will accrue to the PLA manufacturing value chain in 2020. About $367 million/yr of new revenues will go to the agriculture community for harvesting, collection, and transportation of the feedstock. Energy benefits are estimated to save 202 trillion kJ/yr equivalent of fossil derived fuels in 2020 by the displacement of 8 billion/yr of fossil fuel-based polymers with PLA (http://www.oit.doe.gov/cfm/full article.cfm/id=305).

1.2 Lactic Acid (Monomer)

Lactic acid was first isolated in 1780 by Swedish chemist, Carl Wilhelm Scheele, who isolated the lactic acid from sour milk as impure brown syrup and gave it a name based on its origins: 'Mjölksyra'. The French scientist Frémy produced lactic acid by fermentation and this gave rise to industrial production in 1881(http://www.lactic-acid.com/history.html). Lactic acid is a chemical compound which plays very important role in several biochemical processes. It has a hydroxyl group adjacent to the carboxyl group, it can lose a proton from the acidic group, producing the lactate ion $CH_3CH(OH)COO^-$. It is miscible with water or ethanol, and is hygroscopic. Lactide is a six member ring, it has significant enough ring strain (22.9 kJ mol^{-1}) that ring opening is favored over reversal of the addition of the alkoxide to the carbonyl (Duda and Penczek, 1990). In 2006, global production of lactic acid reached 275,000 tons with an average annual growth of 10% (http://www.nnfcc.co.uk/publications/nnfcc-renewable-chemicals-factsheet-lactic-acid). The lactic acid dimerises to give lactide, which upon ring-opening polymerization yield Poly(lactic acid), PLA.

1.3 Poly(lactic acid), PLA

Poly(lactic acid), PLA is a bio-degradable, thermoplastic polymer and can be made from renewable resources such as sugarcane and corn. It is highly versatile aliphatic polyesters commonly made from α-hydroxy acid. It is one of the most promising biodegradable polymers (biopolymers) and has been the subject of abundant study over the last two decades. It is relatively cheap and has some remarkable properties, which make it suitable for different applications. High molecular weight polylactide is a colorless, glossy, stiff thermoplastic polymer with properties similar to polystyrene. The physical and mechanical properties of PLA make it a good material as replacement for petrochemical thermoplastics in several application areas. While the high price of PLA long restricted its use to medical applications, recent breakthroughs in lactide polymerization technology opened up possibilities for the production of PLA in bulk for other applications.

The physical characteristics of high molecular weight PLA are to a great extent dependent on its transition temperatures for common qualities such as density, heat capacity, and mechanical and rheological properties. In the solid state, PLA can be either amorphous or semi-crystalline, depending on the stereochemistry and thermal history. The amorphous PLA is soluble in most organic solvents such as tetrahydrofuran (THF), chlorinated solvents, benzene, acetonitrile and dioxane. For amorphous PLAs, the glass transition (T_g) determines the upper use temperature for most commercial applications. For semi-crystalline PLAs, both the T_g (~58 °C) and melting point (T_m), 130 - 230 °C (depending on structure) are important for determining the use temperatures across various applications. Above T_g, amorphous PLAs changes from glassy to rubbery and behaves as a viscous fluid upon further heating. Below T_g, PLA behaves as a glass with the ability to creep until cooled to its β-transition temperature of approximately 45 °C. Below this temperature, PLA will only behave as a brittle polymer.

PLA has numerous advantages over other polymers such as: (1) it is produced from renewable resources, (2) permits considerable energy savings, (3) can be recycled back to lactic acid which is a non-toxic and naturally occurring metabolite through hydrolysis or alcoholysis, (4) helps in capturing carbon dioxide, (5) compostable, (6) improvement of farm economics, (7) decline of landfill volumes (Auras *et* al. 2004 and Dorgan *et* al. 2001).

1.4 Applications of PLA (http://cipetians-zone.blogspot.com/2010/09/bio-degradable-plastics-introduction.html)

1) Stereo complex blends of PDLA and PLLA have a wide range of applications, such as woven shirts (iron ability), microwavable trays, hot fill applications and even engineering plastics (in this case, the stereo complex is blended with a rubber like polymer such as ABS). Such blends also have good form-stability and visual transparency, making them useful for low-end packaging applications. Progress in biotechnology has resulted in the development of commercial production of the D enantiomer form that was not possible until recently.
2) PLA is currently used in a number of biomedical applications, such as sutures, stents, dialysis media and drug delivery devices. It is also being evaluated as a material for tissue engineering. Because it is biodegradable, it can also be employed in the preparation of bioplastic, useful for producing loose fill packaging, compost bags, food packaging, and disposable tableware. In the form of fibers and non-woven textiles, PLA also has many potential uses, for example as upholstery, disposable garments, feminine hygiene products, and nappies.
3) PLA has been used as the hydrophobic block of amphiphilic synthetic block copolymers used to form the vesicle membrane of polymersomes.
4) PLA is a sustainable alternative to petrochemical derived products, since the lactide from which it is ultimately produced can be derived from the fermentation of agricultural by-products such as corn starch or other carbohydrate-rich substances like maize, sugar or wheat.
5) PLA has also been developed in the United Kingdom to serve as sandwich packaging.
6) PLA has also been used in France to serve as the binder in Isonat Natisol, an hemp fiber building insulation.
7) PLA is used for biodegradable and compostable disposable cups for cold beverages, the lining in cups for hot beverages, containers for food packaging.

In spite of its good properties, the applications are limited due to its low flexibility and impact strength. Hence it shows some disadvantages too:

1) PLA has high cost in comparison to other polymers because of lower scales of production. PLA is more expensive than the majority of commodity polymers.

2) The plastic softens at a temperature of about 60 °C, which limits its suitability for the production of cups for hot drinks.
3) PLA has moisture of sorption properties.
4) 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 its 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.

1.5 Ring-opening polymerization of PLA

PLA can be prepared by two different methods- by polycondensation of hydroxyl -carboxylic acids or, by ring-opening polymerization (ROP) of cyclic esters. The ROP can be performed either as a bulk polymerization, or in solution, emulsion or dispersion (Sosnowski *et* al., 1996 and Gadzinowski *et* al., 1996). An initiator is necessary to start the polymerization. Under rather mild conditions, high molecular weight aliphatic polyesters of low polydispersity can be prepared in short periods of time. The polycondensation technique is less expensive than ROP, but it is difficult to obtain high molecular weight polylactide to achieve specific end groups. Problems associated with condensation polymerization, such as the need for exact stoichiometry, high reaction temperatures and the removal of low molecular weight by products (e.g. water) are excluded in ROP (Brode *et* al., 1972).

The ROP of lactide has been thoroughly investigated during the last 40 years, due to its versatility to produce a variety of biomedical polymers in a controlled manner. ROP of lactide can be carried out by cationic, anionic, and coordination-insertion mechanisms depending on the initiator. A number of initiators were used for the synthesis of polylactide but among them, stannous octoate is usually preferred because it provides high reaction rate, high conversion rate, and high molecular weights, even under rather mild polymerization conditions. Use of triphenylphosphine (TPP) as co-initiator to enhance the polymerization rate and molecular weight of polylactide resulted in increase in molecular weight from thousands to several ten thousands. Fig. 1.1 shows the formation of polylactide from lactide by ROP.

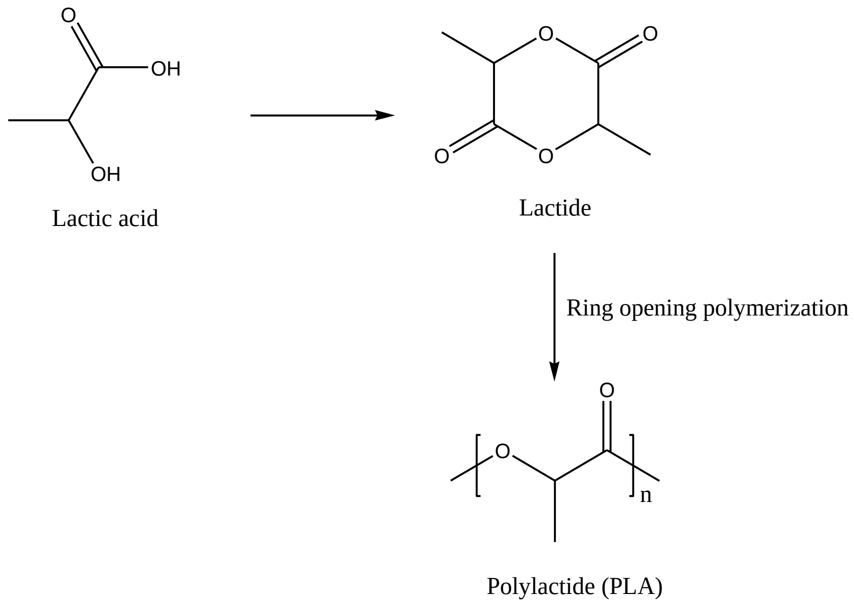


Figure 1.1 Ring-opening polymerization of lactide

1.6 Need for Mathematical Modeling of the ROP of PLA

Hundreds of research papers and patents based on the synthesis of PLA have appeared in the literature. Now large size manufacturing units for PLA are being set-up. But, there is lack of data concerning the rate constants for initiation, propagation and termination steps of PLA polymerization except some data about the apparent rate constant. Also, it is extremely difficult to experimentally find the absolute values of different rate constants. Thus, there is a need for mathematical modeling which when used with the readily available experimental data for the average molecular weights, can be used to predict the polymerization rate constants with sufficient accuracy in a short time. Mehta, (2006) and Mehta *et* al., (2005, 2007) have developed a model for ring-opening polymerization of PLA and computed the kinetic rate constants for five different initiators. Additionally, they showed quantitatively presence of even trace amount of impurities like water can lead to a drastic reduction in molecular weight of the product.

CHAPTER – 2

LITERATURE REVIEW

CHAPTER 2 LITERATURE REVIEW

2.1 Overview

Poly(lactic acid), PLA, a degradable, thermoplastic, can be made from renewable resources such as sugarcane and corn. Due to a growing market for the biodegradable and renewable polymers like PLA, the world demand for lactic acid is rapidly increasing. PLA does not have any reactive side-chain groups. PLA has good mechanical properties and, performs well compared to standard thermoplastics. The hardness, stiffness, impact strength and elasticity of PLA, important for applications such as beverage flasks, are similar to those for PET.

PLA films show better ultraviolet light barrier properties than polyethylene, but were slightly worse than polystyrene (PS) and polyethylene terephthalate (PET). PLA films show better mechanical properties than PS, and comparable to those of PET. PLA has lower melting and glass transition temperature than PET and PS. Solubility parameter predictions indicate that PLA will interact with nitrogen compounds, anhydrides, and some alcohols, and it will not interact with aromatic hydrocarbons, ketones, esters, and water. In terms of barrier, PLA showed O_2 and CO_2 permeability coefficients lower than PS and higher than PET. PLA, totally degraded in aerobic or anaerobic environments in two months to five years, and early chain fragmentation can be obtained at higher humidity and temperature in composting facilities as soon as fifteen days (Auras *et* al, 2005).

The life cycle of Poly(lactic acid), PLA is shown in Fig. 2.1 starting with fermentation of starch to give lactic acid, the dimer form lactide is obtained, which is polymerized to give high molecular weight PLA. The PLA on hydrolysis degrades to lactic acid which is further broken to give CO_2 and H_2O.

Among all biodegradable polyesters, PLA is the product that has one of the highest potential due to its availability on the market and its low price (Lunt, 1998, Sinclair, 1996 and Vert *et* al., 1995). Some commercial biopolyesters like Poly(lactic acid), PLA, Poly (3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV, Polycaprolactone, PCL, Poly (ester amide), PEA, Poly (butylene succinate-co-adipate), PBSA and Poly (butylene adipate-co-terephthalate), PBAT show their different properties like density, glass transition, melting point, crystallinity, modulus etc. in Table 2.1.

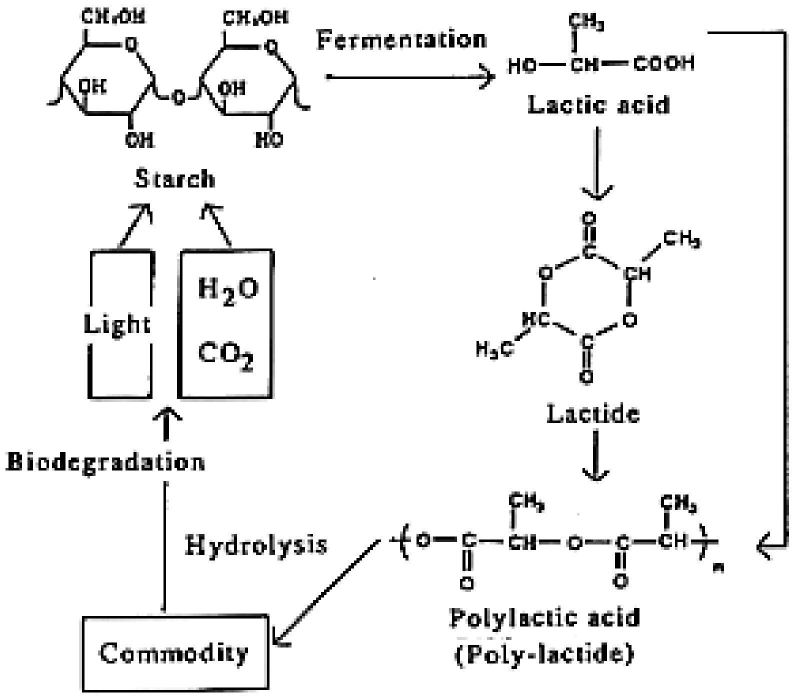


Figure 2.1 Life cycle of polylactic acid

Table 2.1 Main Commercial Biopolyesters (http://www.biodeg.net/bioplastic.html)

Parameters	Poly(lactic acid), PLA Dow-Cargill (Nature Works)	Poly (3-hydroxybutyrate-co-3-hydroxyvalerate), PHBV Monsanto (Biopol D400G) HV=7 mol%	Polycaprolactone, PCL Solway (CAPA 680)	Poly (ester amide), PEA Bayer (BAK 1095)	Poly (butylene succinate-co-adipate), PBSA Showa (Bionolle 3000)	Poly (butylene adipate-co-terephthalate), PBAT Eastman (eastar bio 14766)
Density	1.25	1.25	1.11	1.07	1.23	1.21
Melting point, in °C (DSC)	152	153	65	112	114	110-115
Glass transition, in °C (DSC)	58	5	-61	-29	-45	-30
Crystallinity (in %)	0-1	51	67	33	41	20-35
Modulus, in MPa (NFT 51-035)	2050	900	190	262	249	52
Elongation at break, in % (NFT 51-035)	9	15	>500	420	>500	>500
Tensile stress at break or max., in MPa (NFT 51-035)	-	-	14	17	19	9
Biodegradation* Mineralization in %	100	100	100	100	90	100
Water permeability WVTR at 25 °C (g/m2/day)	172	21	177	680	330	550
Surface tension** (g) in mN/m. gd (Dispersive component) gp (Polar component)	50 37 13	- - -	51 41 11	59 37 22	56 43 14	53 43 11

(*) At 60 days in controlled composting according to ASTM 5336

(**) Determinations from contact angles measurements of probes liquids

2.2 Synthesis of PLA from Lactic Acid

There are two major routes to produce PLA from the lactic acid monomer (Fig. 2.2). The first route involves removal of water by the use of solvent under high vacuum and high temperature (condensation polymerization) to yield low molecular weight of polylactide. In the other route, water is removed under mild conditions to give an intermediate dimer, the lactide, which on ring-opening polymerization gives high molecular weight PLA (http://www.nonwoven.co.uk/reports/Prague%202000.html). In order to get high molecular weight of polylactide, ring-opening polymerization method was used.

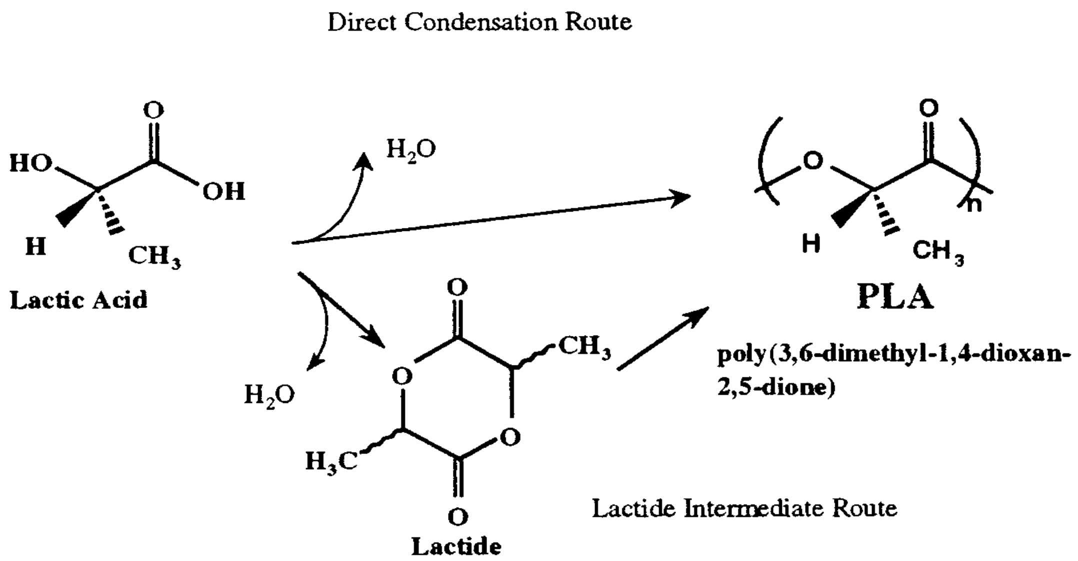


Figure 2.2 Synthesis of PLA by two routes

(Source: http://www.nonwoven.co.uk/reports/Prague%202000.html)

2.2.1 Lactic Acid (Monomer)

Lactic acid can be used in food technology as taste enhancing additive and the source of polylactic acid, (PLA) a polymer used as biodegradable plastic. Lactic acid exits in two enantiomeric forms: L- and D- lactic acid. Lactide ring bears two identical asymmetric carbon atoms in L- lactide, D- lactide and D, L- lactide which is a 50/50 mixture of L- and D- lactide, or two different ones in meso- lactide. As fermented, lactic acid is 99.5% L- isomer and 0.5% D- isomer. Polymerization of the lactide rich in the L- form gives crystalline products, whereas those rich in the D- form (>15%) are more amorphous. The thermal, mechanical, and biodegradation characteristics of lactic acid polymers are known to depend on the choice and distribution of stereoisomers within the polymer chains. High purity L- and D- lactides form stereo regular isotactic poly (L- lactide) (PLLA) and poly (D- lactide) (PDLA), respectively. Fig. 2.3 shows the three different forms of lactide.

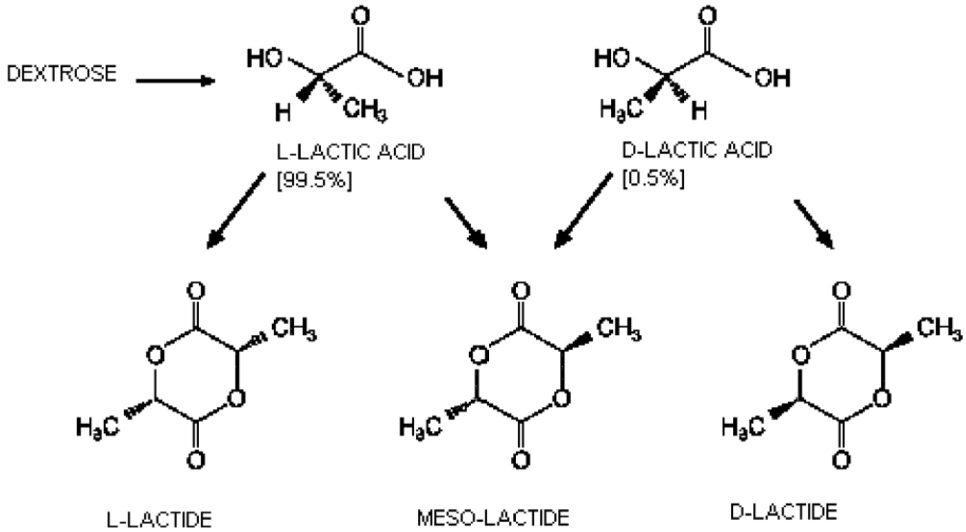


Figure 2.3 Different forms of lactide

(Source: http://www.nonwoven.co.uk/reports/Prague%202000.html)

Lactide has a characteristic quartet in its ^{1}H NMR spectrum with peaks at 5.13, 5.05, 4.97, 4.89 ppm and a doublet having peaks at 1.69 and 1.61 ppm (McNeill and Leiper, 1985). The principal bands of the infrared (IR) spectrum of lactide can be found in the literature, and they can be utilized for example in kinetic studies (McNeill and Leiper, 1985, Moravek *et* al., 2009). When lactide is polymerized to PLA, the wavenumbers associated with C-H stretching of CH_3 (3010 and 2930 cm^{-1}), C-H stretching of the carbonyl CH (2950 cm^{-1}), and the C=O stretch shift to slightly lower wavenumbers, that is, to 3000 and 2890, 2940, and 1750 cm^{-1}, respectively. The bands related to C-H bending of CH_3 (1445 and 1380 cm^{-1}) and C-H bending of the carbonyl CH (1350 cm^{-1}) are reported to shift to higher wave numbers, that is, 1450 and 1375 cm^{-1} and 1360 cm^{-1}. No shift should be observed for the bands assigned to the C-O stretch of lactide at 1260 and 1100 cm^{-1} due to ROP (McNeill and Leiper, 1985).

2.2.2 Synthesis of PLA by Condensation Polymerization

Polycondensation leads to the formation of a polymer by the linking of molecules of a monomer with the release of water, or a similar simple substance. The major disadvantage of this synthesis is that it does not produce high molecular weight PLA due to complication in removing impurity and water. Other drawbacks of these techniques are the need for large reactor, evaporation, solvent recovery and increased racemization (Fisher *et* al., 1973). The synthesis of PLA through polycondensation of the lactic acid monomer leads to weight average molecular weights lower than 1.6×10^4, whereas ring-opening polymerization of lactide results in average molecular weights ranging from 2×10^4 to 6.8×10^5 (Hyon *et* al., 1997). Direct synthesis of poly (L-lactic acid) (PLLA) from an L- lactic acid oligomer has been performed in supercritical carbon dioxide ($scCO_2$) using an esterification promoting agent, dicyclohexyldimethylcarbodiimide (DCC), and 4-dimethylaminopyridine (DMAP) as a catalyst. PLLA within M_n of 13,500 g/mol was synthesized in 90% yield at 3500 psi and 80 °C after 24 h. The molecular weight distribution of the products was narrower than PLLA prepared with melt–solid phase polymerization under conventional conditions (Yoda *et* al., 2004).

Lactic acid polymers consist mainly of lactyl units, of only one stereoisoform or combinations of D and L lactyl units in various ratios. There have been studies to obtain a high molar mass polymer by manipulating the equilibrium between lactic acid, water and polylactic acid in an organic solvent (Ajioka *et* al., 1995) or a multifunctional branching agent was used to give star-shaped polymers (Kim and Kim, 1999). In the presence of bifunctional agents (dipoles and di acids) they form telechelic polymers, which can be further linked to give high molar mass polymers using linking agents like diisocynate (Hiltunen *et* al., 1997). In order to reduce the production cost of PLA, L- lactic acid was polymerized by direct polycondensation (DP) under vacuum without initiators, solvents and initiators. Experiments were conducted at polymerization temperatures (T_p) of 150–250 °C. The maximum PLA molecular weight obtained was 90 kDa at 200 °C after 89 h under vacuum. Above 200 °C, PLA is thermally degraded by specific scission (Achmad *et* al., 2009).

Poly (ester urethane) (PEU) consisting of poly (L- lactic acid) and poly (ethylene succinate) was successfully prepared via chain-extension reaction of poly (L- lactic acid) - diol (PLLA-OH) and poly (ethylene succinate) - diol (PES-OH) using 1,6-hexamethlyene diisocyanate (HDI) as a chain extender. PLLA-OH was obtained by direct polycondensation of L- lactic acid in the presence of 1, 4-butanediol. PESOH was synthesized by condensation polymerization of succinic acid with excessive ethylene glycol. The data of GPC analysis indicated that high molecular weights than 200,000 g mol^{-1} were easily synthesized through chain-extension reaction (Zeng *et* al., 2009).

High molecular weight PLA can be synthesized by adopting the process of polycondensation followed by solid state polycondensation. In this method, the residual monomer present in the polymer is substantially less because, during the solid-state polycondensation process, the monomer and catalyst are concentrated in the amorphous regions of the polymer and as a result almost 100 % of the monomer is converted to polymer (Maharana *et* al., 2009).

Various metal triflates were employed for direct polycondensation of lactic acid to obtain Poly(lactic acid). Screening of the metal triflates was conducted with the polycondensation of lactic acid at 160–180 °C for 16 h under reduced pressure (1.4 kPa) after a pre-dehydration process under an air atmosphere. Examined metal triflates are scandium, yttrium, ytterbium, lanthanum, hafnium, copper, and silver triflates. Polycondensation using scandium triflate afforded poly(lactic acid) with high molecular weights ($M_n = 4.3 \times 10^4$) with good yields (62%) under following conditions; initiator amount = 0.05 mol%, pre-dehydration at 180 °C for 2 h, and polycondensation at 180 °C for 16 h (Konishi *et* al., 2010).

2.2.3 Synthesis of PLA by Ring-Opening Polymerization

The polymerization of lactones is generally carried out in bulk or in solution (THF, toluene, chloroform etc.), emulsion, (Sosnowski *et* al., 1996) or dispersion (Gadzinowski *et* al., 1996). The temperature of bulk polymerization is generally in the range of 100-150 °C, whereas in solution polymerization, low temperatures have been used (0-25 °C) to minimize side reactions (inter and intra molecular transesterification). Racemic lactide was polymerized with various initiators containing Zn and Al. Three groups of initiators can be distinguished in view of their influence on transesterification: $ZnCl_2$ having the strongest transesterification activity, $ZnEt_2$ and $ZnEt_2$/Al $(OiPr)_3$ having medium activity and $Al(acac)_3$ with no transesterification activity at all (Kasperczyk *et* al., 1990). The mechanism of polymerization depends on the type of initiator. Three major reaction mechanisms are cationic, anionic, and coordination-insertion. However, high molecular weight polyesters have only been obtained by using anionic or coordination-insertion ring-opening polymerization.

2.2.3.1 Cationic Ring-Opening Polymerization

The cationic ring-opening polymerization involves the formation of a positively charged species which are subsequently attacked by a monomer. The attack results in ring opening of the positively charged species through the SN^2 type process. The cationic ring-opening polymerization reaction of lactones has been achieved using alkylating agents, acylating agents, Lewis acids and protic acids.

Methyl triflate (MeOTf) was found to be a useful initiator for the cationic ring-opening polymerization reaction of L- lactide. The reactions were performed in nitrobenzene for 48 hr and at optimized 50 °C. The methyl ester end groups were formed when methyl triflate was used as the initiator and it was suggested that the polymerization proceeds by cleavage of the alkyl-oxygen bond rather than the acyl-oxygen bond. According to their proposal, reaction propagates through the activation of the monomer by methylation with methyl triflate followed by SN^2 attack of the triflate anion on the positively charged lactide ring with the inversion of stereochemistry. Propagation was proposed to proceed by nucleophilic attack by lactide on the activated cationic chain end with inversion, leading to net retention of the configuration (Kricheldorf and Dunsing, 1986). The polymerization proceeded by the cleavage of the alkyl-oxygen bond rather than the acyl-oxygen bond (Fig. 2.4).

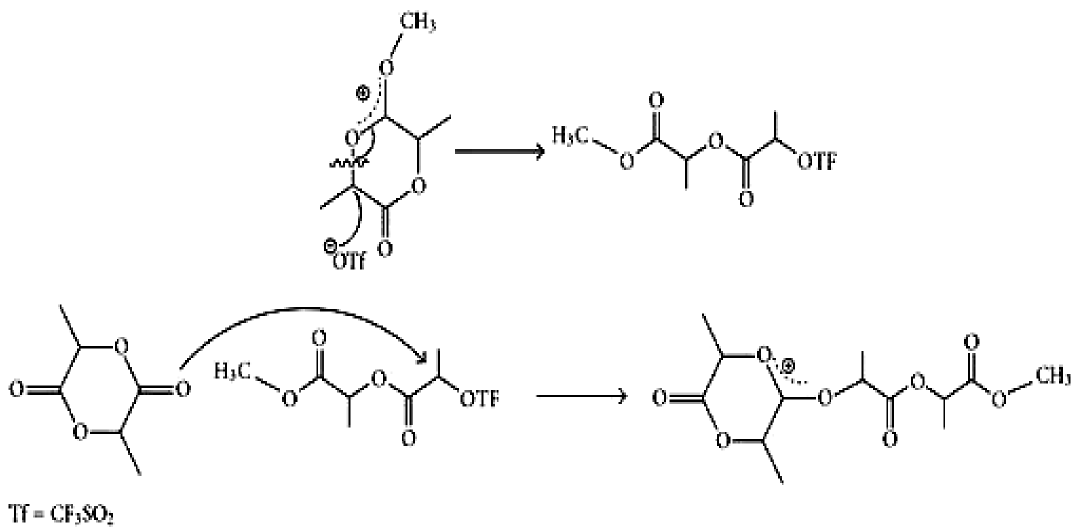


Figure 2.4 Proposed pathways for cationic ring-opening polymerization of lactone

Atthoff and co-workers reported bulk ring-opening polymerization of lactide at 130 °C using 5 mol% diphenylammonium triflate (DPAT) as an acid-proton initiator in ethanol as initiator. Under these conditions, they were able to get PLA with molecular weight up to 12000 g/mol with dispersity 1.24 to 1.51 in 4 days. They also suggested that such a high dispersity is due to transesterification with prolonged reaction time (Atthoff *et* al., 2003).

2.2.3.2 Anionic Ring-Opening Polymerization

The effective initiators for anionic polymerization of lactones are alkali metals, alkali metal oxides, alkali metal naphthalenide complexes with crown ethers, etc. The reaction is initiated by nucleophilic attack of negatively charged initiator on the carbon of the carbonyl group or on the alkyl-oxygen, resulting in formation of linear polyester (Albertsson and Varma, 2003). The polymerization of *β*- lactones proceeds through alkyl-oxygen or acyl-oxygen cleavage giving both carboxylate and alkoxide end groups (Fig. 2.5).

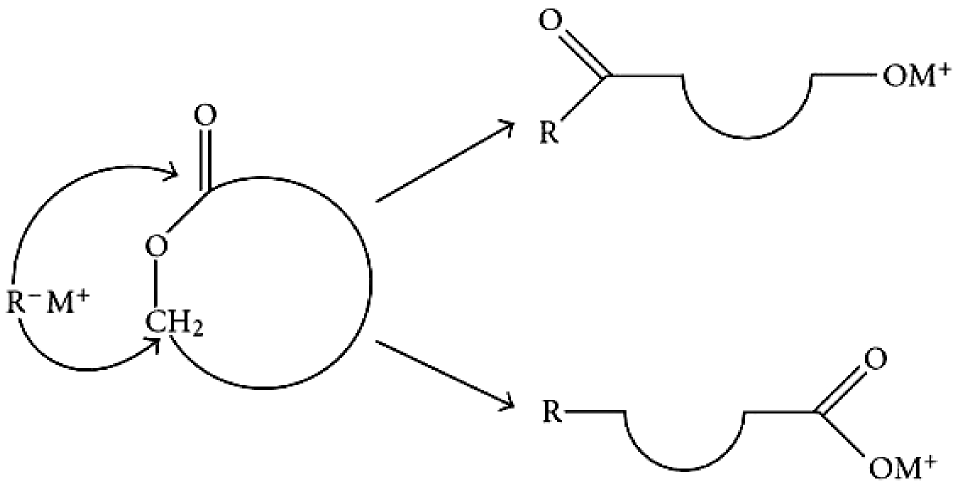


Figure 2.5 Initiation of ring-opening polymerization of lactones

In larger lactones, such as caprolactone or lactide, the reaction proceeds by the acyl-oxygen scission only thereby leading to the formation of an alkoxide ion as the propagating species (Fig. 2.6).

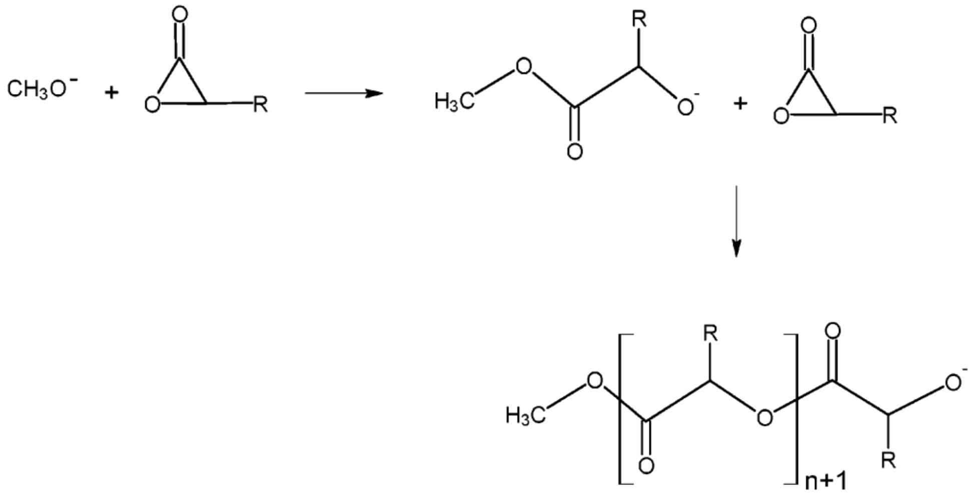


Figure 2.6 Anionic polymerization of lactone showing acyl oxygen

2.2.3.3 Co-ordination Insertion Ring-Opening Polymerization

Coordination insertion polymerization has been extensively used for the preparation of aliphatic polyesters with well defined structure and architecture. The most widely used initiators are various aluminum and tin alkoxides and carboxylates. The covalent metal alkoxides or carboxylates with vacant "d" orbital react as coordination initiators and not as anionic initiators in these polymerizations. These initiators are capable of producing stereoregular polymers of narrow MWD and controlled molecular mass, with well defined end groups. The carboxylates are weaker nucleophiles in comparison to alkoxides. The polymerization proceeds via acyl oxygen cleavage of the lactone with insertion of the monomer into the metal-oxygen bond of initiator (Kowalski *et* al., 1998, Kricheldorf *et* al., 1995, In't Veld *et* al., 1997, Du *et* al., 1995, Schwach *et* al., 1997, Zhang *et* al., 1994). The coordination of the exo-cyclic oxygen to the metal results in the polarization and makes the carbonyl carbon of the monomer more susceptible for nucleophilic attack (Fig. 2.7).

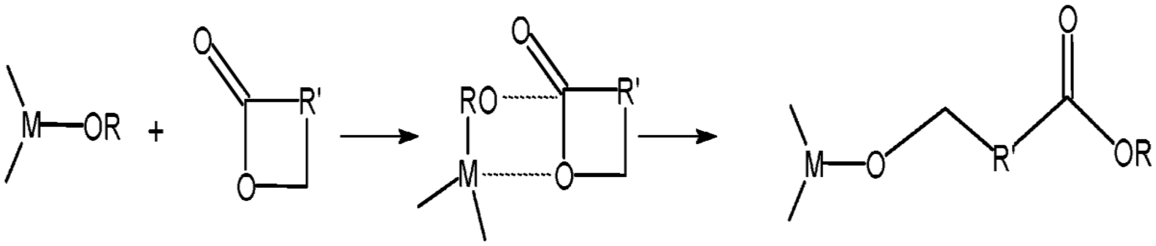


Figure 2.7 Coordination insertion mechanism of lactone polymerization

Kricheldorf *et* al. (2000) observed the formation of octanoic acid when tin (II) 2- ethylhexanoate was heated above 100 °C. The acid, thus liberated, may bring about the esterification of alcohol (active hydrogen co-initiator) leading to the formation of water, which may react with $Sn(Oct)_2$ to form stannoxanes and tin hydroxides. Under such conditions, it would be difficult to control the molecular mass and side reactions because the presence of water or other hydroxyl compounds is likely to initiate polymerization. The relative reactivity of different metal alkoxide initiators for transesterification reaction depends on the metal and is lowest for aluminum alkoxides. The following order has been observed:

$$Bu_2Sn\,(OR)_2 > Bu_3SnOR > Ti\,(OR)_4 > Zn\,(OR)_2 > Al\,(OR)_3$$

Stannous octoate has been the most widely used initiator because of high reaction rates, the solubility in the monomer melt and the ability to produce high molecular weight polylactide (Swift 1993, Schwach *et* al., 1994, Cabaret *et* al., 2004). The addition of an equimolar amount of Lewis base, particularly triphenylphosphine into 2-ethylhexanoic acid, significantly enhances the lactide polymerization rate in bulk. Triphenylphosphine has two beneficial effects: it increases the polymerization rate and delays the occurrence of the undesirable back biting reactions at monomer/initiator ratios greater or equal to 5000 (Degee *et* al., 1999).

Engel *et* al. (1997) studied the ring-opening polymerization of lactide cyclic monomers in the bulk in the presence of tin (II) 2- ethylhexanoate. It was reexamined under appropriate conditions for the end-group characterization of growing chains by high-resolution ^{1}H NMR. The formation of a side product, hydroxytin (II) lactate, was found which appeared to initiate lactide polymerization and to yield a high molecular weight PLA50 polymer. However, the polymerization with stannous octoate was faster than with hydroxytin (II) lactate.

Schwach *et* al. (1998) reported that the polymerization was moisture sensitive and that only a fraction of zinc used was active. Small quantities of a side-product was detected and identified as zinc lactate. This compound appeared to be an efficient initiator of the ring-opening polymerization in the bulk. Initiation by zinc lactate yielded high molecular weight polymers with a high degree of conversion and high polymerization rates.

Kleawkla *et* at. (2005) discussed the co-ordination insertion mechanism of the ring-opening polymerization of the cyclic esters. Originally it was assumed that stannous octoate was the initiator but this was later disproved by the fact that the polymer molecular weight did not depend upon the monomer: stannous octoate molar ratio. Instead it was concluded that hydroxyl containing impurities (e.g. hydroxyl acids) in the system, including any trace amounts of moisture, were the true initiating species with the stannous octoate acting as a initiator to activate the carbonyl of the monomer towards nucleophilic attack by OH group. This was then followed by acyl-oxygen bond cleavage and ring opening of the monomer. It is now believed that rather than effecting simple complexation with the stannous octoate , the alcohol (ROH) actually reacts with it to form a tin alkoxides, $Sn(OR)_2$, and that it is this $Sn(OR)_2$ which is the true initiating specie. Thus, the stannous octoate is more correctly termed as initiator and the ROH as the co-initiator.

Copolymers with various compositions were synthesized by bulk ring-opening polymerization of glycolide and ε-caprolactone, using stannous (II) octoate or zirconium (IV) acetylacetonate as initiator. Reaction time and temperature were varied to induce different chain microstructures. Stannous (II) octoate leads to less transesterification than zirconium (IV) acetylacetonate, and lower temperatures lead to less transesterification than higher ones (Kasperczyk *et* al., 2005).

Aluminum-alkoxide initiated polymerization of lactones proceeds according to a coordination-insertion mechanism. Aluminum isopropoxide coordinates to the exocyclic carbonyl oxygen, and the acyl-oxygen cleavage yields an isopropyl ester end-group. Termination of growing chain with dilute HCl leads to the formation of a hydroxy end-group. A narrow molecular mass distribution and an increase in DP with an increase in [M]/[I] ratio confirmed the living character of the polymerization (Loefgren *et* al., 1994).

Ferric alkoxides were used as initiators for bulk ring-opening polymerization of lactides. The molecular weight decreased and the molecular weight distribution broadened as the polymerization temperature increased. Intermolecular transesterification took place during polymerization of D, L- lactide as evidenced by the results of MALDITOF MS analysis, and the quantitative evaluation for each initiation system was made by ^{13}C NMR analysis. ^{1}H NMR, and MALDI-TOF MS analyses indicated that the polymerization of lactides proceeded via a coordination-insertion mechanism involving cleavage of the acyl-oxygen bond of the lactides (Wang *et* al., 2005). ROP of lactones with these organometallic initiators at high temperatures or long reaction time leads to both inter- as well as intra-molecular transesterification reactions. Both types of transesterification reactions lead to an increase in dispersity of the polyesters (Fig. 2.8).

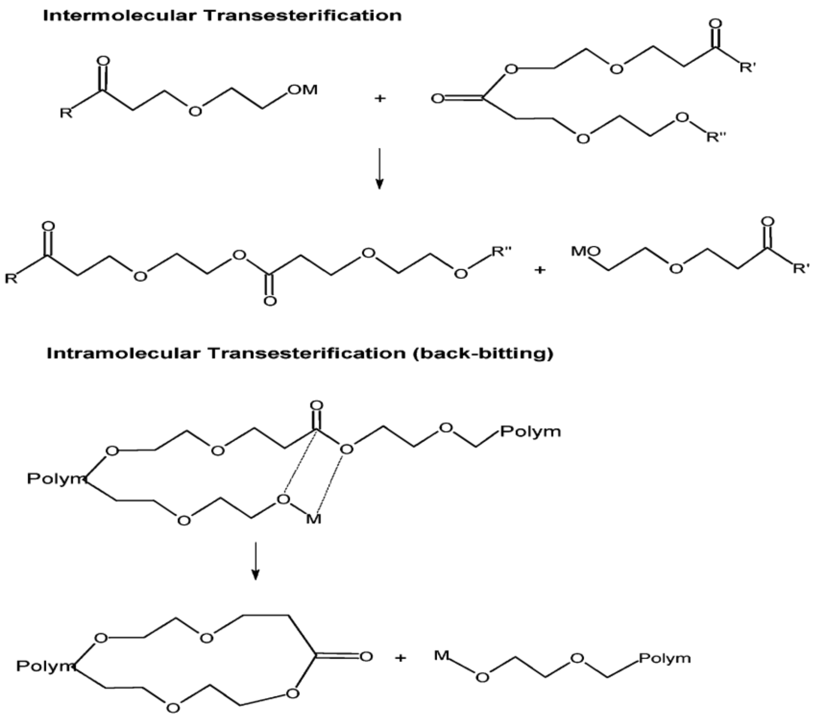


Figure 2.8 Inter- and intra-molecular transesterification reactions

The reaction parameters which influence transesterification reactions are temperature, reaction time, the type and concentration of initiator and the nature of the lactone or lactide (Dubois *et* al., 1965). Higher flexibility of the polyester backbone leads to an increase in the extent of side reactions (transesterification).

Bu_3SnOMe and $Bu_2Sn(OMe)_2$ are effective transesterification catalysts and cause ‘back-biting’ degradation even at 90 °C. In all series of polymerizations initiated with tin methoxides two tendencies are detectable: increasing randomization of the stereosequence with increasing reaction time and with higher reaction temperatures. In contrast, Sn(II) octoate does not cause transesterification at ≤ 120°C and even at 180°C randomization of the stereosequences is slow (Kricheldorf *et* al., 1992). 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 (Kricheldorf and Saunders, 1990, Kricheldorf and Boettcher, 1993, Kricheldorf and Serra, 1985 and Kleine and Kleine, 1959).

Poly (L- lactide), PLLA with ultra-high weight average molecular mass and narrow polydispersity index was synthesized by ring-opening polymerization. A synthetic purification method involving a water bath and two time recrystallization could improve the purity of L- lactide to 100%. The yield of L- lactide reached 40.6% and increased 12.1% compared with the recrystallization method. Poly (L-lactide) with a weight average molecular mass of about 102.4 × 10^4 and a polydispersity index of 1.16 was obtained when polymerization was conducted with molar ratio of monomer to initiator $[M_0]/[I_0]$ of 12000 for 24 h at 140 °C (Zhou *et* al., 2008).

2.2.4 PLA Composites and Nanoparticles

Bioresorbable composite plates have been made from poly (glycolic acid), PGA fibers embedded in a PLA matrixes. These composites are bioresorbable, exhibit good biocompatibility with the tissues in which they are implanted, and have adjustable resorption rates, depending on the relative amounts of L- and D- lactic acid units as well as on the quantities of glycolic acid and lactide repeating units. This concept of bioresorption or biodegradability is an important one in many areas of bioimplants (Boretos and Eden, 1984). Composites of PLA have been made with jute fibers (Ouchi *et* al., 2003) and bioactive glass (Roether *et* al., 2002).

Lipase catalyzed ring opening graft copolymerization can be employed to graft hydrophobic polyesters onto hydrophilic cellulose based polymers. The reaction resulted in polyester grafted HEC with DSs between 0.10 and 0.32 in terms of per anhydroglucose unit (Li *et* al., 1999). Organoclay plays an important role in the preparation of polymer/clay nanocomposites and dispersing the clay into less polar polymer matrixes (Maiti *et* al., 2002). New polylactide (PLA)/layered silicate nanocomposites have been prepared by simple melt extrusion of PLA and organically modified montmorillonite. The d spacing of both the organically modified montmorillonite and intercalated nanocomposites were investigated by wide-angle X-ray diffraction (WAXD) analysis, and the morphology of these nanocomposites was examined by transmission electron microscopy (TEM) (Ray *et* al., 2002). PHB/layered silicate nanocomposites were prepared successfully through melt extrusion (Maiti *et* al., 2007).

PLA nanocomposites with nano-sized precipitated calcium carbonate (NPCC) and organically modified montmorillonite (MMT) clay were prepared by melt extrusion. Morphologies, tensile mechanical properties, dynamic mechanical and rheological properties, polymer–nanoparticles interactions, and toughening mechanisms of the PLA/NPCC and PLA/MMT nanocomposites were compared. MMT and NPCC showed significantly different effects on the strength, modulus and elongation of the PLA nanocomposites (Jiang *et* al., 2007).

The specific moduli of both solid and microcellular components were improved by addition of nanoclay into bio-based polylactide and facilitated the formation of smaller cell sizes and higher cell densities. Addition of nanoclay also reduced the strain at break and the specific toughness of solid polylactide nanocomposite components. However, the strain at break and specific toughness of microcellular polylactide nanocomposite components were largely improved in comparison with microcellular polylactide components, especially when the loading level of the nanoclay was at 3% and 5%, presumably due to the lack of large voids, as well as the smaller cell size and higher cell density (Kramschuster *et* al., 2007).

Poly(lactic acid)/organo-montmorillonite (OMMT) nanocomposites were prepared by melt intercalation technique. Maleic anhydride-grafted ethylene propylene rubber (EPMgMA) was added into the PLA/OMMT in order to improve the compatibility and toughness of the nanocomposites. The samples were prepared by single screw extrusion followed by compression molding. The thermal properties of the PLA/OMMT nanocomposites have been investigated by using differential scanning calorimeter (DSC) and thermo-gravimetry analyzer (TG). The melting temperature (T_m), glass transition temperature (T_g), crystallization temperature (T_c), degree of crystallinity (χ_c), and thermal stability of the PLA/OMMT nanocomposites have been studied. It was found that the thermal properties of PLA were greatly influenced by the addition of OMMT and EPMgMA (Chow and Lok, 2009).

Poly(lactic acid) PLA and polycaprolactone (PCL) nanocomposites prepared by adding two organically modified montmorillonites and one sepiolite were obtained by melt blending. Materials were characterized by Wide Angle X-ray analysis (WAXS), Scanning Electron Microscopy (SEM), Transmission Electron Microscopy (TEM), Differential Scanning Calorimetry (DSC), Thermo Gravimetric Analysis (TGA) and Dynamic-Mechanical Thermal Analysis (DMTA) (Fukushima *et* al., 2009). A new manufacturing process similar to papermaking, which enables the production of thin sheets made of uniformly dispersed microfibrillated cellulose (MFC) with polylactic acid (PLA) fibers was devised, and the composites were obtained by compression molding of the stacked sheets (Nakagaito *et* al., 2009).

The Taguchi method of experimental design (TMED) was used for the preparation of PLA nanoparticles via a nano precipitation technique. The effect of four pertinent parameters, such as concentration of PLA, solvent to non solvent (S/NS) volume ratio, molecular weight of PLA and type of solvent, were studied on the yield and size of nanoparticles. The size of PLA nanoparticles obtained was around 100 nm (Maharana *et* al., 2010).

Jonoobi et al., (2010) develop cellulose nanofiber (CNF) reinforced polylactic acid (PLA) by twin screw extrusion. Nanocomposites were prepared by premixing a master batch with high concentration of CNFs in PLA and diluting to final concentrations (1, 3, 5 wt. %) during the extrusion. The tensile modulus and strength increased from 2.9 GPa to 3.6 GPa and from 58 MPa to 71 MPa, respectively, for nanocomposites with 5 wt.% CNF.

2.2.5 Polymerization Mechanism

Poly(lactic acid), PLA can undergo cationic, anionic and co-ordiantion insertion polymerization mechanisms. The mechanism through which the initiator works has been suggested for some systems. Trifluoromethane sulfonic acid (triflic acid) and methyl trifluoromethanes sulfonic acid (methyl triflate) are the only cationic initiators to polymerize lactide (Kricheldorf and Kreiser, 1987, Kricheldorf and Sumbel, 1989 and Dittrich, 1971). The polymerization proceeds via triflate ester end-groups instead of free carbenium ions, which yields, at low temperatures (<100 °C), an optically active polymer without racemization. The chain growth proceeds by cleavage of the alkyl oxygen bond. The propagation mechanism begins with the positively charged lactide ring being cleaved at the alkyl-oxygen bond by an SN^2 attack by the triflate anion. The triflate end-group reacts with a second molecule of lactide again in an SN^2 fashion to yield a positively charged lactide. Then the triflate anion again opens the charged lactide, and polymerization proceeds (Kricheldorf and Dunsing, 1986). The cationic polymerization mechanism with methyl trifluoromethanes sulfonic acid (methyl triflate) initiator is shown in Figure 2.9.

Zhang *et* al. (1994) studied the effect of hydroxyl and carboxylic acid substances on lactide polymerization in the presence of stannous octoate. Stannous alkoxide, a reaction product between stannous octoate and alcohol, was proposed as the substance initiating the polymerization through coordinative insertion of lactide. Alcohol could affect the polymerization through reactions leading to initiator formation, chain transfer, and transesterification. Carboxylic acids affect the polymerization though a deactivation reaction.

Aluminum isopropoxide is an effective initiator for the polymerization of lactides in toluene at 70 °C. The ring-opening polymerization proceeds through a coordination-insertion mechanism. The mechanism involves the insertion of the lactide into the aluminum-alkoxide bond with lactide acyl-oxygen cleavage is shown in Figure 2.10 (Dubois *et* al., 1991).

Nijenhuis *et* al. (1992) studied the kinetics and mechanism of L- lactide bulk polymerization using stannous octoate and zinc bis (2,2-dimethyl-3,5-heptanedionate-O,O'). Up to 80% conversion, the rate of polymerization using tin compound was higher than that with zinc-containing catalyst, while at conversions beyond 80%, the latter catalyst gave the higher rate of polymerization. Crystallization of the newly formed polymer has an accelerating effect on the polymerization. The differences in the rate of polymerizations at high conversion for the two catalysts have been suggested to be caused by a difference in crystallinity of the newly formed polymer. It is further suggested that contaminants in the catalyst (such as tin-oxy or tin-hydroxyl contaminants) and the monomer are the true initiators. Initiation as well as polymerization proceeds through a Lewis acid catalyzed transesterification reaction between an activated lactone and a hydroxyl group.

Schwach *et* al. (1997) reexamined the ring-opening polymerization of PLA in the presence of stannous octoate under conditions allowing for the end-group characterization of growing chains by high-resolution ^{1}H-NMR. For low values of monomer to initiator ratios, the DL- lactide ring was opened to yield lactyl octoate-terminated short chains.

Various authors have described mechanisms for the tin octoate catalyzed polymerization of lactide but only a few have incorporated the effect the impurities on the polymerization. Figure 2.11 is a hypothetical reaction mechanism put forth by (Du *et* al., 1995) which includes the effect of different hydroxylic compounds.

Stannous (II) triflouromethane sulfonate and scandium(III) trifoloromethane sulfonate have also been studied as catalysts for PLA synthesis (Moller *et* al., 2001). It was found that polymers of predictable molecular weights and narrow polydispersities could be obtained. The addition of base either as a solvent or as an additive significantly enhanced the polymerization rate with minimal loss to the polymerization control.

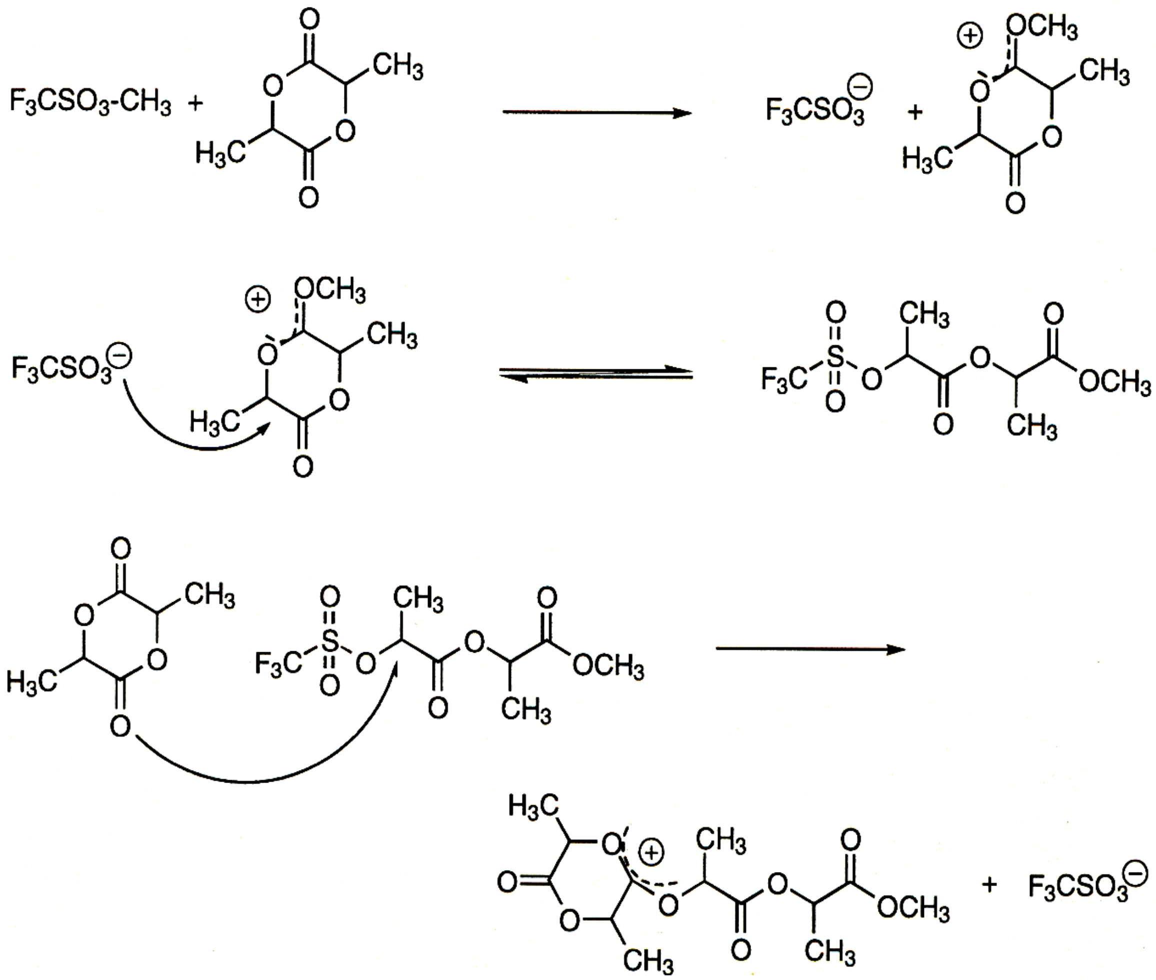


Figure 2.9 Cationic ring-opening polymerization mechanism of PLA using methyl triflate (Source: Kricheldorf and Dunsing, 1986)

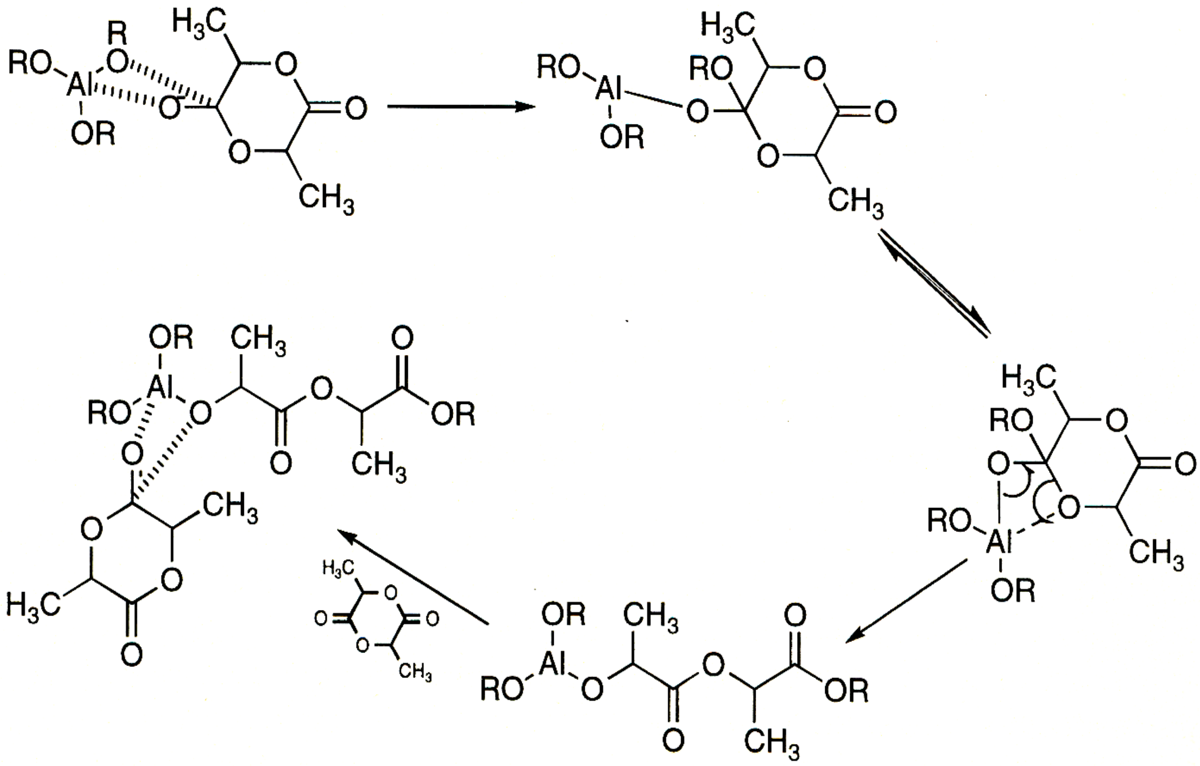


Figure 2.10 Polymerization mechanism of PLA using Aluminum Isopropoxide

(Source: Dubois *et* al., 1991)

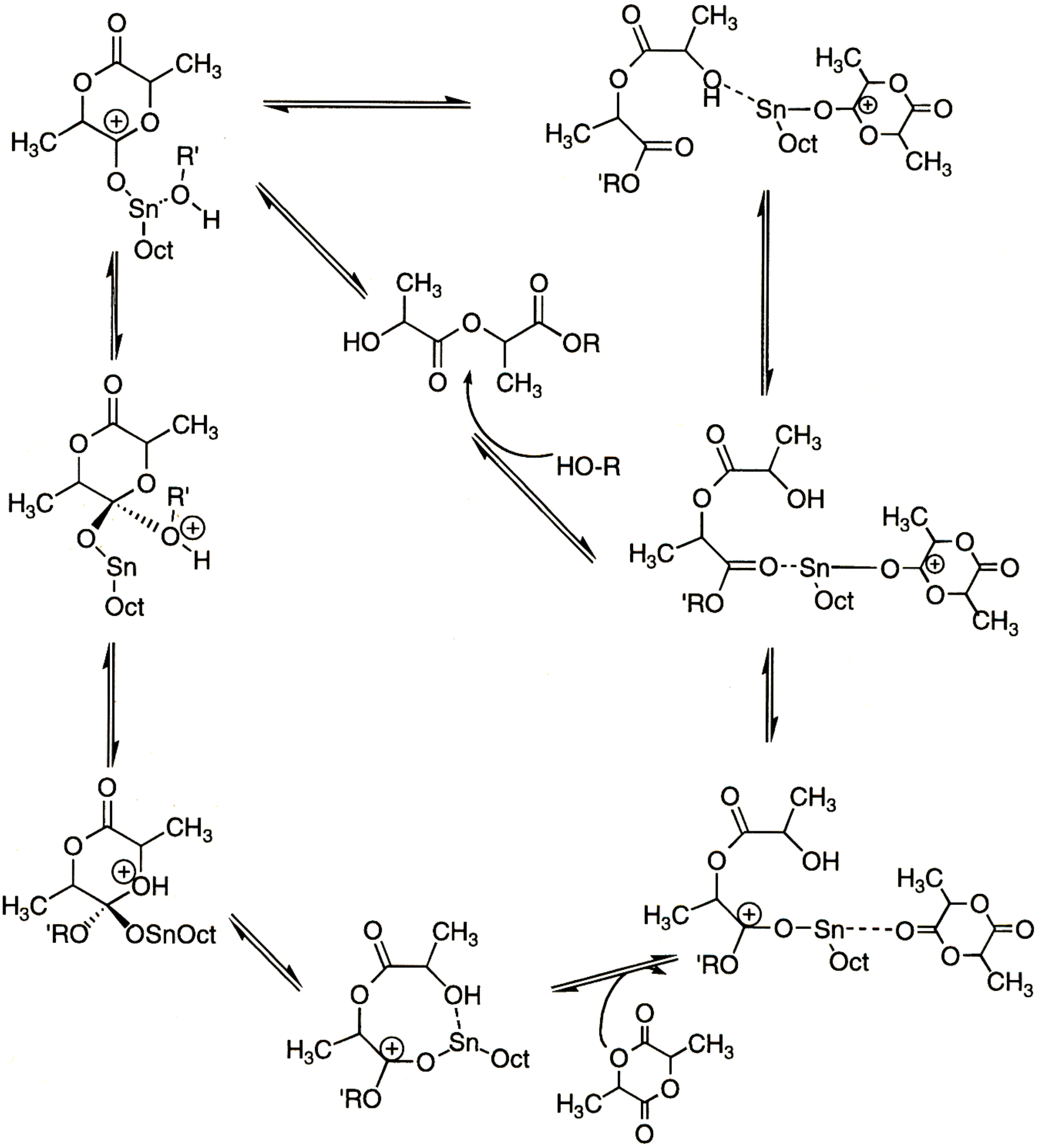


Figure 2.11 Polymerization mechanism of lactide in presence of stannous octoate (Source: Du *et* al., 1995)

2.2 Effect of Different Parameters on the ROP of Polylactide

In view of the growing importance and application of PLA it would be useful to examine the effects of various parameters like polymerization temperature, polymerization time, monomer/initiator ratio, nature of the initiator, amount of water or other impurities etc. which are likely to affect the degree of polymerization and molecular weight distribution etc.

Zhang *et* al. (1994) reported that the hydroxyl and carboxylic acid substances in the presence of stannous octoate affect the ring-opening polymerization of polylactide. Stannous alkoxide, a reaction product between stannous octoate and alcohol is proposed as the molecule initiating the polymerization through coordinative insertion of lactide. Alcohol can affect the polymerization through the initiator formation, chain transfer and transesterification. Carboxylic acid can affect the polymerization through a deactivation reaction. Experimental analyses showed that alcohol increased the PLLA production while carboxylic acid decreased it. Both alcohol and carboxylic acid reduced the final molecular weight of PLLA. The polymerization induction period was observed at high carboxylic acid concentration due to the deactivation reaction caused by carboxylic acid. The polymerization reactions were carried out in glass ampoules which were sealed under high vacuum and put in an oven at 130 °C to start the polymerization. Samples were removed at 2, 5, 10, 30 and 72 hr. The yield increased with polymerization time and then levelled off. At a polymerization time of 72 hr, all yields were around 95%. Without adding hydroxy and carboxylic acid substances, the highest PLLA molecular weight (24.4×10^4) was obtained after polymerization for 30 hr. At the monomer to alcohol molar ratios of 5,000 and 500, the final PLLA molecular weights were 19.7×10^4 and 8.0×10^4, respectively, corresponding to the degree of polymerizations of 2,700 and 1,100.

Schwach *et* al. (1994) reported that five variables, namely time, temperature, monomer to initiator ratio, nature of the initiator and monomer degassing time affect the polymerization. These are arranged according to their average effect on transesterification in Tables 2.2 to 2.4.

Table 2.2 shows the variables, which were retained for factorial analysis, together with their selected levels (Schwach *et* al., 1994). Table 2.3 shows the polymerization conditions for tin and zinc based initiators and Table 2.4 lists the main as well as interaction effects.

Table 2.2 Selected variables and levels (Schwach *et* al., 1994)

Variables	Levels
A: Initiator	Stannous octoate or zinc powder
B: Monomer to initiator ratio (w/w)	1,000 or 10,000
C: Polymerization temperature (°C)	130 or 160
D: Polymerization time (hr)	24 or 120
E: Monomer degassing time (min)	15 or 30

Table 2.3 Polymerization conditions for Zn and Sn (Schwach *et* al., 1994)

S.No.	Initiator	Time (hr)	Temp. (°C)	M/I	Degassing time (min)	M_w	TEC (%)
1	Zn powder	24	130	10000	30	11000	9.7
2	Sn octoate	24	130	10000	15	216000	0.0
3	Zn powder	120	130	10000	30	216000	28.9
4	Sn octoate	120	130	10000	15	162000	0.0
5	Zn powder	24	160	10000	30	146000	26.1
6	Sn octoate	24	160	10000	15	120000	8.3
7	Zn powder	120	160	10000	30	110000	81.4
8	Sn octoate	120	160	10000	15	364000	16.4
9	Zn powder	24	130	1000	15	231000	21.6
10	Sn octoate	24	130	1000	30	137000	23.9
11	Zn powder	120	130	1000	15	75000	15.1
12	Sn octoate	120	130	1000	30	328000	33.4
13	Zn powder	24	160	1000	15	127000	71.7
14	Sn octoate	24	160	1000	30	254000	43.4
15	Zn powder	120	160	1000	15	172000	89.0
16	Sn octoate	120	160	1000	30	85000	92.5

Table 2.4 Estimated main effects and interaction effects on transesterification coefficients (TEC) (%) (Schwach *et* al., 1994)

Variables and/or interactions	Effects (%)	Reduced effects	Significance
C: Polymerization temperature	37.2	11.3	Significant
B: M/I ratio (+AE)	-27.3	-8.3	Significant
D: Polymerization time	20.2	6.1	Significant
A: Initiator (+BE)	15.5	4.7	Significant
CD	14.6	4.4	Significant
E: Monomer degassing time (+AB)	14.5	4.4	Significant

The largest average effect was shown by the polymerization temperature. A 30 °C increase in this variable resulted in a 37.2% increase in transesterification coefficient (TEC). However, the temperature was found to significantly interact with time (average interaction effect: 14.6%). Increasing the polymerization temperature from 130 to 160 °C resulted in a 25% increase in TEC for a 24 hr polymerization time, whereas, for a 120 hr polymerization time, the same increase in temperature resulted in a 50% increase in TEC. The second largest average effect was ascribed to the monomer to initiator ratio, an increase in this variable causing a 27.3% decrease in TEC. The third main effect was due to the polymerization time, by increasing the value of this variable from 24 to 120 hr increased TEC by 20.2%, on the average. The fourth main effect was ascribed to the initiator type. Finally, increasing the monomer degassing time from 15 min up to 30 min increased TEC by 14.5%. Within the ranges of selected variables, a hierarchy of average effects was established: polymerization temperature>monomer to initiator ratio>polymerization time> initiator >monomer degassing time.

Kohn *et* al. (2003) studied the effect of recrystallization of the lactide using ethyl acetate for at least 3 time to remove meso-lactide, which absorbs moisture, and reported that it helped in the polymerization. Bis (trimethyltriazacyclohexane) praseodymium triflate catalyzed the polymerization of D, L- lactide in various solvents without the requirement of any additional reagent. The 95% yield at M/I = 1000 and a molecular weight of 18,000 was obtained in melt polymerization at 170 °C in 18 hr. Under the same conditions praseodymium triflate was found to be a poor initiator giving a lower molecular weight (5700) with medium yields (74%).

Effect of Solvent on Polymerization

The polymerization reaction was carried for 24 hr in refluxing THF, dichloromethane, ethyl acetate and toluene at 80 °C, respectively. In case of non-solvent, polymerization reaction was carried for 18 hr at 170 °C and the monomer to initiator ratio was the same in both the cases. Although the molecular weight and yields were less at 170 °C but results were better than that for praseodymium triflate. Effect of the various solvents is shown in Table 2.5 (Kohn *et* al., 2003).

Table 2.5 Effect of various solvents on the polymerization of D, L- lactide (Kohn *et* al., 2003)

Solvent	**THF**[a]	**Dichloromethane**[a]	**Ethyl acetate**[a]	**Toulene**[a]	**No solvent**[b]
Yield (%)	88	82	79	84	95
M_n X 10^{-4}	1.03	0.83	1.26	1.18	1.80

[a] Monomer to initiator ratio=1000, reflux or, 80 °C, 24 hr,

[b] Monomer to initiator ratio=1000, 170 °C, 18 hr, vacuum

Effect of Temperature and Time on Polymerization

Polymerization results had been reported at different temperatures and time. The increase in yield follows a first order kinetics up to about 20 hr. This is followed by drop in yield at long reaction time due to transesterification reactions leading to soluble low molecular weight oligomers. The GPC results of the polymers obtained after 5 and 18 hr showed nearly identical number of polymer chains indicating that the production of cyclic polymer chains from transesterification and reinsertion of the cyclic esters into the polymer chains are in equilibrium after 5 hr and then a slow increase and eventual drop in molecular weight with time is due to increase in poly dispersity index (PDI) (Kohn *et* al., 2003).

The molecular weight of the resulting poly (D, L- lactide) increased with the temperature at the initial stage and reached the maximum values at 170 °C, then followed by rapid decrease with a broader distribution of the molecular weight afterwards (Kohn *et* al., 2003).

Effect of the Molar Ratio [LA]/[Cat] on the Polymerization

The molecular weight increased gradually but not linearly with the monomer to initiator ratio as a result of transesterification. The melt polymerization of D, L- lactide with bis (trimethyltriazacyclohexane) praseodymium triflate can be efficiently carried out at 170 °C for 18 hr and is first order w.r.t. lactide and half order w.r.t. initiator concentrations and is accompanied by a large degree of transesterification (Kohn *et* al., 2003).

Wang *et* al. (2004) carried out polymerization in bulk using creatinine as initiator and L- lactide as monomer. Polymerization reaction was carried out at 160 °C for 96 hr. Monomer/initiator ratio was 100. Polymerization gave a polymer with high yield (97%), moderate MW ($M_n = 1.56 \times 10^4$) and narrow MWD (PDI = 1.28). Polymerization temperature and time affected the polymerization reaction. With the increase of temperature, reaction yield and molecular weight of the product increased. Under the examined conditions the optimum temperature was 160 °C, below this temperature both the reaction yield and molecular weight of the polylactide were relatively low (yield ≤ 87%, $M \leq 1.0 \text{ X } 10^4$). This is due to the fact that in melt polymerization the decrease of reaction temperature increases the viscosity of the polymerization system, which reduces the activity of macromolecular propagation species. Effect of polymerization temperature on ring-opening polymerization of lactide in bulk is shown in Table 2.6 (Wang *et* al., 2004).

Table 2.6 Influence of polymerization temperature on ring-opening polymerization of lactide in bulk (Wang *et* al., 2004)

S.No.	Temperature (°C)	Yield (%)	$M_n \times 10^{-4}$	PD
1	120	80.4	0.67	1.25
2	135	85.7	0.88	1.20
3	150	87.0	0.92	1.44
4	160	97.0	1.56	1.28
5	165	96.5	1.40	1.30
6	180	96.0	0.93	1.53

The polymerization time plays a significant role on the bulk polymerization of lactide catalyzed by creatinine. Experimental results show that after 96 hr, the reaction goes to completion. Prolonged reaction time cannot increase the polymer yield; it causes a decrease in molecular weight and broadening of the molecular weight distribution of formed polymers. This is probably due to the fact that transesterification side reaction in polymerization gets intensified at prolonged time. Effect of polymerization temperature on ring-opening polymerization of lactide in bulk is shown in Table 2.7 (Wang *et* al., 2004).

Table 2.7 Influence of polymerization time on ring-opening polymerization of lactide in bulk (Wang *et* al., 2004)

S.No.	Time (hr)	Yield (%)	$M_n \times 10^{-4}$	PD
1	24	67.2	0.71	1.40
2	48	85.2	0.91	1.41
3	72	90.1	1.17	1.34
4	96	96.5	1.40	1.30
5	110	96.6	1.16	1.47
6	120	96.4	1.20	1.57

Experimental analyses showed that monomer to initiator ratio also affected the polymerization reaction as maximum yield and molecular weight was obtained at M/I ratio = 100, thereafter with increase in monomer to initiator ratio, yield kept on decreasing (Table 2.8). The main advantage of creatinine in the synthesis of polylactide is that the material is metal free, highly biosafe and suitable for the carrier materials of controlled drug release devices.

Table 2.8 Influence of monomer to initiator ratio on ring-opening polymerization of lactide in bulk (Wang *et* al., 2004)

S.No.	Monomer to initiator ratio	Yield (%)	$M_n \times 10^{-4}$	PD
1	100	96.5	1.40	1.30
2	250	90.0	1.27	1.29
3	500	70.1	1.23	1.25
4	1000	67.4	1.34	1.23

Zhang *et* al. (2004) reported that rare earth 2, 6- dimethylaryloxide are successful initiators for the ROP of polylactide. Polylactide with viscosity average molecular weight as high as 4.5×10^4 g mol^{-1} with over 95% yield can be prepared with $Ln(ODMP)_3$ as initiator at 100 °C in 45 min. Table 2.9 shows the effect of solvent polarity on lactide polymerization. The monomer conversion and molecular weight of polylactide obtained in chloroform and THF are lower than those in toluene. It indicates that polar solvents are not beneficial for the lactide polymerization with (rare earth 2, 6-dimethylaryloxide) $Ln(ODMP)_3$, which is consistent with the coordination mechanism. It has been found that the conversion and molecular weight of polylactide could be controlled easily by varying monomer concentration, monomer to initiator molar ratio, polymerization temperature and time. Effect of temperature and time on polymerization is shown in Table 2.10 (Zhang *et* al., 2004).

Table 2.9 Effect of solvent in polymerization (Zhang *et* al., 2004)

S.No.	**Solvent**	**$Ln(ODMP)_3$**	**Conversion (%)**	**$M_v \times 10^{-4}$**
1	Toluene	La	97.2	4.51
2	Chloroform	La	65.7	1.93
3	THF	La	50.0	1.47
4	Toluene	Sm	79.4	3.58
5	Chloroform	Sm	41.7	1.56
6	THF	Sm	32.5	1.13

Table 2.10 Effect of temperature and time on polymerization (Zhang *et* al., 2004)

S.No.	**Temperature (°C)**	**Time (min)**	**Conversion (%)**	**$M_v \times 10^{-4}$**	**$M_n \times 10^{-4}$**
1	90	45	89.4	3.93	3.55
2	100	45	97.2	4.51	4.27
3	110	45	92.7	3.75	3.40
4	120	45	85.6	2.98	2.49
5	100	15	43.0	2.44	2.03
6	100	25	66.6	3.67	3.16
7	100	35	89.1	4.33	4.01
8	100	55	94.3	4.40	4.15

The favourable conditions for the synthesis of polylactide with high molecular weight and yield with $Ln(ODMP)_3$ in toluene are: lactide = 2.0 mol/l, monomer to initiator ratio = 1000, polymerization temperature and time are 100 °C and 45 min.

Wang *et* al. (2005) reported that the ferric alkoxide were efficient initiators for bulk ring-opening polymerization of lactide with the higher than 90% of monomer conversions polymerized at 130 °C for 36 hr. The amount of initiator varied corresponding to [I]/[M] mole ratios of 0.5×10^{-3} to 2.0×10^{-3}. Maximum molecular weights were achieved at 1/1000 of [I]/[M] mole ratio and then decreased gradually with increasing amount of initiator and prolonging polymerization time. As shown in Table 2.11 (Wang *et* al., 2005), the monomer conversion increased with the increase of [I]/[M] ratio, when the [I]/[M] ratio was higher than 1.0×10^{-3}, over 90% monomer conversion was obtained. A very small difference between molar ratios was found in all the ferric alkoxides. The maximum molecular weight was achieved at a [I]/[M] ratio of 1.0×10^{-3}. It is possible that a higher initiator concentration will result in more growing chains, thus giving a lower molecular weight product while a lower initiator concentration will produce less initiation sites, thus leading to lower monomer conversion and higher molecular weight of polylactide.

Table 2.11 Effect of monomer to initiator molar ratio on polymerization of D, L- lactide in bulk (Wang *et* al., 2005)

Initiators	[I]/[M]	Conversion (%)	$M_n \times 10^{-4}$	PD
$Fe(OEt)_3$	0.5×10^{-3}	86.2	4.36	1.62
	1.0×10^{-3}	94.4	6.14	1.61
	1.5×10^{-3}	95.4	5.87	1.60
	2.0×10^{-3}	96.8	5.26	1.63
$Fe(OPr)_3$	0.5×10^{-3}	85.3	3.94	1.65
	1.0×10^{-3}	93.9	5.08	1.68
	1.5×10^{-3}	95.3	4.20	1.68
	2.0×10^{-3}	96.5	3.61	1.69
$Fe(O^iPr)_3$	0.5×10^{-3}	83.4	2.10	1.72
	1.0×10^{-3}	91.6	2.96	1.73
	1.5×10^{-3}	92.1	2.87	1.74
	2.0×10^{-3}	92.6	2.77	1.76
$Fe(OBu)_3$	0.5×10^{-3}	86.0	1.90	1.98
	1.0×10^{-3}	96.2	1.86	1.92
	1.5×10^{-3}	96.8	1.84	1.92
	2.0×10^{-3}	96.9	1.78	1.88

In bulk polymerization, the polymerization temperature is chosen higher than the melting point of the lactide monomers (127 °C). Table 2.12 shows the results of the ring-opening polymerizations of D, L- lactide performed at temperatures ranging from 130 to 150 °C at 48 hr (Wang *et* al., 2005). It is seen that with increase in temperature, the monomer conversion also increases for each polymerization system. However, the molecular weight decreases and the molecular weight distribution get broadened for all ferric alkoxides. The highest molecular weight was achieved by polymerization at 130 °C for each ferric alkoxide. This may be ascribed to the acceleration of transesterification as the polymerization temperature increases.

Table 2.12 Effect of temperature on polymerization of D, L - lactide in bulk (Wang *et* al., 2005)

Initiators	Temp (°C)	Conversion (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PD
$Fe(OEt)_3$	130	94.4	6.14	9.88	1.61
	140	94.9	5.82	9.66	1.66
	150	96.0	4.98	9.16	1.84
$Fe(OPr)_3$	130	93.9	5.08	8.53	1.68
	140	94.3	4.77	8.20	1.72
	150	95.2	4.60	8.19	1.78
$Fe(O^iPr)_3$	130	91.6	3.34	5.78	1.73
	140	92.4	3.01	5.47	1.82
	150	93.0	2.76	5.13	1.86
$Fe(OBu)_3$	130	90.5	2.07	3.97	1.92
	140	91.7	1.82	3.57	1.96
	150	92.1	1.74	3.45	1.98

The results of the ring-opening polymerizations of L- lactide by ferric alkoxides at 130 °C for different time are shown in Table 2.13 (Wang *et* al., 2005). The highest molecular weight of the products was achieved by polymerization for 36 hr and then it decreased with prolonging polymerization time. This may also be due to the thermal depolymerization as the polymerization time increases.

Table 2.13 Effect of time on polymerization of DL- lactide in bulk (Wang *et* al., 2005)

Initiators	Time (hr)	Conversion (%)	$M_n \times 10^{-4}$	$M_w \times 10^{-4}$	PD
$Fe(OEt)_3$	24	92.6	12.98	19.98	1.54
	36	97.5	13.97	21.71	1.55
	48	98.0	10.63	16.36	1.54
	72	100.0	8.42	12.83	1.52
$Fe(OPr)_3$	24	90.8	9.83	15.92	1.62
	36	95.3	10.07	16.39	1.63
	48	96.7	9.03	14.76	1.63
	72	100.0	8.60	14.13	1.64
$Fe(O^iPr)_3$	24	86.2	6.24	10.73	1.72
	36	92.1	6.31	10.95	1.74
	48	96.5	5.43	9.45	1.74
	72	100.0	5.32	9.35	1.76
$Fe(OBu)_3$	24	90.5	2.37	4.42	1.87
	36	95.5	4.08	7.64	1.87
	48	96.5	3.03	5.71	1.89
	72	100.0	2.67	5.11	1.91

It was observed that ferric alkoxides showed high initiation activity in the bulk polymerization of lactide. Ferric alkoxide with larger ligand gave a lower molecular weight and a broader molecular weight distribution (Wang *et* al., 2005).

It can be concluded from the above data that parameters show very significant effect on the polylactide polymerization. In most of the cases, the effect of polymerization temperature and time is positive. Molecular weight and yield both increased up to a certain value and after that they decreased. It also causes the broadening of molecular weight distribution. This is probably due to the transesterification side chain reaction. The average molecular weight decreases at very high monomer-to-initiator ratio. This may be due to the reason that with such less number of growing polymer chains, presence of even a trace amount of chain terminating agent can limit the molecular weight.

2.4 Estimation of Kinetic Rate Constants

2.4.1 Polymerization Mechanism and Kinetics

Initiation prepares an ionic reactive centre, which adds many monomer units in a chain reaction or propagation and grows to a large size. The chain produced may be 'living' or 'terminated'. Ring-opening polymerization is initiated by primary initiators that could be ionic or molecular species. Initiation results in opening of the ring to form secondary initiator species M*, which may be either an ion or neutral molecule depending on the initiator. This can be generalized as

$$\text{R----Z} + \text{I} \longrightarrow \text{M*} \tag{2.1a}$$

where Z is the functional group in the monomer and I is the ionic or molecular initiator. Ionic ring-opening polymerization includes the reactions initiated by species such as Na^+, RO^-, HO^{--}, H^+ and BF_3. The prime initiator of molecular type is water. Ionic initiators are normally more reactive than the molecular ones. The initiator species grow by successive ring-opening additions of many monomer molecules.

$$\text{M*} + \text{nR—Z} \longrightarrow \text{M---(R—Z)}_n\text{*} \tag{2.1b}$$

The nature of the chain-growth process in ring-opening polymerization bears a superficial resemblance to chain polymerization. Only monomer adds to the growing chain in the propagation step. Species larger than monomer do not react with the growing chains. However, ring-opening polymerizations can have the characteristics of either chain or step polymerization or both.

Model: Termination by Transfer to the Monomer

The first step in the modeling of polymerization reactions is the postulation of a kinetic mechanism, which governs the set of reactions comprising the polymerization process. Initiation, propagation and termination reactions are characterized by rate constant k_o, k_j *and* k_t, respectively. In the ring-opening polymerization, for both (D, L) – lactide, initiation results in opening of the ring to form secondary initiator species P_1 (Odian, 1991). This can be generalized as:

$$M + I \xrightarrow{k_o} P_1 \tag{2.2}$$

where, M is the monomer, I is the initiator and P_1 is the activated polymer of single monomer unit . Initiation is characterized by a rate constant k_0. The initiator species grow by successive ring-opening additions of monomer molecules:

$$P_j + M \xrightarrow{k_{pj}} P_{j+1} \quad \text{, for all j} \geq 1 \tag{2.3}$$

where, Pj is the active polymer chain of j units. The rate constant k_{pj} refers to the jth propagation step on a chain.

The termination mechanism can be assumed to be the chain transfer to monomer, giving:

$$P_j + M \xrightarrow{k_{tj}} M_j + P_1 \text{, for all j} \geq 1 \tag{2.4}$$

In equation (2.4), it is assumed that the charged ring spontaneously forms P_1. Here M_j is the deactivated polymer of j repeat units, which will not participate in any reaction. It is assumed that each initiator molecule initiates one polymer chain. The growth of polymer chain continues till the monomer is completely consumed. The termination mechanism has been assumed to be the chain transfer to monomer only. There is no chain transfer to impurities such as water.

2.4.2 Determination of Kinetic Parameters by Modeling and Simulation

In order to design a reactor for the production of a polymer, the reactor configuration is optimized such that the polymer properties such as molecular weight distribution (MWD) are suitable for end-use. This MWD is expressed in terms of the distribution function itself or in terms of moments of this distribution. For a particular reactor type, say a batch reactor, this mechanism may lead via the mass balance equations to a set of equations governing the evolution of the concentrations of polymer with a given chain length. These equations might be solved in order to obtain the information necessary to understand the polymerization.

There are several ways to solve the mass balance equations. The first is the numerical method. Many attempts have been made for an approximate solution. One way is to replace the discrete variable of infinite range, the polymer chain length, by a continuous variable (Ray, 1972). The difference – differential equations become partial differential equations. (Bamford *et* al., 1958, Bamford and Jenkins 1960, Bamford and Tompa, 1954) used this procedure in their analysis of vinyl (radical chain growth) polymerization. (Zeman and Amundson, 1965 a,b) used it extensively to study batch and continuous polymerizations. Analytical solutions were obtained by taking terms from the Taylor series expansion of the activated polymer concentration function. It has been found that the accuracy of approximation is very strongly dependent on the number of terms retained in the Taylor's series expansion, as well as on the polymer chain length (Penczek *et* al., 1980). Falkovitz and

Segal, (1982) concluded that at least a second- order approximation is required in these analyses.

For chain length independent rate constants, the kinetic equations for free radical polymerization have been exactly solved (Kumar and Gupta, 1998, Venkateshwaran and Kumar, 1992). For chain length dependent rate constants, a series solution has been developed (Sailaja and Kumar, 1995, 1997). It is shown that the various rate constants can be directly determined from the experimental data on molecular weight distribution. Also, if the monomer concentration as a function of reaction time is known, differential equations describing the generation of activated polymer specie become linear equations with time dependent coefficients and its series solution has been given in terms of monomer conversion (Sailaja and Kumar, 1995, 1997). The authors have used a technique similar to the finite element method for boundary problems to divide the conversion into sub domains. The size of these steps is decided by a convergence criterion and results were determined at the end of the conversion domain through sequential computation. Other numerical methods make the use of a steady-state assumption (or a stationary state assumption) (Bamford *et* al., 1958) that the concentration of ions increases initially, but almost instantaneously reaches a steady state value. This method also assumes that the rate of initiation is equal to the rate of termination. In slower polymerizations, as in the PLA synthesis, the validity of steady-state assumption is not justified.

The steady-state may not be achieved if rate of initiation is greater than rate of termination. The concentration of propagating centers slowly increases throughout the polymerization, reaching a maximum late during the reaction, and then decreases. The expressions derived in the textbooks usually make the assumption of steady-state. The existence of steady-state can be ascertained by measuring the concentration of propagating specie as a function of time. This is certainly not an easy task. It should be mentioned that contrary to these considerations for rate of polymerization, the derivations for the expressions for number average degree of polymerization do not assume steady-state conditions. The ratios of various rate constants can be ascertained by careful experimentation. However, the determination of individual rate constants is a difficult task.

The other methods to solve mass balance equations include the discrete transform methods (Abraham, 1970, 1963, Bharucha-Reid, 1960; Feller, 1959, Howe, 1955). The limitation of the discrete transform methods (including method of moments) is that in complex polymerization mechanism it may not be possible to invert the generating function to give the polymer chain length distribution. Thus it would be difficult to handle the mass balance equations characterized by polymer chain length dependent rate constants. Also, with the advent of gel permeation chromatography, it has become possible to obtain the experimental determination of the entire polymer chain length distribution (rather than restricted to average molecular weights) (Tirrel *et* al., 1986, 1996). In another approach, the mass balance equations are bypassed and a statistical approach is adopted (Case, 1958, Kilkson, 1964, Lopez *et* al., 1980, Lowry, 1970, Macosko and Miller, 1976, Miller and Macosko, 1978). The statistical approach has the disadvantage of relying too heavily on intuition and so lacks the methodic reliability of the mass balance approach. Mehta, (2006) and Mehta *et* al., (2005, 2007) have developed a model for ring-opening polymerization of PLA and computed the kinetic rate constants for five different initiators. Additionally, they showed quantitatively presence of even trace amount of impurities like water can lead to a drastic reduction in molecular weight of the product.

2.5 Determination of Intrinsic Viscosity Using Ubbelohde Viscometer

Schlinder *et* al. (1979) plotted intrinsic viscosities of partly hydrolyzed PLA samples versus their number average molecular weights derived from carboxyl end group determinations. The data was represented by Mark-Houwink equations of the form

$$[\eta] = KT\ (a + 2)\ M_n^{a} \qquad (2.5)$$

where the gamma function of a + 2 takes into consideration that randomly degraded polymers will posses most probable molecular weight distribution in which M_w / M_n = 2.

Kricheldorf *et* al. (1988) reported that in case of PLA, the number average molecular weight (M_n) was determined by two independent methods, namely vapour pressure, osmometry and viscometry in combination with the Mark-Houwink equation. The Mark-Houwink equation is based on end-group titrations and includes two negative aspects. Firstly, the usefulness of the equation (2.6) is highly sensitive to variations of the molecular weight distribution. Secondly, the basic titration might have caused partial saponification of the polylactide samples.

$$[\eta] = 5.72 \times 10^{-4}\ M_n^{0.72} \qquad (2.6)$$

Dubois *et* at. (1991) reported that the universal calibration method was applied for poly (D, L- lactide) on the basis of the following viscometric relationships, valid in THF at 30 °C:

$$[\eta] = 1.25 \times 10^{-2}\ M^{0.717}, \quad \text{polystyrene} \qquad (2.7a)$$

$$[\eta] = 5.49 \times 10^{-2}\ M^{0.639}, \quad \text{poly (D, L- lactide)} \qquad (2.7b)$$

Nijenhuis *et* al. (1992) determined the molecular weights by using an Ubbelohde viscometer (Type Oa, ASTM, D-445). From the intrinsic viscosity of PLLA solutions in chloroform at 25 °C, the M_v and M_n were determined by using formula

$$[\eta] = 5.45 \times 10^{-4}\ M_v^{0.73} \qquad (2.8a)$$

$$[\eta] = 3.25 \times 10^{-4}\ M_n^{0.77} \qquad (2.8b)$$

Kricheldorf *et* al. (1994) reported that the [η] measurements were all conducted in chloroform, because benzene, the alternative solvent used in previous studies, is for health reasons not recommended anymore. The molecular weights calculated from equations (2.9a)-(2.9d) for selected polylactide were compiled. The molecular weight data show satisfactory agreement between the results obtained from equations (2.9b) and (2.9c). However, the values obtained from equations (2.9a) and (2.9d) do not agree with each other, nor with those obtained from equations (2.9b) or, (2.9c) and thus the origin and significance of this set of equations need a discussion.

$$[\eta] = 5.45 \times 10^{-4} M_n^{0.73} \quad \text{(for poly (L- lactide) at 30 °C)} \qquad (2.9a)$$
$$[\eta] = 2.21 \times 10^{-4} M_n^{0.77} \quad \text{(for poly (D, L- lactide) at 30 °C)} \qquad (2.9b)$$
$$[\eta] = 7.4 \times 10^{-4} M_n^{0.87} \quad \text{(for poly (L- lactide) at 20 °C)} \qquad (2.9c)$$
$$[\eta] = 1.32 \times 10^{-4} M_n^{0.58} \quad \text{(for poly (D, L- lactide) at 20 °C)} \qquad (2.9d)$$

All the four Mark-Houwink equations have in common the fact that the calibration is based on number average molecular weight (M_n). In the case of equations (2.9b) and (2.9c), the M_n values were determined by titration of the carboxyl end-groups. This method is risky because the ester bonds of the polylactide are sensitive to any kind of basic or, hydrolytic cleavage, even at room temperature in (neutral) water. The problem here is the existence of two different Mark-Houwink equations i.e. for poly (L- lactide) and poly (D, L- lactide). The samples used for calibrations were hydrolysed in THF. However, it was found that the high molecular weight poly (L- lactide) (η_{inh} > 1.0 dlg^{-1}) is not completely soluble in this solvent. Incomplete solubility leads to a non statistical hydrolysis, and therefore to problems with the calibrations as pointed out by Schindler and Harper.

Hyon *et* al. (1997) measured intrinsic viscosities of polylactide in chloroform at 25 °C and the viscosity average molecular weight (M_v) was calculated from the following equations:

$$[\eta] = 5.45 \times 10^{-4} M_v^{0.73} \quad \text{Poly (L- lactide)} \qquad (2.10a)$$
$$[\eta] = 2.21 \times 10^{-4} M_v^{0.77} \quad \text{Poly (D, L- lactide)} \qquad (2.10b)$$

Liang *et* al. (2003) determined intrinsic viscosity of PLA in chloroform determined by Ubbelohde viscometer at 25 °C. The viscosity average molecular weight was calculated according to the following equation

$$[\eta] = 2.21 \times 10^{-4} M_\eta^{0.77} \text{ (dl/g)} \qquad (2.11)$$

Dorgan *et* al. (2005) reported that Mark-Houwink and Schulz-Blaschke constants for dilute PLA solutions in chloroform at 30 °C, and in THF were determined.

For chloroform $[\eta] = 0.0131M_v^{\,0.777}$, (2.12a)

$[\eta] = 0.0153M_w^{\,0.759}$ mL/g, and $k_{SB} = 0.302.67$ (2.12b)

For THF, $[\eta] = 0.0174M_v^{\,0.736}$ mL/g and $k_{SB} = 0.289$ (2.12c)

In Mark-Houwink equation $[\eta] = kM^{\alpha}$; the values of α is 0.5 at the theta state and is in the range of 0.65 - 0.8 for linear random coils in the good solvent. It has been observed that α of the six- and four- armed polymers are smaller than the linear counterparts with the similar molecular weight, which indicates a smaller hydrodynamic size and a more compact structure of the branched polymers. These results further confirm the star-shaped structures of the polymers. It is observed that some of the molecular weights are not in accordance with the theoretical ones. This is because the Sn $(Oct)_2$ catalyzes transesterification reactions and the conversion did not reach 100% (Guo *et* al. 2010).

It can be seen that there are a large number of Mark-Houwink constants values reported in the literature. It would be advantageous to develop a generalized correlation between intrinsic viscosity and molecular weight.

CHAPTER – 3

MATERIALS AND METHODS

CHAPTER 3 MATERIALS AND METHODS

3.1 Materials

Stannous octoate, dibutyltindimethoxide, zinc stearate and triphenylphosphine (Sigma Aldrich, India) were obtained from suppliers and used as received. Polylactide samples (PDLLA, 0.18 dl/g), (PDLLA, 0.45 dl/g), (PDLLA, 0.68 dl/g), (PLLA, 0.90-1.20 dl/g) were obtained from Gangwal Chemicals Private Limited, Mumbai and used as received. Chloroform, acetone, diethyl ether, dry toluene and methanol (Ranbaxy Ltd., India) were also used without further purification. Tetrahydrofuran of analytical grade was from Central Chem, Slovakia. It was distilled immediately before use and stabilized with 0.2 g L^{-1} of 2, 6-di-terc-butyl-4-methyl phenol.

3.1.1 L- lactide ({3S, 6S}-3, 6-Dimethyl-1, 4-dioxane-2, 5- dione)

L- lactide was used as monomer in polymerization and purchased from Sigma Aldrich, India. It was purified through recrystallization in dry toluene and dried under vacuum in a dessicator overnight before use. The recrystallization of L- lactide was done three times with dry toluene (solvent) to improve the purity and the yield of L- lactide. The ^{1}H NMR analysis was performed on the recrystallized monomer after drying to confirm the absence of water and dry toluene. Figure 3.1 shows the chemical structure of the L- lactide monomer.

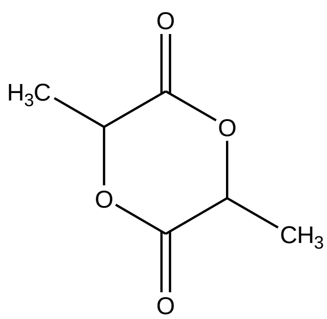
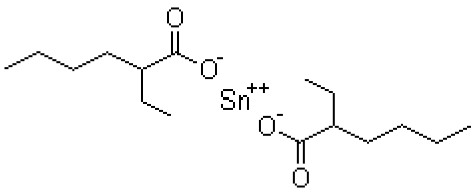
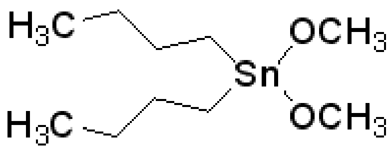
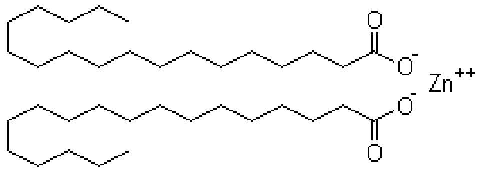
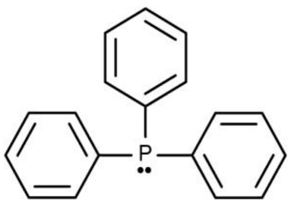


Figure 3.1 Chemical structure of L- lactide

3.1.2 Initiator (s) and Co-Initiator

Stannous octoate, dibutyltindimethoxide and zinc stearate were used as initiators during polymerization reactions. Triphenylphosphine, a Lewis base, was used as co-initiator. Table 3.1 shows the chemical structures of various initiator (s) and co-initiator.

Table 3.1 Chemical structures of various initiator (s) and co-initiator

S.No.	Initiator (s)/Co-initiator	Chemical structure
1.	Stannous Octoate (Initiator)	
2.	Dibutyltindimethoxide (Initiator)	
3.	Zinc Stearate (Initiator)	
4.	Triphenylphosphine (Co-initiator)	

3.2 Experimental Set-up

Two different experimental set-ups were used for polymerization experiments with very fine temperature control. In one set-up, polymerization reactions were carried out under nitrogen atmosphere and in the other, reactions were carried out under vacuum.

3.2.1 Polymerization Under Nitrogen Atmosphere

The experimental set up has the provision of evacuating the batch reactor and fluxing it with dry nitrogen (Fig. 3.2). The reaction vessel consisted of four necked round bottom borosil flask of 250 ml capacity. A teflon stirrer driven by a variable speed motor was inserted into the vessel through the middle neck. The first side neck of glass rector was used for the supply of nitrogen through drylite (silica mesh) from nitrogen cylinder ('A' grade). Vacuum was applied by another side neck to the glass reactor by using a vacuum pump. Fourth neck was used to release nitrogen gas through glass trap containing oil (bubbles indicated the release of nitrogen gas). Vacuum and nitrogen gas was allowed to pass through the glass reactor alternatively for three times at the start of reaction for achieving complete inert atmosphere inside the glass reactor. The glass reactor was heated in an oil bath and stirred with a teflon stirrer. The synthesis was carried out under a blanket of dry nitrogen till the completion of the polymerization. The entire set up was housed in a fume hood.

3.2.2 Polymerization Under Vacuum

Some experiments were carried out under vacuum only after the dispersion of initiator was done in the recrystallized monomer with the solvent diethyl ether. After proper dispersion, solvent was evaporated with rotaevaporator. Polymerization was carried out in five different bottles (Fig. 3.3). Each bottle was sealed under vacuum and then immersed in an oil bath which has a very fine control over temperature.

Figure 3.2 Experimental set-up for polymerization under nitrogen atmosphere

Figure 3.3 Experimental set-up for polymerization under vacuum

3.3 Polymerization

Exploratory Experiments

Poly(lactic acid), (PLA) was successfully synthesized in the very first experiment, which was carried out in air and with relatively poor temperature control. The monomer (L- lactide), 1 gm, and a drop of initiator (stannous octoate) were heated and stirred for approximately 3 hrs at 120 °C. Solid product obtained was dissolved in 10 ml of acetone and shaken for 30 min at 50 °C. The solution was filtered and the polymer was precipitated with methanol (30 ml for 7 hr). The solid precipitate was filtered and kept in a vacuum dessicator for about 24 hrs. The precipitate was indeed PLA, as confirmed by FTIR.

After that, an experimental set up has been established for polymerization experiments with very fine control over temperature and dry nitrogen cover in the reaction flask.

3.3.1 Synthesis of Polylactide Under Nitrogen Atmosphere

Different initiators (stannous octoate, dibutyltindimethoxide, and zinc stearate with and without triphenylphosphine as co-initiator) were used for the synthesis of polylactide over a wide range of monomer to initiator ratios (500 to 5000) under nitrogen atmosphere. The recrystallized monomer and initiator was dispersed with diethylether and after proper dispersion, solvent was evaporated using rotaevaporator. The monomer and initiator were vigorously mixed in a four-necked round bottom flask (glass reactor) equipped with a PTFE stirrer. Flask was thermostated in an oil bath at 130 (± 1) °C. One neck of glass reactor was used for applying vacumm with a vacuum pump. Nitrogen gas was applied through drylite to another side neck of glass reactor. Vacuum was applied at the start of reaction and dry nitrogen gas was allowed to pass through the reation mixture through out the course of the reaction. The third neck of the glass reactor was used to vent nitrogen gas. In each polymerization, different samples were taken from the glass reactor with glass spatula into a conical flask by increasing the nitrogen gas flow for kinetic estimation. The maximum polymerization time was 30 hr with stannous octoate, 45 hr with dibutyltindimethoxide and 60 hr with zinc stearate. The products obtained were dissolved in chloroform and precipitated in cold methanol. These were dried in a vacumm dessicator for 24 to 30 hr.

3.3.2 Synthesis of Polylactide Under Vacuum

Different initiators (stannous octoate, dibutyltindimethoxide, and zinc stearate with and without triphenylphosphine as co-initiator) were used for the synthesis of polylactide over a wide range of monomer to initiator ratios (500 to 5000) under vacuum. The recrystallized monomer and initiator were dispersed with diethylether and after proper dispersion, the solvent was evaporated using rotaevaporator. The resultant mixture was equally distributed among five different reagent bottles, and vacuum was applied at the start of the reaction. Reagent bottles were thermostated in an oil bath at 130 (± 1) °C. In each polymerization, at different intervals of time, bottles were taken out from the oil bath for kinetic estimation. The maximum polymerization time was 30 hr with stannous octoate, 133 hr with dibutyltindimethoxide and 76 hr with zinc stearate. The products obtained were dissolved in chloroform and precipitated in methanol. These were dried in a vacumm dessicator for 24 to 30 hr.

3.4 Viscometry Method

Ubbelohde viscometer was used to find the intrinsic viscosity of synthesized polymer samples. The Ubbelohde viscometer is also called as "suspended level viscometer" because the liquid initially drawn into the small upper bulb is not connected to the reservoir as it flows down the capillary during measurement. The capillary is suspended above the reservoir. In conjunction with the pressure-equalization tube, this ensures that the only pressure difference between the top of the bulb and the bottom of the capillary is that due to the hydrostatic pressure i.e., the weight of the liquid. Ubbelohde viscometer with polymer sample was placed in viscometer bath which was controlled at 30(±0.1) °C. An automatic cooling/heating system maintained the desired temperature. (Fig. 3.4). Time of flow of solution and solvent was determined using the viscometer.

Figure 3.4 Intrinsic viscosity set-up

Time of flow of polymer solution = $t_{solution}$

Time of flow of solvent = $t_{solvent}$

Relative viscosity $\eta_{rel} = t_{solution} / t_{solvent}$ (3.1)

Specific viscosity $\eta_{sp} = (\eta_{solution} - \eta_{solvent}) / \eta_{solvent}$ (3.2)

Reduced viscosity $\eta_{red} = \eta_{sp} / C$ (3.3)

Inherent viscosity $\eta_{inh} = \ln\eta_{rel} / C$ (3.4)

Figure 3.5 shows the graph between reduced and inherent viscosity on the y-axis and concentration on the x-axis. Intercept on the y-axis gives the value of intrinsic viscosity.

Intrinsic viscosity $$[\eta] = \lim_{c \to 0} \frac{\eta_{sp}}{c} \equiv \lim_{c \to 0} c^{-1} \ln \eta_{rel} \quad (3.5)$$

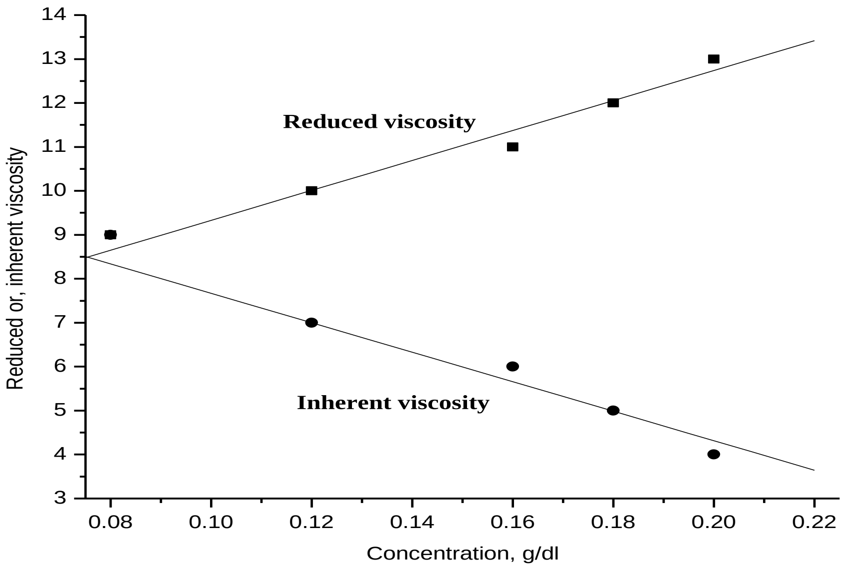


Figure 3.5 Graph between η_{red} and η_{inh} vs concentration

The intrinsic viscosity is defined as the limiting value of the specific viscosity/concentration ratio at zero concentration. Intrinsic viscosity is determined by measuring the relative viscosity at several concentrations and then extrapolating the specific viscosity to zero concentration.

3.5 Characterization Techniques

Characterization of synthesized polylactide was done by Size Exclusion Chromatography (SEC), Proton Nuclear Magnetic Resonance (^{1}H NMR) and Fourier Transform Infrared (FTIR) spectroscopy.

3.5.1 Size Exclusion Chromatography (SEC)

The molar masses of products were determined by SEC analysis using THF. Differential Refractometric Detector was from Waters, USA. Two polystyrene/divinylbenzene linear columns from PSS, Germany were applied. Injection volume was 50 µL and injected concentration was 2 mg ml^{-1}. Elution rate was 1 ml min^{-1}. Molar mass averages M_w and M_n of samples were calculated by means of DataApex software applying calibration with polystyrene standards. According to the IUPAC terminology, the molar mass values obtained in this way are to be called as “polystyrene equivalent molar masses”.

3.5.2 Proton Nuclear Magnetic Resonance (^{1}H NMR)

The ^{1}H NMR spectra were recorded on Brucker Avance II Spectrometer operating at 400 MHz. NMR spectrum was recorded in $CDCl_3$ solvent. NMR is unique technique for the direct detection of hydrogen bonding interactions, chemical identification and conformational analysis of chemicals whether synthetic or natural. The sample amount depends on the experiment you are performing. The higher concentration will lead to difficult shimming and broadened lines. It is recommended to keep the amount of sample below 20 mg. The most used NMR solvent is deuterated chloroform ($CDCl_3$).

3.5.3 Fourier Transform Infrared (FTIR) Spectroscopy

FTIR spectra were recorded using KBr pellets on Perkin Elmer FTIR Spectrometer. FTIR spectroscopy is used primarily for qualitative and quantitative analysis of organic compounds, and also for determining the chemical structure of many inorganic compounds. The finely powdered potassium bromide will absorb more humidity (it is hygroscopic) from the air and therefore lead to an increased background in certain ranges. Add about 1 to 2 % of sample, mix and grind to a fine powder. For very hard samples, add the sample first, grind, add KBr and then grind again.

CHAPTER – 4

RESULTS AND DISCUSSION

CHAPTER 4 RESULTS AND DISCUSSION

4.1 Synthesis of Polylactide, PLA using Stannous Octoate with/without Triphenylphosphine

4.1.1 Synthesis of PLA with Stannous Octoate

Synthesis of PLA has successfully been carried out using stannous octoate as an initiator under two different environments: inert atmosphere and vacuum. The anionic ring-opening polymerization mechanism proposed for the situation as discussed in section 4.1.1.3,

(i) Under inert atmosphere, and

(ii) Under vacuum

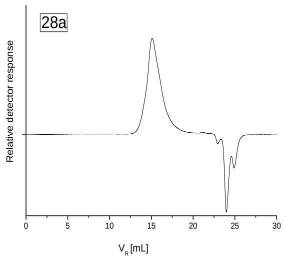
4.1.1.1 Polymerization Under Inert Atmosphere

Initially, in the runs with (M_o/I_o) ratios 346 and 693, very low molecular weight of polylactide was produced. After proper dispersion of initiator in monomer with diethyl ether as solvent, polylactide of high molecular weight was obtained and a single peak or, unimodality was observed in the SEC chromatograms. A set of experiments were then carried out over a wide range of monomer to initatior ratios (346 to 5076). The monomer and initiator were vigorously mixed in a four-necked round bottom flask equipped with a teflon stirrbar. The reactants were maintained at a constant temperature of 130 (± 1) °C by putting fask in an oil bath. One neck of the glass reactor was used for applying vacumm with a vacuum pump. Nitrogen gas was applied through drylite to the other side neck of glass reactor. Vacuum was applied at the start of reaction and dry nitrogen gas was allowed to pass through the reaction mixture throughout the course of the reaction. The third neck of the glass reactor was used to vent nitrogen gas. The maximum polymerization time was 29 hr. The products obtained were dissolved in chloroform and precipitated in methanol. These were dried in a vacumm dessicator for 24 to 30 hr. The polymer samples were then subjected to separation using the size exclusion chromatography. Table 4.1 lists the values of M_n, M_w and PD for different monomer to initiator ratios and polymerization time for the synthesis of polylactide with stannous octoate at 130 (± 1) °C. Figure 4.1 shows the SEC chromatograms of PLA synthesized with stannous octoate.

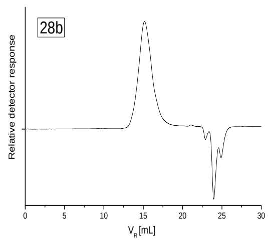
Table 4.1 Synthesis of PLA (under inert atmosphere) with stannous octoate (initiator) at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
346	3	602	1866	3.10
693	4	460	1478	3.21
693	4	869	2000	2.30
527	0.42	23781	63502	2.67
	28.5	30535	67649	2.21
1048	0.75	31604	55050	1.74
	28.42	27962	59661	2.13
2561	1	34021	53051	1.55
	28.25	14266	43698	3.06
5076	2.5	8017	12852	1.60
	2.92	7932	13491	1.70
	27.42	9754	18589	1.90

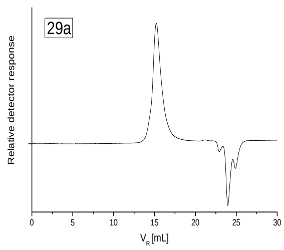
From the data presented in Table 4.1 it is seen that at higher (M_o/I_o) ratio values PD's are relatively independent of reaction time and M_w values. The highest molecular weight (M_n = 34021) of the products was achieved by polymerization with narrow polydispersity (PD = 1.55) for 1 hr with (M_o/I_o) ratio 2561, and then it decreased (M_n = 14266) with prolonging polymerization time and broadening of the polydispersity (PD = 3.06). This may also be due to the thermal depolymerization as the polymerization time increases. It also has been observed that with the increase of monomer to initiator (M_o/I_o) ratio 346 to 2561, molecular weight goes on increasing (M_n = 602 to 34021) but after that it decreased gradually (M_n = 8017) with decreasing amount of initiator and prolonging polymerization time. It is possible that a higher initiator concentration will result in more growing chains, thus giving a lower molecular weight product while a lower initiator concentration will produce less initiation sites, thus leading to lower monomer conversion and higher molecular weight of polylactide. The average molecular weight decreases at very high monomer to initiator ratio. This may be due to the reason that with such less number of growing polymer chains, presence of even a trace amount of chain terminating agent can limit the molecular weight.



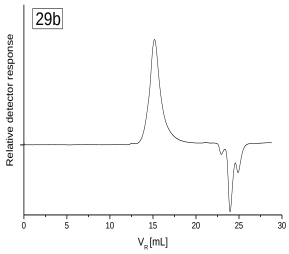
$V_r = 15.1$ $M_n = 23781$ $M_w = 63502$



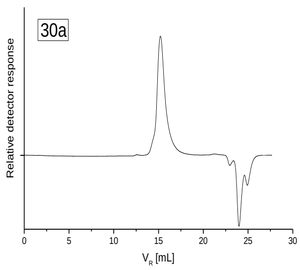
$V_r = 15.15$ $M_n = 30535$ $M_w = 67649$



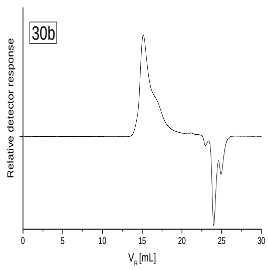
$V_r = 15.21$ $M_n = 31604$ $M_w = 55050$



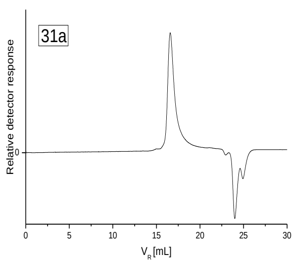
$V_r = 15.18$ $M_n = 27962$ $M_w = 59661$



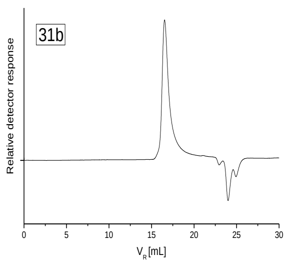
$V_r = 15.21$ $M_n = 34021$ $M_w = 53051$



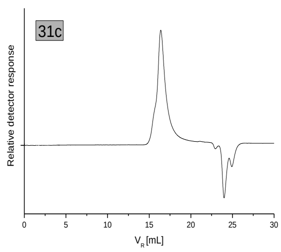
$V_r = 15.14$ $M_n = 14266$ $M_w = 43698$



$V_r = 16.58$ $M_n = 8017$ $M_w = 12852$



$V_r = 16.53$ $M_n = 7932$ $M_w = 13491$



$V_r = 16.39$ $M_n = 9754$ $M_w = 18589$

Figure 4.1 SEC of PLA synthesized (under inert atmosphere) with stannous octoate

Single peak or, unimodality is observed in the SEC chromatograms of polylactide synthesized by stannous octoate (Fig. 4.1). Here V_r represents the retention volume in ml. and other symbols have their usual meanings. The multiple positive and negative peaks at high V_r's may be due to initiators, air, etc. The large negative peak with V_r in the range 22 – 24 ml may be due to the unreacted monomer or traces of solvents left during the sample purification. Their presence (unreacted monomer or, solvents) is not too important as far as the solvent peaks are separated from the polymer peaks in SEC chromatograms. They serve as internal standards and do not affect the calculated molar values. The reason for single or, unimodal peaks in SEC chromatograms are due to the proper dispersion of initiator in monomer with diethyl ether (solvent).

The FTIR analysis showed that polylactide had been formed. The IR spectrum of PLLA shows that the strong band at 1758.0 cm^{-1} corresponds to C=O bond stretching and the bands at 2999.2 cm^{-1} and 2948.7 cm^{-1} are assigned to C-H stretching of $–CH_3$. The most characteristic absorption of ester C-O stretching at 1189.2 cm^{-1} is also observed. The peak at 3507.6 cm^{-1} is due to the stretching of hydroxyl group O-H. Figure 4.2 shows the FTIR of polylactide.

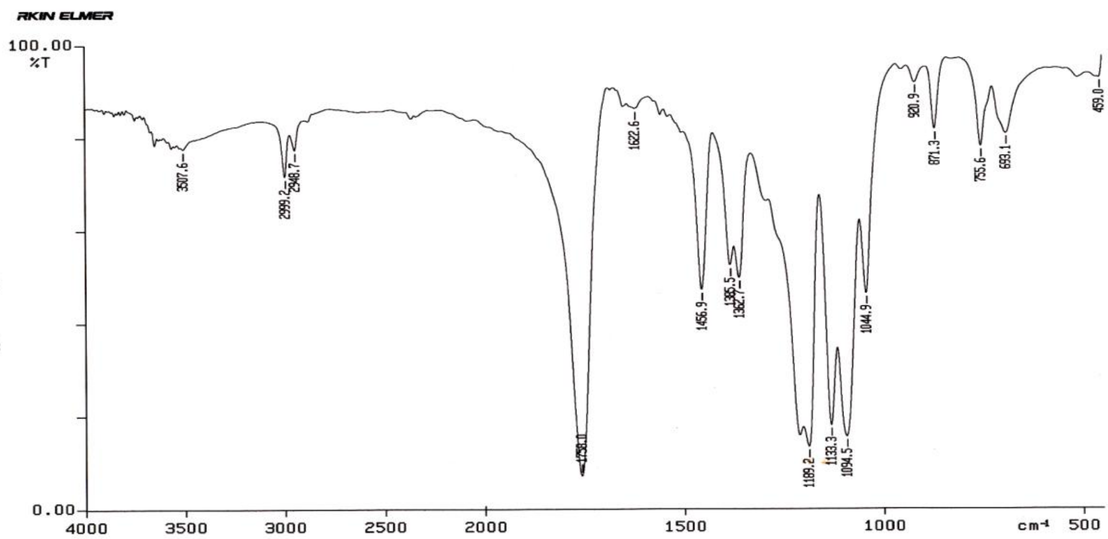


Figure 4.2 FTIR spectra of polylactide

The [1]H NMR spectra were recorded on Brucker Avance II Spectrometer operating at 400 MHz using $CDCl_3$ as solvent. Poly (L- lactic acid), PLLA product bears –OH and –COOH as its two end groups. Figure 4.3 shows the structure of polylactide. The ^{1}H NMR spectrum of PLA is shown in Fig. 4.4. The resonance signal at (δ = 1.57) and (δ = 5.13 - 5.20) are assigned to PLLA. The resonance signal at (δ = 4.35) corresponds to the methine linked to the end group –OH. Thus, the characterization explained above demonstrates the fine structure of PLLA formed in the ring-opening polymerization. Figures 4.5 and 4.6 show the ^{1}H NMR spectra of PLLA and PDLLA. The ^{1}H NMR showed the presence of pure PLLA (monomer used was L- lactide), and not its enantiomer or a racemic mixture of polylactide.

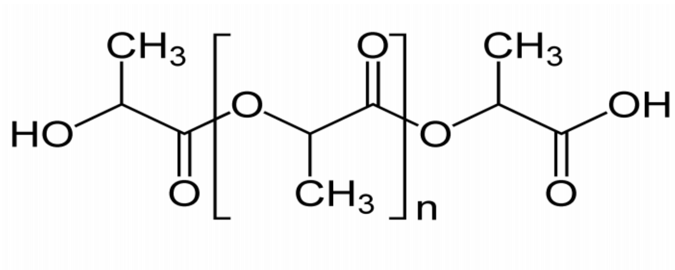


Figure 4.3 Structure of polylactide

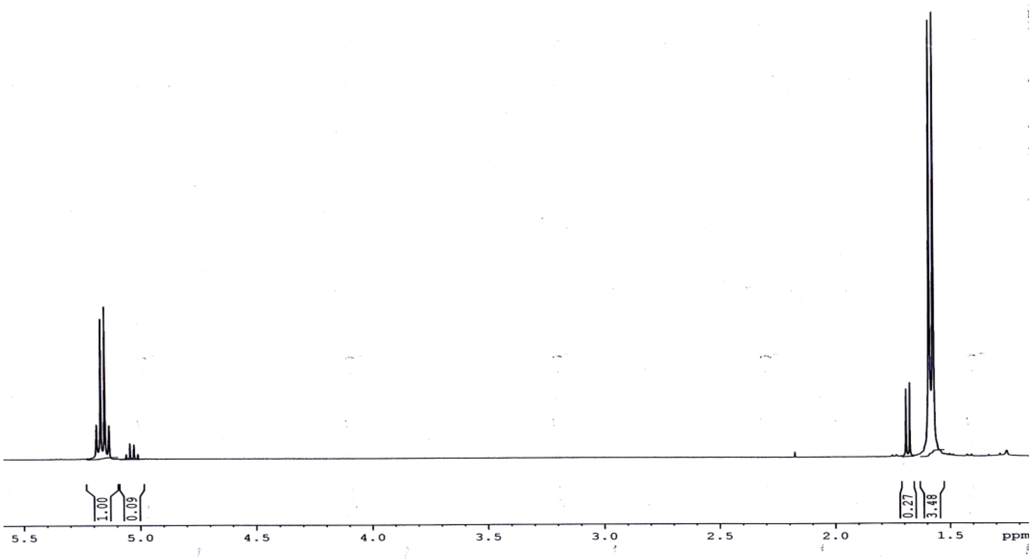


Figure 4.4 ^{1}H NMR spectra of PLLA

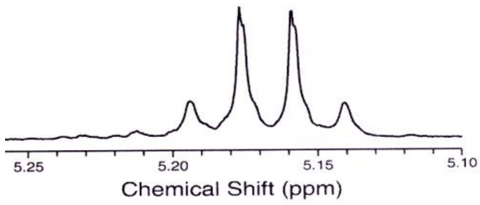


Figure 4.5 ^{1}H NMR spectra of PLLA

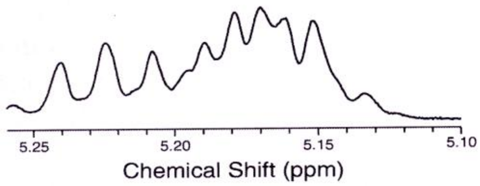


Figure 4.6 ^{1}H NMR spectra of PDLLA

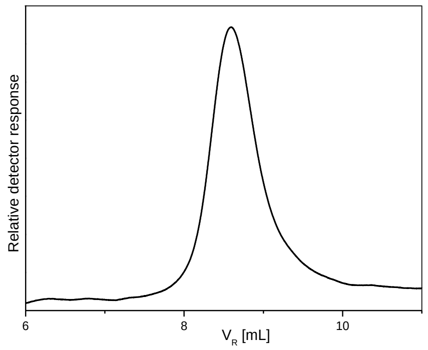
4.1.1.2 Polymerization Under Vacuum

Stannous octoate (initiator) was used for the synthesis of polylactide under vacuum. The recrystallized monomer and initiator were dispersed in diethylether and after proper dispersion, the solvent was evaporated using a rotaevaporator. The resultant mixture was equally distributed among five different reagent bottles, and vacuum was applied at the start of reaction. Reagent bottles were thermostated in an oil bath at 130 (± 1) °C. The monomer to initiator (M_o/I_o) ratio 2549 was used for polymerization because it has been observed from the previous polymerization (Table 4.1) that maximum molecular weight was produced at this range of monomer to initiator. The maximum polymerization time was 28 hr. The products obtained were dissolved in chloroform, precipitated in methanol and were dried in a vacumm dessicator for 24 to 30 hr. The polymer samples thus obtained were separated into PLA of different M_w using SEC technique. The resulting SEC chromatograms are shown in Fig. 4.7. Table 4.2 lists the values of M_n, M_w and PD for the PLA synthesized with stannous octoate at 130 (± 1) °C at different reaction time.

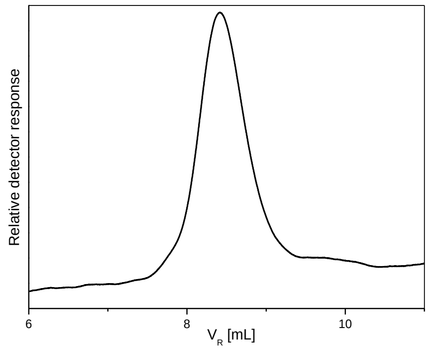
Table 4.2 Synthesis of PLA (under vacuum) with stannous octoate at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
2549	0.50	14656	19416	1.25
	1	18667	24645	1.32
	3	25435	29577	1.16
	5	22345	27188	1.21
	28	32502	44922	1.38

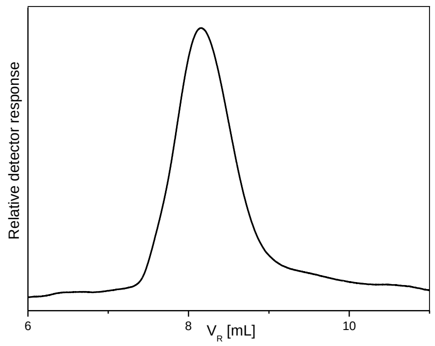
From Table 4.2 it is seen that values of PD's are quite less and are more or less independent of reaction time. The number and weight average molecular weight of polylactide goes on increasing with increase of polymerization time.



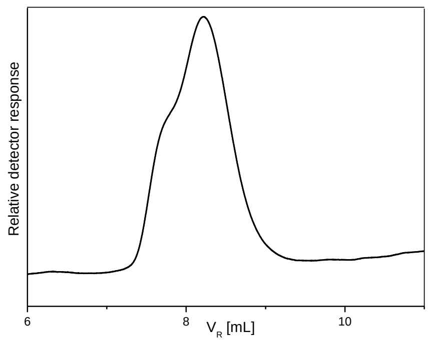
V_r = 8.6 M_n = 14656 M_w = 19416



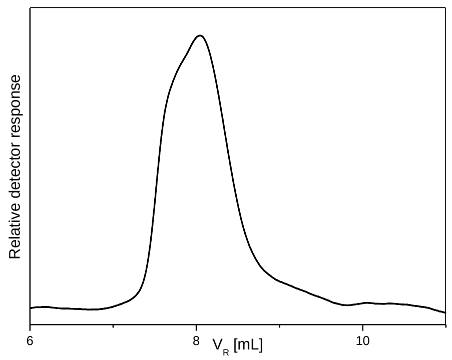
V_r = 8.42 M_n = 18667 M_w = 24645



V_r = 8.22 M_n = 25435 M_w = 29577



V_r = 8.15 M_n = 22345 M_w = 27188



V_r = 8.05 M_n = 32502 M_w = 44922

Figure 4.7 SEC of PLA synthesized (under vacuum) with stannous octoate

Mostly, single or unimodal peaks were observed in SEC chromatograms of PLA synthesized with stannous octoate, and as discussed earlier it suggests uniform dispersion of the initiator.

4.1.1.3 Proposed Anionic Ring-Opening Polymerization Mechanism of Stannous Octoate

The sequence of ring-opening polymerization mechanism for PLA using stannous octoate is shown in Fig. 4.8. The Stannous octoate opens the ring at O=CH−O− position of the monomer molecule giving rise to product P_j and the sequence continues further as shown ultimately giving a polymer M_j and stannous octoate back.

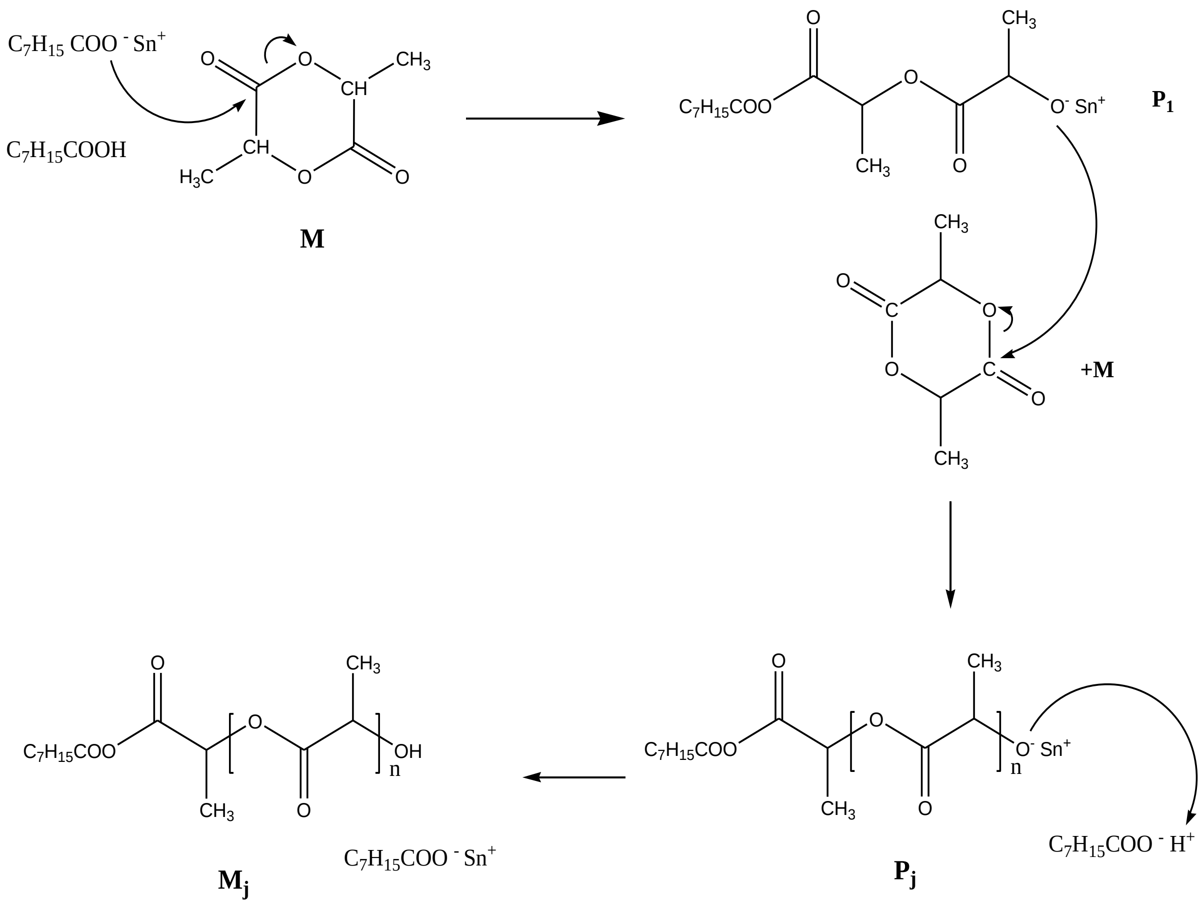


Figure 4.8 Proposed anionic ring-opening polymerization mechanism of stannous octoate

4.1.2 Synthesis of PLA with Stannous Octoate/Triphenylphosphine

Triphenylphosphine as co-initiator has been used along with stannous octoate as an initiator for the synthesis of polylactide, PLA under two different environments. An anionic ring-opening polymerization mechanism has been proposed and shown in Fig. 4.1.2.3.

(i) Under inert atmosphere, and
(ii) Under vacuum

Use of Triphenylphosphine as Co-initiator with Stannous Octoate

The addition of an equimolar amount of a Lewis base, particularly triphenylphosphine into 2-ethylhexanoic acid, significantly enhances the lactide polymerization rate in bulk. Triphenylphosphine has two beneficial effects: it increases the polymerization rate and delays the occurrence of the undesirable back biting reactions at least at monomer/initiator ratio greater or equal to 5000 (Degee *et* al., 1999). So, triphenylphosphine as co-initiator was used to enhance the polymerization rate and molecular weight of polylactide. Molecular weight increased from few thousands to several ten thousands g mol^{-1}.

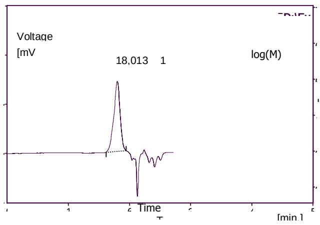
4.1.2.1 Polymerization Under Inert Atmosphere

Polymerization was carried out using stannous octoate (initiator) with triphenylphosphine (co-initiator) over a wide range of monomer to initiator ratios (540 to 4940) under nitrogen atmosphere. Procedure is same as explaind earlier in section 4.1.1.1. The maximum polymerization time was 28 hr. Table 4.3 lists the values of M_n, M_w and PD for the PLA synthesized with stannous octoate at different monomer to initiator ratios and reaction time. Figure 4.9 shows the SEC chromatograms of PLA synthesized with stannous octoate/triphenylphosphine.

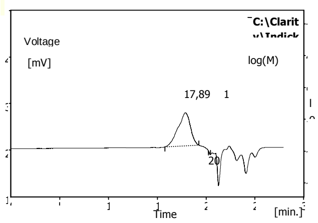
Table 4.3 Synthesis of PLA (under inert atmosphere) with stannous octoate/ triphenylphosphine at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
524	0.66	9527	11995	1.26
	25.58	31216 8795	39680 10005	1.27 1.13
1040	2.16	4921	7116	1.44
	7.83	7425	9762	1.31
2557	1.5	5760	6819	1.18
	2.5	6200	7208	1.16
	3.5	45206 7081	49151 8163	1.08 1.15
	4.5	122495 7343	133120 8596	1.08 1.17
	25.33	9942	14270	1.43
4940	1.5	6244	7546	1.20
	2.5	5689	8356	1.46
	27.42	22682 7134	26978 8013	1.18 1.12

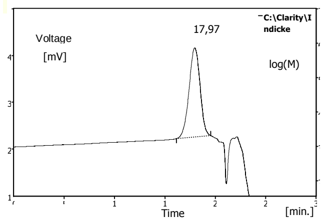
From Table 4.3 it is seen that values of PD's are nearly independent of reaction time for higher (M_o/I_o) ratios and decrease gradually for M_o/I_o ratio = 524. It has also been observed that polydispersity has been reduced with the use of triphenylphosphine as co-initiator during polymerization. Table 4.3 shows that with the increase of polymerization time, the number and weight average molecular weight goes on increasing and after prolonged reaction time, the molecular weight decreased gradually. It has also been seen that with increase of monomer to initiator ratio (M_o/I_o ratio = 1040 to 2557), molecular weight of polylactide increased and with further increase of monomer to initiator ratio (M_o/I_o ratio = 4940), molecular weight of polylactide decreased. Maximum molecular weight (M_n = 122495) and narrow polydispersity (PD = 1.08) was observed in M_o/I_o ratio = 2557 and the reason is same as explained earlier in section 4.1.1.1. The bimodal behavior of SEC as reflected in some of the average molecular weight values in Table 4.3 is proverbially due to poor dispersion of initiator in the polymerization mass. This is discussed in detail in section 4.1.3.



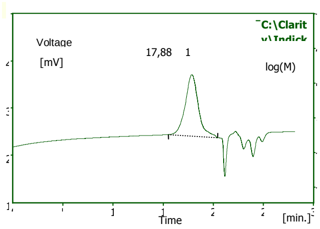
V_r = 18.01 M_n = 4921 M_w = 7116



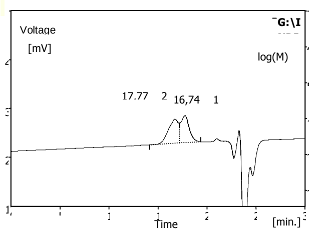
V_r = 17.89 M_n = 7425 M_w = 9762



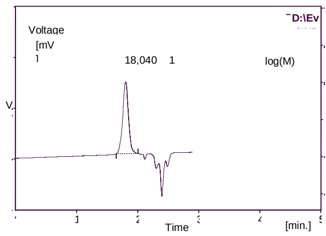
V_r = 17.97 M_n = 6244 M_w = 7546



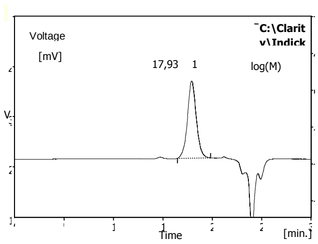
V_r = 17.88 M_n = 5689 M_w = 8356



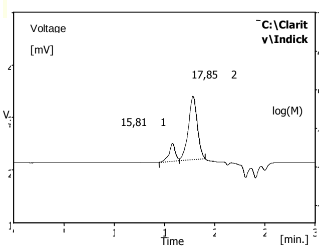
V_r1 = 16.74 M_n1 = 22682 M_w1 = 26978
V_r2 = 17.77 M_n2 = 7134 M_w2 = 8013



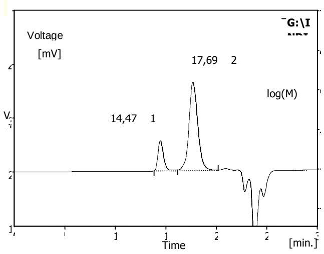
V_r = 18.04 M_n = 5760 M_w = 6819



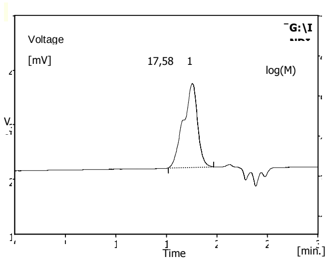
V_r = 17.93 M_n = 6200 M_w = 7208



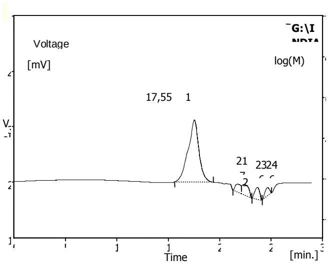
V_r 1 = 15.81 M_n1 = 45206 M_w1 = 49151
V_r 2 = 17.85 M_n2 = 7081 M_w2 = 8163



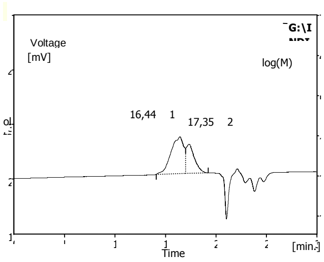
V_r 1 = 14.47 M_n1 = 122495 M_w1 = 133120
V_r 2 = 17.69 M_n2 = 7343 M_w2 = 8596



V_r = 17.58 M_n = 9942 M_w = 14270



V_r = 17.55 M_n = 9527 M_w = 11995



V_r 1 = 16.44 M_n1 = 31216 M_w1 = 39680
V_r 2 = 17.35 M_n1 = 8795 M_w1 = 10005

Figure 4.9 SEC of PLA synthesized (under inert atmopshere) with stannous octoate/ triphenylphosphine

The large negative peak with V_r in the range 22 – 24 mL may be the unreacted monomer. The shifts in V_r of this peak are strange. The multiple positive and negative peaks at high V_r may be from initiators, air, etc. Due to the non dispersion of initiator with monomer, bimodality and even trimodality was seen in SEC chromatograms (Fig. 4.9). Some trimodal samples contain three different polymer species with distinct molar mass and polydispersity.

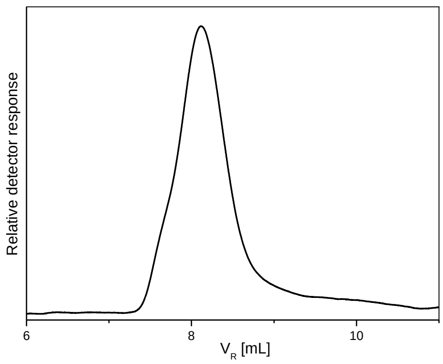
4.1.2.2 Polymerization Under Vacuum

Stannous octoate (initiator) and triphenylphosphine (co-initiator) were used for the synthesis of polylactide under vacuum only. Procedure is same as explaind earlier in section 4.1.1.2. The maximum polymerization time was 26 hr. Table 4.4 lists the values of M_n, M_w and PD at various polymerization times for PLA synthesized with stannous octoate/triphenylphosphine at 130 (± 1) °C. Fig. 4.10 shows the SEC chromatograms of PLA synthesized with stannous octoate/triphenylphosphine. Mostly, single or, unimodal peaks are observed in SEC chromatograms. Figure 4.11 shows the proposed anionic ring-opening polymerization mechanism of stannous octoate/triphenylphosphine.

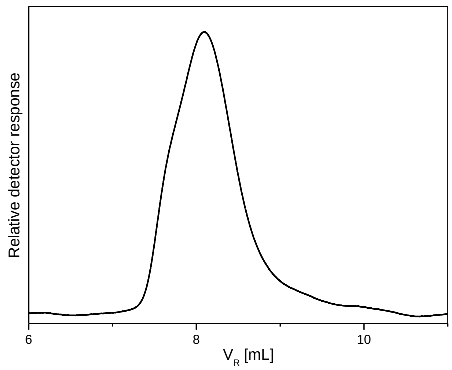
Table 4.4 Synthesis of PLA (under vacuum) with stannous octoate/triphenylphosphine at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
2557	1	21972	35814	1.63
	2	24303	39245	1.61
	4	41689	53237	1.27
	6	36142	50059	1.38
	26	33093	48114	1.45

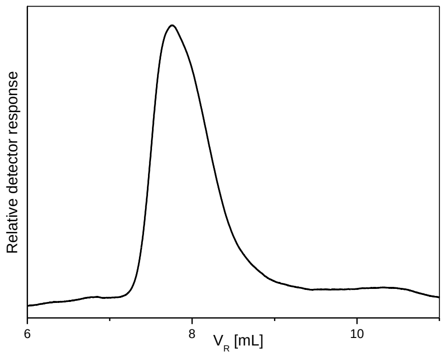
Table 4.4 shows that with the increase of polymerization time (1 to 4 hr), the number and weight average molecular weight increased (M_n = 21972 to 41689) and then decreased gradually. Single monomer to initiator (M_o/I_o) ratio 2557 was used during polymerization. Maximum molecular weight of polylactide (M_n = 41689) gave narrow polydispersity (PD = 1.27). It has also been observed that increase in molecular weight of polylactide, decrease the polydispersity value and decrease in molecular weight of polylactide, increase the polydispersity value. The reason is same as explained earlier in section 4.1.1.1.



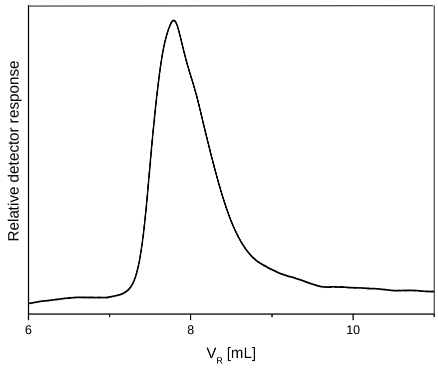
V_r = 8.11 M_n = 21972 M_w = 35814



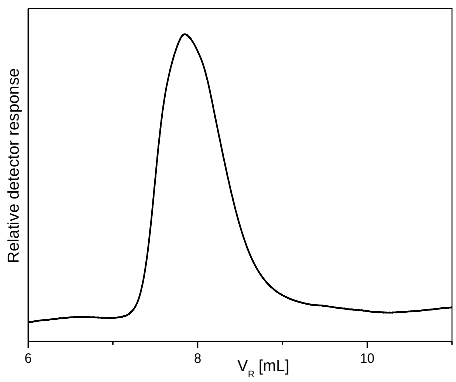
V_r = 8.10 M_n = 24303 M_w = 39245



V_r = 7.76 M_n = 41689 M_w = 53237



V_r = 7.79 M_n = 36142 M_w = 50059



V_r = 7.85 M_n = 33093 M_w = 48114

Figure 4.10 SEC of PLA synthesized (under vacuum) with stannous octoate/ triphenylphosphine

4.1.2.3 Proposed Anionic Ring-Opening Polymerization Mechanism of Stannous Octoate/Triphenylphosphine

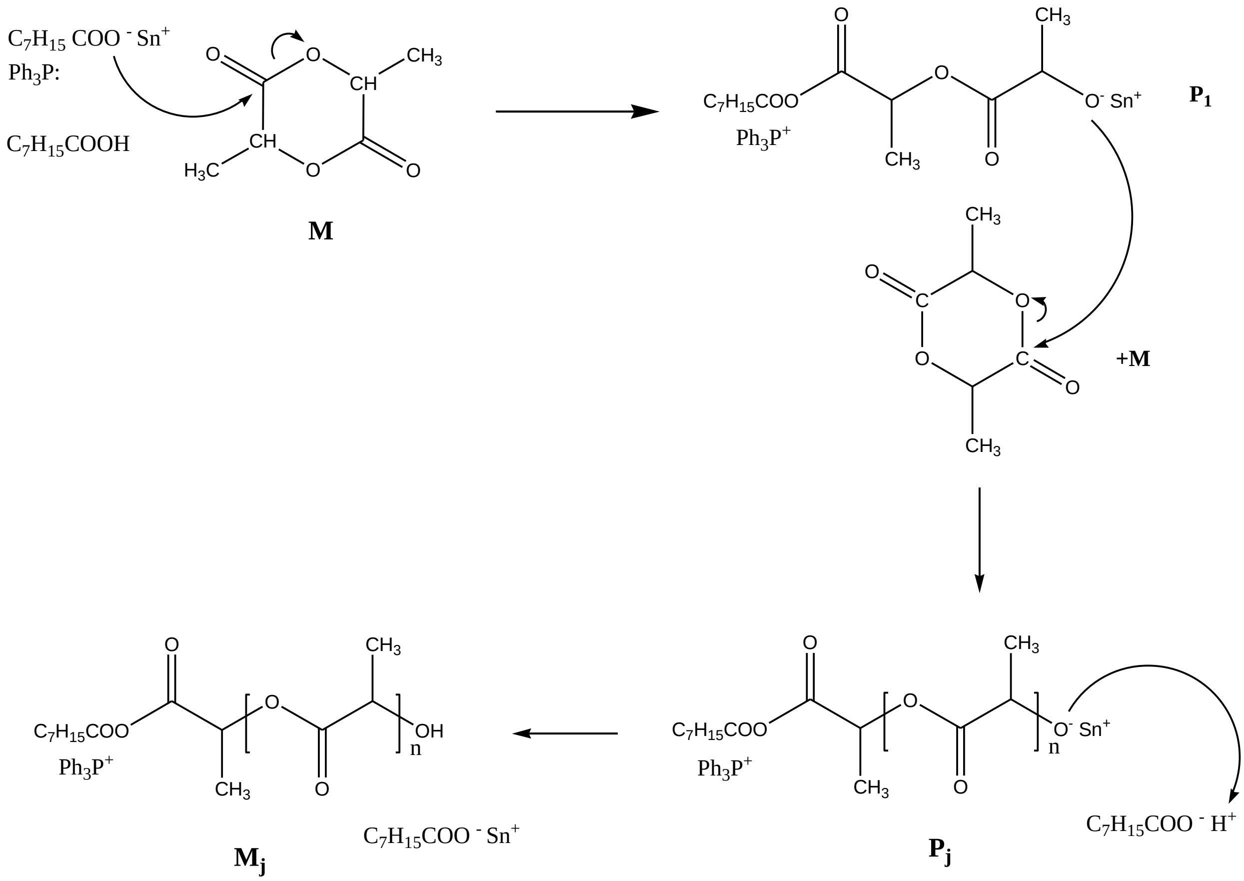


Figure 4.11 Proposed anionic ring-opening polymerization mechanism of stannous octoate/triphenylphosphine

4.1.3 Effect of Dispersion of Initiator on the Synthesis of Polylactide

Data with stannous octoate showed single values of molecular weight while data with stannous octoate/triphenylphosphine showed double values of molecular weight of PLA. The reason for bimodality or trimodality in SEC chromatogram was due to non dispersion of initiator with the monomer molecules. We did some experiments by taking monomer (L- lactide) and initiator (stannous octoate/triphenylphosphine) in round bottom flask and mixture was heated to 130 (± 1) °C and stirred with Teflon stirrer. Doublet peak was observed in SEC chromatogram. Out of double peaks, one peak showed high molecular weight and other peak showed low molecular weight. To reduce bimodality or, trimodality in the SEC chromatogram, it is very necessary to disperse initiator in the monomer molecules with diethylether (solvent). High molar mass polylactide were obtained and significantly sharp unimodal peaks were observed in the SEC chromatograms.

The number and weight average molecular weight has been determined by SEC. Fig. 4.12 showed the SEC chromatogram for PLA product using stannous octoate with triphenylphosphine as initiator under nitrogen atmosphere. The following are the results obtained from SEC chromatograms of product of polymerization under two conditions used in this work.

1. PLA with stannous octoate and triphenylphosphine under nitrogen atmosphere: M_{n1} = 122495 M_{w1} = 133120, M_{n2} = 7343 M_{w2} = 8596

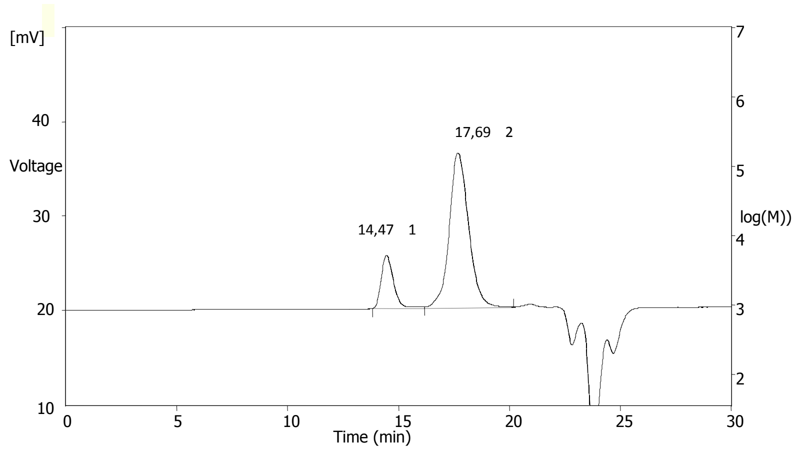


Figure 4.12 SEC of PLA (with stannous octoate and triphenylphosphine)

It was initially thought that the doublet observed in SEC might be due to two competing reactions: i) the lower MW peak due to polycondensation reactions (which normally give low MW polymer or oligomers at the same reaction temperature with tin compounds as initiators) and; ii) the higher MW peak due to ring-opening polymerization of lactide (Moon *et* al., 2000).

2. The second possibility is that the doublet may be due to the formation of cyclic and linear polylactide. The linear PLA has a higher molecular weight while cyclic has lower molecular weight (Stanford *et* al., 2010). As published in a recent study (http://www.almaden.ibm.com/st/chemistry/ps/initiators/RingOpening), a special emphasis is placed on mechanistic features of novel organo initiators that enable high reactivity and selectivity for the construction of complex polymer architectures. For example, in the presence of alcohols, N-heterocyclic carbenes are potent initiators for the ring-opening polymerization of lactide to generate linear polylactide (Fig. 4.13, pathway A). In the absence of alcohols, N-heterocyclic carbenes mediate the polymerization of lactide to cyclic polylactide of high molar mass and narrow molar mass distribution (Fig. 4.13, pathway B).

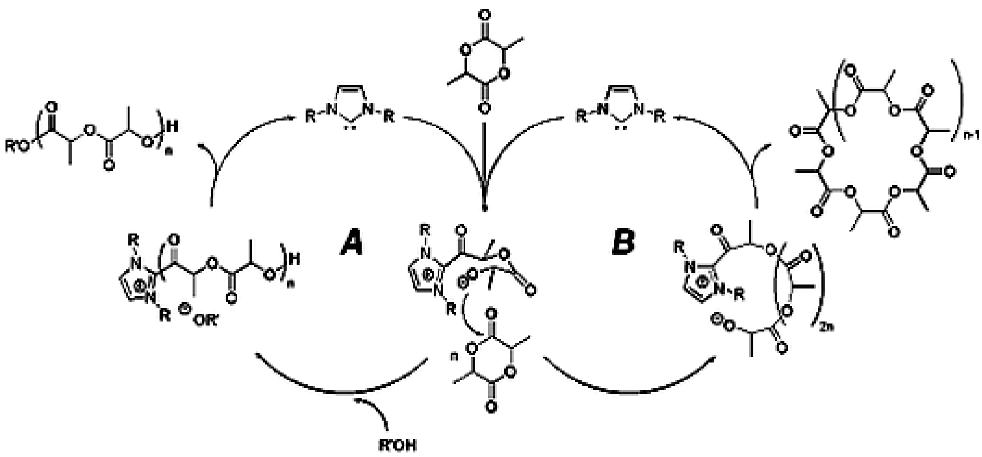


Figure 4.13 Pathway-A shows the production of linear PLA and pathway-B shows the formation of cyclic PLA

(Source: http://www.almaden.ibm.com/st/chemistry/ps/initiators/RingOpening)

The above pathways can possibly explain the bimodality in the SEC chromatogram of PLA; one peak shows the presence of linear PLA which gives high molecular weight while other peak shows the formation of cyclic PLA which gives low molecular weight compared to the linear PLA. When bimodality was observed in the first two sets of experiments, a third set of polymerization experiment was performed. These results are presented in Fig. 4.14 and discussed below.

SEC chromatogram of the PLA (pure stannous octoate) obtained in which the reaction was carried out under dry nitrogen atmosphere gives M_n = 34021 M_w = 53051. The negative peaks with high retention volumes are so called system peaks and are due to air dissolved in injected polymer solution and traces of water present in sample and possibly also due to the unreacted monomer. They can be ignored because they do not interfere with the PLA peaks.

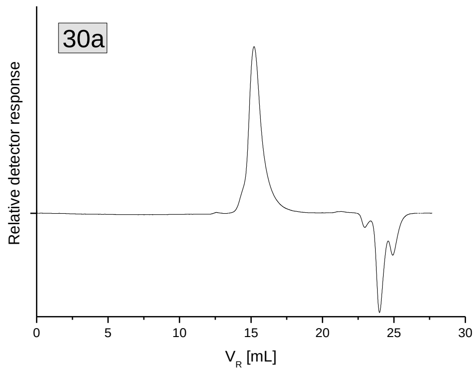


Figure 4.14 SEC of PLA (with pure stannous octoate)

It was observed that the pronounced bimodality or trimodality of PLA observed on the SEC chromatograms has been in principle removed with a proper dispersion of initiator in the monomer. Thus, bimodal or multimodal PLA was formed as result of the incomplete, imperfect mixing of initiator with monomer (Fig. 4.12).

As a cross-check of the result obtained, we also analyzed some of the commercial samples of polylactide, and found single peak in their SEC chromatogram (Fig. 4.15) indicating the accuracy of the SEC results obtained with prepared samples.

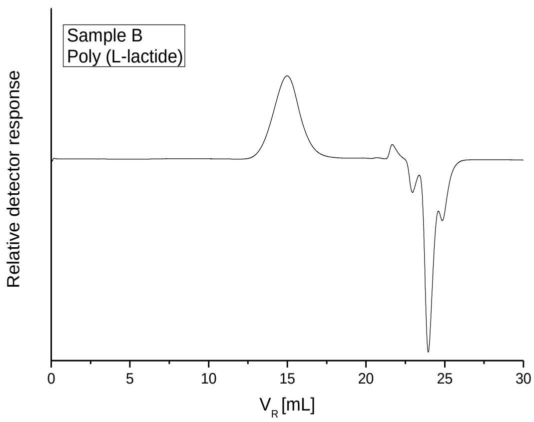


Figure 4.15 SEC of PLA (commercial sample)

The multimodality in the SEC chromatograms of the samples prepared, which were not mixed sufficiently, may be due the following reason. If there are a given number of initiator molecules at a particular location in the polymerizing mass, then the given number of monomer molecules will distribute themselves among the growing number of chains. Now, if the number of initiator molecules is less (relative to number of monomer molecules), then there will be few initiating chains and polymerization will result in longer polymer chains. If the number of initiator molecules is more, then more chains will be initiated resulting in a lower average molecular weight product.

Therefore, if there is poor dispersion, we can expect to get bimodality or, multimodality in the SEC chromatogram of the product thus formed.

4.1.4 Effect of Monomer to Initiator Ratio on Degree of Polymerization

Monomer to initiator ratio was varied from (500 to 5000) for the synthesis of PLA. The maximum molecular weight of PLA has been obtained when the (M_o/I_o) ratio was 2500 to 2600. Eenink (1987) reported that at lower values of (M_o/I_o) ratio, the initiator concentration I_o is considerably high. As (M_o/I_o) ratio increases, the number of initiator molecules decreases. So with an increase in (M_o/I_o) ratio there is a reduction in the number of chains onto which given monomer molecules can distribute themselves. Thus, the molecular weight increases with an increase in (M_o/I_o) ratio. With further increase in (M_o/I_o) ratio, the number of initiated chains decreases so much that with the same termination rate constant, there is quick termination of a significant percentage of chains, which results in lowering of molecular weight and peak formation in the curve (Fig. 4.16). It is possible that a higher initiator concentration will result in more growing chains, thus giving a lower molecular weight product while a lower initiator concentration will produce less initiation sites, thus leading to lower monomer conversion and higher molecular weight of polylactide. The average molecular weight decreases at very high monomer to initiator ratio. This may be due to the reason that with such less number of growing polymer chains, presence of even a trace amount of chain terminating agent can limit the molecular weight. A plot of experimentally observed polydispersities at various (M_o/I_o) ratios is compared with values predicted from Model 1 and 2. It is seen that at Model 2 predictions are closer to observed values up to (M_o/I_o) ratio 20000. Beyond which both models predict similar values which are much higher than experimental values.

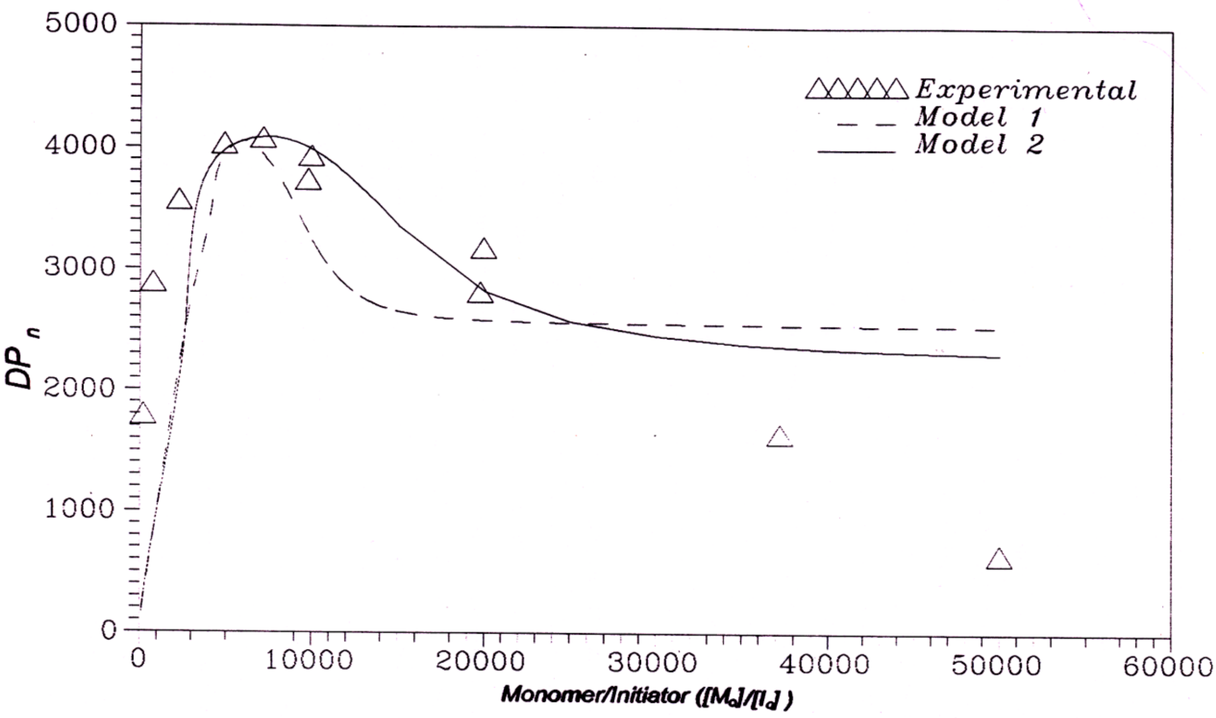


Figure 4.16 Effect of monomer to initiator ratio on degree of polymerization

(Source: Eenink, 1987)

4.2 Synthesis of Polylactide, PLA using Dibutyltindimethoxide with/ without Triphenylphosphine

4.2.1 Synthesis of PLA with Dibutyltindimethoxide

Dibutyltindimethoxide as an initiator was used for the synthesis of polylactide under two different environments: inert atmosphere and vacuum. An anionic ring-opening polymerization mechanism has been proposed which is same as shown earlier in section 4.1.1.3.

(i) Under inert atmosphere, and
(ii) Under vacuum

Low molecular weight of PLA was obtained during polymerization. The reason might be due to the fact that Bu_3SnOMe and $Bu_2Sn(OMe)_2$ are effective transesterification catalysts and cause 'back-biting' degradation even at 90°C. In all series of polymerizations initiated with tin methoxides two tendencies are detectable: increasing randomization of the stereosequence with increasing reaction time and with higher reaction temperatures (Kricheldorf *et* al., 1991).

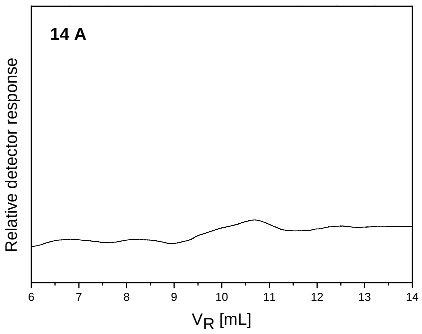
4.2.1.1 Polymerization Under Inert Atmosphere

Synthesis of PLA was carried out with dibutyltindimethoxide (as an initiator) with different monomer to initiator ratios (1040 and 2555) under nitrogen atmosphere at 130 (± 1) °C. Procedure is same as described earlier in section 4.1.1.1. The maximum polymerization time was 40 hr. Mostly, single or, unimodal peaks were seen in most of the SEC chromatograms but in some SEC chromatograms, bimodality or, even trimodality was observed. Table 4.5 lists the values of M_n, M_w and PD for PLA synthesized with dibutyltindimethoxide/triphenylphosphine at two (M_o/I_o) ratios and different reaction time. Fig. 4.17 shows the SEC chromatograms of PLA synthesized with dibutyltindimethoxide.

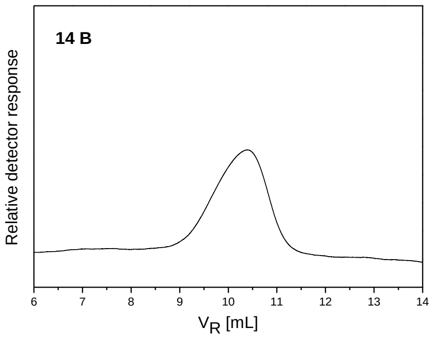
Table 4.5 Synthesis of PLA (under inert atmosphere) with dibutyltindimethoxide (initiator) at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
1040	11.5	2921	3459	1.18
	16.75	3360	4300	1.28
	23.5	3759	4928	1.31
	28.75	4412	5838	1.32
	34.5	3504	4988	1.42
2555	10.92	3662	4300	1.17
	13.42	3637	4506	1.23
	16.42	3978	4962	1.24
	18.42	4229	5582	1.32
	39.66	4461	7896	1.77

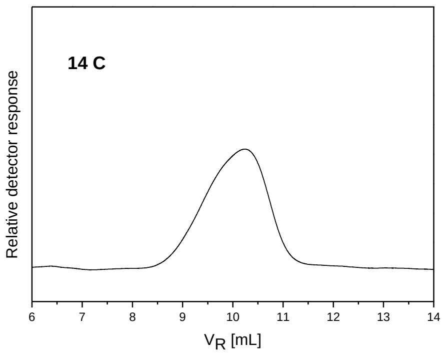
The maximum molecular weight (M_n = 4561) was observed in monomer to initiator ratio (M_o/I_o ratio) 2555. The reason for low molecular weight of polylactide obtained with dibutyltindimethoxide is only due to the occurrence of transesterification reaction (as explained in above paragraph).



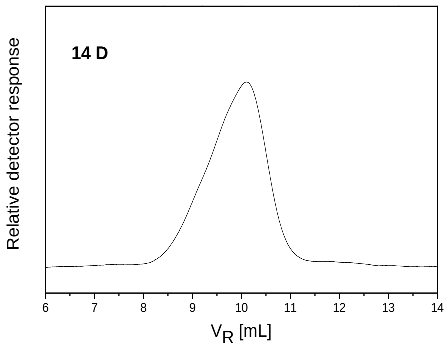
$V_r = 9$ $M_n = 2921$ $M_w = 3459$



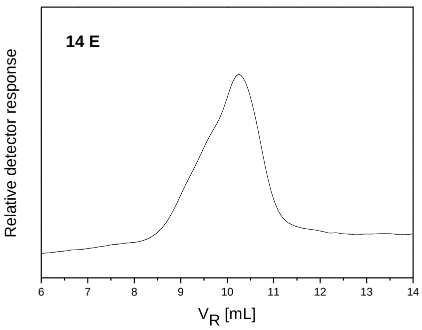
$V_r = 7.37$ $M_n = 3360$ $M_w = 4300$



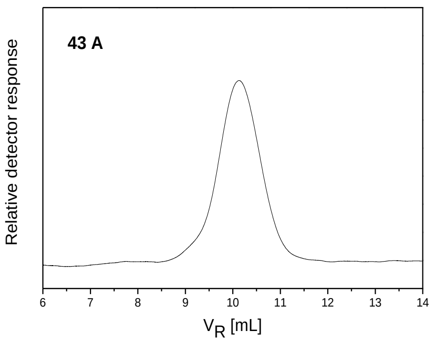
$V_r = 7.62$ $M_n = 3759$ $M_w = 4928$



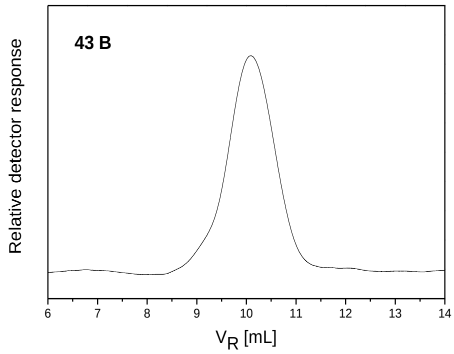
$V_r = 7.86$ $M_n = 4412$ $M_w = 5838$



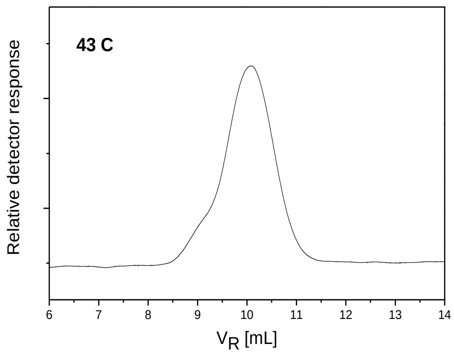
$V_r = 7.6$ $M_n = 3504$ $M_w = 4988$



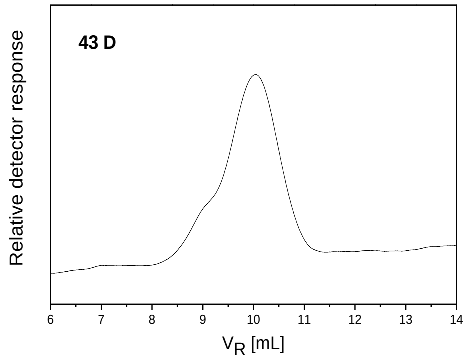
$V_r = 8.41$ $M_n = 3662$ $M_w = 4300$



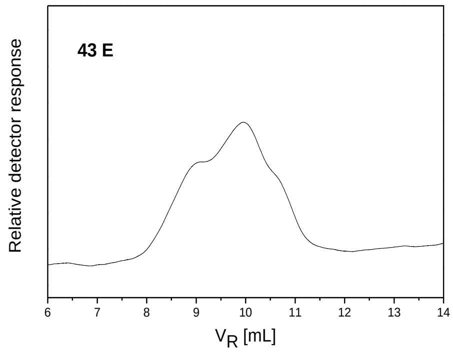
V_r = 8.29 M_n = 3637 M_w = 4506



V_r = 8.02 M_n = 3978 M_w = 4962



V_r = 7.91 M_n = 4229 M_w = 5582



V_r = 7.12 M_n = 4461 M_w = 7896

Figure 4.17 SEC of PLA synthesized (under inert atmosphere) with dibutyltindimethoxide

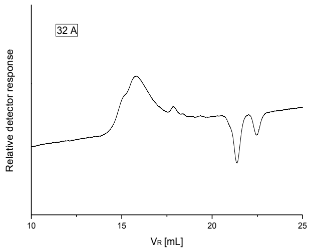
4.2.1.2 Polymerization Under Vacuum

Dibutyltindimethoxide (initiator) was used for the synthesis of polylactide under vacuum. Different experiments were carried out over a wide range of monomer to initiator ratios (525 to 5054) at 130 (± 1) °C. The procedure is same as explained earlier in section 4.1.1.2. The maximum polymerization time was 133 hr. Table 4.6 lists the lists the values of M_n, M_w and PD of PLA synthesized with dibutyltindimethoxide at different M_o/I_o ratios and reaction time. Unimodality, bimodality and even trimodality was seen in SEC chromatograms (Fig. 4.18).

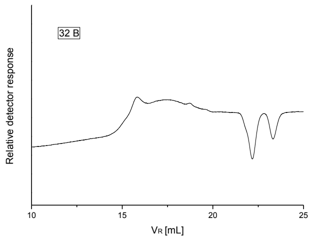
Table 4.6 Synthesis of PLA (under vacuum) with dibutyltindimethoxide at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
525	10	2020	3007	1.49
	20	1506	3164	2.10
	30	1647	3105	1.88
	40	2347	4700	2.00
	50	3149	7474	2.37
1047	14.5	3317, 496	3468, 779	1.04, 1.98
	36.75	341	1308	3.83
	40.5	855	2516	2.94
	46.5	829	2350	2.83
	60.5	908	2427	2.67
2573	16.5	3383, 210	3539, 416	1.04, 1.98
	32.5	290	1083	3.73
	58.33	393	1352	3.44
	80.33	415	1688	4.07
	102.33	2106	3166	1.50
5054	85	779	2388	3.06
	97	1365	2278	1.67
	109	438	3319	7.58
	116	484	3831	7.91
	133	1270	3460	2.72

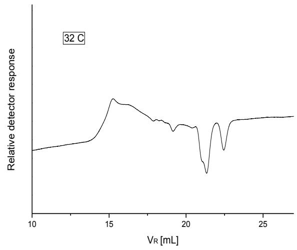
The maximum molecular weight (M_n = 3383) of polylactide with narrow value of polydispersity (PD = 1.04) was observed in monomer to initiator ratio (M_o/I_o ratio) 2573. The reason is same as explained earlier in section 4.1.1.1.



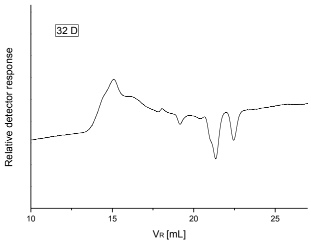
V_r = 15.80 M_n = 2020 M_w = 3007



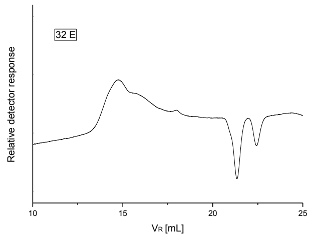
V_r = 15.26 M_n = 1506 M_w = 3164



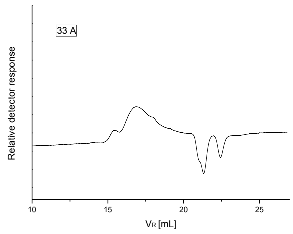
V_r = 15.27 M_n = 1647 M_w = 3105



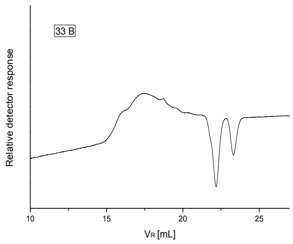
V_r = 15.07 M_n = 2347 M_w = 4700



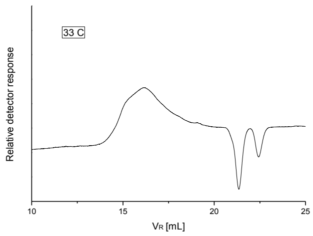
V_r = 14.76 M_n = 3149 M_w = 7474



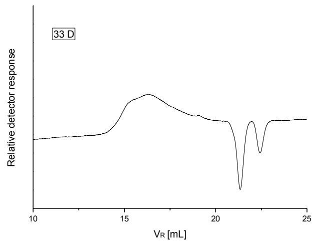
V_r 1 = 15.46 M_n 1 = 3317 M_w 1 = 3468
V_r 2 = 16.83 M_n 2 = 496 M_w 2 = 779



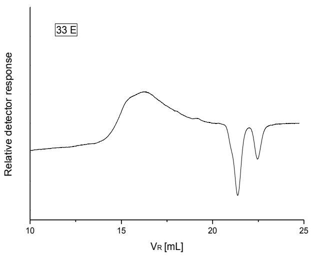
V_r = 17.47 M_n = 341 M_w = 1308



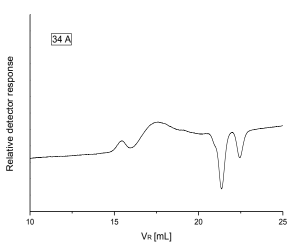
V_r = 16.14 M_n = 855 M_w = 2516



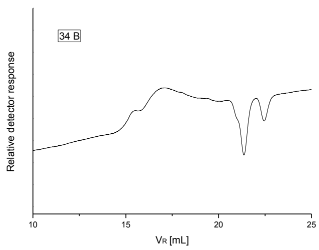
V_r = 16.35 M_n = 829 M_w = 2350



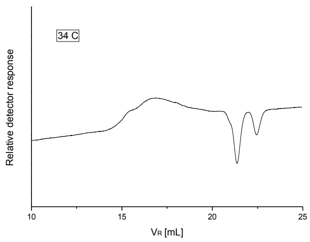
V_r = 16.27 M_n = 908 M_w = 2427

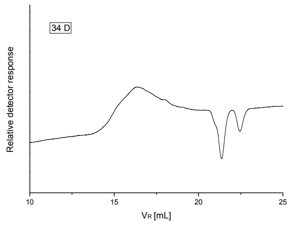


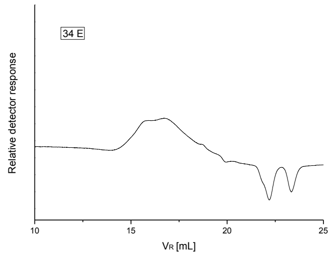
V_r 1 = 15.46 M_n 1 = 3383 M_w 1 = 3539
V_r 2 = 17.61 M_n 2 = 210 M_w 2 = 416



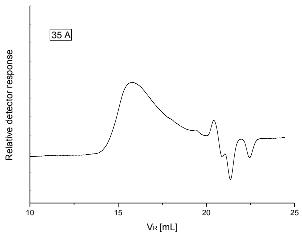
V_r = 17.04 M_n = 290 M_w = 1083

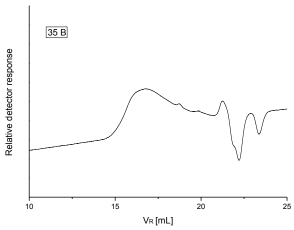


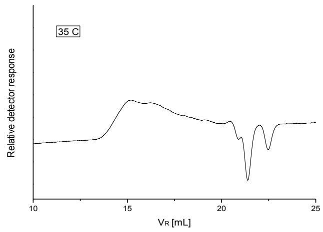




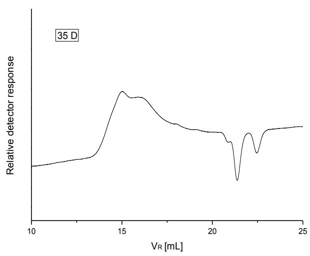
V_r = 16.81 M_n = 393 M_w = 1352 V_r = 16.43 M_n = 415 M_w = 1688 V_r = 16.91 M_n = 2106 M_w = 3166

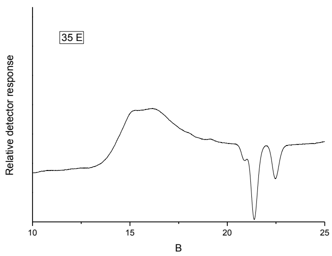






V_r = 15.80 M_n = 779 M_w = 2388 V_r = 16.76 M_n = 1365 M_w = 2278 V_r = 15.18 M_n = 438 M_w = 3319





V_r = 15.01 M_n = 484 M_w = 3831 V_r = 16.18 M_n = 1270 M_w = 3460

Figure 4.18 SEC of PLA synthesized (under vacuum) with dibutyltindimethoxide

4.2.2 Synthesis of PLA with Dibutyltindimethoxide/Triphenylphosphine

Triphenylphosphine as co-initiator with dibutyltindimethoxide as an initiator was used for the synthesis of PLA under two different environments: inert atmosphere and vacuum. An anionic ring-opening polymerization mechanism is proposed which is similar as shown in section 4.1.2.3.

(i) Under inert atmosphere, and
(ii) Under vacuum

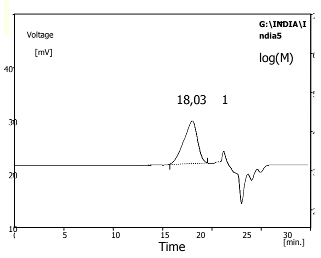
4.2.2.1 Polymerization under Inert Atmosphere

Synthesis of PLA was carried out with dibutyltindimethoxide (as an initiator) and triphenylphosphine (co-initiator) over a wide range of monomer to initiator ratios (518 to 5085) under nitrogen atmosphere at 130 (± 1) °C. The procedure is same as explained earleir in section 4.1.1.1. The maximum polymerization time was 38 hr. Table 4.7 lists the values of M_n, M_w and PD for PLA synthesized with dibutyltindimethoxide/ triphenylphosphine using different (M_o/I_o ratios) and reaction time. Mostly, single or, unimodal peaks were seen in most of the SEC chromatograms but in some SEC chromatograms, bimodality was also seen. Figure 4.19 shows the SEC chromatograms of PLA synthesized with dibutyltindimethoxide/triphenylphosphine.

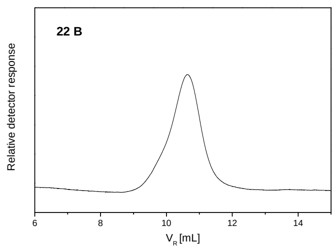
Table 4.7 Synthesis of PLA (under inert atmosphere) with dibutyltindimethoxide/ triphenylphosphine at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
518	8	2318	2826	1.21
	17.08	2662	3496	1.31
	18.75	2845	3777	1.32
	36.25	3326	5602	1.68
1061	10.25	2594	4649	1.79
	15.25	2240	2688	1.19
	20	2515	3081	1.22
	31.5	2913	3870	1.32
	37.25	3115	4186	1.34
1073	33	6828	9387	1.37
2564	7.33	5962	7788	1.30
	11	6222	8969	1.44
	28	6923	10825	1.56
5085	20	2455	2986	1.21
	26.33	3876	4718	1.21
	30.16	2843	3763	1.32
	33.75	2944	3993	1.35
	36.08	3098	4273	1.37

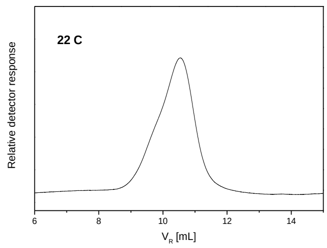
The maximum molecular weight (M_n = 6923) of polylactide with polydispersity value (PD = 1.56) was observed in monomer to initiator ratio (M_o/I_o ratio) 2564. The reason is similar as explained earleir in section 4.2.1.1.



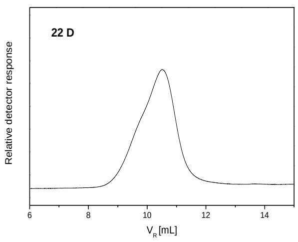
$V_r = 18.03$ $M_n = 6828$ $M_w = 9387$



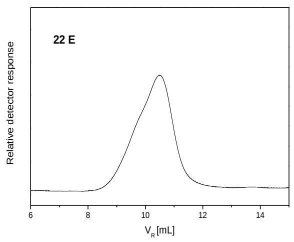
$V_r = 10.64$ $M_n = 2455$ $M_w = 2986$



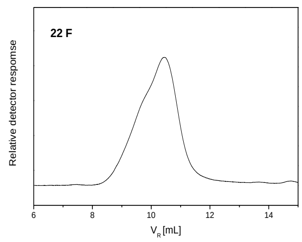
$V_r = 10.54$ $M_n = 3876$ $M_w = 4718$



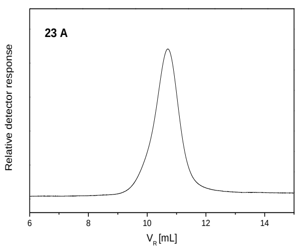
$V_r = 10.52$ $M_n = 2843$ $M_w = 3763$



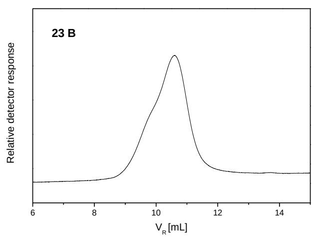
$V_r = 10.5$ $M_n = 2944$ $M_w = 3993$



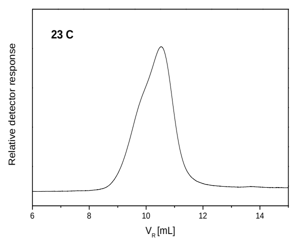
$V_r = 10.45$ $M_n = 3098$ $M_w = 4273$



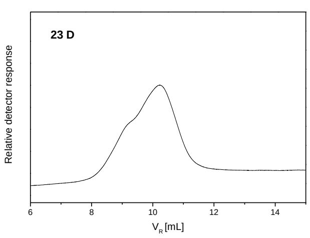
$V_r = 10.71$ $M_n = 2318$ $M_w = 2826$



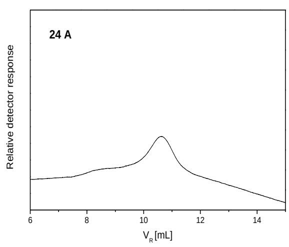
$V_r = 10.6$ $M_n = 2662$ $M_w = 3496$



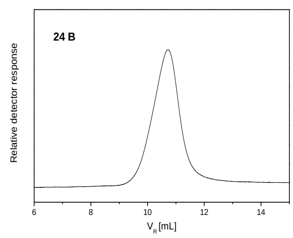
$V_r = 10.53$ $M_n = 2845$ $M_w = 3777$



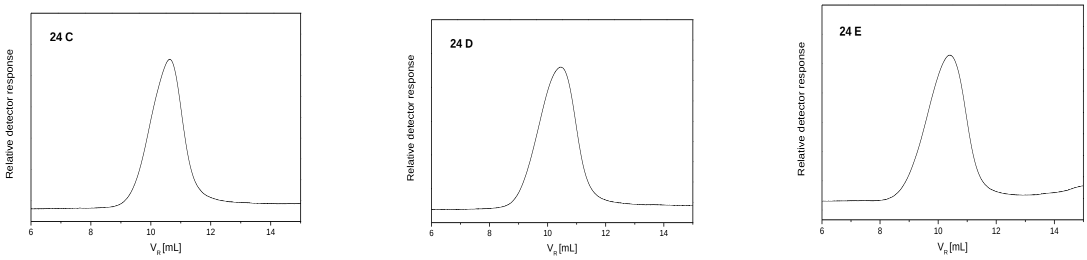
$V_r = 10.22$ $M_n = 3326$ $M_w = 5602$



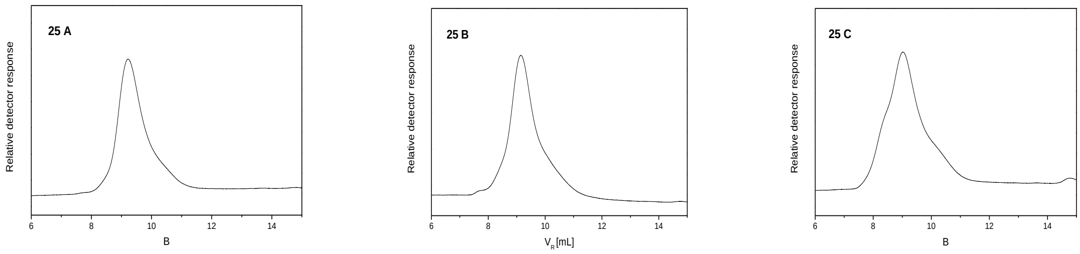
$V_r = 10.64$ $M_n = 2594$ $M_w = 4649$



$V_r = 10.72$ $M_n = 2240$ $M_w = 2688$



V_r = 10.63 M_n = 2515 M_w = 3081 V_r = 10.44 M_n = 2913 M_w = 3870 V_r = 10.4 M_n = 3115 M_w = 4186



V_r = 9.22 M_n = 5962 M_w = 7788 V_r = 9.15 M_n = 6222 M_w = 8969 V_r = 9.02 M_n = 6923 M_w = 10825

Figure 4.19 SEC of PLA synthesized (under inert atmosphere) with dibutyltindimethoxide/triphenylphosphine

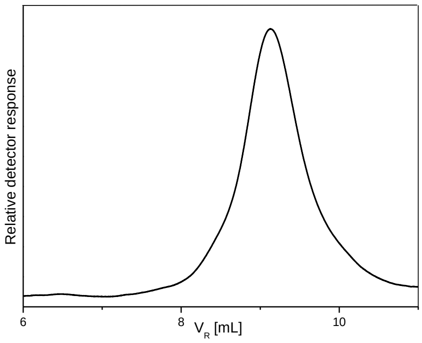
4.2.2.2 Polymerization Under Vacuum

Dibutyltindimethoxide as an initiator and triphenylphosphine as co-initiator were used for the synthesis of polylactide under vacuum only at 130 (± 1) °C. The procedure is similar as described earlier in section 4.1.1.2. The monomer to initiator ratio (M_o/I_o ratio) 2572 was used during polymerization. The maximum polymerization time was 55 hr. Table 4.8 lists the values of M_n, M_w and PD for PLA synthesized with dibutyltindimethoxide/ triphenylphosphine at 130 (± 1) °C at different reaction time. Mostly single or, unimodality was observed in SEC chromatograms. Figure 4.20 shows the SEC chromatograms of PLA synthesized with dibutyltindimethoxide/triphenylphosphine.

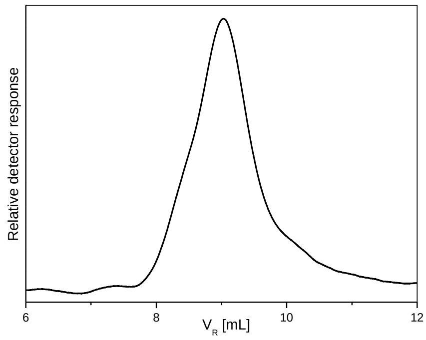
Table 4.8 Synthesis of PLA (under vacuum) with dibutyltindimethoxide/ triphenylphosphine at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
2572	22.50	6722	10155	1.51
	32.50	9628	13271	1.37
	35.50	9701	15155	1.56
	38.50	10953	16967	1.54
	55	10256	18022	1.75

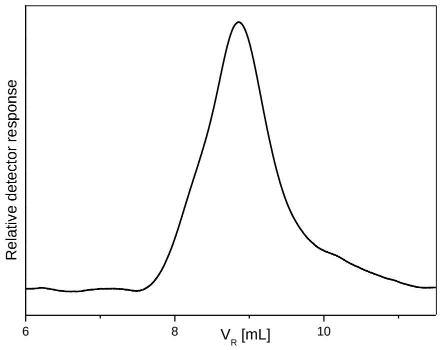
Table 4.8 shows that maximum molecular weight (M_n = 10953) of polylactide with polydispersity value (PD = 1.54) was observed. It has been seen that molecular weight of polylactide increased when polymerization was carried out under vacuum as compare to in an inert atmosphere. The polydispersity value also decreased in case of vacuum. The reason for decrease in molecular weight after prolonged reaction time is described in section 4.1.1.1.



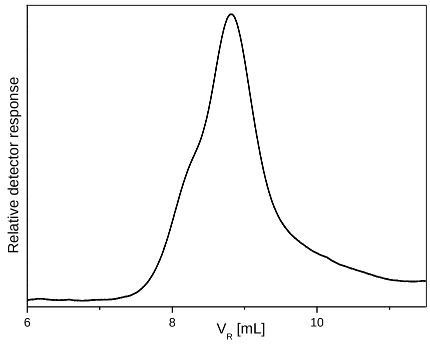
V_r = 9.13 M_n = 6722 M_w = 10155



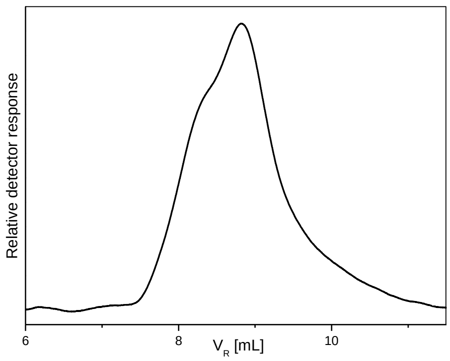
V_r = 9.03 M_n = 9628 M_w = 13271



V_r = 8.86 M_n = 9701 M_w = 15155



V_r = 8.81 M_n = 10953 M_w = 16967



V_r = 8.82 M_n = 10256 M_w = 18022

Figure 4.20 SEC of PLA synthesized (under vacuum) with dibutyltindimethoxide/ triphenylphosphine

4.3 Synthesis of Polylactide, PLA using Zinc stearate with/without Triphenylphosphine

4.3.1 Synthesis of PLA with Zinc stearate

Zinc stearate (as an initiator) was used for the synthesis of PLA under two different environments: inert atmosphere and vacuum. An anionic ring-opening polymerization mechanism has been proposed which is same as shown in section 4.1.1.3.

(i) Under inert atmosphere, and

(ii) Under vacuum

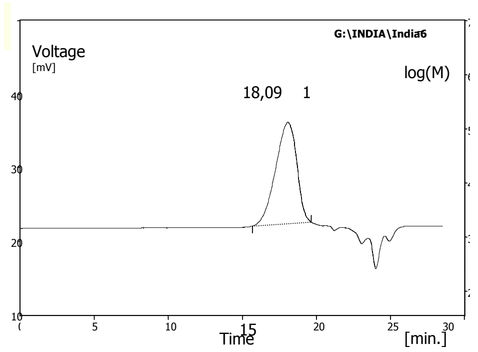
4.3.1.1 Polymerization Under Inert Atmosphere

Synthesis of PLA was carried out with zinc stearate (as an initiator) over different monomer to initiator ratios (693, 1040 and 2594) under nitrogen atmosphere at 130 (± 1) °C. The procedure is similar as explained earlier in section 4.1.1.1. The maximum polymerization time was 65 hr. Table 4.9 lists the values of M_n, M_w and PD for PLA synthesized with zinc stearate at different monomer to initiator ratios and reaction time. Fig. 4.21 shows the SEC chromatograms of PLA synthesized with zinc stearate. Mostly unimodal peaks are shown in SEC chromatograms but some SEC chromatograms also show bimodality.

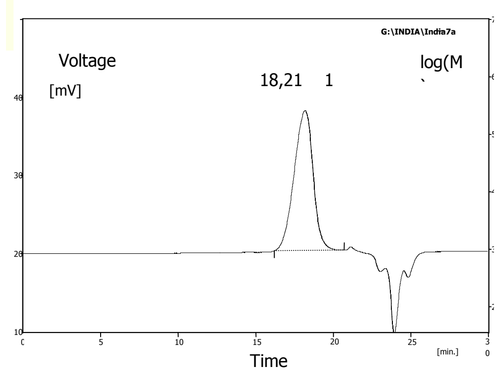
Table 4.9 Synthesis of PLA (under inert atmosphere) with zinc stearate at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
693	34	6071	8278	1.36
1040	19.66	5379	6869	1.27
	25.92	6183	7910	1.28
	29.42	6763	8883	1.31
	39.16	6356	8316	1.31
2594	30.58	3848	5178	1.34
	32.58	4055	5337	1.31
	41.42	4299	6102	1.41
	46.42	4718	7105	1.50
	65	12679 4464	19124 5596	1.14 1.25

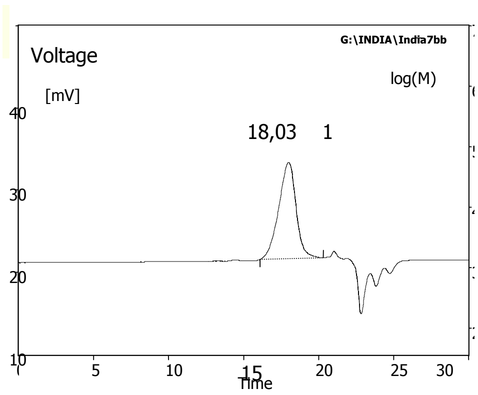
The maximum number average molecular weight (M_n = 12679) of polylactide with narrow polydispersity (PD = 1.14) was obtained with monomer to initiator ratio (M_o/I_o ratio) 2594. The reason is same as explained earlier in section 4.1.1.1.



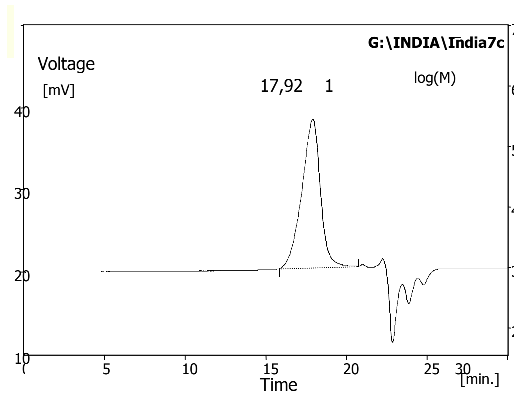
V_r = 18.09 M_n = 6071 M_w = 8278



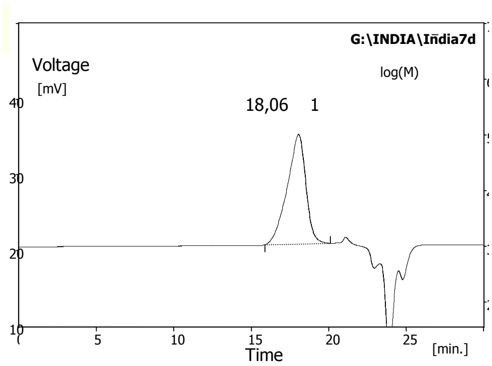
V_r = 18.21 M_n = 5379 M_w = 6869



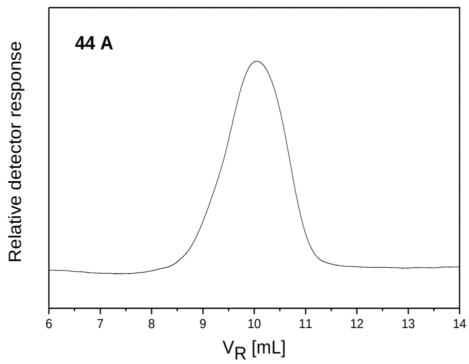
V_r = 18.03 M_n = 6183 M_w = 7910



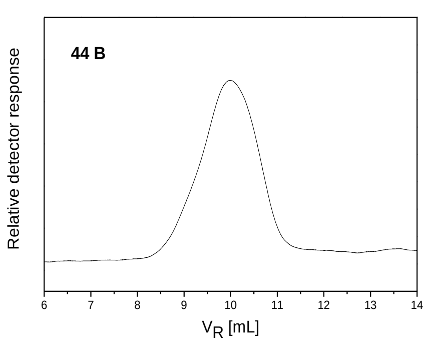
V_r = 17.92 M_n = 6763 M_w = 8883



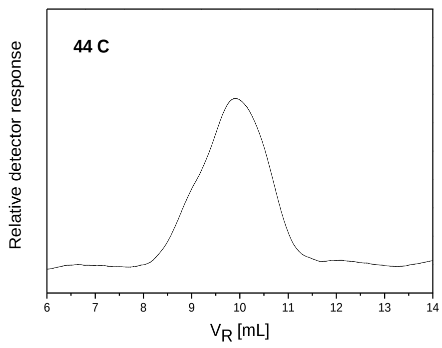
V_r = 18.06 M_n = 6356 M_w = 8316



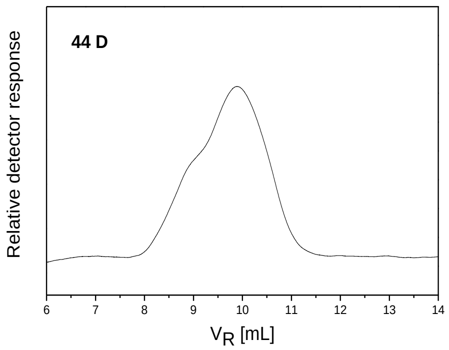
V_r = 7.52 M_n = 3848 M_w = 5178



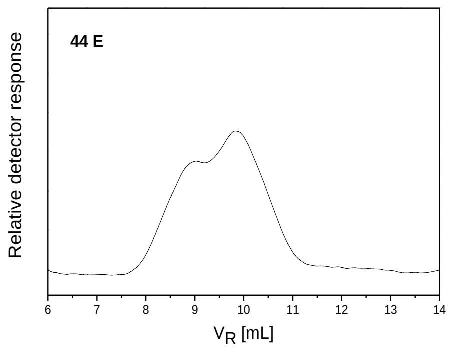
V_r = 7.7 M_n = 4055 M_w = 5337



V_r = 12.23 M_n = 4299 M_w = 6102



V_r = 7.66 M_n = 4718 M_w = 7105



V_r1 = 7.31 M_n1 = 19124 M_w1 = 21866

V_r2 = 8.99 M_n2 = 4464 M_w2 = 5596

Figure 4.21 SEC of PLA synthesized (under inert atmosphere) with zinc stearate

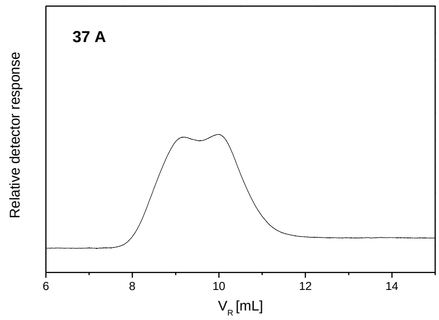
4.3.1.2 Polymerization Under Vacuum

Zinc stearate (initiator) was used for the synthesis of polylactide under vacuum. Polymerization was carried out over different monomer to initiator ratios (520 to 2299) at 130 (± 1) °C. The procedure is similar as explained earlier in section 4.1.1.2. The maximum polymerization time was 76 hr. Table 4.10 lists the values of M_n, M_w and PD for PLA synthesized with zinc stearate at two (M_o/I_o) ratios and different reaction time. Figure 4.22 shows the SEC chromatograms of PLA synthesized with zinc stearate. Mostly single or unimodal peaks are shown in SEC chromatograms but some SEC chromatograms also show bimodality.

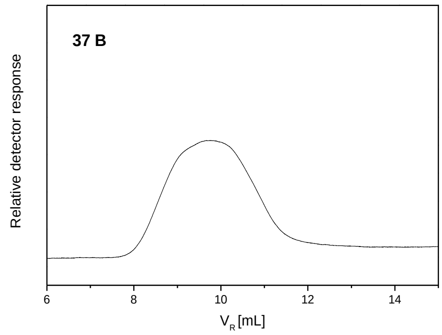
Table 4.10 Synthesis of PLA (under vacuum) with zinc stearate at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
520	48.5	13330 3361	14648 4597	1.09 1.36
	52	3294	6358	1.93
	55	14638 3539	16034 4818	1.09 1.36
	59	8887 2600	11464 3031	1.29 1.16
	76	13090 3616	15663 4314	1.19 1.19
2299	7	15398	25154	1.65
	11	9400	19066	2.02
	15	7551	14438	1.91
	18	8285	15664	1.89
	34.5	14389	27534	1.91

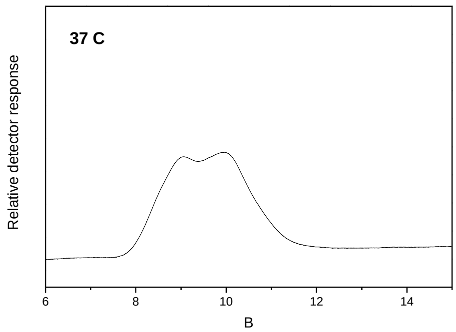
The maximum number average molecular weight (M_n = 15398) of polylactide with narrow polydispersity (PD = 1.65) was obtained with monomer to initiator ratio (M_o/I_o ratio) 2299. The reason is same as explained earlier in section 4.1.1.1.



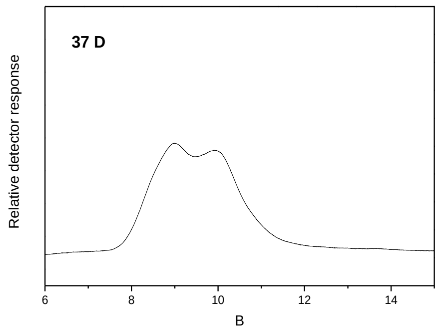
V_r 1 = 9.16 M_n 1 = 13330 M_w 1 = 14648
V_r 2 = 9.99 M_n 2 = 3361 M_w 2 = 4597



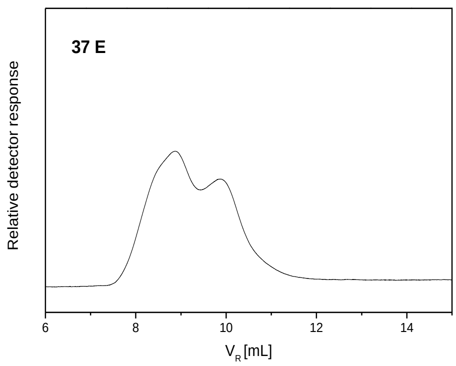
V_r = 9.77 M_n = 3294 M_w = 6358



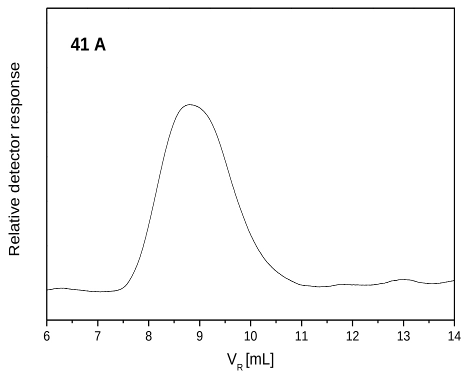
V_r 1 = 9.05 M_n 1 = 14638 M_w 1 = 16034
V_r 2 = 9.96 M_n 2 = 3539 M_w 2 = 4818



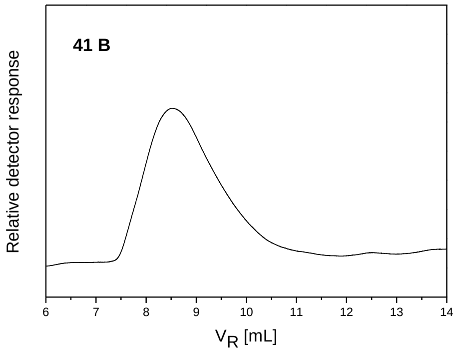
V_r 1 = 8.99 M_n 1 = 8887 M_w 1 = 11464
V_r 2 = 9.95 M_n 2 = 2600 M_w 2 = 3031



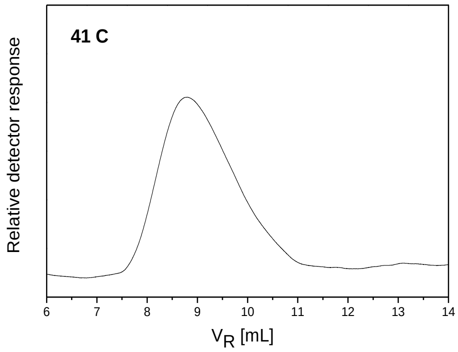
V_r 1 = 8.88 M_n 1 = 13090 M_w 1 = 15663
V_r 2 = 9.87 M_n 2 = 3616 M_w 2 = 4314



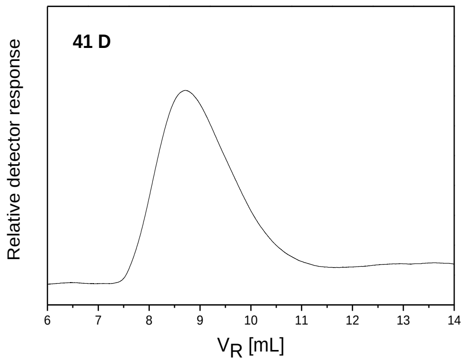
V_r = 7.06 M_n = 9288 M_w = 15398



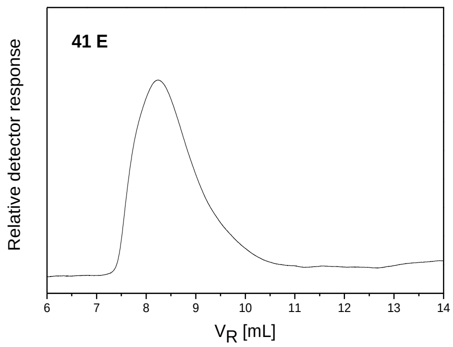
V_r = 7.17 M_n = 9400 M_w = 19066



V_r = 6.8 M_n = 7551 M_w = 14438



V_r = 7.22 M_n = 8285 M_w = 15664



V_r = 7.07 M_n = 14389 M_w = 27534

Figure 4.22 SEC of PLA synthesized (under vacuum) with zinc stearate

4.3.2 Synthesis of PLA with Zinc Stearate/Triphenylphosphine

Zinc stearate (initiator) and triphenylphosphine (co-initiator) was used for the synthesis of polylactide under two different environments: inert atmosphere and vacuum. An anionic ring-opening polymerization mechanism has been proposed which is same as shown in section 4.1.2.3,

(i) Under inert atmosphere, and
(ii) Under vacuum

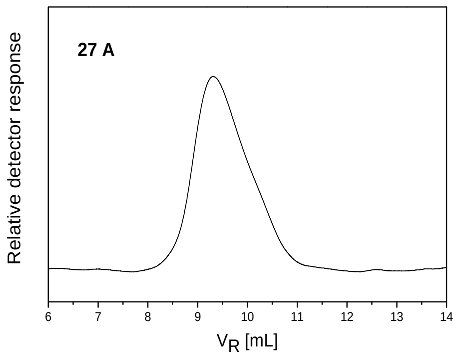
4.3.2.1 Polymerization Under Inert Atmosphere

Synthesis of PLA was carried out with zinc stearate (as an initiator) and triphenylphosphine (co-initiator) over different monomer to initiator ratios (508 and 2568) under nitrogen atmosphere at 130 (± 1) °C. The procedure is similar as explained earlier in section 4.1.1.1. The maximum polymerization time was 66 hr. Table 4.11 lists the values of M_n, M_w and PD for PLA synthesized with zinc stearate/triphenylphosphine at two M_o/I_o ratios and several reaction times. Mostly single or unimodal peaks are shown in SEC chromatograms but some SEC chromatograms also show bimodality. Fig. 4.23 shows the SEC chromatograms of PLA synthesized with zinc stearate/triphenylphosphine.

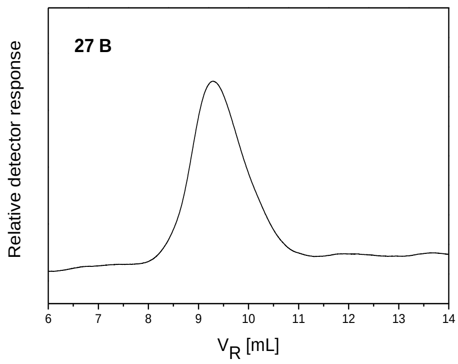
Table 4.11 Synthesis of PLA (under inert atmosphere) with zinc stearate/ triphenylphosphine at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
508	14.25	5570	7768	1.39
	18	3718	8060	2.16
	20	6665	9336	1.40
	23	5979	9073	1.51
	30.50	6945	12154	1.75
2568	59.08	4706	7235	1.53
	60.08	4778	7350	1.53
	61.08	4697	7303	1.55
	63.08	4799	8148	1.69
	66.08	4316	9491	2.19

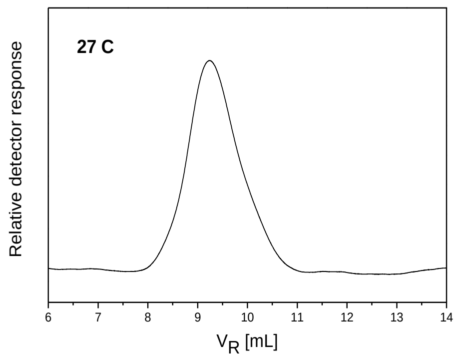
The maximum number average molecular weight (M_n = 6945) of polylactide with polydispersity (PD = 1.75) was obtained with monomer to initiator ratio M_o/I_o ratio = 508.



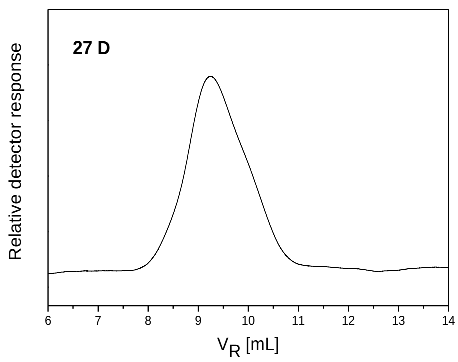
V_r = 7.71 M_n = 5570 M_w = 7768



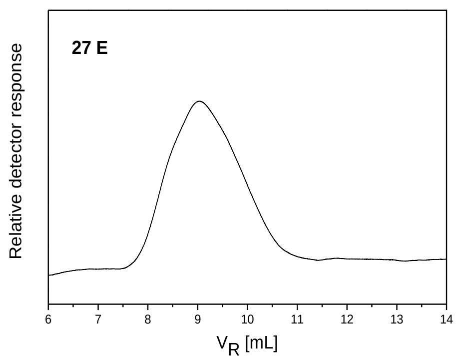
V_r = 7.67 M_n = 3718 M_w = 8060



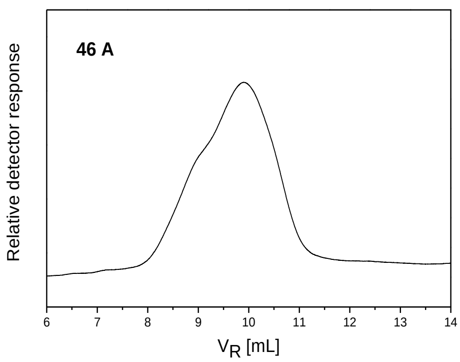
V_r = 7.55 M_n = 6665 M_w = 9336



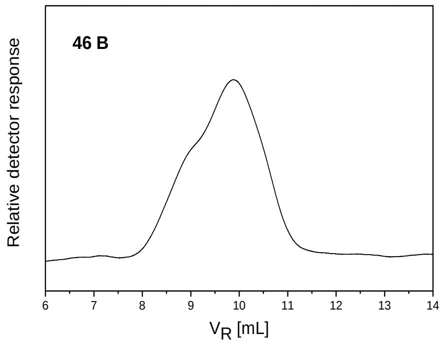
V_r = 7.43 M_n = 5979 M_w = 9073



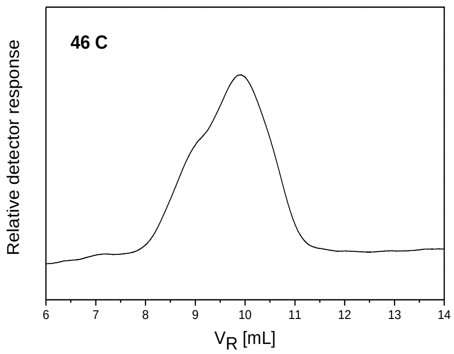
V_r = 7.42 M_n = 6945 M_w = 12154



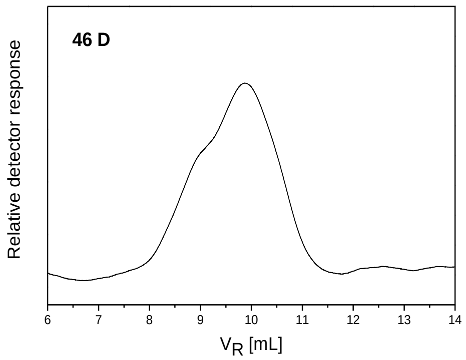
V_r = 7.49 M_n = 4706 M_w = 7235



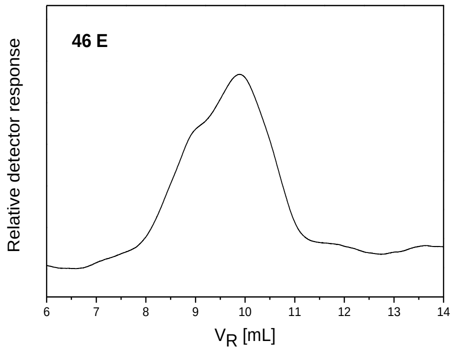
V_r = 7.65 M_n = 4778 M_w = 7350



V_r = 7.36 M_n = 4697 M_w = 7303



V_r = 7.02 M_n = 4799 M_w = 8148



V_r = 6.59 M_n = 4316 M_w = 9491

Figure 4.23 SEC of PLA synthesized (under inert atmosphere) with zinc stearate/ triphenylphosphine

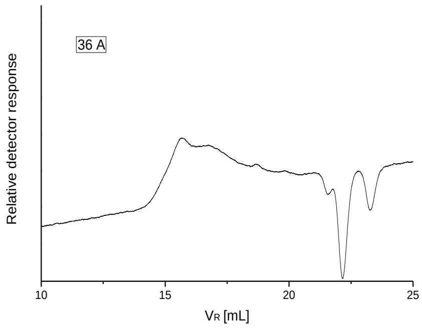
4.3.2.2 Polymerization Under Vacuum

Synthesis of PLA was carried out with zinc stearate (as an initiator) and triphenylphosphine (co-initiator) over two different monomer to initiator ratios (518 and 2602) under vacuum only at 130 (± 1) °C. The procedure is similar as explained earlier in section 4.1.1.2. The maximum polymerization time was 155 hr. Table 4.12 lists the values of M_n, M_w and PD for PLA synthesized with zinc stearate/triphenylphosphine at two M_o/I_o ratios and several reaction times. Figure 4.24 shows the SEC chromatograms of PLA synthesized with zinc stearate/triphenylphosphine. Mostly single or unimodal peaks are shown in SEC chromatograms but some SEC chromatograms also show bimodality.

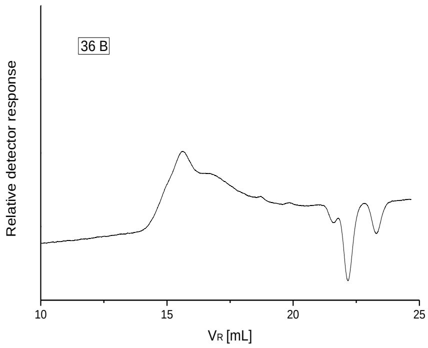
Table 4.12 Synthesis of PLA (under vacuum) with zinc stearate/triphenylphosphine at 130 (± 1) °C

M_o/I_o ratio	Polymerization time (hr)	M_n	M_w	PD
518	42.5	4699	5064	1.08
	45.5	4901	5412	1.10
	48.5	1484	3628	2.44
	52.5	2046	3956	1.93
	66	1233	3428	2.78
2602	78.25	6447	9629	1.49
	123	5138	8698	1.69
	148.58	6870	12419	1.80
	154.08	7776	13297	1.70
	155.25	5455	8411	1.54

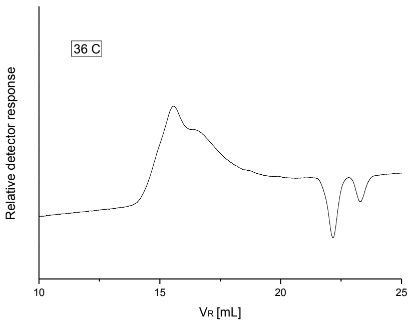
The maximum number average molecular weight (M_n = 7776) of polylactide with polydispersity (PD = 1.70) was obtained with monomer to initiator ratio (M_o/I_o ratio = 2602). The reason is same as explained earlier in section 4.1.1.1.



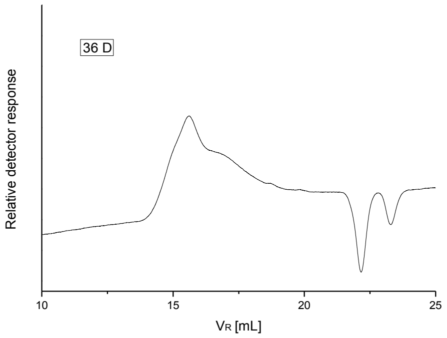
V_r = 15.73 M_n = 4699 M_w = 5064



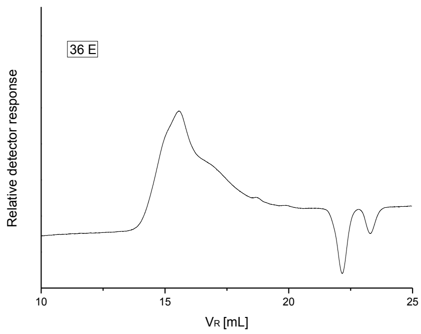
V_r = 15.64 M_n = 4901 M_w = 5412



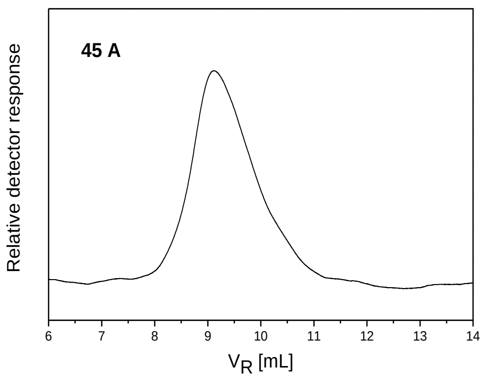
V_r = 15.57 M_n = 1484 M_w = 3628



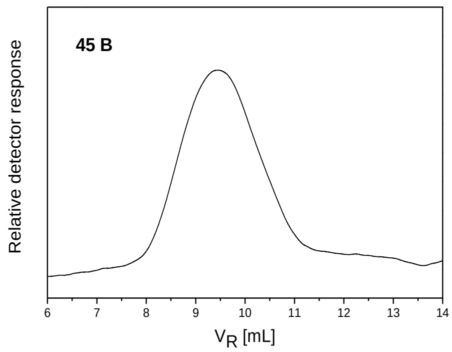
V_r = 15.61 M_n = 2046 M_w = 3956



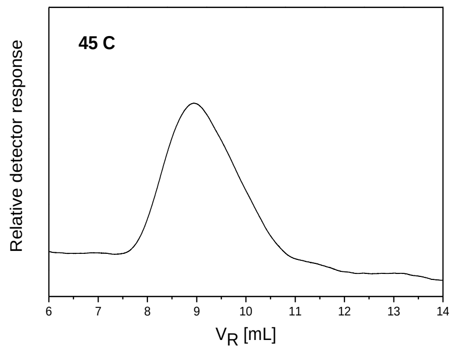
V_r = 15.57 M_n = 1233 M_w = 3428



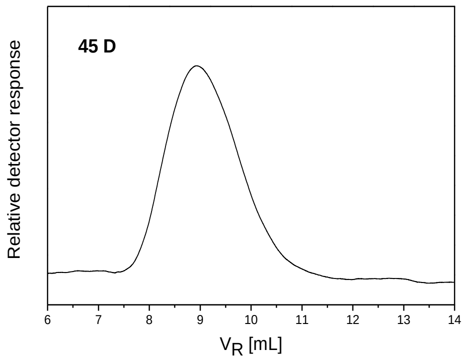
V_r = 7.51 M_n = 6447 M_w = 9629



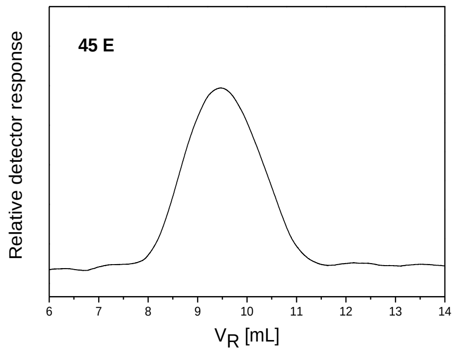
V_r = 7.24 M_n = 5138 M_w = 8698



V_r = 7.34 M_n = 6870 M_w = 12419



V_r = 7.31 M_n = 7776 M_w = 13297



V_r = 7.39 M_n = 5455 M_w = 8411

Figure 4.24 SEC of PLA synthesized (under vacuum) with zinc stearate/ triphenylphosphine

4.4 Determination of Mark-Houwink Parameters

A correlation has been developed between intrinsic viscosity and molecular weight using Mark-Houwink equation as basis of k and a have been determined for PLA using the viscosity data obtained with (section 3.4) in chloroform solution at 30 °C.

Mark-Houwink equation

$$[\eta] = K.M_n^a$$

The intrinsic viscosity, [η] is calculated by using the data obtained with Ubbelohde viscometer, and the values of number average molecular weight, M_n are obtained from size exclusion chromatography, SEC.

Plot between log [η] vs log M_n is a straight line (Fig. 4.25). The slope of this line gives the "a" value and the intercept is equal to the log of the "k" value. The values of $k = 5.98 \times 10^{-4}$ and a = 0.72 have been determined by regression analysis.

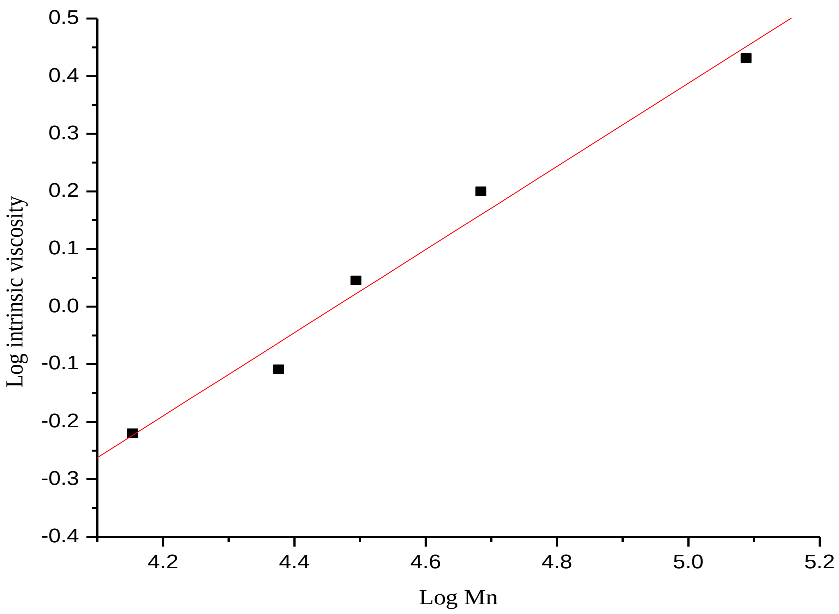


Figure 4.25 Graph between log M_n vs logarithmic intrinsic viscosity

4.5 Mathematical Modeling of the PLA Ring-Opening Polymerization Kinetics

The modeling of ring-opening polymerization of L- lactide to Poly(lactic acid) (PLA) has been carried out. The progress of lactide polymerization has been simulated using an available computer program wherein the mechanism is assumed to be a ring-opening reaction comprising of chain initiation, chain propagation, and chain termination (Mehta 2006). First of all the computer program takes numerical values of all required parameters such as the values of initial monomer concentration, initial initiator concentration and values of rate constants for initiation, propagation and termination, etc. The differential equations are solved by Euler's method and average molecular weights obtained corresponding to concentration of active and terminated polymer chains. Starting from zero, the time variable is incremented by 0.01 min till it reaches a predefined total reaction time. The program outputs are the values of average molecular weights as a function of polymerization time.

Except some reported data on the apparent rate constant, there is lack of data in the literature on the rate constants for initiation, propagation and termination steps of PLA polymerization. Using a simple numerical technique, the individual rate constants are evaluated theoretically and the results are compared with the available experimental data for the ring-opening polymerization of PLA.

4.5.1 Polymerization Mechanism

In ring-opening polymerization, for both D- and L- lactides, initiation results in opening of the ring to form secondary initiator species P_1 (Odian, 1991). This can be generalized as:

$$M + I \xrightarrow{k_o} P_1 \qquad (4.1)$$

where M is the monomer, I is the initiator and P_1 is the activated polymer of one unit (Fig. 4.26). The initiator species grow by successive ring-opening additions of monomer molecules:

$$P_j + M \xrightarrow{k_j} P_{j+1} \quad , \text{j=1, 2, 3,…} \qquad (4.2)$$

where P_j is the active polymer chain of j units. The rate constant k_j refers to the jth propagation step on a chain. In the present case, the termination mechanism has been assumed to be the chain transfer to monomer, giving:

$$P_j + M \xrightarrow{k_t} M_j + P_1 \tag{4.3}$$

In equation (4.3), it is assumed that the charged ring spontaneously forms P_1. Here M_j is the deactivated polymer of j repeat units, which will not participate in any reaction.

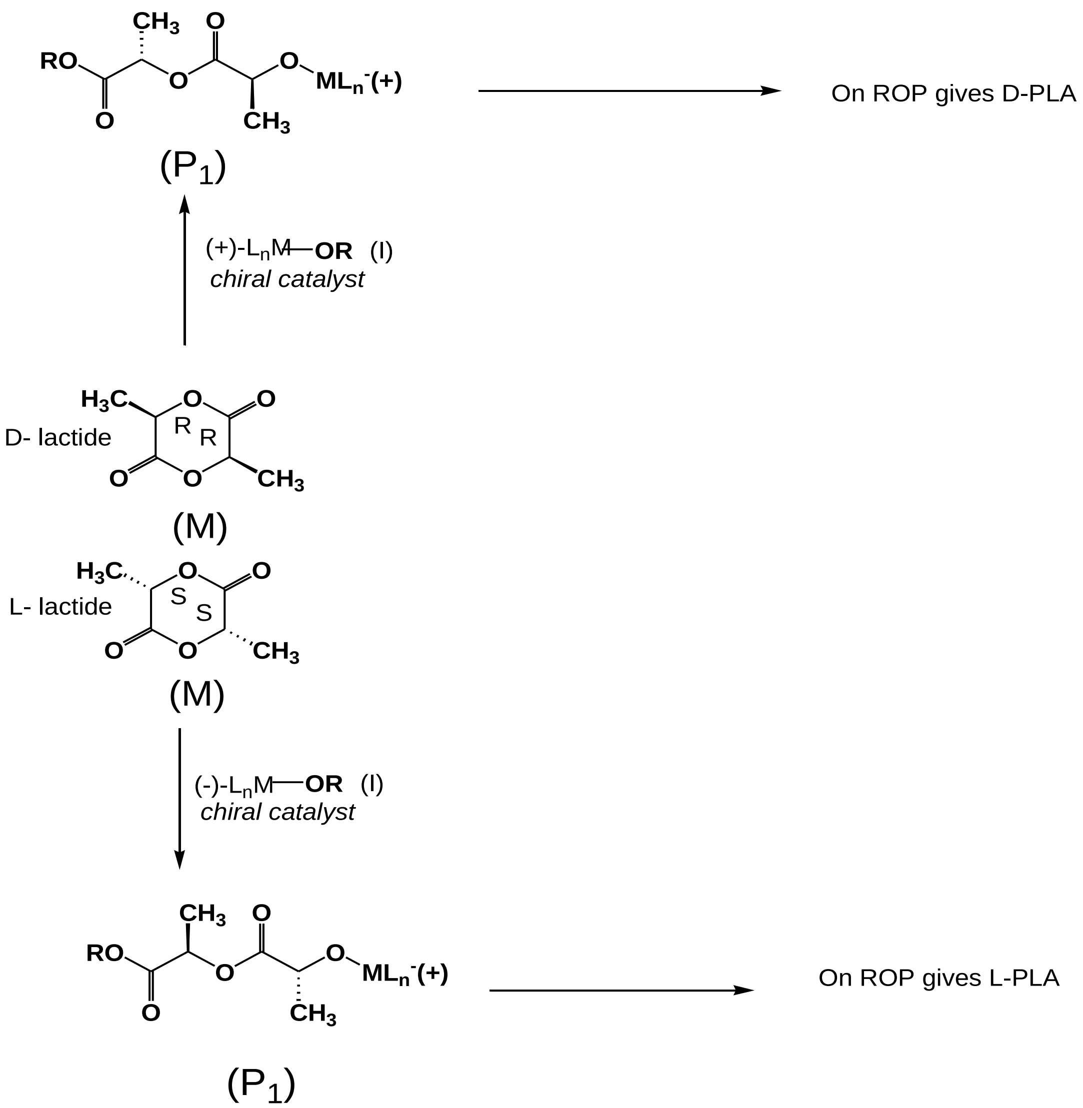


Figure 4.26 Initiation of L- lactide and D- lactide

4.5.2 Mathematical Model

Mass balance equations for a batch reactor may be written for the above kinetic scheme as follows:

The monomer is consumed in the initiation, propagation and termination reactions. Therefore, the rate of change of monomer concentration can be obtained by adding the rate of consumption of monomer due to all three steps as given in equations (4.1) to (4.3).

$$\frac{d[M]}{dt} = -[M]\{k_0[I] + \sum_{j=1}^{n} k_j[P_j] + \sum_{j=1}^{n} k_{tj}[P_j]\} \tag{4.4}$$

$$\frac{d[I]}{dt} = -k_0[I][M] \tag{4.5}$$

$$\frac{d[P_1]}{dt} = k_0[I][M] - k_1[P_1][M] + \sum_{j=2}^{n} k_{tj}[P_j][M] \tag{4.6}$$

$$\frac{d[P_j]}{dt} = [M]\{k_{(j-1)}[P_{j-1}] - k_j[P_j] - k_{tj}[P_j]\},\ j > 1 \tag{4.7}$$

and

$$\frac{d[M_j]}{dt} = k_{tj}[P_j][M],\ j \geq 1 \tag{4.8}$$

with initial conditions, at $t = 0$

$$[M_j] = 0 \text{ and } [P_j] = 0,\ j \geq 1 \tag{4.9}$$

$$[M] = [M_o] \tag{4.10}$$

$$[I] = [I_o] \times s \tag{4.11}$$

where, the symbols in square brackets represent respective molar concentrations and subscripts of rate constants (*k*s) indicate chain length dependent values. In equation (4.11), '*s*' represents number of chains initiated by an initiator molecule. In the absence of solution of the differential equations given by equations (4.4) to (4.8), earlier investigators used continuous variable approach, statistical methods, the method of moments or some discrete transform methods which are related to the average molecular weight. Most of these methods involve several assumptions and provide only approximate solutions. Using method of moments, particularly for complex polymerization mechanisms, it is not possible to invert the generating function to give $[P_j]$. With the advent of techniques, through which one can now experimentally obtain the entire chain length distribution (Tirrel *et* al., 1986), a more general modeling with direct solution of differential equations is required. This has now become possible with the availability of high-speed computers.

The summation over j in equations (4.4) and (4.6) should continue to infinity, however, it is practically impossible to do so in numerical techniques. In the present case, n = 5000, which is well above the experimentally reported values for PLA, was taken. It was observed that a value more than this has no effect on the results. These equations were solved on a PC using a simple numerical technique using a very small step size (Mehta 2006).

For the purpose of comparison with the experimental data, the number average molecular weight, M_n and weight average molecular weight, M_w were also calculated using:

$$M_n = m \frac{\sum_{j=1}^{n} j([P_j]+[M_j])}{\sum_{j=1}^{n} ([P_j]+[M_j])} \tag{4.12}$$

$$M_w = m \frac{\sum_{j=1}^{n} j^2([P_j]+[M_j])}{\sum_{j=1}^{n} j([P_j]+[M_j])} \tag{4.13}$$

where, m is the molecular weight of the repeat unit (in the present case m=144).

4.5.3 Method

The molecular weight of polymer formed is more sensitive to k_p than k_t for shorter reaction time whereas effect of k_t is pronounced for prolonged reaction time. M_n, however, is not very sensitive to k_o. With a decrease in k_o, the number average molecular weight, M_n, is lower for short reaction time, and as the reaction proceeds M_n becomes higher. Due to low value of k_o, the number of initiated chains are less and with the availability of same monomer molecules for the growth of fewer number of chains, the average chain length increases. It is known that ratio of rate of initiation to sum of the rates of initiation, propagation and termination, affects the molecular weight distribution (Odian, 1991). Thus, k_o values can be fine-tuned using the polydispersity (M_w/M_n) data.

The parameters k_o, k_p and k_t were selected from M_n and M_w vs polymerization time curves for different values of rate constant parameters by comparing the simulated and experimental curves. The values giving a close fit were chosen. Thus the curve fitting was optimized by trial and error and model comparison was done by visual assessment. An average simulation took about 30 minutes for simulating polymerization.

The rate constant parameters k_o, k_p and k_t for stannous octoate and stannous octoate/ triphenylphosphine were calculated because high molecular weight of polylactide was obtained with these initiators under two different environments: nitrogen atmosphere and vacuum. In case of dibutyltindimethoxide and zinc stearate initiators, rate constant parameters cannot be calculated due to the some following reasons:

1. Low molecular weight of polylactide was obtained (<10,000 g/mol).
2. SEC characterization is not that accurate enough to provide correct values of both average molecular weight and polydispersity.
3. These polymerization reactions are rather difficult to reproduce because of too many reaction parameters.

Figs. 4.27 and 4.28 show the comparison of experimental and model results (number average molecular weight) for the polymerization of L- lactide, using stannous octoate and stannous octoate/triphenylphosphine under nitrogen atmosphere. Table 4.13 shows the summary of rate constants determined with various initiators for the polymerization carried out under nitrogen atmosphere at 130 (± 1) °C.

Figs. 4.29 and 4.30 show the comparison of experimental and modeling results (number average molecular weight) for the polymerization of L- lactide, using stannous octoate and stannous octoate/triphenylphosphine under vacuum. Table 4.14 shows the summary of rate constants determined with various initiators for the polymerization carried out under vacuum at 130 (± 1) °C.

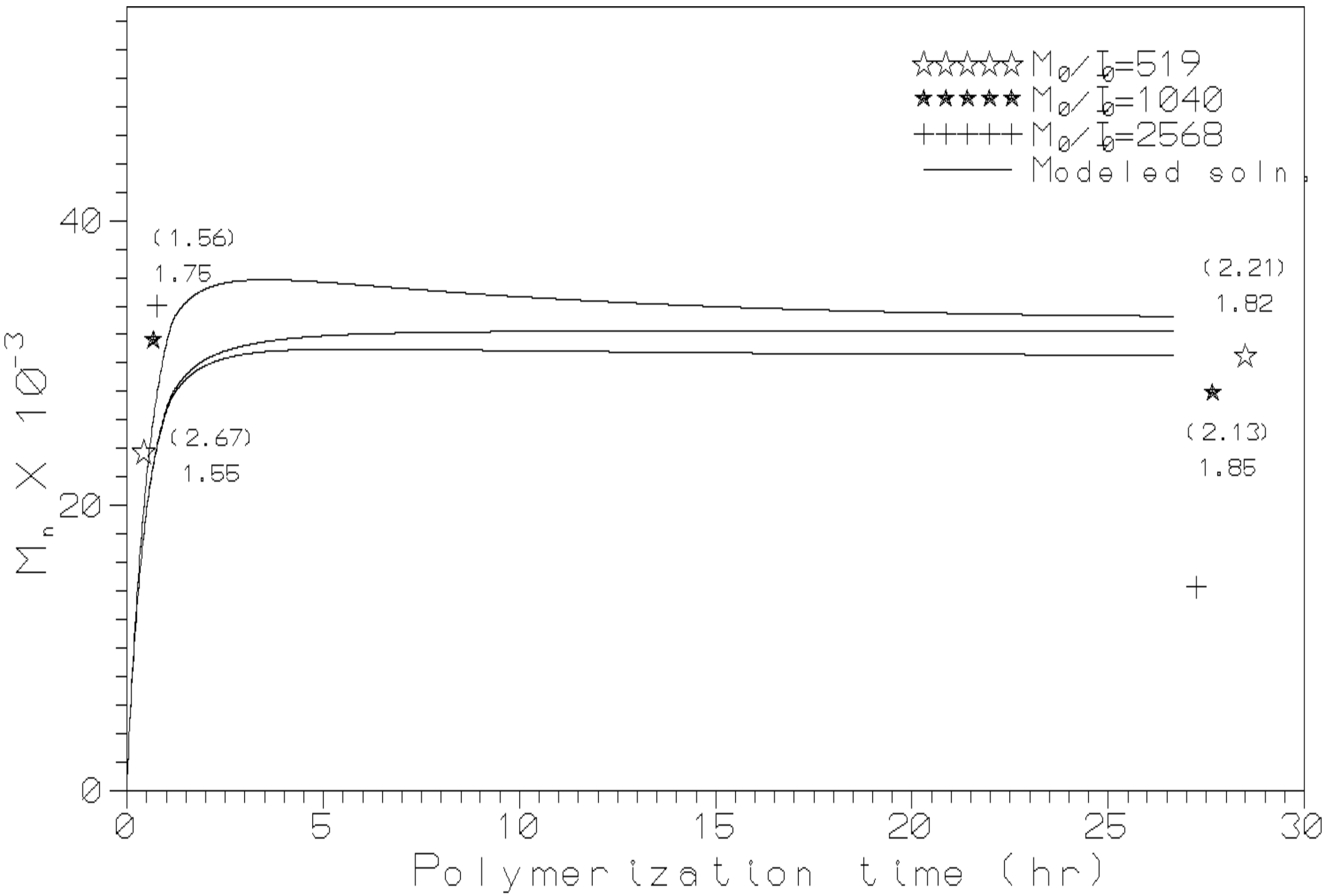


Figure 4.27 Comparison of experimental and modeling results (number average molecular weights) for the polymerization of L- lactide, using stannous octoate under nitrogen atmosphere. The solid lines are the solutions obtained from the model and points are the experimental values.

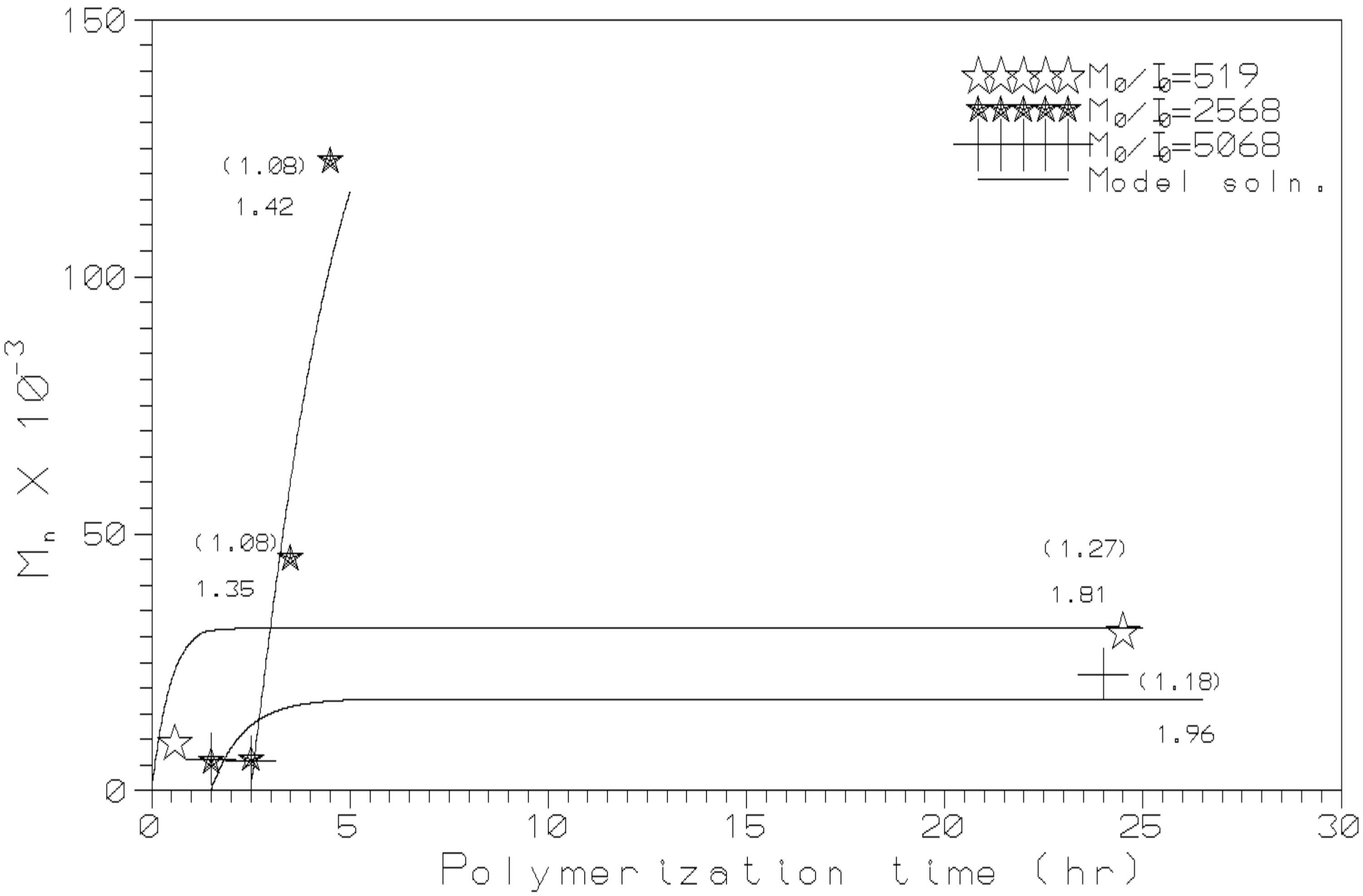


Figure 4.28 Comparison of experimental and modeling results (number average molecular weights) for the polymerization of L- lactide, using stannous octoate and triphenylphosphine under nitrogen atmosphere. The solid lines are the solutions obtained from the model and points are the experimental values.

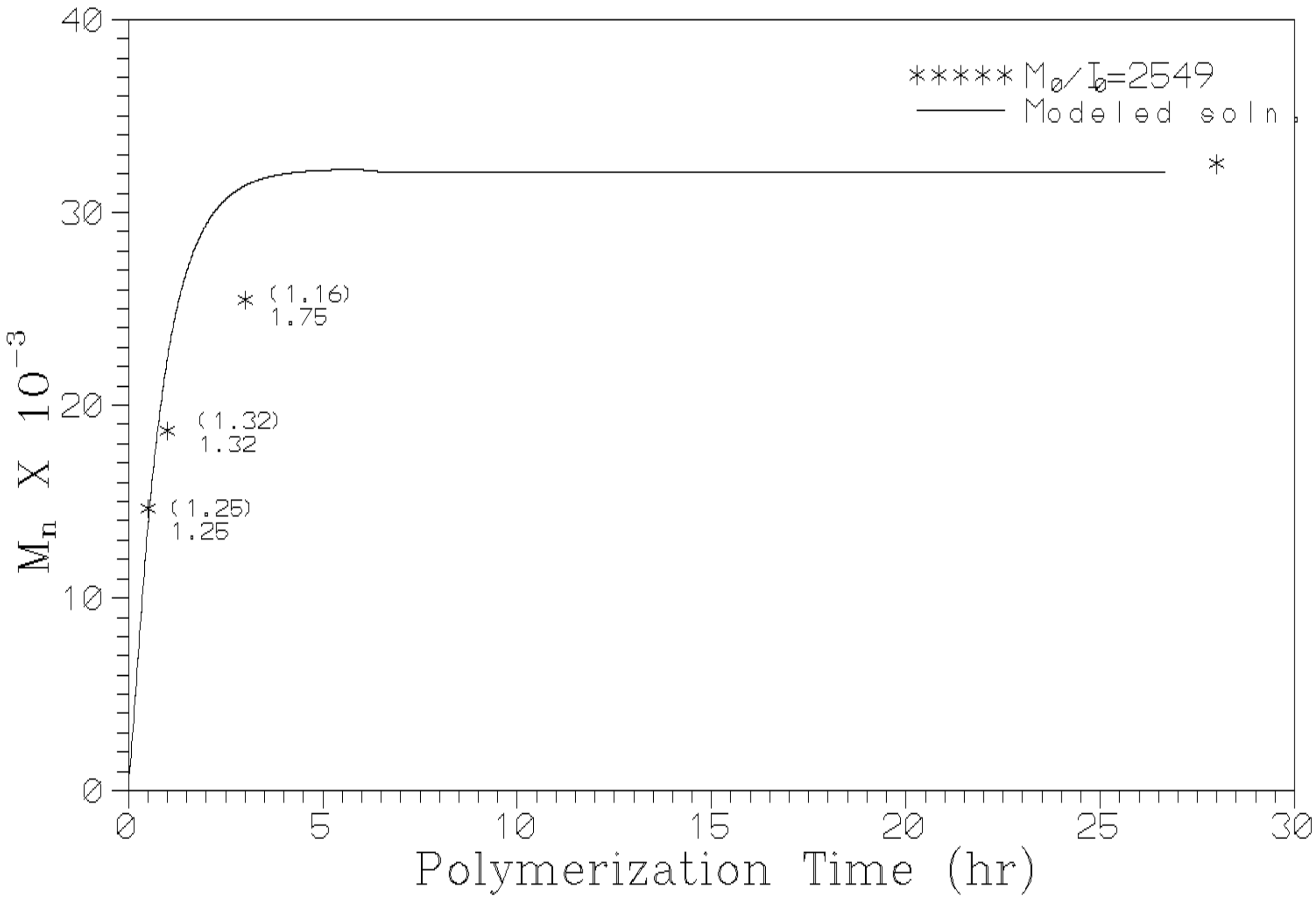


Figure 4.29 Comparison of experimental and modeling results (number average molecular weights) for the polymerization of L- lactide, using stannous octoate under vacuum. The solid lines are the solutions obtained from the model and points are the experimental values.

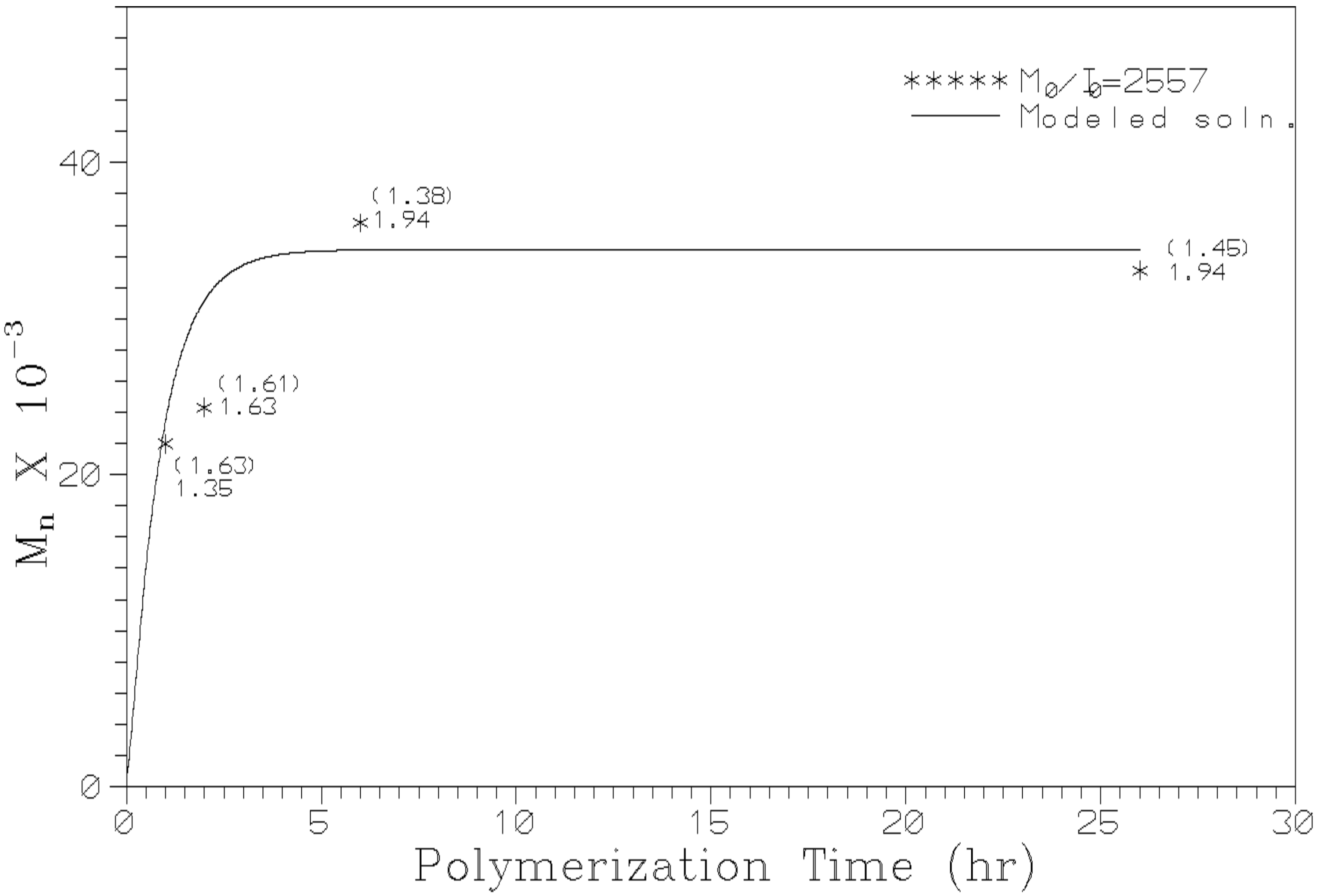


Figure 4.30 Comparison of experimental and modeling results (number average molecular weights) for the polymerization of L- lactide, using stannous octoate and triphenylphosphine under vacuum. The solid lines are the solutions obtained from the model and points are the experimental values.

Table 4.13 Summary of rate constants determined with various initiators for the polymerization carried out under nitrogen atmosphere at 130 (± 1) °C

S.No.	Initiators	k_o (l/mol.min)	k_p (l/mol.min)	k_t (l/mol.min)
1.	Stannous Octoate	0.003	15	0.060
2.	Stannous Octoate and Triphenylphosphine	0.200	15	0.023

Table 4.14 Summary of rate constants determined with various initiators for the polymerization carried out under vacuum at 130 (± 1) °C

S.No.	Initiators	k_o (l/mol.min)	k_p (l/mol.min)	k_t (l/mol.min)
1.	Stannous Octoate	0.200	5	0.020
2.	Stannous Octoate and Triphenylphosphine	0.200	5	0.020

Comparing the kinetic rate constants for the two initiators: stannous octoate and stannous octoate with triphenylphosphine (polymerization carried out under two different environments: nitrogen atmosphere, vacuum), a few interesting observations can be seen:

1. The propagation rate constant, k_p, is same for both the initiators. This means that the polymer chain once initiated will grow at the same rate in both cases (also, there is an assumption in the analysis that the propagation rate constant is independent of the chain length).
2. The initiation rate constant, k_o, is comparatively very less for pure stannous octoate initiator (nitrogen atmosphere). This would also explain the high experimental values of PD (implying a very broad molecular weight distribution). The growing polymer chains will start and terminate at different time leading to a broad MWD. In contrast, for stannous octoate with triphenylphosphine initiator, the experimental PD is very less which would be a desirable attribute of this system. For the vacuum atmosphere polymerizations, k_o, (Table 4.14) is identical for both stannous octoate and stannous octoate/triphenylphosphine. Thus, it is possible that the nitrogen atmosphere provided in the reaction kettle somehow decreases the rate constant.

3. The termination rate constant, k_t, for pure stannous octoate initiator is about 2.6 time that for stannous octoate with triphenylphosphine initiator. This could be the major reason for the difference in the average molecule weights achieved in PLA synthesis in the two cases. In case of vacuum, k_t, is same for both.
4. In the case of stannous octoate with triphenylphosphine initiator there is an induction time up to about 2.5 hr. It is interesting to note that initially it was not possible to curve fit the data for any value of k_p and k_t. However, once the time axis was shifted by an amount up to 2.5 hr, an excellent fit was obtained for particular k_p and k_t. This induction time is possibly due to the fact that the catalyst has to be thermally activated in the beginning of the polymerization in order to be effective. For the vacuum atmosphere polymerizations, the induction time decreases.
5. In both cases, the highest values of the average molecular weights are observed at initial monomer to initiator ratio of 2568. Thus, the polymerizations (vacuum atmosphere) were carried out only at this monomer to initiator ratio. The increase in molecular weights with increasing initial monomer to initiator ratio is because as this ratio increases, there will be fewer initiating sites for same number of monomer molecules and thus will lead to longer polymer chains. However, it is observed that at initial monomer to initiator ratio of 5068, the average molecular weights values fall dramatically. This could be because the numbers of initiating sites are reduced to such a level that chain termination by impurities or other molecules becomes significant and thus results in a lower chain length.

CHAPTER – 5

CONCLUSIONS AND RECOMMENDATIONS

CHAPTER 5 CONCLUSIONS AND RECOMMENDATIONS

5.1 Conclusions

On the basis of experiments conducted in the present study and modeling approach used for PLA polymerization, the following significant conclusions may be drawn:

1. PLA has been synthesized with a molecular weight above one-lac at laboratory scale using stannous octoate as an initiator. Also, a Lewis base namely triphenylphosphine has been used as co-initiator with this initiator. Molecular weight has increased from thousands to several ten thousands g mol^{-1}, when triphenylphosphine was used as co-initiator.
2. Low molecular weight of polylactide up to a few thousands was obtained with dibutyltindimethoxide and zinc stearate (with or, without triphenylphosphine) initiators. In dibutyltindimethoxide and dibutyltindimethoxide/triphenylphosphine initiators, low molecular weight of polylactide has been obtained because these initiators are known to be effective transesterification catalysts and also known to cause 'back-biting' degradation. Zinc stearate and zinc stearate/triphenylphosphine (initiator) gave lower molecular weight PLA than stannous octoate but higher than dibutyltindimethoxide because it is a weaker base, requires higher nucleophilicity to initiate lactide and that too only at higher temperatures. Some experiments were also performed with zinc stearate at 180 °C, but degradation took place at this temperature.
3. The maximum molecular weight of PLA is observed when the M_o/I_o ratio is 2500 to 2600.
4. The effect of dispersion of the initiator plays a very important role in polymerization. Double or even triple peaks in SEC chromatograms got reduced to single when initiator was well dispersed in monomer with the help of a solvent diethyl ether.
5. A correlation has been developed between intrinsic viscosity and molecular weight and values of $k = 5.98 \times 10^{-4}$ and $a = 0.72$ have been determined in the Mark-Houwink equation for PLA solution in chloroform at 30 °C.
6. High molecular weight of polylactide was obtained when polymerization was carried out under nitrogen atmosphere as compared to that carried out under vacuum.

7. A simple and reliable model has been presented for the polymerization of lactide to PLA. The model enables numerical solution of rate equations for initiation, propagation, and termination steps. It is easily extendable to more complex polymerization mechanisms. The simulation can be done in conjunction with the experimental data to yield individual rate constants. It is possible to obtain unique values for various rate constants using M_n versus time and polydispersity data. Accurate rate constants can be predicted using appropriate and reproducible rate data. This methodology offers greater opportunity for capturing high, non-equilibrium polymer yield through appropriately timed termination of the polymerization reaction.
8. A comparison of polymerization kinetics has been done when the initiator used is stannous octoate with and without triphenylphosphine under two different environments: nitrogen atmosphere and vacuum at 130 (± 1) °C. It is interesting that even though higher molecular weight product is obtained in a shorter time period with the latter, the propagation rate constant is same for both cases.
9. In the case of stannous octoate with triphenylphosphine initiator there is an induction time up to about 2.5 hr. It is interesting to note that initially it was not possible to curve fit the data for any value of k_p and k_t. However, once the time axis was shifted by an amount up to 2.5 hr, an excellent fit was obtained for particular k_p and k_t. This induction time is possibly due to the fact that the catalyst has to be thermally activated in the beginning of the polymerization in order to be effective. For the vacuum atmosphere polymerizations, the induction time decreases.
10. The termination rate constant is higher for stannous octoate as compared to the case when triphenylphosphine is also added to the polymerization kettle and this would lead to lower molecular weights under nitrogen atmosphere. In case of vacuum, k_t, is same for both.
11. Also, the initiation rate constant is much lower in case of stannous octoate which is responsible for a higher polydispersity value, and hence a broader molecular weight distribution under nitrogen atmosphere. For the vacuum atmosphere polymerizations, k_o, is identical for both stannous octoate and stannous octoate/triphenylphosphine. Thus, it is possible that the nitrogen atmosphere provided in the reaction kettle somehow decrease the rate constant.

5.2 Recommendations for Future Work

The synthesis and present modeling approach needs further improvement. For this the following are recommended:

1. Synthesis of PLA may be carried out using other co-initiators in place of triphenylphosphine which can then be used with stannous octoate, dibutyltindimethoxide and zinc stearate.
2. Purification methods other than recrystallization may be used to increase the purity of L- lactide (monomer) and yield of PLA.
3. The model can be made more accurate if the propagation reaction is made reversible to account for the depropagation reaction.

REFERENCES

Abraham, W. H., 1970. The Flory-Schultz distribution in reversible semi-batch polymerization, *Chem. Eng. Sci.,* 25, 331-335.

Abraham, W. H., 1963. Path-dependent distribution of molecular weights in linear polymers, *Ind. Eng. Chem. Fund*., 2, 221-224.

Achmad, F., Yamane, K., Quan, S., Kokugan, T., 2009. Synthesis of polylactic acid by direct polycondensation under vacuum without catalysts, solvents and initiators, *Chemical Engineering Journal*, 151(1-3), 342-350.

Ajioka, I., Suzuki, H., Higuchi, C., Kashima, T., 1998. Aliphatic polyesters and their coplymers synthesized through the direct condensation polymerization. *Polymer Degradation and Stability*, 59(1-3) 137-143.

Alaaeddine, A., Amgoune, A., Thomas, C. M., Dagorne, S., Laponnaz, S. B., Carpentier, J. F., 2006. Bis [bis (oxazolinato)] Complexes of Yttrium and Lanthanum: Molecular Structure and Use in Polymerization of dl-Lactide and dl-β- Butyrolactone. *European Journal of Inorganic Chemistry*, 18, 3652-3658.

Albertsson, A. C., Varma, I. K., 2003. Recent developments in ring-opening polymerization of lactones for biomedical applications. *Biomacromolecules*, 4(6), 1466-1486.

Andreopoulos, A.G., Hatzi, E., Doxastakis, M., 1999. Synthesis and properties of Poly(lactic acid). *Journal Of Materials Science: Materials In Medicine*, 10(1), 29-33.

Atthoff, B., Hilborn, J., Bowden, T., 2003. Polymeric Materials Science and Engineering (PMSE) Preprints, 88, 369.

Auras, R. A., Harte, B., Selke, S., Hernandez, R. J., 1998. Biopolymers from renewable resources, D. L. Kaplan (Ed.), *Springer-Verlag,* Berlin, 367–411.

Auras, R., Harte, B., Selke, S., 2004. An overview of polylactide as packaging materials. *Macromolecular Biosciences,* 4(9), 835–864.

Auras, R., Harte, B., Selke, S., 2005. Polylactides. A new era of Biodegradable Polymers for Packaging Application. ANTEC, 3240-3244.

Bamford, C. H., Tompa, H., 1954. The calculation of molecular weight distributions from kinetic schemes, *Trans. Faraday Soc*., 50, 1097-1115.

Bamford, C. H., Barb, W. G., Jenkins, A. D., Onyon, P. F., 1958. The Kinetics of Vinyl Polymerization by Radical Mechanisms, Academic Press, New York.

Bamford, C. H., Jenkins, A. D., 1960. The coupling of polymers. Part1. Size distributions and intrinsic viscosities, *Trans. Faraday Soc*., 56, 907-931.

Benoit, H., Grubisic, Z., Rempp, P., Decker, D., Zilliox, J. G. 1966. Study of chromatography in liquid phase of linear polystyrene and branched in known structure**.** *J. Chem. Phys.*, 63: 1507-1514.

Bero, M., Kasperczyk, J., Jedlinski, Z. J., 1990. Coordination polymerization of lactides, 1. Structure determination of obtained polymers. *The Macromolecular Chemistry*, 191(10), 2287–2296.

Bharucha-Reid, A. T., 1960. Elements of the theory of Markov processes and their applications, McGraw-Hill, New York.

Bonsignore, P., 1995. Production of high molecular weight polylactic acid. US5470944.

Boretos, J. W., Eden, M., (eds.), 1984. Contemporary Biomaterials: Material and Host Response, Clinical applications, New Technology and Legal Aspects, Noyes Med. Publ., Park Ridge, NJ.

Brode, G. L., Koleske, J. V., 1972. Lactone polymerization and polymer properties. *J. Macromol. Sci. – Chem.*, A6(6), 1109-1144.

Cabaret, O. D., Vaca, B. M., Bourissou, D., 2004. Controlled ring-opening polymerization of lactide and glycolide. *Chem. Rev*., 104(12), 6147-6176.

Case, L. C., 1958. Molecular weight distributions in polycondensations involving unlike reactants. II. Linear distributions. *J. Polym. Sci*., 29, 455-495.

Chow, W. S., Lok, S. K., 2009. Thermal properties of poly(lactic acid)/organo-montmorillonite nanocomposites. *Journal of Thermal Analysis and Calorimetry*, 95(2), 627-632.

Degee, O., Dubois, P., Jacobsen, S., Fritz, S. G., Jerome, R., 1999. Beneficial effect of triphenylphosphine on the bulk polymerization of L, L- lactide promoted by 2-ethylhexanoic acid tin(II) salt. *J. Polym. Sci. Part A: Polym. Chem*., 37, 2413-2420.

Dittrich, V. W., Schulz, R. C., 1971. Kinetics and mechanism of ring-opening polymerization of L (-)-lactide. *The Macromolecular Chemistry*, 15, 109–126.

Dobrzynski, P., Li, S., Kasperczyk, J., Bero, M., Gasc, F., Vert, M., 2005. Structure-Property Relationships of Copolymers Obtained by Ring-Opening Polymerization of Glycolide and ε -Caprolactone. Part 1. Synthesis and Characterization. *Biomacromolecules*, 6, 483-488.

Dorgan, J. R., Lehermeier, H. J., Palade, L. I., Cicero, J., 2001. Polylactides: properties and prospects of an environmentally benign plastic from renewable resources. *Macromol. Symp.*, 175, 55-66.

Dorgan, J. R., Janzen, J., Knauss, D. M., Hait, S. B., Limoges, B. R., Hutchinson, M. H., 2005. Fundamental solution and single chain properties of polylactides. *J. Polym. Sci., Part B: Polym. Phys*. 43, 3100-3111.

Du, Y. J., Nijenhuis, A. J., Bastiaansen, C., Lemstra, P. J., 1995. New approaches to ring opening polymerization-evidences of step transfer polymerization. *J.Macromol. Sci. Pure Appl. Chem.*, A32, 1061-1069.

Du, Y. J. Lemstra, P. J., Nijenhuis, A. J., Van Aert, H. A. M., Bastiaansent, C., 1995. ABA Type Copolymers of Lactide with Poly (ethy1ene glycol). Kinetic, Mechanistic, and Model Studies, *Macromolecules*, 28, 2124-2132.

Dubois, Ph., Degée, Ph., Jacobsen, S., Fritz, H. G., Jerome, R., 1999. Beneficial effect of triphenylphosphine on the bulk polymerization of L, L-lactide promoted by 2-ethylhexanoic acid tin (II) salt. *Journal of Polymer Science Part A: Polymer Chemistry*, 37(14), 2413-2420.

Dubois, Ph., Jerome, R., Jacobs, C., Teyssie, Ph., 1991. Macromolecular engineering of polylactones and polylactides. Mechanism and Kinetics of lactide homopolymerization by Aluminium isopropoxide. *Macromolecules*, 24, 2266-2270.

Dubois, P., Ropson, N., Jerome, R., Teyessie, P., 1996. Macromolecular Engineering of Polylactones and Polylactides. 19. Kinetics of Ring-Opening Polymerization of ε-Caprolactone Initiated with Functional Aluminum Alkoxides. *Macromolecules*, 29 (6), 1965–1975.

Duda, A., Penczek, S., 1990, Thermodynamics of L-Lactide Polymerization. Equilibrium Monomer Concentration, *Macromolecules*, 23, 1636–1639.

Eenink, M. J. D., 1987. Ph.D. Thesis, Twente University.

Espartero, J. L., Rashkov, I., Li, S. M., Manolova, N., Vert, M., 1996. NMR analysis of polylactic acid macromolecules. *Macomolecules*, 59, 3535-3539.

Engel, R., Schwach, G., Coudane, J., Vert, M., 1997. More about the polymerization of lactides in the presence of stannous octoate, *Journal of Polymer Science Part A: Polymer Chemistry*, 35 (16), 3431-3440.

Falkovitz, M. S., Segal, L. A., 1982. Some analytic results concerning the accuracy of the continuous approximation in a polymerization problem, *SIAMJ. Appl. Math.*, 42 (3), 542-548.

Feller, W., 1959. An introduction to probability and its applications. Wiley, New York.

Finne, A., Reema, Albertsson, A.C., 2003. Use of germanium initiators in ring-opening polymerization of L- lactide. *Journal of Polymer Science Part A: Polymer Chemistry*, 41(19), 3074-3082.

Fisher, E. W., Sterze, H. J., Wegner, G., 1973. Investigation of the structure of solution grown crystals of lactide copolymers by means of chemical reactions. Kolloid ZZ, *Polym.*, 251, 980-990.

Fukushima, K., Tabuani, D., Camino, G., 2009. Nanocomposites of PLA and PCL based on montmorillonite and sepiolite. *Materials Science and Engineering: C*, 29(4), 1433-1441.

Gadzinowski, M., Sosnowski, S., Slomkowski, S., 1996. Kinetics of the dispersion ring-opening polymerization of ε-caprolactone initiated with diethylaluminum ethoxide. *Macromolecules*, 29, 6404-6407.

Ghosh, P., Ray, L., Katiyar, V., Raihan, M. J., Nanavati, H., Shaikh, M. M., 2006. First Example of a Gold(I) N-Heterocyclic- Carbene -Based Initiator for the bulk ring-opening polymerization of L- lactide, *European Journal of Inorganic Chem*., 18, 3724-3730.

Guo, B., Wistrand, A. F., Albertsson, A. C., 2010. Molecular Architecture of Electroactive and Biodegradable Copolymers Composed of Polylactide and Carboxyl-Capped Aniline Trimer. *Biomacromolecules*, 11, 855–863.

Harper, C. A., 2000. Modern Plastics Handbook. New York: McGraw-Hill.

Hedrick, J. L., Myers, M., Connor, E. F., Glauser, T., Mock, A., Nyce, G., 2001. Phosphines: Nucleophilic organic catalysts for the controlled ring-opening polymerization of lactides. *Journal of Polymer Science Part A: Polymer Chemistry*, 40 (7), 844-851.

Hedrick, J. L., Moller, M., Nederberg, F., Lim, L. S., Kange, R., Hawker, C. J., Gu, Y., Shah, R., Abbott, N. L., 2002. Stannous(II) trifluoromethane sulfonate: a versatile catalyst for the controlled ring-opening polymerization of lactides: Formation of stereoregular surfaces from polylactide "brushes". *Journal of Polymer Science, Part A: Poly. Chemistry*, 39 (20), 3529-3538.

Hiltunen, K., Seppala, J. V., Harkonen, M., 1997. Effect of catalyst and polymerization conditions on the preparation of low molecular weight lactic acid polymer. *Macromolecules*, 30(3), 1091-1100.

Howe, J. P., 1955. Method of integrating the rate equations for free radical initiated. *Journal of Chemical Physics*, 23 (5), 899-902.

Hyon, S. H., Jamshidi, K., Ikada, Y., 1997. Synthesis of polylactides with different molecular weights. *Biomaterials*, 18 (22), 1503-1508.

Inata, H., Matsumura, S., Ogasawa, M., 1983. Process for producing aromatic polyesters having an increased degree of polymerization, these aromatic polyesters, process for producing molded articles composed thereof, and these molded articles. EP0020944.

In't Veld, P. J. A., Velner, E. M., VanDeWitte, P., Hamhuis, J., Dijkstra, P. J., Feijen, J., 1997. Melt Block Copolymerization of ε-Caprolactone and L- lactide. *J. Polym. Sci, Polym. Chem.*, 35 (2), 219-226.

Jacobson, S., Fritz, H. G., Degee, P., Dubois, P., Jerome, R., 2002. New developments on the ring-opening polymerization of polylactide. *Industrial crops and products*, 11(2-3), 265-275.

Jiang, L, Zhang, J., Wolcott, M. P., 2007. Comparison of polylactide/nano-sized calcium carbonate and polylactide/montmorillonite composites: Reinforcing effects and toughening mechanisms. *Polymer,* 48(26), 7632-7644.

Jing, S. Peng, W., Tong, Z., Baoxiu, Z., 2006. Microwave-irradiated ring-opening polymerization of D,L- lactide under atmosphere. *Journal of Applied polymer science*, 100 (3), 2244-2247.

Jonoobi, M., Harun, J., Mathew, A. P., Oksman, K., 2010. Mechanical properties of cellulose nanofiber (CNF) reinforced polylactic acid (PLA) prepared by twin screw extrusion. *Composites Science and Technology,* 70(12), 1742-1747.

Kalmi, M., Lahcini, M., Castro, P., Lehtonen, O., Belfkira, A., Leskelä, M., Repo, T., 2003. Tetrakis Sn (IV) alkoxides as novel initiators for living ring-opening polymerization of lactides. *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (8), 1901-1911.

Kasperczyk, J., Bero, M., 2000. Stereoselective polymerization of racemic DL- lactide in the presence of butyl lithium and butyl magnesium, Structural investigations of the polymers. *Polymer*, 41, 391-395.

Kawasaki, N., Nakayama, A., Maeda, Y., Hayashi, K., Yamamoto, N., Aiba, S., 1998. Synthesis of a new biodegradable co-polyester amide poly lactic acid co-caprolactam. *Macromolecular Chemistry and Physics*, 199, 2407-2415.

Kilkson, H., 1964. Effect of reaction path and initial distribution on the molecular weight distribution of condensation polymers. *Ind. Eng. Chem. Fund*., 4, 281-293.

Kim, S. H., Kim, Y. H., 1999. Direct condensation of polymerization of lactic acid. *Macromolecular Symposium*, 144, 227-287.

Kim, Y., Verkade, J. G., 2005. Living polymerization of lactide using Titanium alkoxide catalysts. *Macromolecular Symposia*, 224 (1), 105-118.

Kleine, V. J., Kleine, H. H., 1959. Proceed over high molecular weight, in particular optically active polyester of lactic acid, a contribution to the connections of macromolecular stereochemistry. *The Macromolecular Chemistry*, 30(1), 23-38.

Kleawkla, A., Suksomran, W., Srisa-ared, M., Baimark, Y., Molloy, R., Siritayananon, J., Punyodom, W., Nalampang, K., Sriyai, M., 2005. Controlled ring-opening polymerization of cyclic eaters, B03.

Kolybaba, M., Tabil, L. G., Panigrahi, S., Crerar, W. J., Powell, T., Wang, B., 2003. Biodegradable Polymers: Past, Present, and Future, Written for presentation at the 2003 CSAE/ASAE Annual Intersectional Meeting Sponsored by the Red River Section of ASAE Quality Inn and Suites 301 3rd Avenue North Fargo, North Dakota, USA.

Konishi, S., Yokoi, T., Ochiai, B., Endo, T., 2010. Effect of metal triflates on direct polycondensation of lactic acid. *Polym. Bull.*, 64, 435–443.

Kowalski, A., Duda, A., Penczek, S., 1998. Kinetics and mechanism of cyclic esters polymerization initiated with tin (II) octoate, 1. Polymerization of ε-caprolactone. *Macromol. Rapid Commun.*, 19, 567-572.

Kramschuster, A., Gong, S., Turng, L. S., Li, T., Li, T., 2007. Injection-Molded Solid and Microcellular Polylactide and Polylactide Nanocomposites**.** *Journal of Biobased Materials and Bioenergy*, 1(1), 37-45.

Kricheldorf, H. R., Serra, A., 1985. Polylactones. *Polymer Bulletin*, 14, 497–502.

Kricheldorf, H. R., Dunsing, R., 1986. Polylactones, 8. Mechanism of the cationic polymerization of L, L-dilactide. *The Macromolecular Chemistry*, 187, 1611–1625.

Kricheldorf, H. R., Kreiser, I., 1987. Polylactones, 11. Cationic copolymerization of glycolide with L, L- dilactide. *The Macromolecular Chemistry*, 188, 1861–1873.

Kricheldorf, H. R., Berl, M., Scharnagl, N., 1988. Polymerization mechanism of metal alkoxide initiated polymerizations of lactide & various lactones. *Macromolecules*, 21, 286-293.

Kricheldorf, H. R., Sumbel, M., 1989. Polylactones—18. Polymerization of L, L-lactide with Sn(II) and Sn(IV) halogenides. *European Polymer Journal*, 25(6), 585–591.

Kricheldorf, H. R., Saunders, I. K., 1990. Polylactones 19. Anionic polymerization of L-lactide in solution. *The Macromolecular Chemistry*, 191(5), 1057–1066.

Kricheldorf, H. R., Boettcher, C., Tonnes, K. U., 1992. Polylactones: 23. Polymerization of racemic and meso-D,L-lactide with various organotin catalysts-stereochemical aspects. *Polymer*, 33(13), 2817-2824.

Kricheldorf, H.R.; Boettcher, C., 1993. Polylactones.XXV, Polymerizations of racemic and meso-D,L –lactide and Zn, Pb, and Bi salts-stereochemical aspects. *Journal of Macromolecular Science-Pure and Applied Chemistry*, *A30* (6-7), 441-448.

Kricheldorf, H. R., Lee, S. R., 1994. Polylactones: 32. High molecular weight polylactides by ring-opening polymerization with dibutylmagnesium or, butyl magnesium chloride, *Polymer*, 36 (15), 2995-3003.

Kricheldorf, H. R., Kreiser-Saunders, I., Boettcher, C., 1995. Polylactones: 31. Sn(II)octoate-initiated polymerization of L-lactide: a mechanistic study. *Polymer,* 36, 1253-1259.

Kricheldorf, H. R., Kreiser-Saunders, I., Stricker, A. 2000. Polylactones 48. $SnOct_2$-Initiated Polymerizations of Lactide: A Mechanistic Study. *Macromolecules*, 33, 702-709.

Kricheldorf, H. R., Lomadze, N., Schwarz, G., 2008. Cyclic Polylactides by Imidazole-Catalyzed Polymerization of L-Lactide. *Macromolecules*, 41, 7812-7816.

Kumar, A., Gupta, R. K., 1998. Fundamentals of Polymers, McGraw-Hill International Edition, Singapore.

Kunioka, M., Wang, Y., Onozawa, S. Y., 2005. Poly(lactic acid) Polymerized by Aluminum Triflate. *Macromolecular Symposia*, 224 (1), 167-180.

Kylma, J., Seppala, J. V., 1997. Synthesis and characterization of a biodegradable polyesters. *Macromolecules*, 30(10), 2876-2882.

Kylma, J., Harkone, M., Seppala, J. V., 1997. The modification of lactic acid based polymer by copolymerization. *Journal of Applied Polymer Science*, 63(13), 1865-1872.

Liao, L., Zhang, C., Liu, L., **2004.** Rapid Ring-Opening Polymerization of D, L- lactide by Microwaves. *Macromolecular Rapid Communications*, 25 (15), 1402-1405.

Li, J., Xie, W., Cheng, H. N., Nickol, R. G., Wang, P. G., 1999. Polycaprolactone-Modified Hydroxyethylcellulose Films Prepared by Lipase-Catalyzed Ring-Opening Polymerization. *Macromolecules*, 32, 2789-2792.

Liang, C., **Sun, J., Shi, W., Chen, D., 2002.** The ring-opening polymerization of D,L-lactide catalyzed by new complexes of Cu, Zn, Co, and Ni Schiff base derived from salicylidene and L-aspartic acid. *Journal of Applied Polymer Science,* 86 (13), 3312-3315.

Liang, C., Kohn, R. D., Pan, Z., Sun, J., 2002. Ring-opening Polymerization of D, L-Lactide with bis (trimethyltriazacyclohexane) praseodymium triflate. *catalysis communication,* 4 (1), 33-37.

Ling, F., Bing, X. Y., Hua, T. K., Quan, S. Z., 2005. Ring-opening Polymerization of D,L-Lactide by Lanthanide Tris (2,4,6-trimethylphenolate): Characteristics and Kinetics. *Chinese Journal of Chem.,* 23 (5), 613-616.

Lee, Y. W., Pack, J. W., Kim, S. H., Park, S. Y., Kim, Y. H., 2005. Ring- opening Polymerization of L-Lactide in supercritical chlorodifluoromethane. *Macromolecular Symposia*, 224 (1), 85-92.

Lopez, F., Castro, J. M., Tirrel, M., 1980. Recursive approach to copolymerization statistics. *Polymer*, 21, 261-273.

Loefgren, A., Albertsson, A. C., Dubois, A. C., Jerome, R., Teyessie, P., 1994. Synthesis and Characterization of Biodegradable Homopolymers and Block Copolymers Based on 1,5-Dioxepan-2-one. *Macromolecules*, 27 (20), 5556-5562.

Lowry, G. G., 1970. Markov chains and Monte Carlo calculations in polymer science, Marcel Dekker, New York.

Lunt, J., 1998. Large-scale production, properties and commercial applications of polylactic acid polymers. *Polym. Deg. Stab*., 59, 145-152.

Macosko, C. W., Miller, D. R., 1976. A new derivation of average molecular weights on nonlinear polymers. *Macromolecules*, 9, 199-206.

Maharana, T., Mohanty, B., Negi, Y. S., 2009. Melt–solid polycondensation of lactic acid and its biodegradability. *Progress in Polymer Science*, 34, 99–124.

Maharana, T., Mohanty, B., Negi, Y. S., 2010. Preparation of Poly(lactic acid) Nanoparticles and Optimization of the Particle Size. *International Journal of Green Nanotechnology: Physics and Chemistry*, 2(2), 100 – 109.

Maiti, P., Yamada, K., Okamoto, M., Ueda, K., Okamoto, K., 2002. New Polylactide/Layered Silicate Nanocomposites: Role of Organoclays. *Chem. Mater*, 14, 4654-4661.

Maiti, P., Batt, C. A., Giannelis, E. P., 2007. New Biodegradable Polyhydroxybutyrate/Layered Silicate Nanocomposites. *Biomacromolecules*, 8, 3393-3400.

Marshall, E. D., McGuinness, D. S., Gibson, V. C., Steed, J. W., 2003. Anionic iron (II) alkoxides as initiators for the controlled ring-opening polymerization of lactide. *Journal of Polymer Science Part A: Polymer Chemistry,* 41 (23), 3798-3803.

McNeill, I. C., Leiper, H. A., 1985. Degradation studies of some polyesters and polycarbonates-1. Polylactide: General features of the degradation under programmed heating conditions. *Polymer Degradation and Stability*, 11 (3), 267–285.

Mehta, R., Kumar, V., Bhunia, H., Upadhyay, S. N., 2005. Synthesis of Polylactic acid: A review. *Journal of macromolecular science, part C, Polymer reviews*, 45, 325-349.

Mehta, R., 2006. PhD Thesis, Modeling and Simulation of Poly(lactic acid) polymerization, Thapar University, Patiala.

Mehta, R., Kumar, V., Upadhyay, S. N., 2007. Mathematical Modeling of Polylactic acid Ring - Opening Polymerization. *Polymer Plastic Technology and Engineering*, 46 (3), 257-264.

Mehta, R., Kumar, V., Upadhyay, S. N., 2007. Mathematical Modeling of Polylactic acid Ring - Opening Polymerization using Stannous Octoate as a Catalyst. Polymer *Plastic Engineering and Technology*, 46, 933-937.

Michael, V., 2000. Winning Technologies: Polylactic Polymers. Industry Week.

Middleton, J. C., Tipton, A. J., 2000. Synthetic biodegradable polymers as orthopedic devices. *Biomaterials*, 21, 2335-2346.

Miller, D. R., Macosko, C. W., 1978. Average property relations for nonlinear polymerizations with unequal reactivity. *Macromolecules*, 11, 656-662.

Moller, M., Nederberg, F., Lim, L. S., Kange, R., Hawker, C. J., Hedrick, J. L., Gu, Y., Shah, R., Abbott, N. L., 2001. Stannous(II) trifluoromethane sulfonate: a versatile catalyst for the controlled ring-opening polymerization of lactides: Formation of stereoregular surfaces from polylactide "brushes". *Journal of Polymer Science, Part A: Polymer Chemistry*, 39, 3529-3538.

Moon, S. I., Lee, C.W., Miyamoto, M., Kimura, Y., 2000. Melt polycondensation of L-lactic acid with Sn(II) catalysts activated by various proton acids: A direct manufacturing route to high molecular weight Poly(L-lactic acid). *J. Polym. Sci. A: Polym. Chem.,* 38 (9), 1673–1679.

Moravek, S. J., Messman, J. M., Storey, R. F., 2009. Polymerization kinetics of rac-lactide initiated with alcohol/stannous octoate using in situ attenuated total reflectance-fourier transform infrared spectroscopy: An initiator study. *J. Polym. Sci., Part A: Polym. Chem*., 47, 797–803.

Mullen, B. D., Storey, R. F., Desai, G. S., Sherman, J. W., Tang, C. N., 2002. Soluble tin (II) macro initiator adducts for the controlled ring-opening polymerization of lactones and cyclic carbonates. *Journal of Polymer Science Part A: Polymer Chem.,* 40 (20), 3434-3442.

Nakagaito, A. N., Fujimura, A., Sakai, T., Hama, Y., Yano, H., 2009. Production of microfibrillated cellulose (MFC)-reinforced polylactic acid (PLA) nanocomposites from sheets obtained by a papermaking-like process. *Composites Science and Technology*, 69 (7-8), 1293-1297.

Nikolic, L., Ristic, I., Adnadjevic, B., Nikolic, V., Jovanovic, J., Stankovic, M., 2010. Novel Microwave-Assisted Synthesis of Poly (D, L- lactide): The Influence of Monomer/Initiator Molar Ratio on the Product Properties. *Sensors*, 10, 5063-5073.

Nijenhuis, A. J., Grijpma, D. W., Pennings, A. J., 1992. Lewis acid catalyzed polymerization of L- lactide. Kinetics and Mechanism of bulk polymerization. *Macromolecules*, 25, 6419-6424.

Odian, G., Principles of Polymerization, Wiley-Interscience: New York, 1991 (Fourth edition).

Ouchi, T., Kontani, T., Ohya, Y., 2003. Modification of polylactide upon physical properties by solution-cast blends from physical and polylactide-grafted dextran. Polymer, *44*(14), 3927-3933.

Penczek, S., Kubisa, P., Matyjaszewski, K., 1980. 'Cationic ring-opening polymerization' in 'Advances in Polymer Science' 37 Springer-Verlag: New York.

Ray, W. H., 1972. On the Mathematical Modeling of polymerization reactors. *J. Macromolecules Sci. Revs.,* C8, 1-56.

Ray, S. S., Maiti, P., Okamoto, M., Yamada, K., Ueda, K., 2002. New Polylactide/Layered Silicate Nanocomposites. 1. Preparation, Characterization, and Properties. *Macromolecules***,** 35, 3104-3110.

Roether, J.A., Gough, J.E., Jerome, R., 2002. Novel bioresorbable and bioactive glass and polylactide for bone tissue engineering. Journal of Materials Science: Materials in Medicine, *13*(12), 1207-1214.

Sailaja, R. R. N., Kumar, A., 1995. Semianalytical solution of irreversible anionic polymerization with unequal reactivity in batch reactors. *Journal of Applied Polymer Science,* 58(10), 1865-1876.

Sailaja, R. R. N., Kumar, A., 1997. Evaluation of rate constants from experimental batch reactor data for anionic polymerization of poly (methyl methacrylate) at high temperatures. *Journal of Applied Polymer Science*, 65(5), 845-859.

Schappacher, M., Save, M., Soum, A., 2002. Controlled ring-opening polymerization of lactones and lactides initiated by lanthanum isopropoxide, 1. General Aspects and Kinetics. *Macromolecular Chemistry and Physics*, 203 (5-6), 889-899.

Schlinder, A., Harper, D., 1979. Polylactide. II. Viscosity-Molecular weight relationships and unperturbed chain dimensions. *Journal of polymer sci.,* 17, 2593-2599.

Schwach, G., Coudane, J., Engel, R., Vert, M., 1994. Stannous-octoate versus zinc-initiated polymerization of racemic lactide-effect of configurational structure. *Polymer Bulletin (Berlin)*, 32 (5-6), 617-623.

Schwach, G., Coudane, J., Engel, R., Vert, M., 1996. Zn lactate as initiator of DL -Lactide ROP of & comparison with Sn octoate. *Polymer Bulletin*, 37, 771-776.

Schwach, G., Coudane, J., Engel, R., Vert, M., 1997. More about the polymerization of lactides in the presence of stannous octoate. *J. Polym. Sci., Polym.Chem.*, 35, 3431-3440.

Schwach, G., Coudane, J., Engel, R., Vert, M., 1998. Ring-opening polymerization of D, L-lactide in the presence of zinc metal and zinc lactate. *Polymer International*, 46 (3), 177-182.

Schwach, G., Coudane, J., Engel, R., and Vert, M., 2002. Influence of polymerization conditions on the hydrolytic degradation of poly (DL-lactide) polymerized in the presence of stannous octoate or zinc-metal. *Biomaterials*, 23 (4), 993-1002.

Shen, Z., Zhang, L., Yu, C., Fan, L., 2004. Ring-opening polymerization of D, L- lactide by rare earth 2,6-dimethylaryloxide. *Polymer International*, 53 (8), 1013-1016.

Sinclair, R. G., 1996. The case for polylactic acid as a commodity packaging plastic. *J. Macromol. Sci., Pure Appl. Chem.*, 33(5), 585-597.

Sosnowski, S., Gadzinowski, M., Slomkowski, S., 1996. Poly (L, L- lactide) microspheres by ring-opening polymerization. *Macromolecules*, 29, 4556.

Stanford, M. J., Pflughaupt, R. L., Dove, A. P., 2010. Synthesis of Stereoregular Cyclic Poly(lactide)s via Thiol−En Click Chemistry. *Macromolecules*, 43, 6538-6541.

Swift, G., 1993. *Acc. Chem. Res*., 26, 105.

Tang, Z., Chen, X., Yang, Y., Pang, X., Sun, J., Zhang, X., Jing, X., 2004. Stereoselective polymerization of rac-lactide with a bulk aluminum/Schiff base complex. *Journal of Polymer Science Part A: Polymer Chemistry*, 42 (23), 5974-5982.

Thomas, C. M., Amgoune, A., Roisnel, T., Carpentier, J. F., 2005. Ring-Opening Polymerization of lactide with group 3 metal complexes supported by dianionic alkoxy-amino-bisphenolate ligands: combining high activity, productivity, and selectivity. *Chemistry a European Journal*, 12 (1), 169-179.

Tirrel, M., Galvan, R., Laurence, R. L., 1986. ‘Polymer Reaction Engineering’, Marcel Dekker, New York.

Tuominen, J., 2003. Chain linked lactic acid polymers: Polymerization and biodegradation studies, Polymer Technology Publication Series, Espoo.

Venkateshwara, G., Kumar, A., 1992. Solution of free radical polymerization. *Journal of Applied Polymer Science*, 45(2), 187-215.

Vert, M., Schwach, G., Coudane, J., 1995. Present and future of PLA polymers. *J. Macromol. Sci., Pure Appl. Chem.,* A32, 787-796.

Vink, E. T. H., Rabago, K. R., Glassner, D. A., Gruber, P. R., 2003. Applications of life cycle assessment to Nature Works TM polylactide (PLA) production. *Polymer Degradation and Stability*, 80, 403-419.

Wang, X., Liao, K., Quan, D., Wu. Q., 2005. Bulk Ring-Opening Polymerization of Lactides Initiated by Ferric Alkoxides. *Macromolecules*, 38, 4611-4617.

Woo, S. I., Kim, B.O., Jun, H. S., Chang, H. S. N., 1995. Polymerization of lactic acid to prepare high molecular weight poly lactic acid by chain extending and hexamethylene diisocyanate. *Polymer bulletin*, 35(4), 415-421.

Xie, W., Chen, D., Fan, X., Li, J., Wang, P. G., Cheng, H. N., Nickol, R. G., 1999. Lithium chloride as catalyst for the ring-opening polymerization of lactide in the presence of hydroxyl-containing compounds. *Journal of poly. Sci. Part A: Polymer Chem*., 37(17), 3486-3491.

Xiong, C., Yuan, M., Li, X., Deng, X., 1999. Polymerization of lactides and lactones. III. Ring-opening polymerization of DL-lactide by the (η3-C3H5)2Sm(μ2-Cl)2(μ3-Cl)2Mg(tmed)(μ2-Cl)Mg(tmed) complex. *Journal of Applied Polymer Science*, 73 (14), 2857-2862.

Yang, Y., Tang, Z., Pang, X., Hu, J., Chen, X., Hu, N., Jing, X., 2005. Controlled and stereospecific polymerization of rac-lactide with a single-site ethyl aluminum and alcohol initiating system. *Journal of Applied Polymer Science*, 98 (1), 102-108.

Yoda, S., Bratton, D., Howdle, S. M., 2004. Direct synthesis of poly (L- lactic acid) in supercritical carbon dioxide with dicyclohexyldimethylcarbodiimide and 4-dimethyl aminopyridine. *Polymer*, 45(23), 7839-7843.

Zeman, R., Amundson, N. R., 1965a. Continuous polymerization models-I : Polymerization in continuous stirred tank reactors. *Chem. Engg. Sci*., 20 (4), 331-361.

Zeman, R., Amundson, N. R., 1965b. Continuous polymerization models-part II : Batch reactor polymerization. *Chem. Engg. Sci.*, 20 (7), 637-664.

Zeng, J. B., Li, Y. D., Li, W. D., Yang, K. K., Wang, X. L., Wang, Y. Z., 2009. Synthesis and Properties of Poly (Ester Urethane)s Consisting of Poly (L- Lactic Acid) and Poly (Ethylene Succinate) Segments. *Ind. Eng. Chem. Res.*, 48, 1706-1711.

Zhao, X., Li, H., Wang, C., Yue, J., Bai, F., 2004. Living ring-opening polymerization of lactides catalyzed by guanidinium acetate. *Journal of Polymer Science Part A: Polymer Chem*., 42 (15), 3775-3781.

Zhang, X., Macdonald, D. A., Goosen, M., Maculey, K., 1994. Mechanism of lactide polymerization in the presence of stannous octoate: The effect of Hydroxy and Carboxylic acid substances. *Journal of Polymer Science Part A: Polymer Chemistry,* 32, 2965-2970.

Zhang, L., Yu, C., Ni, X., Shen, Z., Tu, K., 2004. Ring-opening polymerization of L-lactide by rare-earth tris (4-tert-butylphenolate) single-component initiators. *Journal of Polymer Science Part A: Polymer Chemistry,* 42 (24), 6209-6215.

Zhou, Z. H., Liu, X. P., Liu, L. H., 2008. Synthesis of ultra-high weight average molecular mass of poly (l-lactide). *International Journal of Polymeric Materials*, 57,532–542.

http://www.almaden.ibm.com/st/chemistry/ps/initiators/RingOpening (accessed Sept. 2010).

http://www.wiley-vch.de/books/biopoly/pdf_v04/bpol4008_235_239.pdf (accessed Oct. 2010).

http://cargilldow.com/release.asp?id=92 (accessed May, 2011).

http://www.lactic-acid.com/history.html (accessed May 2011).

http://www.oit.doe.gov/cfm/full article.cfm/id=305 (accessed May 2011).

http://en.wikipedia.org/wiki/Polylactic_acid (accessed July 2011)

http://www.nnfcc.co.uk/publications/nnfcc-renewable-chemicals-factsheet-lactic-acid (accessed July 2011)

APPENDIX A
CHARACTERIZATION OF INITIATORS

Characterization of liquid initiators was done by Fourier Transform Infrared Spectroscopy (FTIR), Hydrogen Nuclear Magnetic Resonance (^{1}H NMR), Ultra Violet and Visible Spectroscopy (UV-visible), Refractive Index, Density. Solid initiators formed homogenous mixture with the monomer, so crystallite size, surface area and particle size need not to be characterized.

Proton Nuclear Magnetic Resonance (^{1}H NMR)

Nuclear magnetic resonance spectroscopy (NMR) was done for liquid initiators (stannous octoate and dibutyltindimethoxide). ^{1}H NMR spectra were recorded on Brucker Avance II Spectrometer operating at 400 MHz. NMR spectrum was recorded in $CDCl_3$ solvent. NMR is unique technique for the direct detection of hydrogen bonding interactions, chemical identification and conformational analysis of chemicals whether synthetic or natural. The ^{1}H NMR spectra of stannous octoate shows that in alkanes, sp^3 hybridized C-H's in range of δ 0.847-1.586 and in acids, sp^3 hybridized C-H's in range of δ 2.199-2.355 (Fig. A.1). The ^{1}H NMR spectra of dibutyltindimethoxide shows that in alkanes, sp^3 hybridized C-H's in range of δ 0.914-1.671 and in ethers, sp^3 hybridized C-H's in range of δ 2.758-3.569 (Fig. A.2).

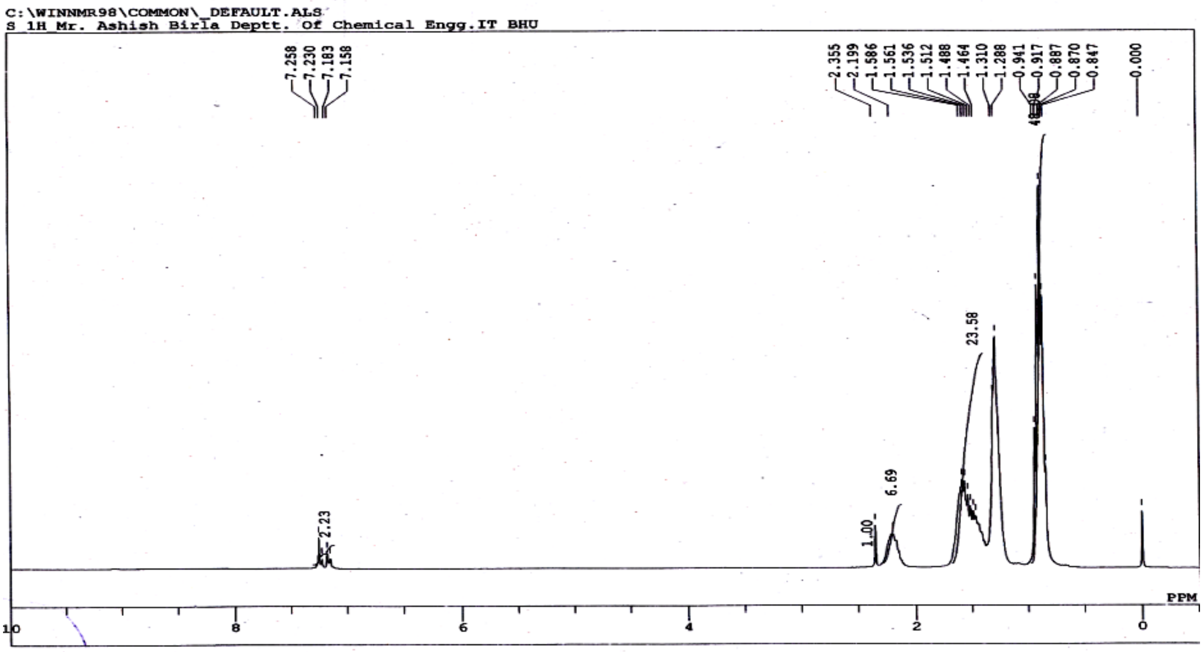


Figure A.1 ¹H NMR spectra of stannous octoate

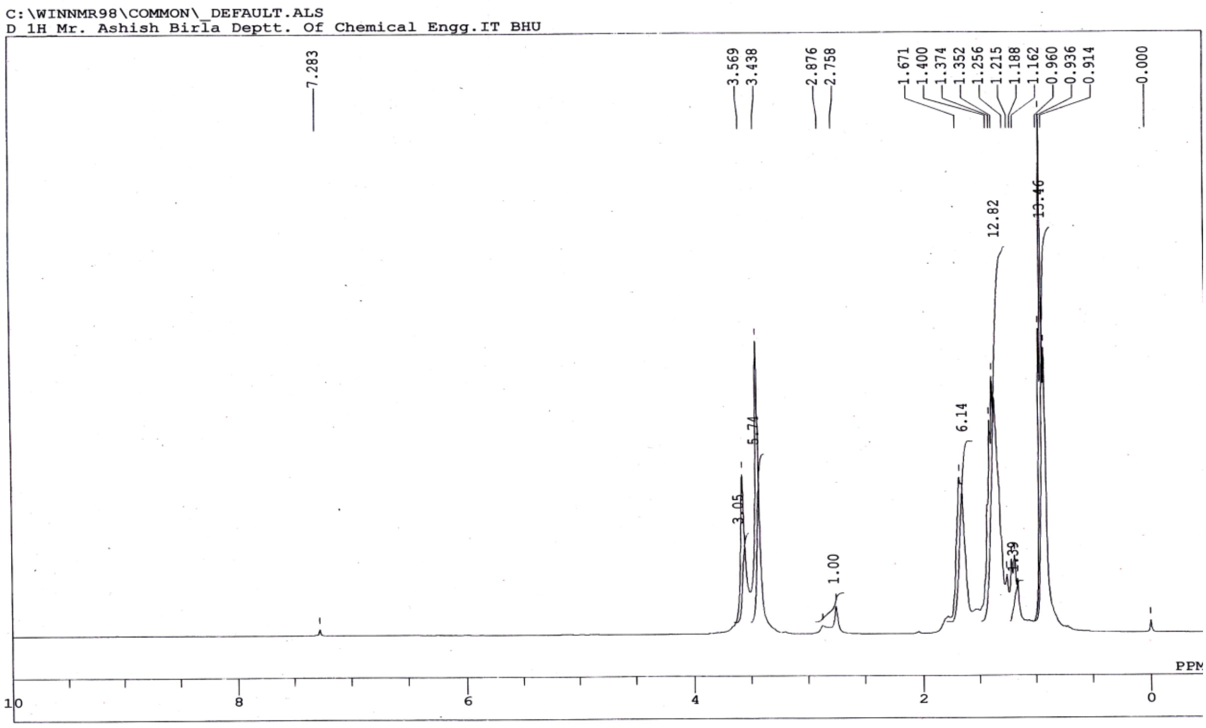


Figure A.2 ¹H NMR spectra of dibutyltindimethoxide

Fourier Transform Infrared Spectroscopy (FTIR)

Fourier Transform Infrared Spectroscopy (FTIR) was done for liquid initiators (stannous octoate and dibutyltindimethoxide). FTIR spectra were recorded using KBr pellets on Perkin Elmer FTIR Spectrometer. FTIR spectroscopy is used primarily for qualitative and quantitative analysis of organic compounds, and also for determining the chemical structure of many inorganic compounds. FTIR spectra of stannous octoate shows that different stretching of C-H stretch (CH_3) at 2960 cm^{-1}, C-O stretch (carboxylic acid) at 1216 cm^{-1} and C=O stretch (carboxylic acid) at 1628 cm^{-1} (Fig. A.3). FTIR spectra of dibutyltindimethoxide shows that different stretching of C-H stretch (CH_3) at 2960 cm^{-1}, C-O stretch (ether) at 1076 cm^{-1} (Fig. A.4).

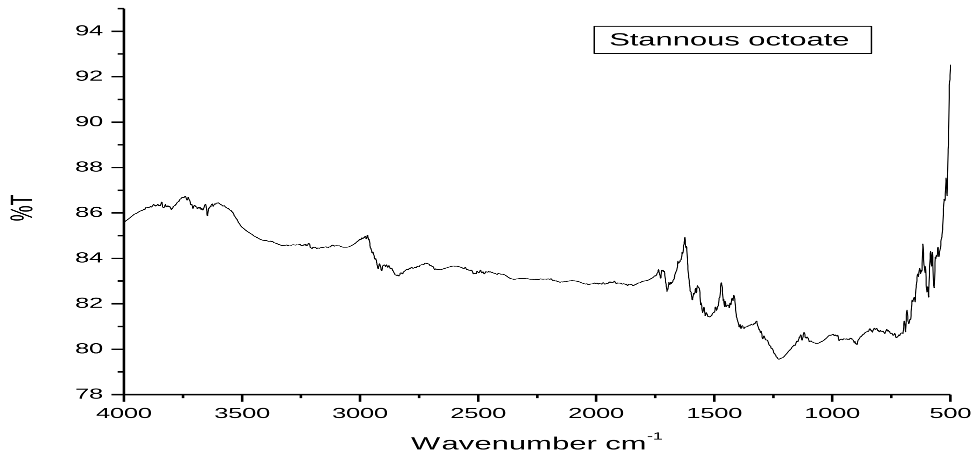


Figure A.3 FTIR spectra of stannous octoate

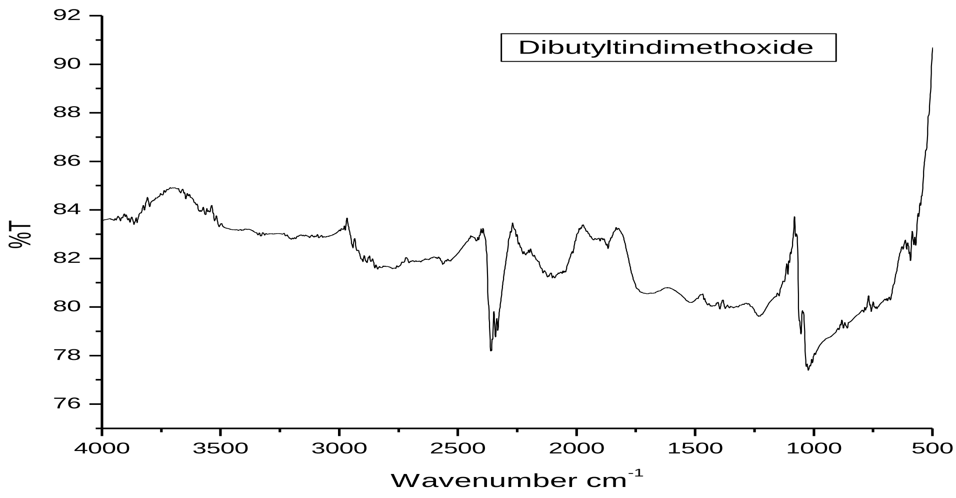


Figure A.4 FTIR spectra of dibutyltindimethoxide

Ultra Violet and Visible Spectroscopy (UV-Visible)

Ultra-violet and visible (UV-Visible) spectroscopy refers to absorption spectroscopy or, reflectance spectroscopy in the ultraviolet-visible spectral region. This means it uses light in the visible and adjacent (near-UV and near-infrared (NIR)) ranges. The absorption or, reflectance in the visible range directly affects the perceived colour of the chemicals involved. The UV-Visible spectra of stannous octoate and dibutyltindimethoxide are shown in Figs. A.5 and A.6. As, both the initiators are colourless, no spectra was observed in Figures A.5 and A.6. In both cases, optical density remains constant with an increase of wavelength.

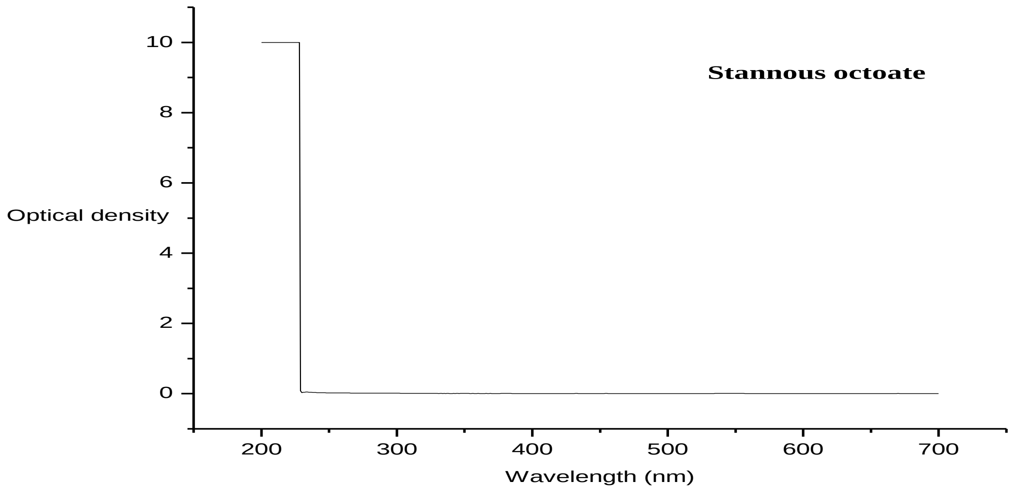


Figure A.5 UV-Visible spectra of stannous octoate

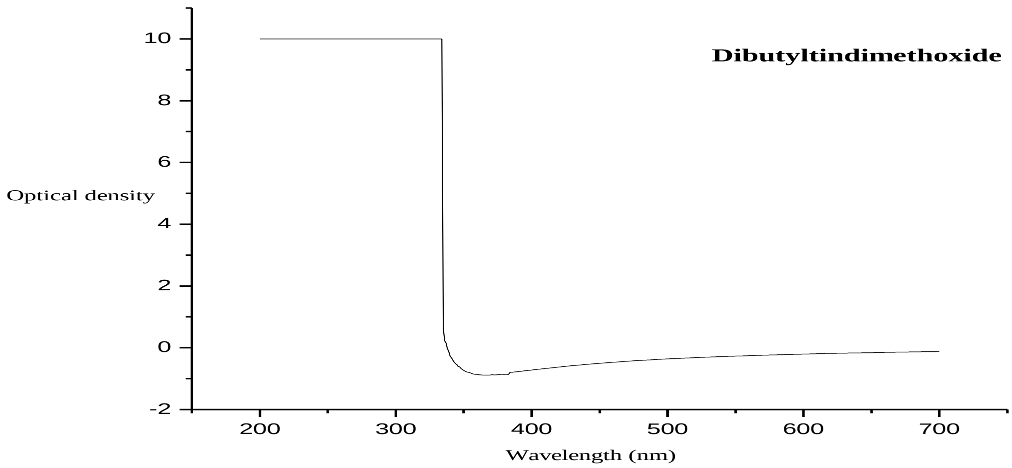


Figure A.6 UV-Visible spectra of dibutyltindimethoxide

Refractive Index and Density

The refractive index or, index of refraction of a substance is a measure of the speed of light in that substance. It is expressed as a ratio of the speed of light in vacuum relative to that in the considered medium. Table A.1 shows the values of refractive index and density of solid and liquid initiators. Density of initiators was expressed in g/ml.

Table A.1 Values of refractive index and density of solid and liquid initiators

S.No.	Initiator (s)/co-initiator	Refractive Index	Density (g/mL)
1.	Stannous octoate	1.493	1.251
2.	Dibutyltindimethoxide	1.487	1.286
3.	Triphenylphosphine	1.59	1.1