January 2018

Synthesis Of Cyclic And Linear Poly(hydroxybutyrates) By Ring-opening Polymerization Of β-Butyrolactone With Amido-Oxazolinate Zinc Catalysts

Muneer Shaik

Recommended Citation

Shaik, Muneer, "Synthesis Of Cyclic And Linear Poly(hydroxybutyrates) By Ring-opening Polymerization Of β-Butyrolactone With Amido-Oxazolinate Zinc Catalysts" (2018). *Theses and Dissertations*. 2344.
https://commons.und.edu/theses/2344

SYNTHESIS OF CYCLIC AND LINEAR POLY(HYDROXYBUTYRATES) BY RING–OPENING POLYMERIZATION OF β-BUTYROLACTONE WITH AMIDO-OXAZOLINATE ZINC CATALYSTS

By

Muneer Shaik
Bachelor of Science, Andhra University, 2008
Master of Science, Osmania University, 2011

A Thesis

Submitted to the Graduate Faculty of the

University of North Dakota

in partial fulfillment of the requirements

for the degree of

Master of Science

Grand Forks, North Dakota

May

2018

This thesis, submitted by Muneer Shaik in partial fulfillment of the requirements for the degree of Master of Science from the University of North Dakota, has been read by the Faculty Advisory Committee under whom the work has been done and is hereby approved.

Guodong D

Committee Chairperson – Dr. Guodong Du

Committee Member – Dr. Harmon B Abrahamson

Lothar Stahl

Committee Member – Dr. Lothar Stahl

This thesis is being submitted by the appointed advisory committee as having met all the requirements of the School of Graduate Studies at the University of North Dakota and is hereby approved.

Dean of the School of Graduate Studies

8/7/18 Date

PERMISSION

Title	Synthesis of Cyclic and Linear Poly(hydroxybutyrates) by Ring Opening Polymerization of β-butyrolactone with Amido–Oxazolinate Zinc Catalysts
Department	Chemistry
Degree	Master of Science

In presenting this thesis in partial fulfillment of the requirements for a graduate degree from the University of North Dakota, I agree that the library of this University shall make it freely available for inspection. I further agree that permission for extensive copying for scholarly purposes may be granted by the professor who supervised my thesis work or, in his absence, by the Chairperson of the department or the dean of the School of Graduate Studies. It is understood that any copying or publication or other use of this thesis or part thereof for financial gain shall not be allowed without my written permission. It is also understood that due recognition shall be given to me and to the University of North Dakota in any scholarly use which may be made of any material in my thesis.

Muneer Shaik
Date

ABBREVIATIONS

1,4-BDM	1,4-benzenedimethanol
BDI	β-diketiminate
rac-BBL	*racemic* β-Butyrolactone
BnOH	Benzyl alcohol
1,4-CHD	1,4-cyclohexanediol
CaH_2	Calcium Hydride
$CDCl_3$	Deuterated Chloroform
CTA	Chain Transfer Agent
DSC	Differential Scanning Calorimetry
Đ	Polydispersity Index
ESI	Electrospray Ionization
GPC	Gel Permeation Chromatography
1,6-HD	1,6-hexanediol
HDPE	High Density Polyethylene
IG-^{13}C	Inverse Gated-^{13}C
LDPE	Low Density Polyethylene
M_n	Number-average molecular weight
MW	Molecular Weight
NMR	Nuclear Magnetic Resonance Spectroscopy

P3HB/PHB	Poly-3-(hydroxybutyrate)
P4HB	Poly-4-(hydroxybutyrate)
PCL	Polycaprolactone
PE	Polyethylene
PET	Polyethylene Terephthalate
PHA	Polyhydroxyalkanoates
PHH	Polyhydroxyhexanoate
PHHx	Poly(3-hydroxybutyrate)-block-poly(3- hydroxyhexanoate)
PHO	Polyhydroxyoctanoate
PHBV	Polyhydroxybutyrate-block-poly(hydroxyvalerate)
PHV	Polyhydroxyvalerate
PLA	Polylactide/ Polylactic acid
P_m	Probability of *meso* diads
P_r	Probability of *racemic* diads
PP	Polypropylene
PS	Polystyrene
PVOH	Polyvinyl Alcohol
ROP	Ring-Opening Polymerization
THF	Tetrahydrofuran
T_m	Melting Temperature

TPS	Thermoplastic Polyolefin Elastomers
TGA	Thermogravimetric Analysis
T_g	Glass Transition Temperature
Zn	Zinc-metal

Table of Contents

LIST OF FIGURES

LIST OF TABLES

LIST OF SCHEMES

ACKNOWLEDGMENTS

Over the last three years, I have greatly benefitted from and been motivated by my interactions with many people in the UND community. I am particularly grateful to the members of my master’s thesis committee: Dr. Harmon Abrahamson and Dr. Lothar Stahl. Their example has served to guide my scientific development, and their professional assistance and teaching have proven to be invaluable in my future career plans. Our collaboration has influenced my research practices in many ways and will continue to be fruitful for years to come.

I am grateful to my research advisor, Dr. Guodong Du. Throughout my scientific development, Dr. Du’s continued patience and advice have been instrumental in my scientific growth. As a researcher, his curiosity and meticulous observations on research aspects have been inspirational in developing my approach and philosophy. As an advisor, he serves as a model to whom I will turn throughout my career.

ABSTRACT

A series of amido-oxazolinate zinc complexes have been employed for the ring opening polymerization of β-butyrolactone (BBL). Experimental results show that these complexes efficiently catalyze the reactions, yielding cyclic poly(hydroxybutyrate)s (PHBs) with high molecular weights (M_n up to 196 kg/mol) and low dispersity. In contrast, in the presence of alcohol co-catalysts, the zinc-catalyzed ring-opening polymerization (ROP) reactions lead to the formation of linear PHBs end-capped by the alcohol initiator and hydroxylbutyrate. A possible mechanism for cyclic PHBs is proposed, in which the zinc catalysts function as a loose Lewis pair at elevated temperature, followed by a fast propagation through a zwitterionic intermediate. Use of diols such as 1,4-cyclohexane diol and 1,4-benzenedimethanol results in the formation of polyester diols. The thermal properties were studied by differential scanning calorimetry (DSC) and thermogravimetric analysis (TGA) to differentiate between the cyclic and linear polyesters.

CHAPTER 1

1.1 Introduction

Plastic has become a beneficial and versatile material used in several applications like product packaging, medicine, household products, garden applications, construction, vehicles, fabrics, and textiles as well as in aerospace.[1] Plastics are of two types: thermoplastics and thermoset plastics. Common thermoplastics include polypropylenes (PP), polyethylene (PE), polyamide, polystyrenes (PS), and polyethylene terephthalate (PET). Thermoset, as the name indicates, is a plastic that maintains its form permanently and cannot be melted by heating because its polymer chains are bonded firmly with crosslinks, as in polyurethane, epoxy resin, and unsaturated polyester.[2] The global market of plastics comprises of readily available, cheap, flexible, durable, and lightweight products.

Most of these plastic materials are produced from petroleum products that do not undergo degradation (decompose or break down), due to the strong carbon-carbon bond between the monomers used resulting in a long life. It is estimated that by 2017, 8.3 billion metric tons of plastic were produced globally, out of which 6.3 billion metric tons have become plastic waste. Only 9% was recycled while 12% was incinerated and 79% dumped in landfills and oceans. The recycling numbers are low because the recycling process and reuse of plastic waste products require vast human resources and huge processing costs, meaning only a minimal amount of plastic waste is recycled or reused.[3] In the landfills and oceans, the plastic waste produces toxins and chemical residues as a byproduct of its decomposition, which adversely affects the wildlife, land, and human habitats.

1.1.1 Biodegradable polymers.

With an increase in environmental awareness related to the problem of effective disposal of plastic waste and its growing demand for biomedical applications, a massive number of research groups have focused on the development and synthesis of biodegradable polymers with a wide range of possible sources (Figure 1).[4] These polymers can be produced from bacterial fermentation or by synthetic methods using different bio-based or synthetic monomers available in the market.

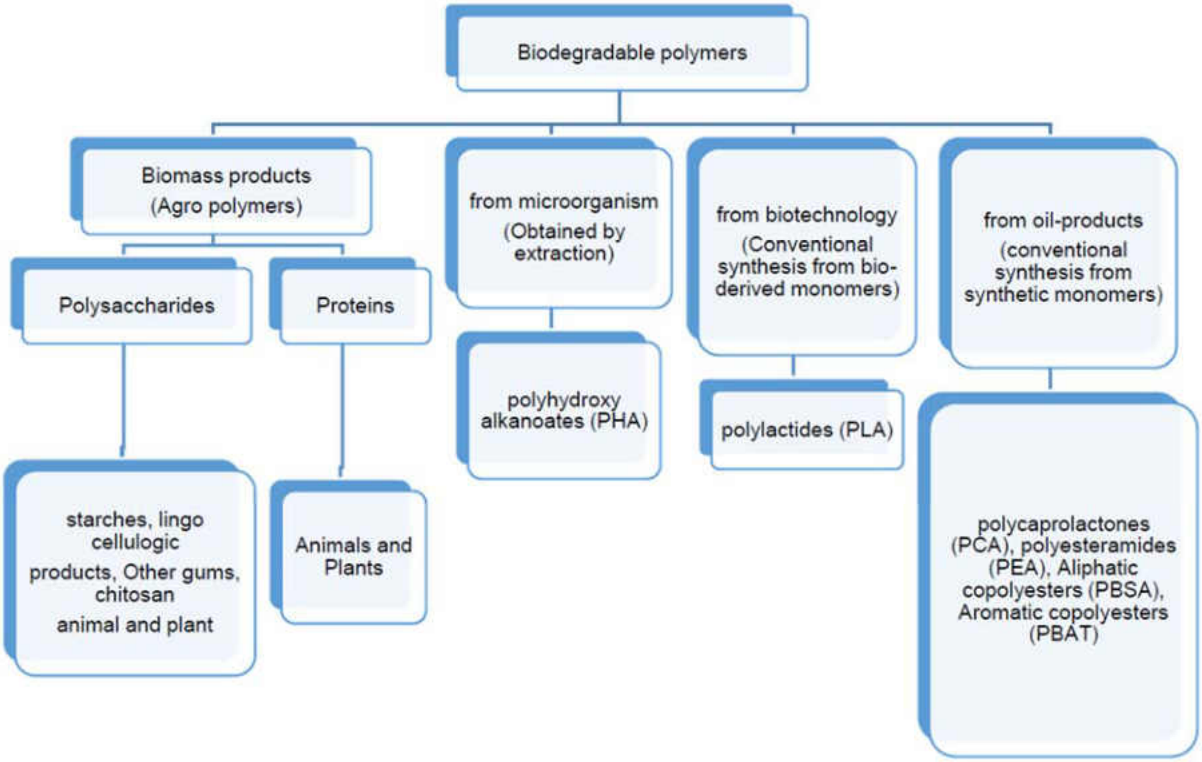


Figure 1. Different classes of polymers, that are bio-based and biodegradable.[4]

A biodegradable polymer is a macromolecule that can be decomposed, or broken down by microbes and bacteria. The biodegradation occurs under physiological conditions with water, catalyzed by enzymatic mediation or under environmental conditions where the presence of oxygen in the air, soil, and seawater is favorable for the action of micro-organisms. Moreover, production of the biodegradable polymer requires only half the energy, which means by using the same amount of energy it is possible to make twice the number of biodegradables as compared to non-biodegradable products, as described in Table 1.[5] The process of recycling is also much more straightforward, and furthermore, they cause no harm to the environment.

Table 1. Energy requirement for synthetic polymers compared to biopolymers.[5]

Type of plastic	Energy requirement, MJ/kg	Global warming, kg CO_2 eq/kg
From non-renewable sources		
HDPE	80.0	4.84
LDPE	80.6	5.04
Nylon 6	120.0	7.64
PET	77.0	4.93
PS	87.0	5.98
PVOH	102.0	2.70
PCL	83.0	3.10
From renewable sources		
TPS	25.4	1.14
TPS C 15% PVOH	24.9	1.73
TPS C 60% PCL	52.3	3.60
PLA	57.0	3.84
PHA	57.0	Not Available

Biodegradable polymers can be used in packaging, agriculture and for medical applications such as drug delivery systems, especially for in-vivo biomedical uses. One of the advantages of the synthetic biodegradable polymers over those produced from bacteria is that one can have greater control over the chemical composition and physical properties of the material. In this field, polyesters are mostly studied, because they are easily hydrolytically degradable at the ester group since the process depends on the chemical and physical properties such as thermosoftening plasticity and crystallinity, which can be controlled by varying the composition.

1.1.2 Polyhydroxyalkanoates

Polyhydroxyalkanoates (PHAs) are a family of aliphatic polyesters considered to be biodegradable polymers. Until now, over 100 distinct types of PHAs have been successfully synthesized using both synthetic and biosynthetic routes. Their unique biodegradable, biocompatible, and thermoplastic characteristics make PHAs suitable for commodity applications, including packaging and plastic containers, and they are especially useful in biomedical applications as surgical sutures, swabs, wound dressings, vascular grafts, blood vessels, and scaffolding for new tissue growth.

PHAs have a general structure of β-substituted poly(β-propiolactone)s as the repeating unit as shown below in Figure 2, which represents an exciting series of polyesters, and the properties can be varied based on the composition of the attached R-group, with various applications as shown in Figure 3.[6]

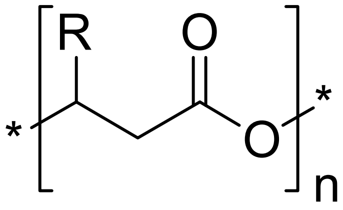


Figure 2. General structure of PHAs

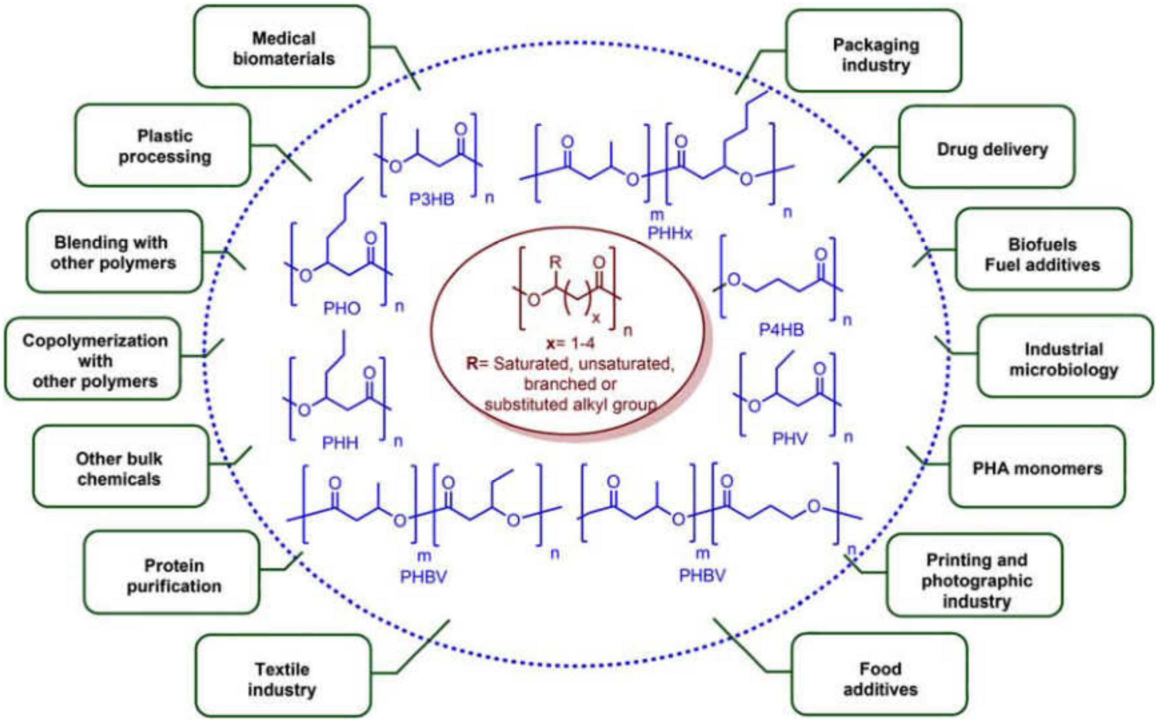


Figure 3. General structure, specific examples, and applications of PHAs.[6]

1.1.2.1 Poly(hydroxybutyrate) (PHB)

Among all the family members of PHAs, poly (3-hydroxybutyrate) (PHB) is a naturally occurring polyester, which is produced by a variety of bacteria and micro-organisms as an internal energy and carbon reserve and thus features biodegradability and biocompatibility. Lemoigne of the Pasteur Institute, France, first detected it in 1926. It is produced by the joining of β-hydroxybutyrate monomers with ester bonds. Different microbial species presenting in the environment able to produce approximately 100 PHAs have been identified. PHB resulting from the bacteria's fermentative process, possessing an isotactic structure with complete (*R*)-configuration, is a typical semi-crystalline material with high melting temperature (T_m) and relatively low thermostability. Therefore, the crystalline PHB is difficult to process, significantly limiting its applications in industrial manufacturing. Biotechnological methods produce most of the PHBs. The only way to achieve the desired low melting transition is by changing the nutrient media of the applied bacteria. Moreover, the bioengineering route to PHB is expensive compared with the chemical synthesis of commodity polymers. However, ring-opening polymerization (ROP) is a potent synthetic methodology for the synthesis of biodegradable aliphatic polyesters from lactones or cyclic esters. ROP of *rac-β*-butyrolactone (*rac*-BBL) usually affords atactic PHB with a low glass transition temperature (T_g) at 5 °C, which does not have any use in plastic industries but has widespread biomaterials applications such as in vitro and in vivo drug delivery systems by blending it with natural PHBs or synthesizing polyurethanes networks.

Some well-defined catalyst systems have been developed to produce PHBs with varying stereotacticity, which alternatively vary the melting point. Among them, yttrium complexes supported by aminoalkoxybis(phenolate) ligands, diamine bisphenolate Salan-type, and binaphthyl Salen-type ligands have shown the excellent ability for stereoselectivity and reactivity to afford syndiotactic PHBs under mild reaction conditions with different syndiotacticity (up to 0.94). The melting temperatures (T_m) of the resultant syndiotactic PHBs varied from 120 to 183 °C depending on their syndiotacticity. Besides, high-molecular-weight PHBs with moderate syndiotacticity (0.55−0.75) could be obtained in the presence of racemic and enantiopure zinc catalysts supported by substituted diaminophenolate ancillary ligands. Isotactic-enriched high-molecular-weight PHBs can be achieved in the presence of chromium (III) salophen complexes. [7]

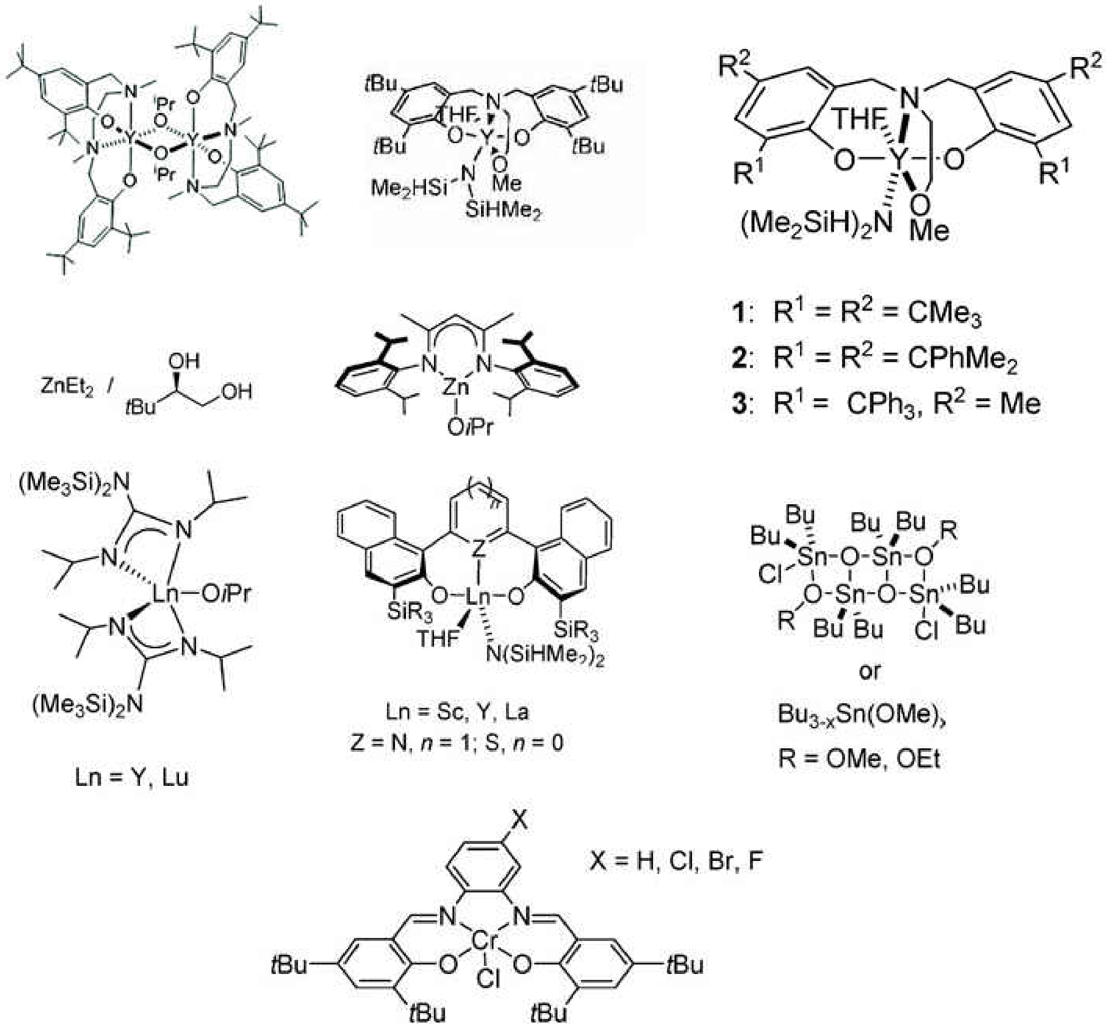


Figure 4. List of catalysts used for ROP of β-butyrolactone.[7]

Distinct types of metal catalysts incorporated with different ligand moieties are used for ROP of β-butyrolactone, and they all result in linear polyester with better control over stereoselectivity. Among the ligands, β-diketiminate (BDI) ligand and its structures assume a unique position due to the remarkable tunability of their steric and electronic properties. Holm and co-workers reported these nitrogen-based, π-conjugated, bidentate chelating ligands with immense potential for the variability of steric protection by manipulating the R_1 and R_2 groups located on nitrogen atoms, and the R_3 and R_4 groups on the carbon backbone. Homoleptic complexes were reported with different divalent transition metals M(II) (M = Ni, Co, Zn, Cu).[8]

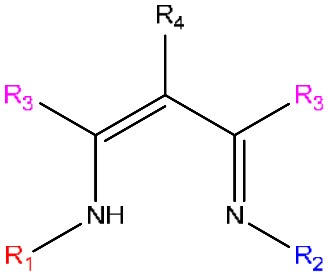


Figure 5. The general form of the β-diketimine ligand

The BDI-metal complexes have found extensive applications in catalytic processes. It is due to the ability of the β-diketiminate ligand supported by coordinatively unsaturated metal centers. For example, these complexes have been used as homogeneous catalysts for olefin polymerization,[9] for the ring opening polymerization of lactides,[10, 23] and in the copolymerization of carbon dioxide and epoxides,[29] copolymerization of oxiranes and cyclic anhydrides,[11] and other applications include cross-metathesis reactions involving the imine functionality of the ligand.[12] Among the different BDI metal complexes, the Zn metal-based complexes show a very high activity towards the ROP of lactones, resulting in cyclic as well as linear polyesters in the presence of alcohols as an initiator.[13]

1.1.3 Cyclic polyester

Condensation polymerizations and ring opening polymerization of lactones provide an essential synthetic route to aliphatic polyesters with end group functionalities. While most of these polyesters possess linear structure, various polyester architectures such as star-shaped, grafted, cross-linked, and hyperbranched structures are possible with an appropriate choice of catalysts and initiators.[14] Among them, macrocyclic polyesters have received considerable interest because of their appealing physical properties that differ from their linear counterparts, including glass transition temperature (T_g), melting temperature (T_m), morphologies, melt viscosities, thermal stability, compatibilities, hydrodynamic volume, and intrinsic viscosity.[15]

In addition to its unusual physical properties, the cyclic topology imparts unique biophysical properties, which may provide enormous advantages for a range of biomedical applications as drug delivery vectors.[16] While the synthesis of high purity cyclic polymers is a challenge, a number of approaches have been reported, such as statistical cyclization of linear polyesters during ester condensation polymerizations,[17] the ring opening polymerization of lactone monomers with metal catalysts, the N-heterocyclic carbenes catalyzed cyclopolymerization of lactides, and the cyclization of α,ω-functionalized linear polymer under high dilution.[18] Each of these techniques have advantages and disadvantages in producing pure cyclic polyesters.

Among the methods for synthesizing cyclic polyesters, ring opening polymerization has become a powerful tool. Detailed studies have been done on the polymerization of lactide into cyclic polyesters,[19] and further, turning it into linear or branched polylactide in the presence of alcohols as initiators and chain transfer agents (CTA).[20] Waymouth et al. were the first to report the cyclic polylactides using the zwitterionic polymerization of lactide (LA) and lactones by N-heterocyclic carbenes (NHCs). The zwitterionic interaction between the intramolecular end groups is the crucial step to create a cyclic structure. Interestingly, polymerization with similar catalyst systems in the presence of alcohol led to the formation of linear or branched polyesters.[21]

CHAPTER 2

2.1 Statement of Purpose

The growing environmental concerns due to plastic wastage have prompted the development of biodegradable and biocompatible polyesters. These two properties are mostly used to describe the capability of polymers to be decomposed by living organisms without harming any living tissue or the environment. Research has been focused on developing end-of-life options that generate materials suitable for recycling or biodegradation. Therefore, to overcome these problems, our group is focused on synthesizing biodegradable polymers with different metal complexes as catalysts.

In this work, the goal is to synthesize chiral amido-oxazolinate zinc complexes (BDI-Zn-N$(SiMe_3)_2$) with aniline and chiral site moieties of different steric groups, which are used as active catalysts for the highly controlled ROP of BBL into high molecular weight (MW) cyclic polyesters.[22] In the presence of mono- and bifunctional alcohols such as ethyl alcohol, benzyl alcohol (BnOH), 1,6-hexanediol (1,6-HD), 1,4-benzenedimethanol (1,4-BDM), and 1,4-cyclohexanediol (1,4-CHD), as initiators the same catalysts remarkably produce linear PHBs with a low dispersity. Low MW oligomers can be produced with increased concentrations of alcohols, but a high concentration of alcohol leads to the deactivation of Zn-complexes.The characterizations of the PHBs and molecular weights were studied by using NMR and GPC techniques. whereas the thermal properties were studied using DSC and TGA.

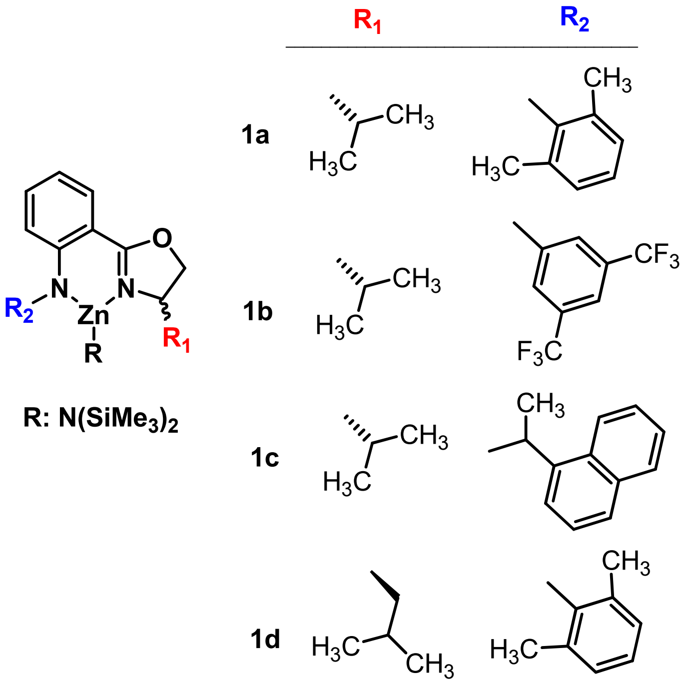


Figure 6. Chiral amido-oxazolinate zinc complexes

CHAPTER 3

3.1 Experimental Section

3.1.1 Materials and methods.

All reactions with air- and/or moisture-sensitive compounds were performed under dry nitrogen using standard glovebox (VAC atmosphere controller) and/or Schlenk line techniques. Deuterated solvents were purchased from Cambridge Isotope Laboratories. Analytical grade THF was purchased from Fisher Scientific and used as received. Other chemicals were purchased from Sigma-Aldrich. β-Butyrolactone was distilled over CaH_2 following three freeze-pump-thaw cycles. $CDCl_3$ was distilled over CaH_2 and degassed prior to use. Toluene was distilled under nitrogen from Na/benzophenone. The synthesis of zinc complexes [**1a–1d**] was conducted according to the literature methods.[22]

3.1.2 Instrumentation.

NMR experiments (1D and 2D) were recorded on a Bruker AVANCE 500 NMR spectrometer, and the spectra were referenced to the residual peaks in $CDCl_3$. The microstructures of PHBs samples were characterized by examination of the carbonyl region in the Inverse gated ^{13}C NMR spectra recorded at room temperature in $CDCl_3$ with concentrations in the range 1 to 1.5 mg/mL. P_m values of the PHBs were determined by $P_m = (I_m/I_m+I_r)$ and $P_r = (I_r/I_m+I_r)$ where I_r and I_m are the integrations of the corresponding inverse gated $^{13}C\{1 H\}$peaks, according to the literature.[23]

Gel permeation chromatography (GPC) analysis was performed on a Varian Prostar instrument with autosampler model 400, using a PLgel 5 mm Mixed-D column, a Prostar 355

RI detector, and THF as eluent at a flow rate of 1 mL min^{-1} (20 ºC). Polystyrene standards from Agilent technologies were used for calibration. Galaxie software was used to operate the instrument, and Cirrus software was used for data processing. A 6210 TOF MS with ESI detection (Agilent Technologies, Santa Clara, CA, USA) was used for mass spectra. The analyte containing solution was introduced into the instrument by direct infusion using a syringe drive (5 mL min^{-1}). The electrospray ionization (e.g., capillary) and collision-induced dissociation (e.g., fragmentor) potentials were set to 3500 V and 150 V, respectively. Acetic acid was used as an electrolyte at 25 mmol L^{-1}. Mass Hunter Qualitative Analysis software was used for data processing.

3.1.3 General procedure for ROP.

An oven-dried 10 mL Schlenk flask equipped with a stir bar was charged with BBL (323 mg, 3.75 mmol, 200 equiv), and catalyst (1 equiv) in toluene (4.0 mL) in a glovebox under nitrogen. The flask was capped and taken out, then heated in an oil bath preset at 100ºC. The reaction was monitored by ^{1}H NMR spectroscopy until the complete conversion of BBL. After removal of the volatile components, the residue was dissolved in DCM (1–3 mL), followed by addition of hexane (4–5 ml). The precipitation of the polymeric products was facilitated by immersing the flask in liquid nitrogen. The supernatant was decanted, and the residues were washed and dried under reduced pressure. Various NMR techniques, ESI-MS, and GPC were then used to characterize the purified polymers.

3.2 Results and Discussion

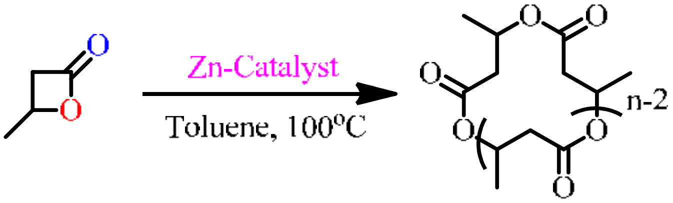
ROP of *rac-β*-butyrolactone. ROP of β-butyrolactone (BBL) using **1a** as a catalyst was first examined, and the progress of the reaction was monitored by ^{1}H NMR spectroscopy. As shown in Table 2, when the reaction was carried out in toluene at 100°C with 0.5 mol% catalyst **1a**, a complete conversion of BBL was achieved after 90 minutes (Table 2, entry 1), leading to high molecular weight (M_n = 26992) with narrow dispersity (Đ = 1.08). Polymerization in DCM (Table 2, entry 2) and THF (Table 2, entry 3) at 60ºC achieved only 15% and 20% conversion after 90 minutes respectively, and 100% conversion was attained at longer times (24 hours) with relatively lower molecular weights. When the reaction was performed under bulk conditions without solvent, maximum conversion of 79% was reached in 30 minutes with M_n of 20000 and a broad dispersity (Đ = 2.56) (Table 2, entry 4). Consequently, the following polymerizations were conducted in toluene as solvent. The activity of other zinc complexes (**1b-d**) was next investigated in the ROP of BBL. Under similar conditions, PHBs with high molecular weights and narrow Đ values were obtained for all the catalysts (Table 2, entries 5-7). The activities of different zinc catalysts were comparable, affording 100% conversion of BBL within 90 minutes. It was noted that the isolated yields of PHBs by the dissolution-precipitation method were somewhat low in general. In addition, the R_1 and R_2 substituent groups in the catalysts may affect the molecular weight and dispersity (**Đ**) of the polymer. As the steric hindrance increased at the R_2 moiety, there was a decrease in the polymer molecular weight.

Table 2. Polymerization of *rac*-β-butyrolactone with amido-oxazolinate zinc complexes

Entry	**Complex**	**Solvent**	***M*n(GPC)**[b]	**Time (min)**	**Đ**	**Conv (%)**	**Pr/Pm**[c]	**Yield**
1	**1a**	Toluene[a]	26992	85	1.08	100	46/54	40
2	**1a**	DCM[a]	7106	1440	1.13	100	57/43	57
3	**1a**	THF[a]	17326	1440	1.49	100	46/54	59
4	**1a**	No Solvent[a]	20132	30	2.56	79	51/49	27
5	**1b**	Toluene	33127	90	1.38	100	48/52	58
6	**1c**	Toluene	26717	90	1.27	100	45/55	42
7	**1d**	Toluene	17520	90	1.2	100	47/53	56

[a] Polymerizations are run with [BBL]/[Zn] = 200/1 in toluene & bulk at 100ºC, and in THF & DCM the reaction runs at 80ºC. [b] Determined by gel permeation chromatography calibrated with polystyrene standards in THF. [c] Determined by Inverse gated decoupling ^{13}C- NMR showing intensities of meso and racemic signals of the carbonyl peak.

We further examined the activity of **1a** by varying the catalyst loadings. Regardless of the BBL/Zn ratio, the polymerization generally reached completion within 60–90 minutes. At [BBL]/[Zn] = 400 (Table 3, entry 4), the polymerization yielded PHB with M_n = 45000 and 100% conversion. Only at low catalyst loadings ([BBL]/[Zn] = 1000 and 2000) did the reaction require longer reaction time (~3 h). Higher molecular weight PHBs (M_n > 100 000) could be achieved at [BBL]/[Zn] = 1000 (Table 3, entry 7), M_n = 140,433 at 99 % conversion and for [BBL]/[Zn] = 2000 (Table 3, entry 8) M_n = 196,538 at 98%. The experimental molecular weights by GPC of the resulting PHBs were generally higher than the M_n calculated from the initial catalyst loading and conversion. At the same time, the molecular weights of the polymers increased roughly linearly with the [BBL]/[Zn] ratio (Appendix A, Figure A2). These observations suggested that the initiation step was slow compared to propagation in the polymerization, and not all catalysts were actively involved in the initiation, but the polymerization was reasonably controlled.



Scheme 1. ROP of BBL to cyclic poly(hydroxybutyrate) in the presence of zinc complexes.[18 a-e]

Table 3. Ring opening polymerization of β-butyrolactone initiated with complex 1a in toluene

Entry[a]	**[BBL]/[Zn]**	**M_n(calcd)**[b]	**M_n(GPC)**[c]	**Đ**[c]	**Time(min)**	**Conv (%)**	**Yield**
1	20:1	1723	2848	1.21	70	100	94
2	100:1	8609	14649	1.31	90	100	31
3	200:1	17218	26992	1.08	90	96	40
4	400:1	34436	45314	1.53	85	99	53
5	600:1	51654	76357	1.35	80	99	61
6	800:1	68872	87291	1.23	60	98	48
7	1000:1	86090	140433	1.81	180	99	72
8	2000:1	172180	196538	1.97	180	98	84

[a]All the polymerization reactions are run with [BBL]/[Zn] = [C]/1 in toluene at 100ºC. [b]Determined by equiv. Of [BBL]*86.09 (mol.wt. of β-butyrolactone). [c]Determined by gel permeation chromatography calibrated with polystyrene standards in THF.

3.3 Microstructure Studies of Cyclic PHBs

The microstructure of the resultant PHBs was evaluated by NMR spectroscopic techniques. Two peaks at 2.45 ppm and 2.56 ppm in the ^{1}H NMR spectrum (Figure 6) could be assigned to the two diastereotopic methylene protons, whereas the peaks at 1.24 ppm and 5.22 ppm assigned to methyl and methine protons respectively. These data agreed with the expected PHB main chain structure; however, the most remarkable feature was the absence of any other signals typically associated with chain ends. A similar observation was noted in the ^{13}C NMR, where only four signals corresponding to the primary chain carbons were present (Figure 7). In other words, no indication of any end groups could be detected, regardless of the molecular weights of the polymers. We took this as evidence that the cyclization took place and cyclic PHBs were obtained. These analyses were supported by an ESI-MS experiment (Appendix A, Figure A3): the primary series of peaks of 86 *Da* difference between consecutive peaks corresponded to the PHB main chain and could be assigned to the $n(C_4H_6O_2)+(CH_3CN)$ series, confirming the macrocyclic polymer structure. Additionally, inverse-gated ^{13}C NMR (IG-^{13}C) shows roughly equal intensities of *meso* and *racemic* signals of the carbonyl peak at 169 ppm (Figure 7), which suggested that the present catalyst was not stereoselective for the ROP of *rac*-BBL, and mostly atatic PHB was obtained. This was entirely different from the ROP of *rac*-lactides by these zinc catalysts, in which highly isotactic polylactides were obtained.[24] Similar contrasts have been noted for the diketiminate zinc catalyzed ROP of BBL and lactides.[25]

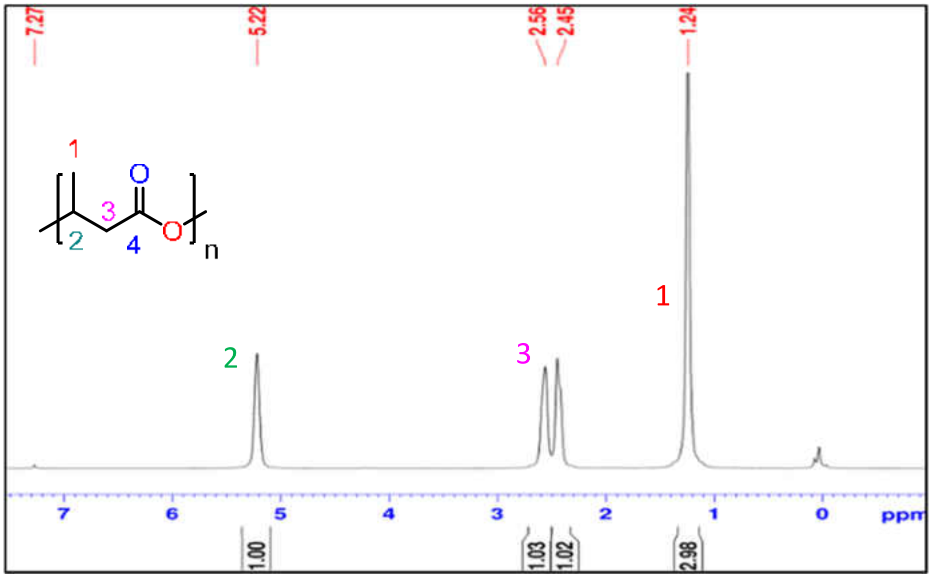


Figure 7. ^{1}H NMR spectrum of cyclic poly(hydroxybutyrate) obtained with complex **1a**

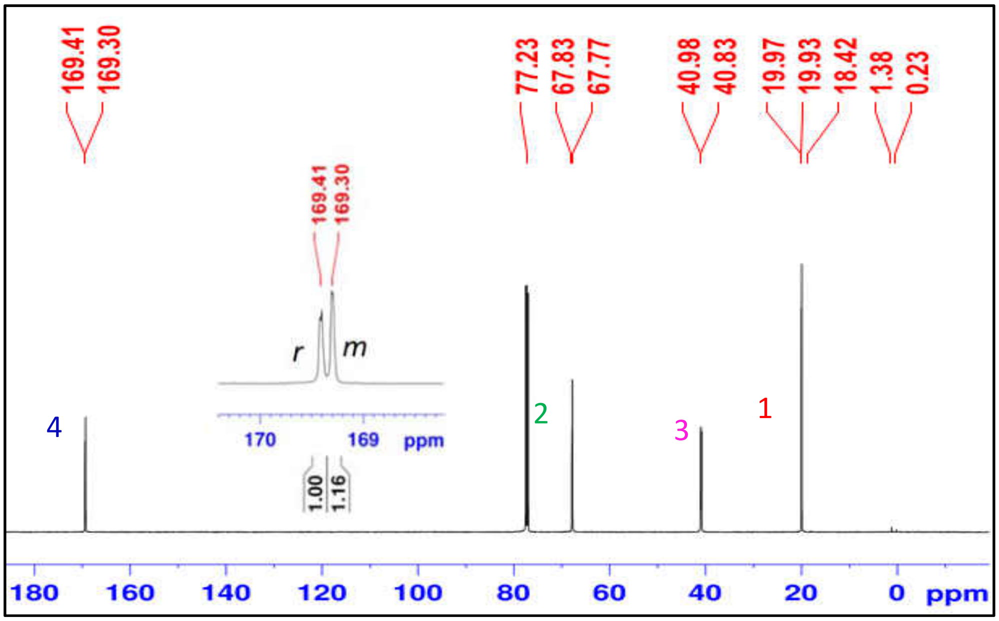
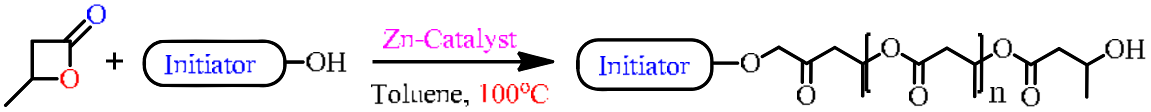


Figure 8. IG-^{13}C-NMR spectrum of cyclic PHB obtained with complex **1a**

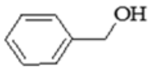
3.4 Synthesis of Linear PHBs with 1a/Alcohols.

Next ROP of BBL was performed with catalyst **1a** in the presence of an alcohol as co-catalyst. Benzyl alcohol (BnOH) and ethanol were used as representatives (Table 4). The resulting polymers showed a good agreement between calculated and experimental molecular weights with relatively narrow dispersities (Đ = 1.09–1.74). Another interesting fact, the molecular weight of the polymer can be controlled by changing the Zn/initiator ratio, with the higher loading of initiator resulting in the formation of PHBs oligomers on 100% conversion and all the PHBs generated with the zinc catalysts are mostly atatic. As the concentration of initiators increases, the polymerization becomes slower. This could be explained by the deactivation of Zn complex by alcohols and can be supported by the entry 8 & 12 in Table 5. We also performed a reaction with high loading of BnOH (Zn:BnOH:BBL=1:50:200). Here BnOH also behaves like a chain transfer agent and short chain oligomer was obtained. The ^{1}H NMR (Figure 8) analysis clearly shows the benzyl and hydroxyl chain ends.



Scheme 2. ROP of BBL to linear poly(hydroxybutyrate) in the presence of alcohol as initiator.[24]

Table 4. Polymerization of BBL in the presence of alcohols as an initiator

Entry[a]	**Initiators**	**[Zn]/[I]/[BBL]**	**Time(min)**	M_n **(calcd)**[b]	M_n **(GPC)**[c]	**Đ**[c]	**Yield**
1		1:1:200	60	17264	9290	1.18	91
2		1:10:200	75	1768	1936	1.09	88
3		1:50:200	120	391	518	1.24	61
4		1:1:200	60	17326	9439	1.13	78
5		1:10:200	40	1830	5363	1.74	54
6		1:50:200	150	452	791	1.18	51

[a] All the polymerization reactions are performed in toluene at 100ºC. [b] Determined by equiv. of {[BBL]/[I]}*86.09 (mol.wt. of β-butyrolactone)+ mol.wt. of initiator. [c] Determined by gel permeation chromatography calibrated with polystyrene standards in THF.

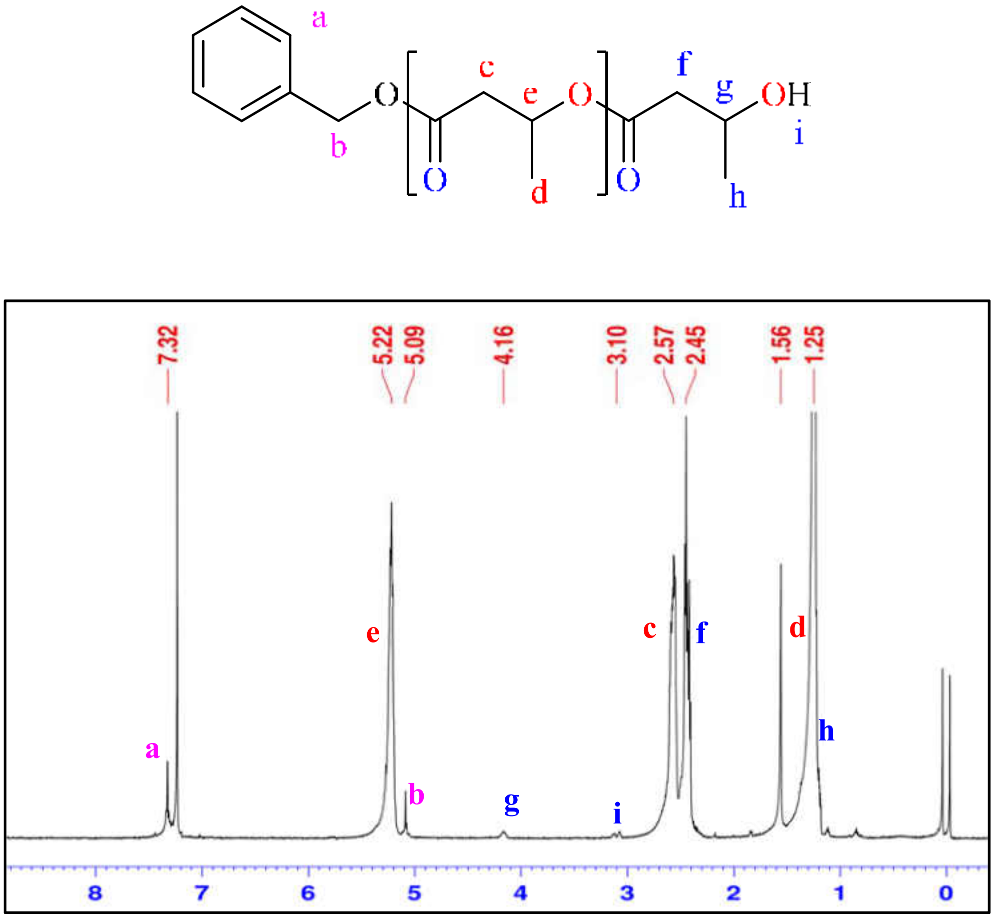


Figure 9. ^{1}H-NMR of poly(hydroxybutyrate) with BnOH ([BnOH]/[Zn] = 1).

The microstructure of the resulting PHBs was investigated by NMR and ESI-MS techniques. Along with the four large ^{1}H NMR peaks at 1.3 (methyl), 2.5 and 2.6 (methylene), and 5.2 (methine) ppm assignable to the main chain repeating butyrate units, small yet consistent peaks were notable that could be attributed to the end groups. A representative spectrum of a PHB sample obtained with excess BnOH initiator (50 equiv vs. Zn, entry 6 in Table 4) is shown in Figure 10. The peaks at 5.12 and 7.36 ppm can be assigned to the benzylic and aryl protons of the benzyloxyl group at one end, whereas the other end of the polymer is characterized by a terminal hydroxybutyrate unit featuring a singlet at 4.21 ppm for methine protons and a broad peak at 3.12 ppm for hydroxyl protons (other signals overlapped with large main chain signals). The integration of the hydroxyl (3.2 ppm) vs. benzylic (5.2 ppm) protons was 1:2, in agreement with them being the two ends of the polymer chain. Further support was provided by the 2D NMR techniques. In the ^{1}H-^{1}H COSY NMR spectrum, only one weak cross peak with methine proton at 4.2 ppm was observed for the hydroxyl protons (3.2 ppm), whereas two additional, stronger cross peaks with methylene (2.3 ppm) and methyl protons (1.2 ppm) were noted for methine protons. Also, the 3.2 ppm signal showed no correlation with ^{13}C signals in the ^{1}H-^{13}C HCCorr NMR spectrum (Figure 11 & 12). In the ^{13}C NMR, besides the main chain carbons, the rest of the peaks can be assigned to benzyl and hydroxybutyrate end groups (Figure 10). Together, these observations indicate that the polymer end groups are hydroxybutyrate at one end and benzyloxyl at the other end. The linear structure and the end groups were further established by the ESI-MS analysis, which showed a significant series of peaks at 107 + 86n + 1 + 23 that could be assigned to the BnO + n($C_4H_6O_2$) + H + Na$^+$ structure (Appendix F, Figure F1).

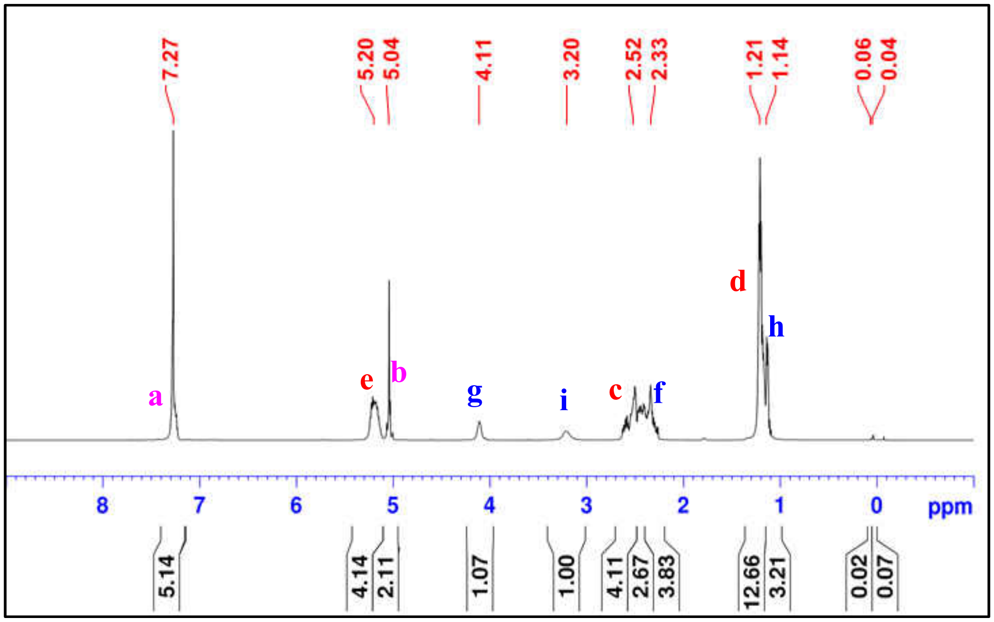


Figure 10. ^{1}H-NMR of poly(hydroxybutyrate) with BnOH ([BnOH]/[Zn] = 50

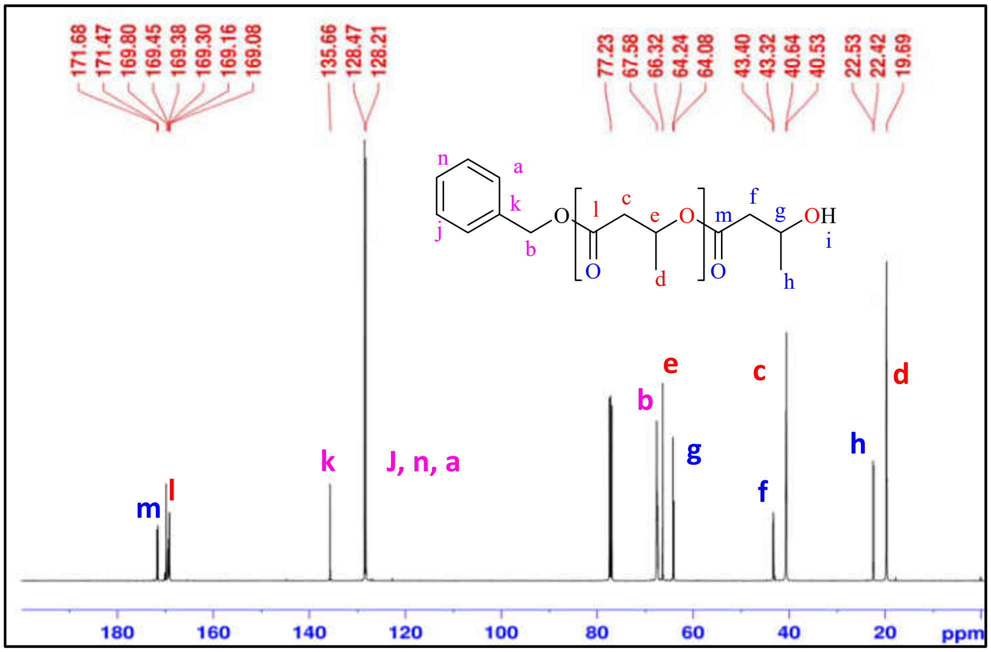


Figure 11. ^{13}C NMR of poly(hydroxybutyrate) with BnOH ([BnOH]/[Zn] = 50).

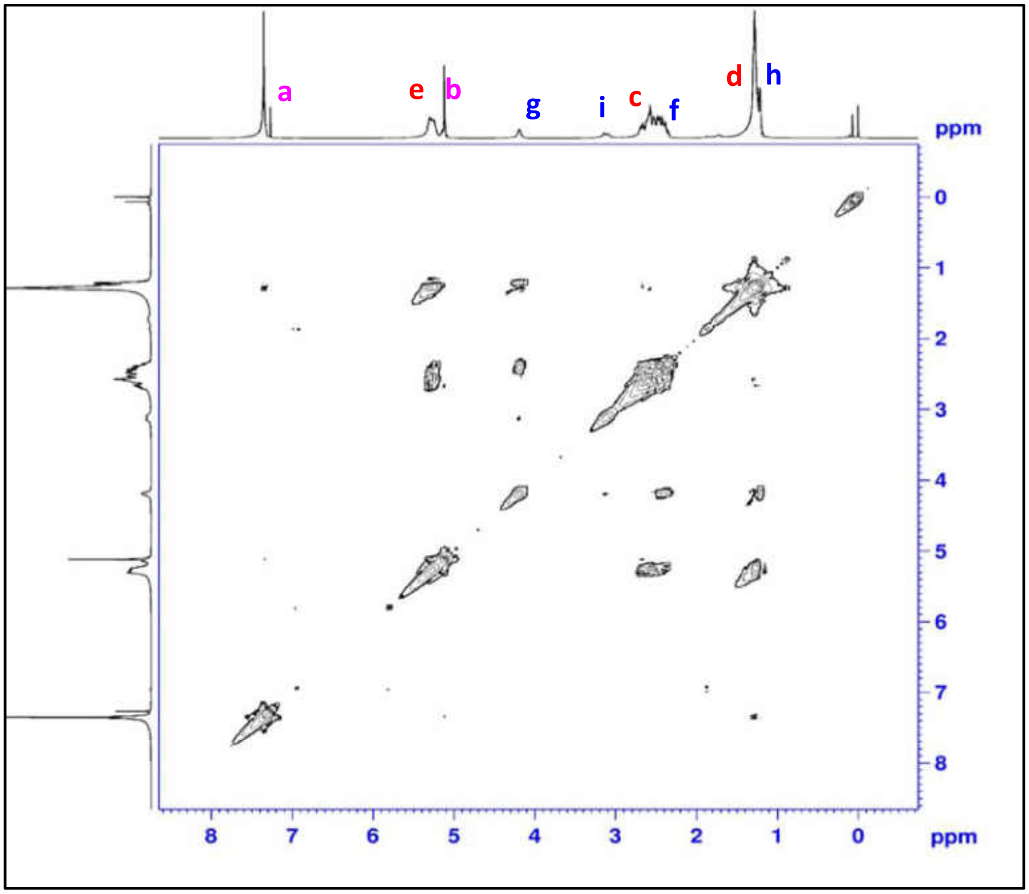


Figure 12. ^{1}H-^{1}H COSY NMR of the polymer with BnOH as an initiator

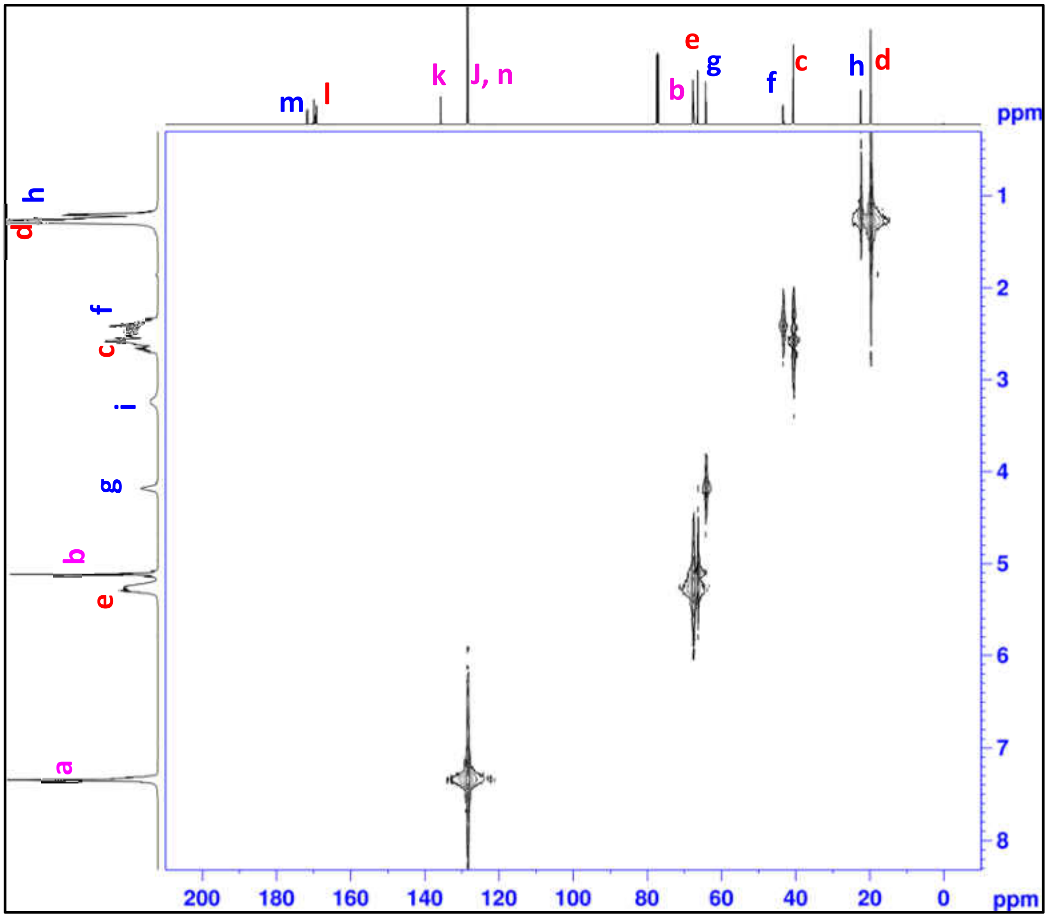
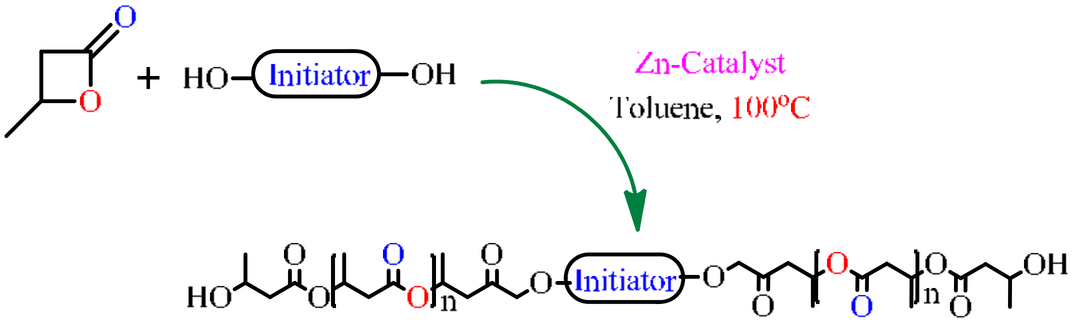


Figure 13. ^{13}C-^{1}H HETCOR NMR of the polymer with BnOH as an initiator

3.5 ROP of BBL in the presence of Diol Initiator

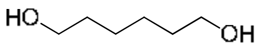
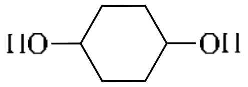
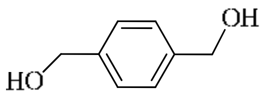
Given the previous observation that BnOH initiator leads to the formation of benzyl and hydroxyl end-capped polyesters, we sought to use the ROP reaction to produce α,ω-dihydroxyl end-capped PHBs by employing diol initiators. Such polyester diols, or telechelic polymers in general, are of great interest and have found uses in various applications such as thermoplastic elastomers and polyurethane coatings.[26] Thus, in the presence of diols such as 1,4-

benzenedimethanol (1,4-BDM), 1,6-hexanediol, and 1,4 cyclohexanediol (1,4-CHD), ROP of BBL was carried out at 100 ºC in toluene with [BBL]:[Zn]:[diol] = 200:1:0.5.



Scheme 3. ROP of BBL to poly(hydroxybutyrate) in the presence of zinc zinc complex 1a with diols as initiators. [11a-d]

Table 5. Polymerization of BBL in the presence of Diols as an initiator

Entry	**Initiators**	**[Zn]/[I]/[BBL]**	**Time (min)**	**M_n (calcd)[b]**	**M_n (GPC)[c]**	**Đ[c]**	**Yield**
1[a]		1:0.5:200	90	34554	16832	1.25	88
2		1:1:200	60	17336	20449	1.34	97
3		1:10:200	90	1840	2668	1.17	89
4		1:20:200	150	980	1468	1.19	72
5[a]		1:0.5:200	110	34553	36318	1.41	62
6		1:1:200	60	17334	9769	1.19	55
7		1:10:200	95	1838	2647	1.27	68
8		1:20:200	90		0	0	0
9[a]		1:0.5:200	90	34574	33137	1.09	68
10		1:1:200	60	17359	18884	1.26	59
11		1:10:200	100	1860	2732	1.23	62
12		1:20:200	90		0	0	0

[a]Polymerization reactions are performed at 80ºC and rest of the reactions are performed at 100 ºC in toluene. [b]Determined by equiv. of {[BBL]/[I]}*86.09 (mol.wt. of β-butyrolactone)+ mol.wt. of initiator. [c]Determined by gel permeation chromatography calibrated with polystyrene standards in THF.

The ^1H NMR spectrum of the polymer synthesized from 1,4-BDM is shown in Figure 13. Along with the four major main chain peaks, similar small resonances peaks at 3.1 and 4.1 ppm for the hydroxyl butyrate group, and 5.1 ppm and 7.3 ppm for the BDM unit were observed, which supports the statement that the diol unit is incorporated between the two growing chains with the terminal hydroxybutyrate units. Although it is possible that diol could be present as a chain end with only one of the two hydroxyl groups reacting, the lack of the NMR signals for the unreacted corresponding benzylic protons (around 4.7 ppm) suggested that the diol was incorporated in the chain. α,ω-Dihydroxyl end-capped PHBs were also obtained with an aliphatic diol, 1,4-CHD. This indicated that secondary alcohols are effective initiators in these reactions as well. The butyrate end group was characterized by the hydroxyl (3.1 ppm) and methine (4.1 ppm) peaks, while the incorporation of CHD unit was evidenced by the α-OC*H* signal of the C_6H_{10} ring at 4.75 ppm. Again, the lack of the NMR signals for the unreacted α-OHC*H* (part of $C_6H_{10}OH$) protons (around 4.0 ppm) suggested that the diol was incorporated in the chain, not at the chain end. These assignments were further supported by the ^{13}C and ^1H-^1H COSY NMR spectra as well as the ESI-MS analysis of the isolated products. The ESI-MS spectrum of BDM derived polymer showed a dominant series of at 136 + 86n + 2 + 23 that could be assigned to the structure of $C_8H_8O_2 + n(C_4H_6O_2) + 2H+Na^+$ (Appendix F, Figure F2). Similarly, the ESI-MS spectrum of CHD derived polymer showed a dominant series of at 114 + 86n + 2 + 23 that could be assigned to the $C_6H_{10}O_2 + n(C_4H_6O_2) + 2H + Na^+$ structure (Appendix F, Figure F3).

It was noted that the integrations of diol unit and the end group signals deviated somewhat from the expected 1:2 ratio. Close inspection of the ^{1}H NMR spectra revealed the presence of two minor peaks at 5.7 and 6.9 ppm when 1,4-BDM and 1,4-CHD were used as initiators. These signals can be assigned to the alkenic protons in *trans*-crotonate group, which is presumably derived from the dehydration of alcohols, and they could amount to up to half of the end groups. These assignments are further supported by the presence of alkenic carbon peaks at ~130 ppm in the ^{13}C NMR. The minor series of peaks in ESI-MS spectrum could be attributed the polymer with crotonate end groups (18 less than the main series of peaks). Similar dehydration has been observed by Coates and coworkers in the polymerization of BBL in the presence of BnOH, which was attributed to elimination reaction promoted by the metal complex.[27] In our case, however, the crotonate end groups were only observed when diols are used as initiators, and no or minimal formation of crotonate signals was noticed when BnOH was used as an initiator (Figure 8). In the earlier example with short chain oligomer obtained from 50 equiv of BnOH, the ^{1}H NMR. Figure 9 clearly shows the benzyl and hydroxybutyrate chain ends; still, there is no or minimal amount of crotonate groups. Since our initial goal was to produce polyester diols, we attempted to explore the conditions to minimize the dehydration reaction. It was noted that when the reaction was allowed to proceed at lower temperature (80 ºC), no crotonate groups were observed in the initial reaction mixture. However, after workup, the crotonate signals showed up in the NMR spectrum, which typically negligible amount at the end groups. Prolonged reaction times and repeated precipitation of the polymer product during purification tend to increase the percentage of crotonate groups.

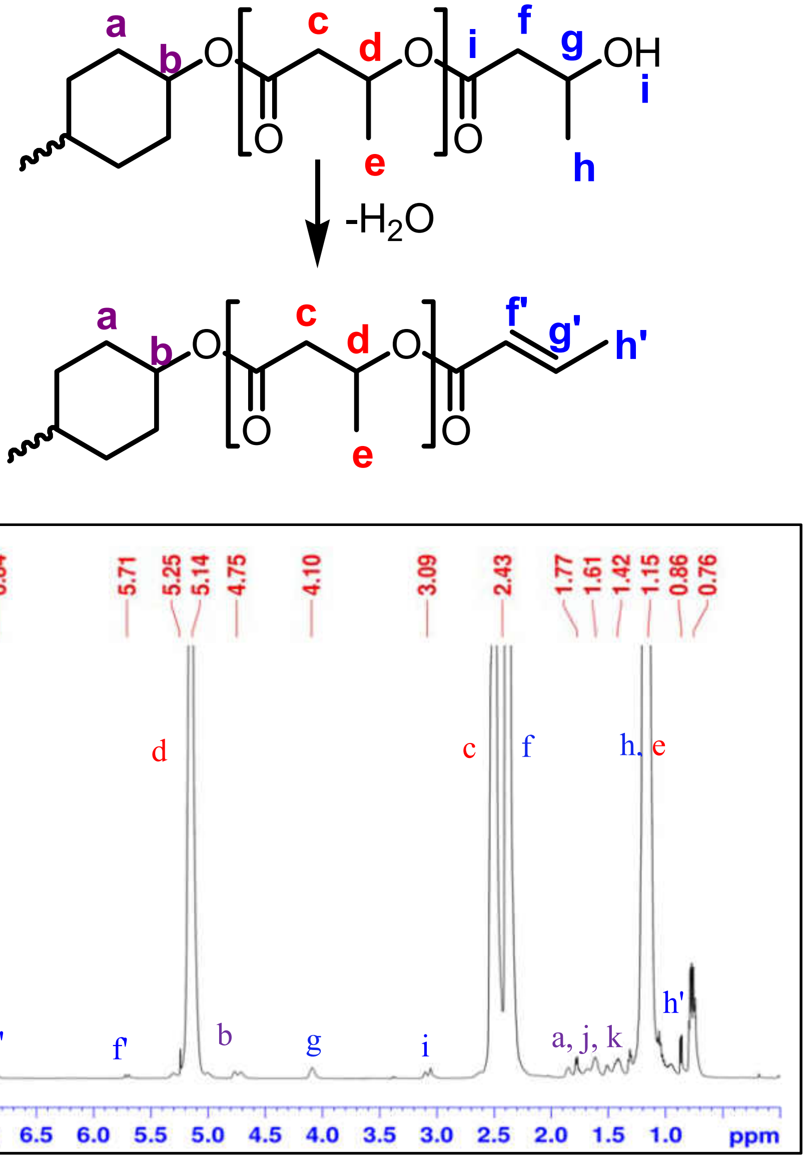


Figure 14. ^{1}H-NMR of isolated poly(hydroxybutyrate) with 1,4-cyclohexane diols ([1,4-CHD]/[Zn] = 0.5) of 80 ºC reaction temperature.

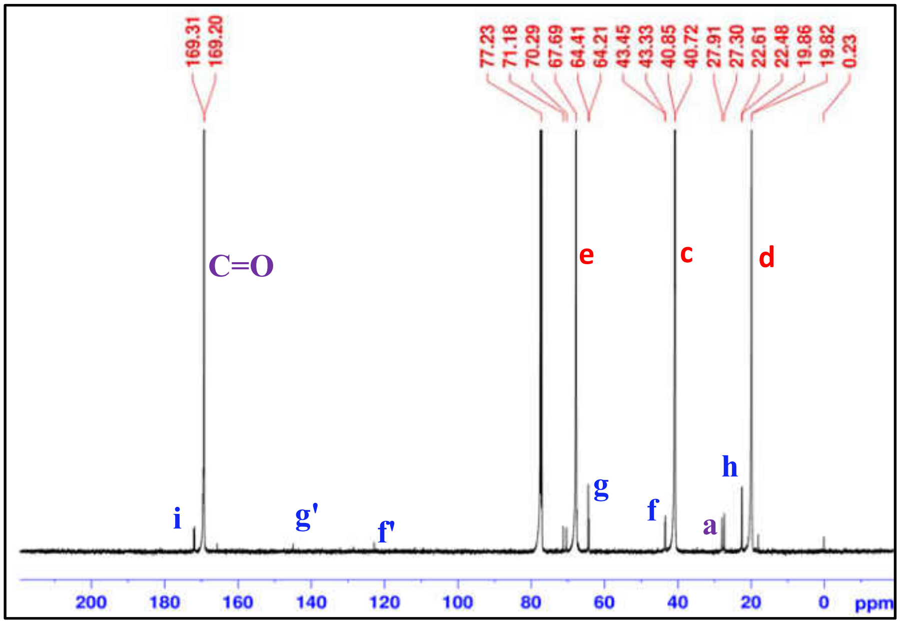
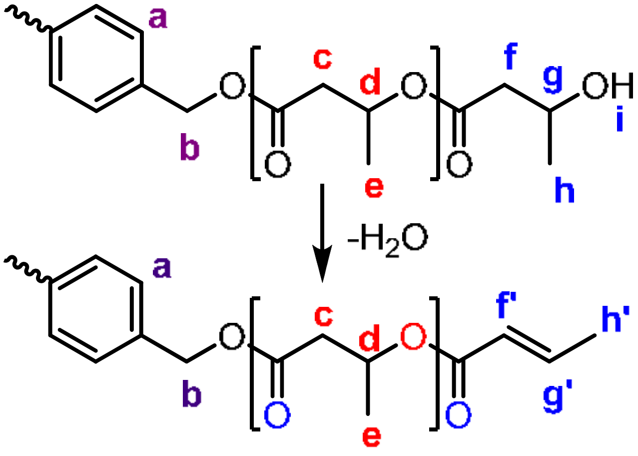


Figure 15.^{13}C-NMR of isolated poly(hydroxybutyrate) with 1,4 cyclohexane diols ([1,4-CHD]/[Zn] = 0.5) of 80 ºC reaction temperature.



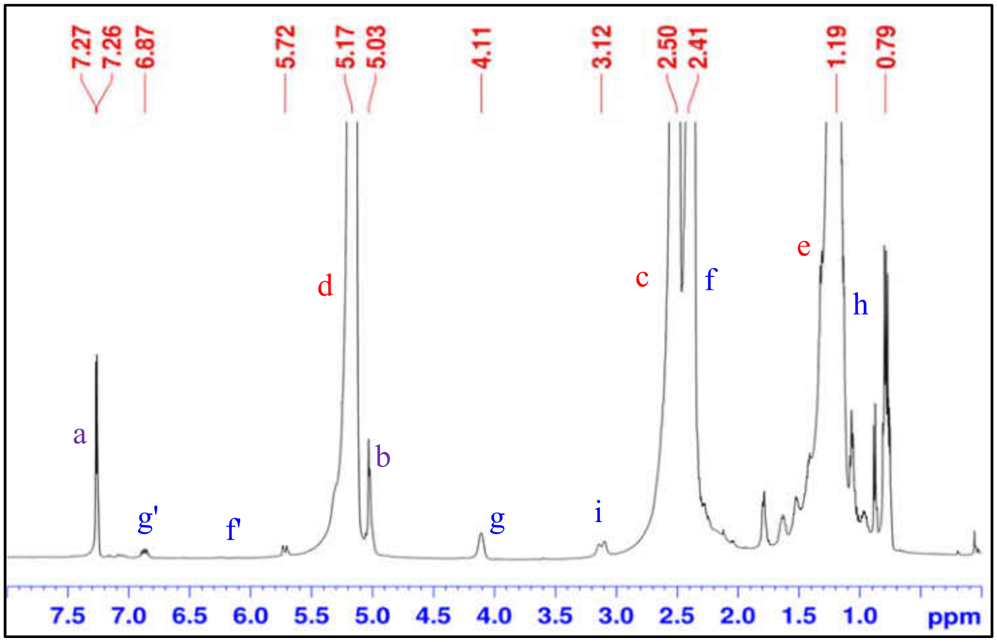


Figure 16. ^{1}H-NMR of isolated poly(hydroxybutyrate) with [1,4-BDM]/[Zn] = 0.5) of 80 ºC reaction temperature.

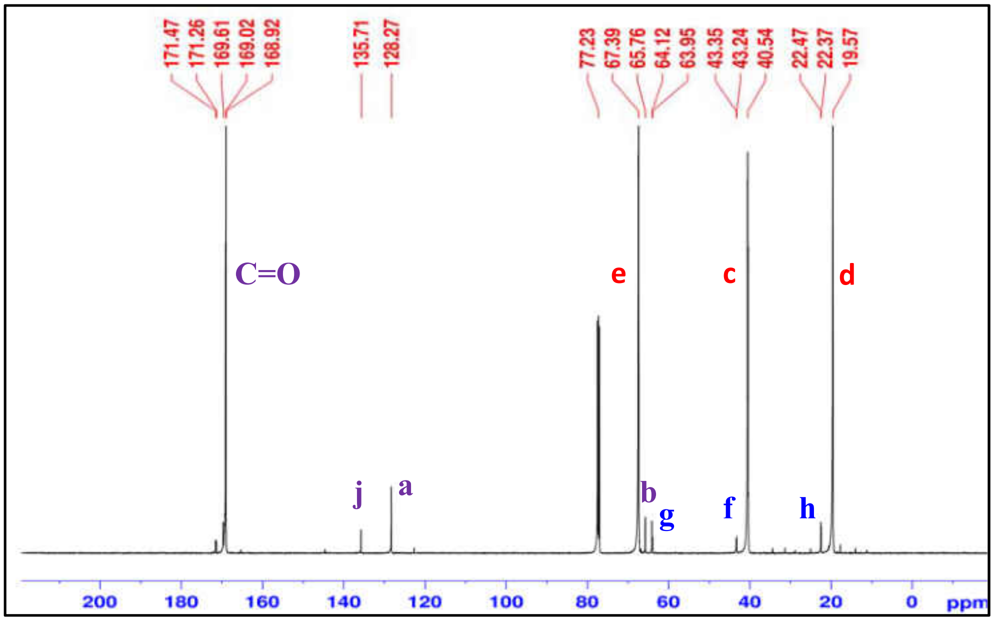
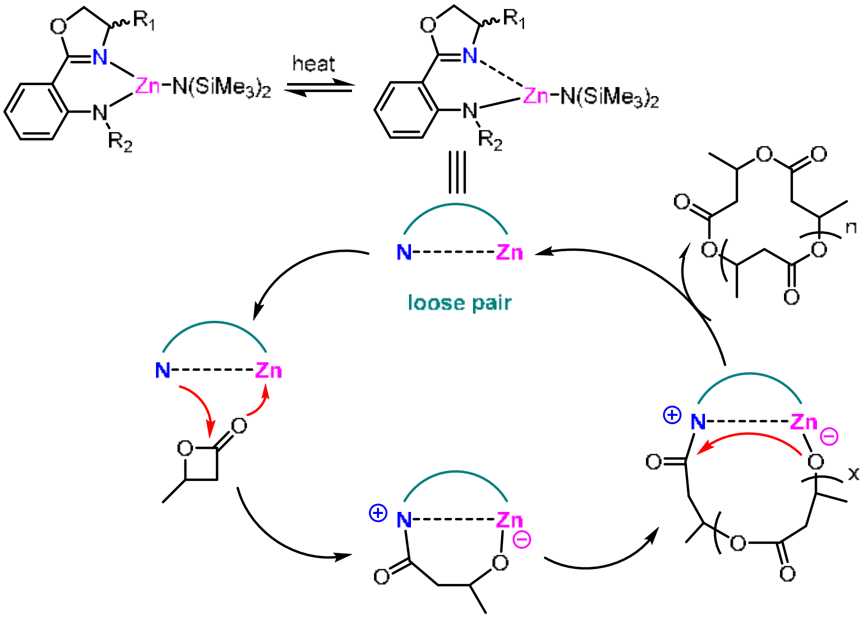


Figure 17. ^{13}C-NMR of isolated poly (hydroxybutyrate) with [1,4-BDM]/[Zn] = 0.5) of 80 ºC reaction temperature.

3.6 Mechanistic Consideration of β-butyrolactone polymerization by Zn complexes.

The cyclic polymers are generally produced from two pathways. In the first case, a linear chain bearing a good leaving group was initially produced and backbiting (or ring closing) under high dilution conditions in the end furnished the cyclic structure. This is usually accompanied by the presence of both linear and cyclic polymers in the products. The present zinc catalysts feature a silylamido group $-N(SiMe_3)_2$ that could serve as an initiating group, however, it tended to be sluggish due to its bulkiness. Furthermore, the linear chain end groups were never observed even at low conversion of BBL and only cyclic PHBs were obtained exclusively. These observations seemed at odds with such a pathway. In the second scenario that could lead to exclusive formation of cyclic polymers, the two ends of the polymer chain were never truly separated. They were held together by electrostatic interactions (or a Lewis pair) as in zwitterionic ring opening polymerization[28] or by a tethered initiating group as in ring expansion polymerization.[29] The present zinc catalysts do not easily fit into these categories but can be viewed as a classical Lewis adduct. The Lewis acidity of the zinc center was significantly attenuated, as they typically do not react with bases such as pyridine at room temperature.[30] However, at elevated temperature, the Lewis adduct could loosen up to become a "loose" pair that initiates the polymerization. ^{1}H NMR studies of **1a** in C_6D_6 at variable temperatures (from 25 to 100ºC) showed a gradual shift (toward free ligands) of signals with increasing temperature, and the largest shifts occurred for the oxazoline ring protons (Figure 18). This suggested that the imino nitrogen mostly likely dissociated from zinc at higher temperature, forming a loose Lewis pair. The notion that the imino nitrogen dissociates instead of the monodentate silylamido nitrogen is not unreasonable, considering that N_{imino} is neutral while N_{amido} is anionic. In the crystal structure of **1a**, the Zn-N_{imino} distance (1.968(9) Å) is significantly longer than the Zn-N_{amido} distance (1.874(9) Å).[30] The Zn and N_{imino} are still associated, but the pair is loose enough to allow for coordination of the monomer, followed by the typical insertion/propagation steps through a zwitterionic intermediate. The situation is analogous to the cyclic polyesters synthesis via ROP promoted by $Zn(C_6F_5)_2$, despite the generation of Lewis adducts between $Zn(C_6F_5)_2$ and Lewis bases.[31] Furthermore, a solution of **1a** and BBL (molar ratio 1:1 or 1:15) in C_6D_6 showed no reaction at room temperature, but BBL was converted to polymers at elevated temperature showing no presence of any intermediate species. Only **1a**, BBL and PHB signals were observed throughout the course of the reaction. This suggested that the initiation step is slow relative to the propagation, which is in agreement with the GPC analysis that the resulting molecular weights are higher than the calculated values based on catalyst loadings and conversions.



Scheme 4. Proposed mechanism for the formation of cyclic PHBs

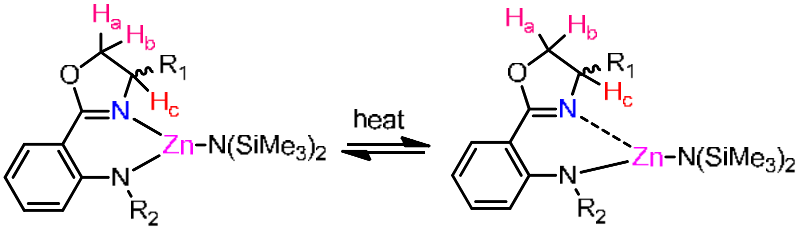


Figure 18. Predicted structures of Zn-complex at high temperature

Table 6. ^{1}H-NMR shifts of **1a**-oxazoline protons defined from variable temperature NMR method.

Temp	**NCH(R$_1$) C*H*$_2$O (H$_a$)**	**NCH(R$_1$) C*H*$_2$O (H$_b$)**	**NC*H*(R$_1$) CH$_2$O (H$_c$)**
25°C	3.5307	3.6475	4.1362
40°C	3.5942	3.6956	4.1655
60°C	3.6626	3.7466	4.1955
80°C	3.7354	3.8070	4.2250
100°C	3.7905	3.8497	4.2596

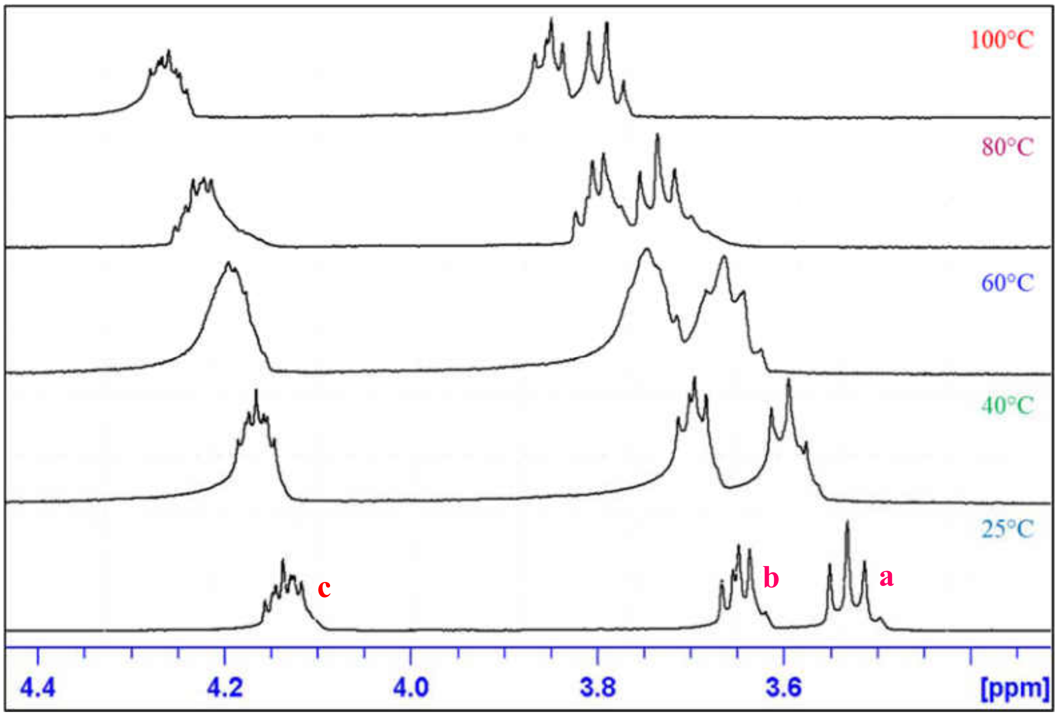


Figure 19. Variable temperature ^{1}H-NMR of catalyst **1a** in C_6D_6

In the presence of an alcohol co-catalyst, the first step would be the substitution of the silylamide by an alkoxide, which can function as a better initiating group. The rest of the reaction proceeds through a typical coordination-insertion mechanism, leading to the formation of linear polyesters end-capped by the initiating alkoxide at one end and hydroxyl butyrate at the other. The absence of any detectable signals for benzyl ether protons in BnOH initiated PHBs supported that only acyl-oxygen scission occurred in the presence of **1a**, in accord with the general depiction of metal-based ROP reaction.

CHAPTER 4

4.1 Conclusion

In summary, a series of Zn complexes have been demonstrated to be highly active in polymerizing BBL. Cyclic PHBs with high molecular weight were obtained in the absence of alcohol, whereas the addition of an alcohol co-catalyst resulted in the formation of linear PHBs with well-defined end groups. Based on experimental observations and catalyst structures, a Lewis pair derived zwitterionic intermediate was proposed for the formation of cyclic polymers. The ROP reaction was employed to synthesize α,ω-dihydroxyl end-capped PHBs with diol initiators, which were incorporated into the polymer chain. However, the mechanistic details, especially those related to the cyclic polymer control and generation, warrant further investigation, which will be the focus of future efforts, as well as improvement of stereocontrol of the ROP process and exploration of the potential applications of polyester diols.

APPENDICES

Appendix A

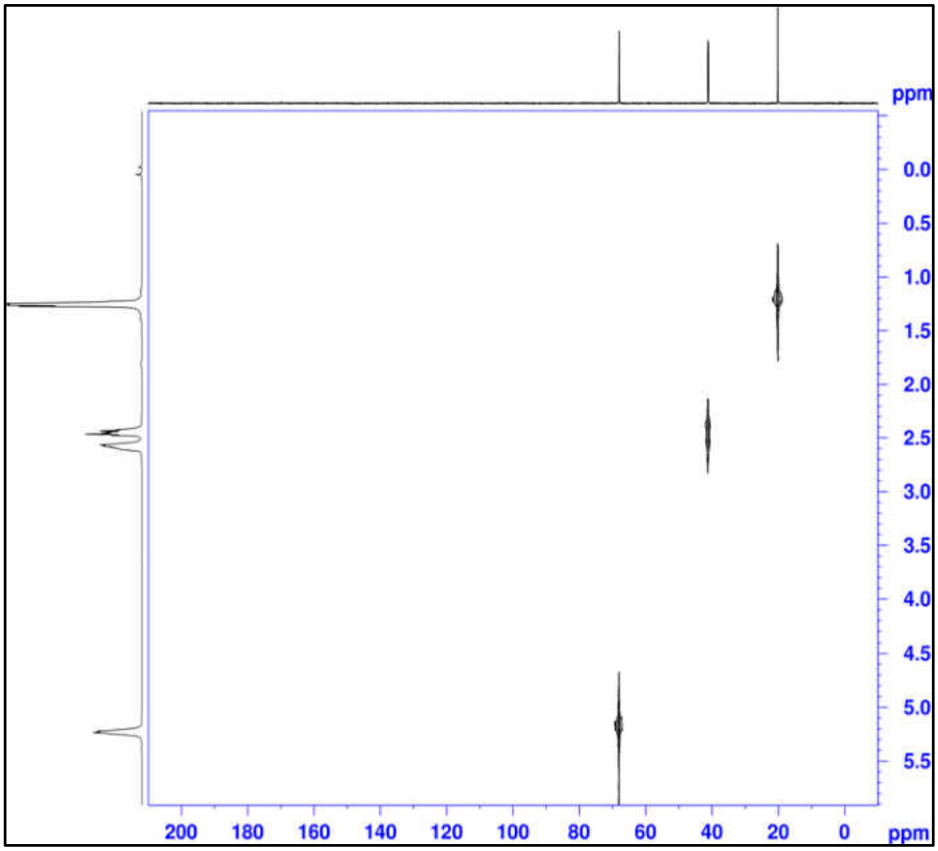


Figure A1. ^{1}H-^{13}C HETCOR NMR of the cyclic poly(hydroxybutyrate)

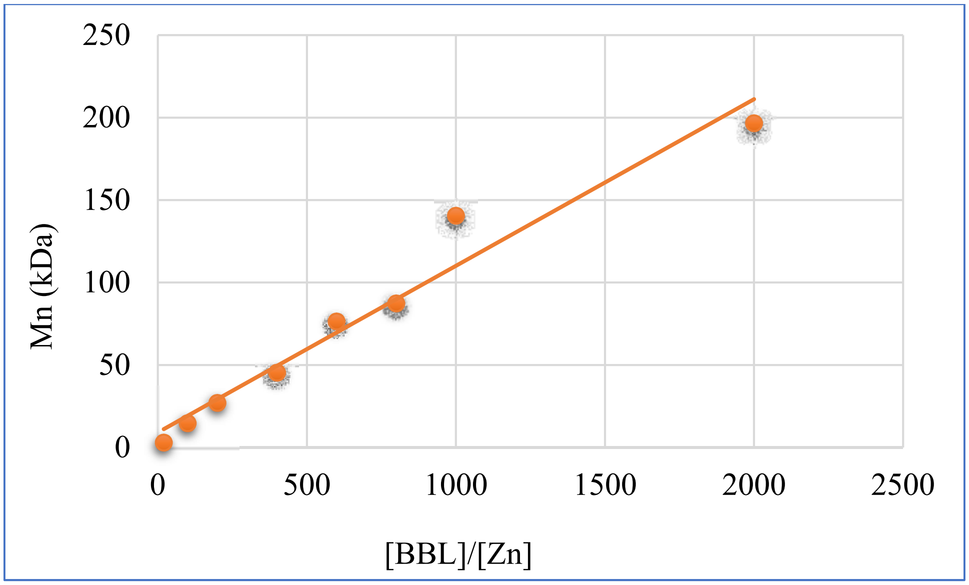


Figure A2. Plots of observed PHB M_n as functions of [BBL]:[Zn] for catalyst 1a

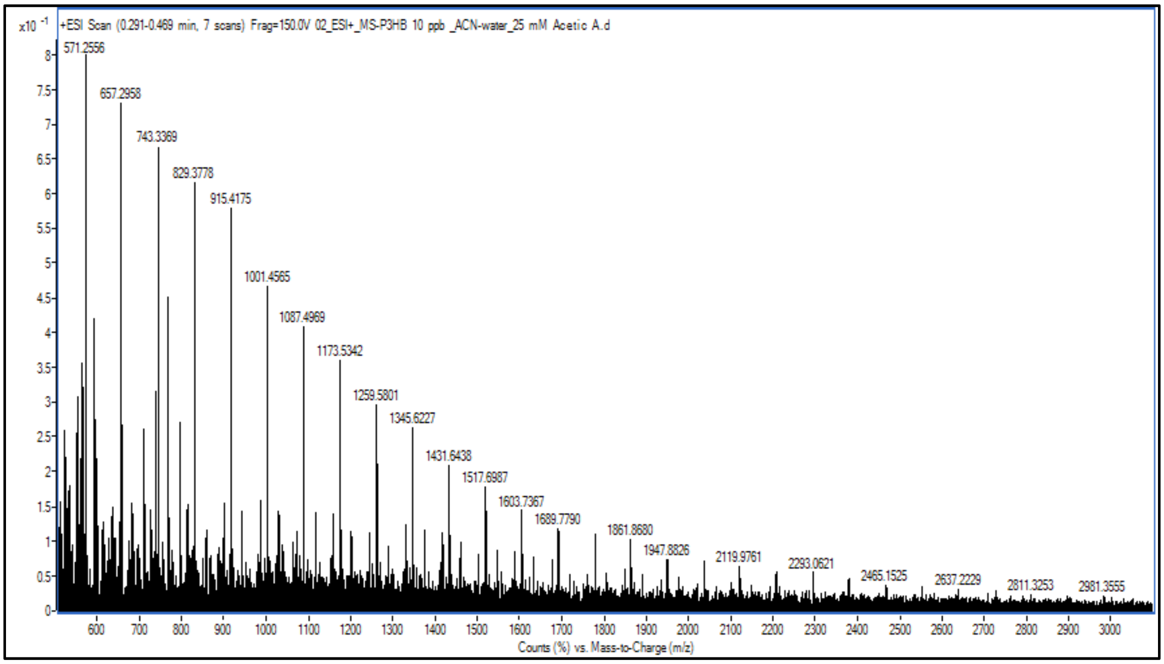
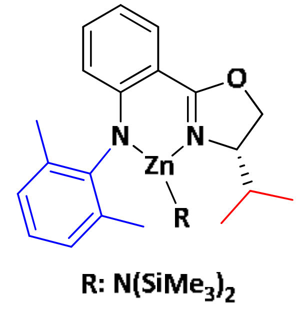
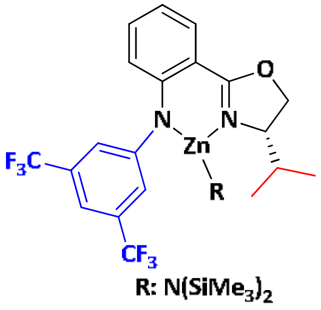


Figure A3: ESI-MS spectrum of cyclic PHB isolated from the polymerization of [BBL]:[1a] ratio of 200:1, in the presence of 25.0 mmol·L^{-1} of acetic acid.

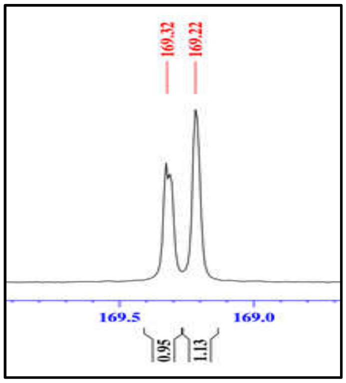
Appendix B

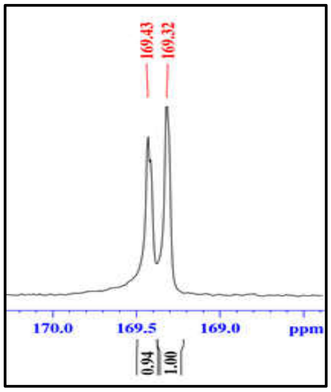


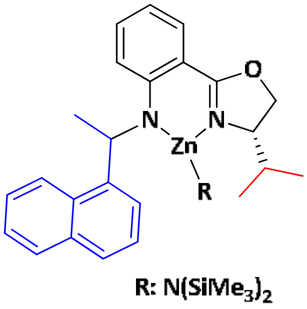
1a, $P_m = 0.54$ (100°C)



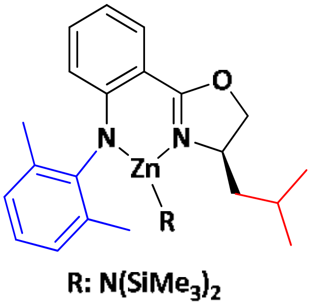
1b, $P_m = 0.52$ (100°C)







1**c**, $P_m = 0.55$ (100°C)



1**d**, $P_m = 0.53$ (100°C)

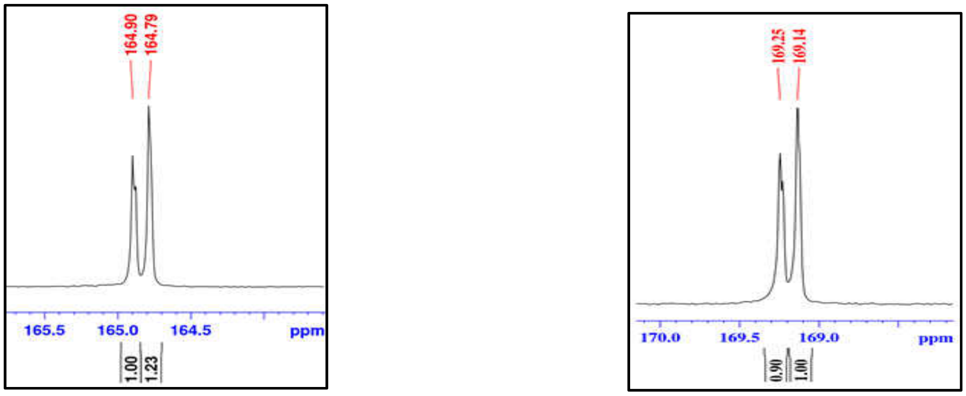


Figure B1. IG ^{13}C{^{1}H} NMR (500 MHz, CDCl3, 25 °C) of cyclic PHBs using different catalysts to investigate P_{m} of the polymer.

Appendix C

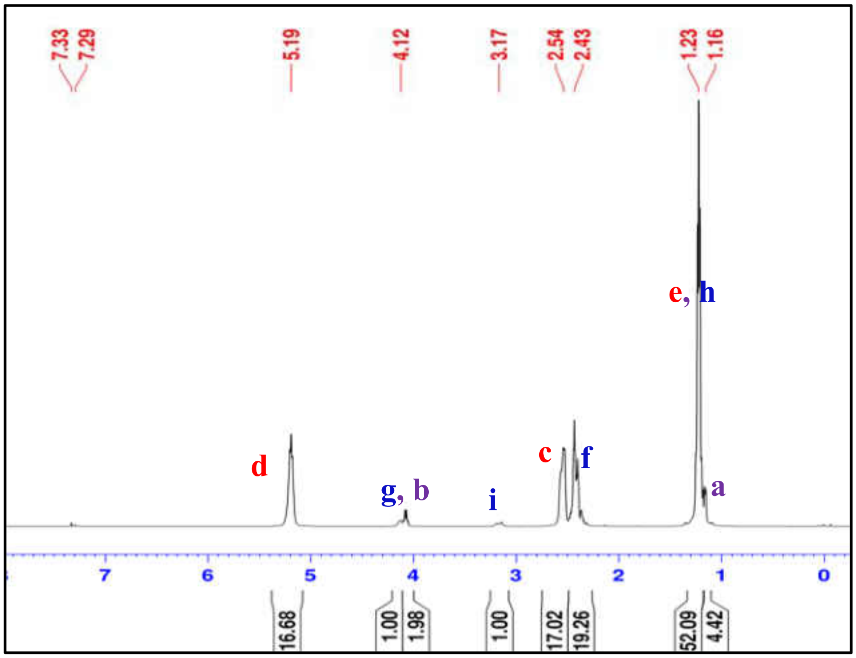
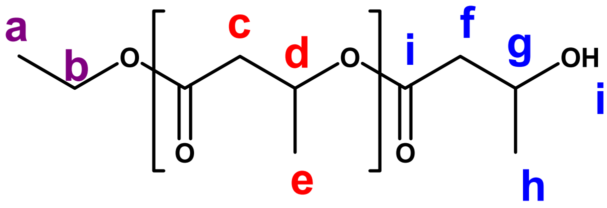


Figure C1. ^{1}H-NMR of poly(hydroxybutyrate) with EtOH ([EtOH]/[Zn] = 10).



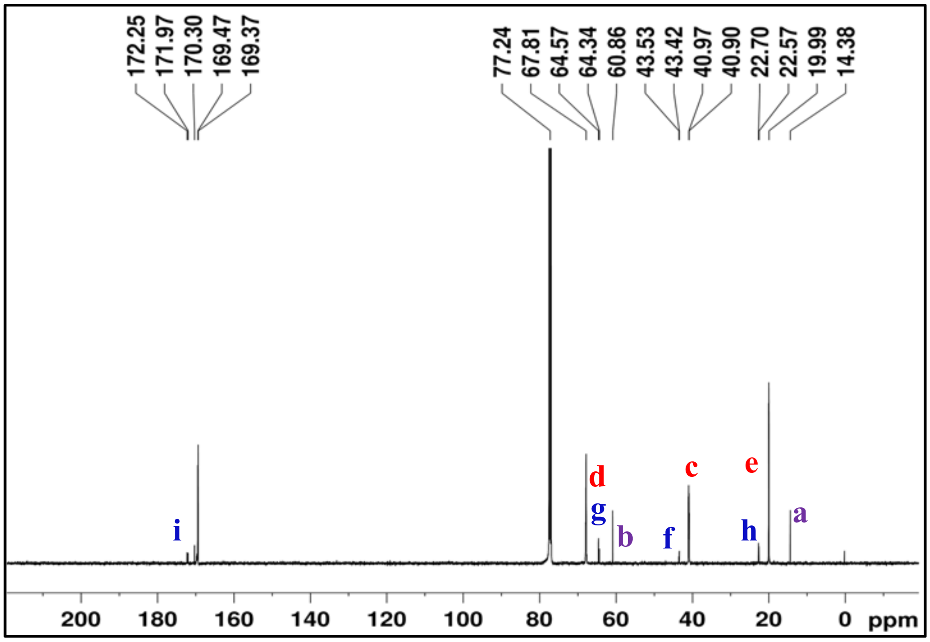


Figure C2. ^{13}C-NMR of isolated poly(hydroxybutyrate) with ethanol ([EtOH]/[Zn] = 10) of 100 ºC reaction temperature.

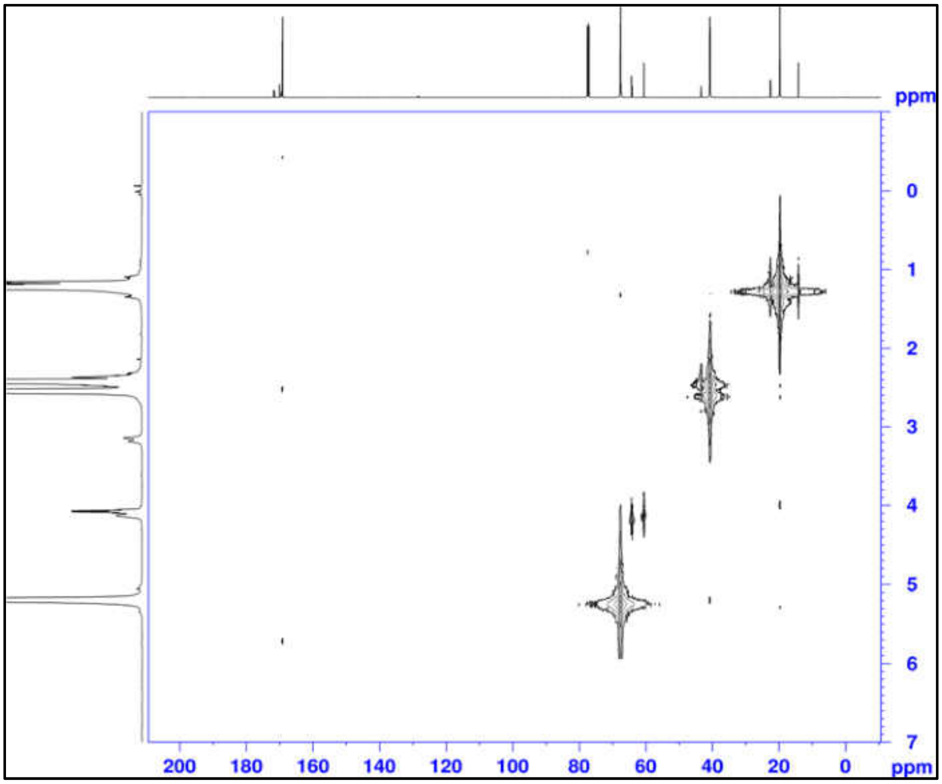


Figure C3. ^{1}H-^{13}C HETCOR NMR of the poly(hydroxybutyrate) with EtOH ([EtOH]/[Zn] = 10).

Appendix D

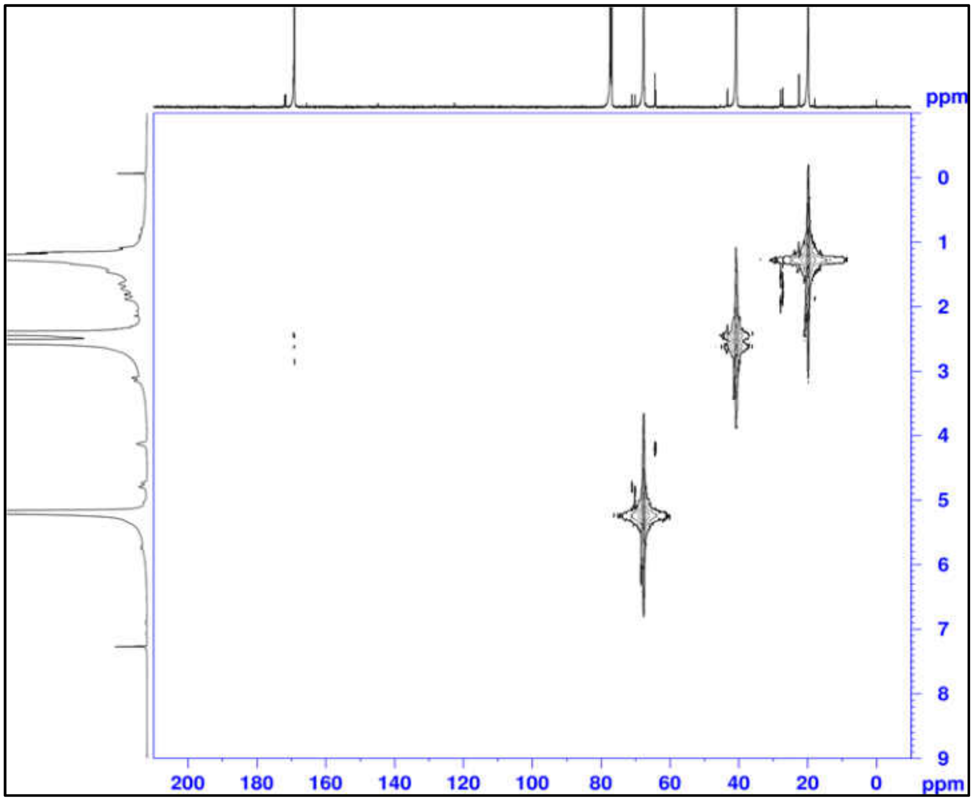


Figure D1. ^{1}H-^{13}C HETCOR NMR of the poly(hydroxybutyrate) with 1,4 CD

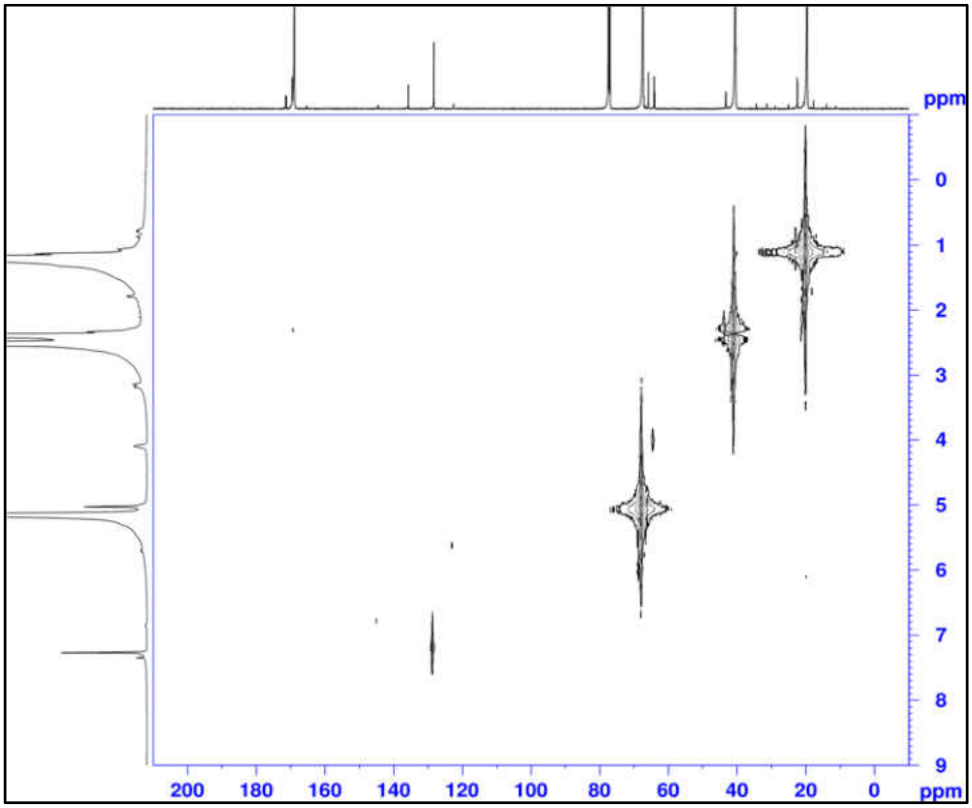


Figure D2. ^{1}H-^{13}C HETCOR NMR of the poly(hydroxybutyrate) with 1,4 BDM.

Appendix E

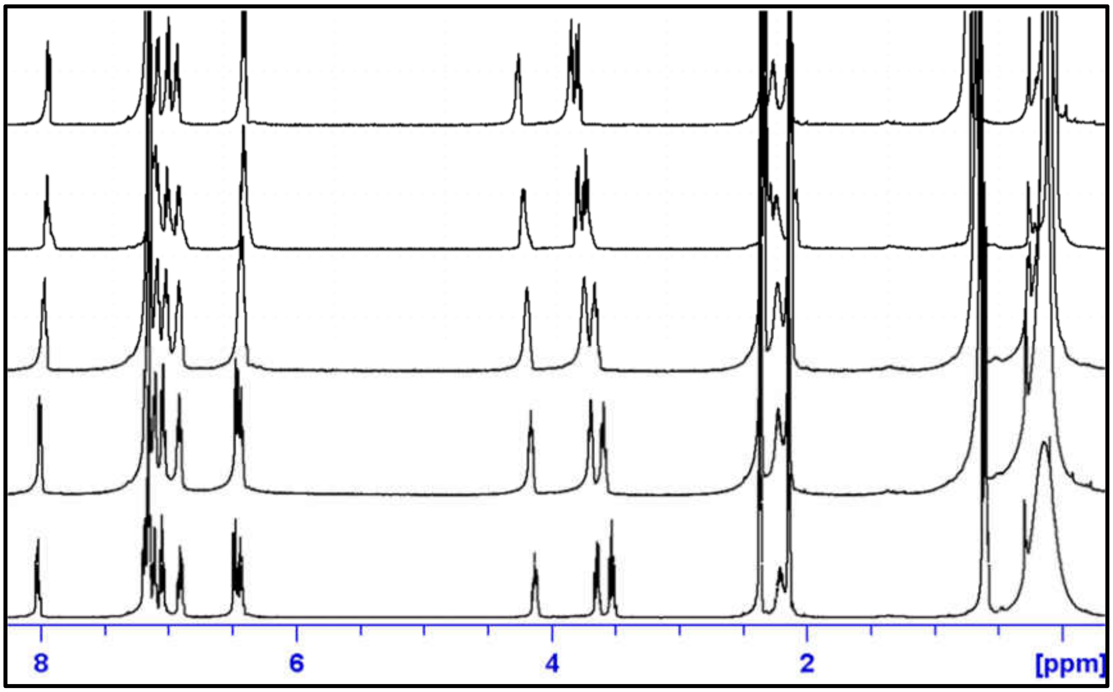


Figure E1. 1H-NMR of catalyst 1a at a variable temperature in C_6D_6

Appendix F

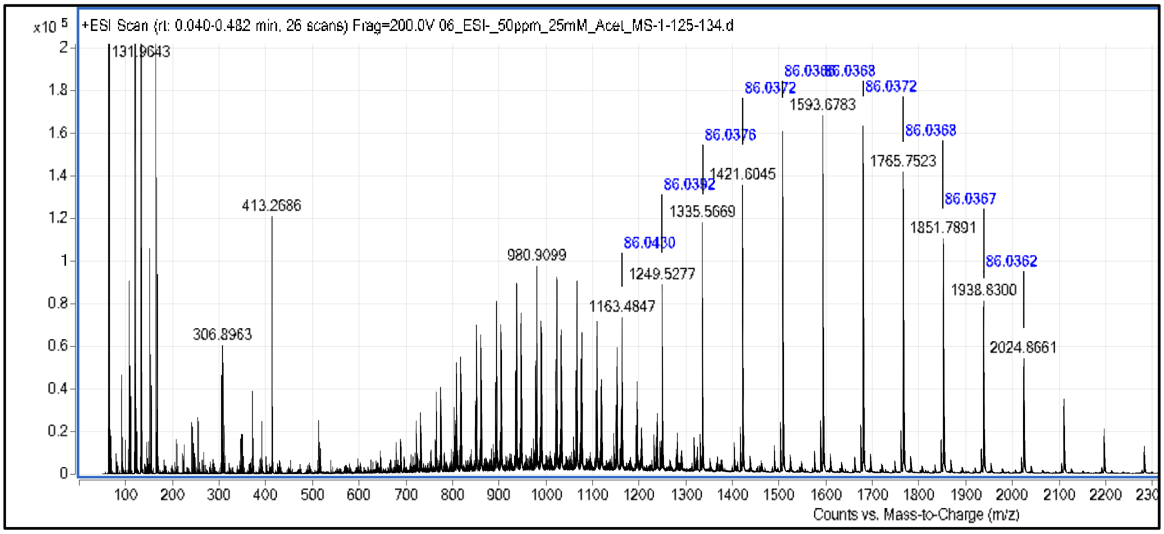


Figure F1. Positive ESI TOF mass spectra of 50 ppm PHBs with benzyl alcohol as an initiator in the presence of 25.0 mmol·L^{-1} of acetic acid.

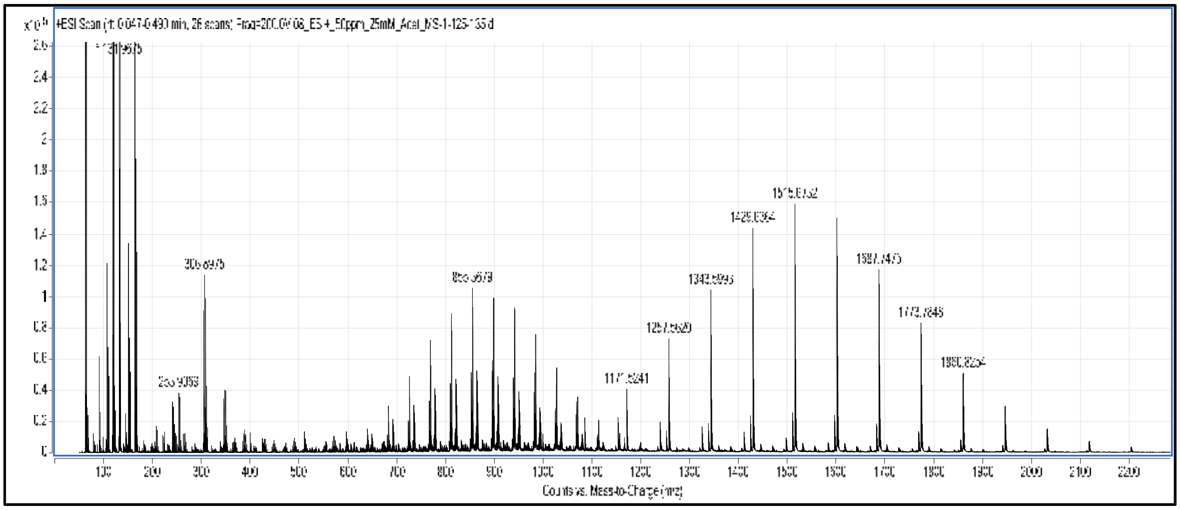


Figure F2. Positive ESI TOF mass spectra of 50 ppm PHBs with 1,4 BDM as an initiator in the presence of 25.0 mmol·L^{-1} of acetic acid.

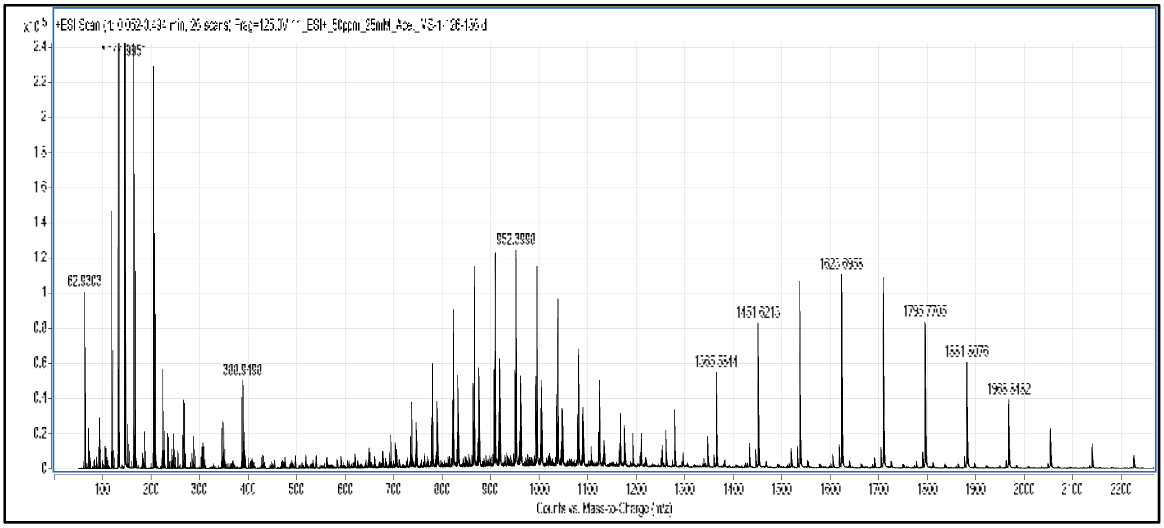


Figure F3. Positive ESI TOF mass spectra of 50 ppm PHBs with 1,4 CHD as an initiator in the presence of 25.0 mmol·L^{-1} of acetic acid.

REFERENCES

---

1. (a) Andrady, A. L.; Neal, M. A. Applications, and societal benefits of plastics. *Philos. Trans. R. Soc. Lond. B Biol. Sci.,* **2009,** *364*, 1977–1984. (b) https://www.regal-plastics.com/plastic-applications/

2. Garg, C.; Jain, A. Green concrete: Efficient & eco-friendly construction materials. *Int. J. Res. Eng. Technol.,* **2014** *2*, 259–264.

3.https://news.nationalgeographic.com/2017/07/plastic-produced-recycling-waste-ocean-trash-debris-environment.

4. Bugnicourt, E.; Cinelli, P.; Lazzeri, A.; Alvarez, V. P. Polyhydroxyalkanoate (PHA): Review of synthesis, characteristics, processing and potential applications in packaging. *Express Polym. Lett.*, **2014,** *8*, 791–808.

5. Gironi, F.; Piemonte, V. Bioplastics and petroleum-based plastics: Strengths and weaknesses. *Energy sourc. A, Recovery util. environ. effects,* **2011***, 33*, 1949–1959.

6. Isikgor, F. H.; Becer, C. R. Lignocellulosic biomass: a sustainable platform for the production of bio-based chemicals and polymers. *Polym. Chem.,* **2015,** *6***,** 4497−4559.

7. Zintl, M.; Molnar, F.; Urban, T.; Bernhart, V.; Preishuber-Pfugl, P.; Rieger, B. Variably isotactic poly(hydroxybutyrate) from *racemic* β-Butyrolactone: Microstructure control by achiral chromium(III) salophen complexes. *Angew. Chem., Int. Ed.* **2008,** *47*, 3458−3460. (b) Hori, Y.; Takahashi, Y.; Yamaguchi, A.; Nishishita, T. Ring opening copolymerization of optically active β-Butyrolactone with several lactones catalyzed by distannoxane complexes: Synthesis of new biodegradable polyesters. *Macromolecules,* **1993,** *26*, 4388−4390. (c)

Kemnitzer, J. E.; McCarthy, S. P.; Gross, R. A. Syndiospecific ring opening polymerization of β-Butyrolactone to form predominantly syndiotactic poly(β-hydroxybutyrate) using tin(1V) catalysts. *Macromolecules,* **1993,** *26*, 6143−6150. (d) Kricheldorf, H. R.; Eggerstedt, S. Polylactones. 41. Polymerizations of β-D, l-butyrolactone with dialkyltinoxides as initiator. *Macromolecules*, **1997,** *30*, 5693−5697. (e) Kricheldorf, H. R.; Lee, S. R.; Scharnagl, N. Polylactones. 28. Syndiotactic poly(β-D, L-hydroxybutyrate) by ring-opening polymerization of β-D,L-Butyrolactone with butyltin methoxides. *Macromolecules*, **1994,** *27*, 3139−3146. (f) Guillaume, C.; Carpentier, J. F.; Guillaume, S. M. Immortal ring opening polymerization of β-Butyrolactone with zinc catalysts: Catalytic approach to poly(3-hydroxyalkanoate). *Polymer*, **2009,** *50*, 5909−5917. (g) Ajellal, N.; Bouyahyi, M.; Amgoune, A.; Thomas, C. M.; Bondon, A.; Pillin, I.; Carpentier, J. F. Syndiotacticm enriched poly(3-hydroxybutyrates) via stereoselective ring opening polymerization of *racemic* β-Butyrolactone with discrete Yttrium catalysts. *Macromolecules*, **2009,** *42*, 987−993. (h) Ajellal, N.; Thomas, C. M.; Carpentier, J. F. J. Functional syndiotactic poly(β-hydroxyalkanoates) via stereoselective ring opening copolymerization of *rac*-β-butyrolactone and *rac*-allyl-β-butyrolactone. *J. Polym. Sci. A Polym. Chem.*, **2009,** *47*, 3177−3189. (i) Ajellal, N.; Durieux, G.; Delevoye, L.; Tricot, G.; Dujardin, C.; Thomas, C. M.; Gauvin, R. M. Polymerization of *racemic* β-butyrolactone using supported catalysts: A simple access to isotactic polymers. *Chem. Commun.* **2010,** *46*, 1032−1034. (j) Jaffredo, C. G.; Carpentier, J. F.; & Guillaume, S. M. Poly(hydroxyalkanoate) block or random copolymers of β-Butyrolactone and benzyl β-Malolactone: A matter of catalytic tuning. *Macromolecules*, **2013,** *46*, 6765−6776. (k) Jaffredo, C. G.; Chapurina, Y.; Guillaume, S. M.;

Carpentier, J. F. From syndiotactic homopolymers to chemically tunable alternating copolymers: Highly active Yttrium complexes for stereoselective ring-opening polymerization of β-Malolactonates. *Angew. Chem., Int. Ed.* **2014,** *53*, 2687−2691. (l) Kramer, J. W.; Coates, G. W. Fluorinated β-lactones and poly(β-hydroxyalkanoates): Synthesis via epoxide carbonylation and ring opening polymerization. *Tetrahedron*, **2008,** *64*, 6973−6978.

8. (a) Parks, J. E.; Holm, R. H. The synthesis, solution stereochemistry, and electron delocalization properties of bis(β-iminoamino) nickel(II) complexes. *Inorg. Chem*. **1968,** *7*, 1408–1416. (b) McGeachin, S. G. Synthesis and properties of some p-diketimines derived from acetylacetone, and their metal complexes. *Can. J. Chem.* **1968**, *46*, 1903-1912. (c) Bonnett, R.; Bradley, D. C.; Fisher, K. J.; Rendall, I. F. Metallo-organic compounds containing metal–nitrogen bonds. Part VII. Synthesis and properties of bis-(*NN′*-diethylbutane-1,3-di-iminato) derivatives of cobalt(II)[2] and zinc. *J. Chem. Soc. A*, **1971**, *0*, 1622-1627. (d) Hohloch, S.; Kriegel, B. M.; Bergman, R. G.; Arnold, J. Group 5 chemistry supported by β-diketiminate ligands. *Dalton Trans.*, **2016,** *45*, 15725–15745. (e) Kronast, A.; Reiter, M.; Altenbuchner, P. T.; Jandl, C.; Pöthig, A.; Rieger, B. Electron-deficient β-Diiminato-Zinc-Ethyl complexes: Synthesis, structure, and reactivity in ring-opening polymerization of lactones. *Organometallics*, **2016,** *35*, 681–685.

9. Delferro, M.; Marks, T. J. Multinuclear Olefin Polymerization Catalysts. *Chem. Rev.* **2011**, *111*, 2450–2485

---

10. Xue, M.; Jiao, R.; Zhang, Y.; Yao, Y.; Shen, Q. Synthesis and Structures of Tris-β-Diketiminate Lanthanide Complexes and Their High Activity for Ring-Opening Polymerization of ε-Caprolactone and L-Lactide. *Eur. J. Inorg. Chem.,* **2009**, *27,* 4110-4118.

11. Jeske, R. C.; DiCiccio, A.M.; Coates, G.W. Alternating Copolymerization of Epoxides and Cyclic Anhydrides: An Improved Route to Aliphatic Polyesters. *J. Am. Chem. Soc.* **2007**, *129*, 11330−11331.

12. Basuli, F.; Huffman, J. C.; Mindiola, D. J. Reductive C–N bond cleavage of the NCCCN β-diketiminate backbone: A direct approach to azabutadienyl and alkylidene-anilide scaffolds *Inorg. Chim. Acta.* **2007**, *360*, 246-254.

13. (a) Ajellal, N.; Carpentier, J. F.; Guillaume, C.; Guillaume, S. M.; Helou, M.; Poirier, V.; Sarazin, Y.; Trifonov, A. Metal-catalyzed immortal ring-opening polymerization of lactones, lactides and cyclic carbonates. *Dalton Trans.*, **2010,** *39*, 8363−8376.

14. (a) Du, Y.; Yan, H.; Huang, W.; Chai, F.; Niu, S. Unanticipated strong blue photoluminescence rom fully bio-based aliphatic hyperbranched polyesters. *ACS Sustainable Chem.* Eng. **2017,** *5*, 6139–6147. (b) Linhardt, A.; König, M.; Iturmendi, A.; Henke, H.; Brüggemann, O.; Teasdale, I. Degradable, dendritic polyols on a branched polyphosphazene backbone. *Ind. Eng. Chem. Res.*, **2018,** *57*, 3602–3609. (c) Ren, J. M.; McKenzie, T. G.; Fu, Q.; Wong, E. H. H.; Xu, J.; An, Z.; Shanmugam, S.; Davis, T. P.; Boyer, C.; Qiao, G. G. Star polymers. *Chem. Rev.*, **2016,** *116*, 6743–6836. (d) Ebrahimi, T.; Hatzikiriakos, S. G.; Mehrkhodavandi, P. Synthesis and rheological characterization of star shaped and linear poly(hydroxybutyrate). *Macromolecules,* **2015,** *48,* 6672–6681.

---

15. (a) Kricheldorf, H. R. Cyclic polymers: Synthetic strategies and physical properties. *J. Polym. Sci. A Polym. Chem.*, **2010,** *48*, 251–284.

16. (a) Zhu, Y.; Hosmane, N. S. Advanced developments in cyclic polymers: Synthesis, applications, and perspectives. *ChemistryOpen*, **2015,** *4*, 408–417. (b) Manavitehrani, I.; Fathi, A.; Badr, H.; Daly, S.; Shirazi, A. N.; Dehghani, F. Biomedical applications of biodegradable polyesters. *Polymers*, **2016,** *8*, 01–32.

17. Wood, B. R.; Hodge, P.; Semlyen, J. A. Cyclic polyesters: 1. Preparation by a new synthetic method, using polymer-supported reagent. *Polymer,* **1993,** *34*, 3052–3058.

18. Tu, X. Y.; Liu, M. Z.; Wei, H. Recent progress on cyclic polymers: Synthesis, bio-properties, and biomedical applications. *J. Polym. Sci. A Polym. Chem.*, **2016,** *54*, 1447–1458.

19. (a) Brown, H. A.; Xiong, S. L.; Medvedev, G. A.; Chang, Y. A.; Abu Omar, M. M.; Caruthers, J. M.; Waymouth, R. M. *Macromolecules*, **2014,** *47*, 2955−2963. (b) Chang, Y. A.; Waymouth, R. M. Ion pairing effects in the zwitterionic ring opening polymerization of δ-valerolactone. *Polym Chem.*, **2015,** *6*, 5212. (c) Hoskins, J. N.; Grayson, S. M. Cyclic polyesters: Synthetic approaches and potential applications. *Polym Chem.***,** **2011,** *2,* 289–299. (d) Culkin, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. Zwitterionic polymerization of lactide to cyclic poly(Lactide) by using N-Heterocyclic carbene organocatalysts. *Angew. Chem. Int. Ed.,* **2007,** *46,* 2627–2630. (e) Shin, E. J.; Jeong, W.; Brown, H. A.; Hedrick, J. L.; Waymouth, R. M. Crystallization of cyclic polymers: Synthesis and crystallization behavior of high molecular weight cyclic poly(ε-Caprolactone)s. *Macromolecules***,** **2011,** *44,* 2773–2779. (f) Kricheldorf, H. R.; Lomadze, N.; Schwarz, G. Cyclic polylactides by imidazole-catalyzed polymerization of l-

---

Lactide. *Macromolecules*, **2008,** *41,* 7812–7816. (g) Piedra-Arroni, E.; Ladaviere, C.; Amgoune, A.; Bourissou, D. Ring-opening polymerization with $Zn(C_6F_5)_2$-Based lewis pairs: Original and efficient approach to cyclic polyesters. *J. Am. Chem. Soc.*, **2013,** *135,* 13306–13309. (h) Phomphrai, K.; Pongchan-o, C.; Thumrongpatanaraks, W.; Sangtrirutnugul, P.; Kongsaeree, P.; Pohmakotr, M. Synthesis of high-molecular-weight poly(ε-Caprolactone) catalyzed by highly active bis(amidinate) tin(II) complexes. *Dalton Trans.,* **2011,** *40,* 2157–2159.

20. (a) Corneillie, S.; Mario Smet, M. PLA architectures: the role of branching. *Polym Chem.,* **2015,** *6*, 850–867. (b) Brown, H. A.; Waymouth, R. M. Zwitterionic ring-opening polymerization for the synthesis of high molecular weight cyclic polymers. *Acc. Chem. Res.*, **2013,** *46*, 2585–2596.

21. (a)Culkin, D. A.; Jeong, W.; Csihony, S.; Gomez, E. D.; Balsara, N. P.; Hedrick, J. L.; Waymouth, R. M. Zwitterionic polymerization of lactide to cyclic poly(Lactide) by using N-Heterocyclic carbene organocatalysts. *Angew. Chem.Int. Ed.*, **2007,** *46*, 2627–2630. (b) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. Zwitterionic polymerization: A kinetic strategy for the controlled synthesis of cyclic polylactide. *J. Am. Chem. Soc.*, **2009**, *131*, 4884–4891. (c) Brown, H. A.; De Crisci, A. G.; Hedrick, J. L.; Waymouth, R. M. Amidine-mediated zwitterionic polymerization of lactide. *ACS Macro Lett*, **2012**, *1*, 1113–1115. (d) Brown, H. A. & Waymouth, R. M. Zwitterionic ring-opening polymerization for the synthesis of high molecular weight cyclic polymers. *Acc. Chem. Res.*, **2013,** *46*, 2585–2596 (e) Shin, E. J.; Brown, H. A.; Gonzalez, S.; Jeong, W.; Hedrick, J. L.; Waymouth, R. M. Zwitterionic copolymerization: Synthesis of cyclic gradient copolymers. *Angew. Chem.Int. Ed.,* **2011,** *50*, 6388–6391.

---

22. Binda, P. I.; Abbina, S.; Du, G. Modular synthesis of chiral β-diketiminato-type ligands containing 2-oxazoline moiety via Palladium-catalyzed amination. *Synthesis,* **2011,** *16*, 2609–2618.

23. Ebrahimi, T.; Aluthge, D. C.; Hatzikiriakos, S. G.; & Mehrkhodavandi, P. Highly active chiral zinc catalysts for immortal polymerization of β-Butyrolactone form melt processable syndio-rich poly(hydroxybutyrate). *Macromolecules,* **2016,** *49*, 8812–8824.

24. Abbina, S.; Du, G. (2014). Zinc-catalyzed highly isoselective ring opening Polymerization of *rac*-lactide. *ACS Macro letters,* **2014,** *3,* 689–692.

25. (a) Chamberlain, B. M.; Cheng, M.; Moore, D. R.; Ovitt, T. M.; Lobkovsky, E. B.; Coates, G. W. Polymerization of lactide with zinc and magnesium β-Diiminate complexes: Stereocontrol and mechanism. *J. Am Chem. Soc.,* **2001,** *123*, 3229–3238. (b) Jeong, W.; Shin, E. J.; Culkin, D. A.; Hedrick, J. L.; Waymouth, R. M. Zwitterionic polymerization: A kinetic strategy for the controlled synthesis of cyclic polylactide. *J. Am. Chem. Soc.,* **2009,** *131*, 4884–4891. (c) Kricheldorf, R. H. Cyclic polymers: Synthetic strategies and physical properties. *J. Polym. Sci. A Polym. Chem.*, **2010,** *48,* 251–284.

26. (a) Brzeska, J.; Heimowska, A.; Janeczek, H.; Kowalczuk, M.; Rutkowska, M. Polyurethanes based on atactic poly[(R,S)-3-hydroxybutyrate]: Preliminary degradation studies in simulated body fluids. *J. Polym. Environ.*, **2014,** *22*, 176–182. (b) Hong, J. H.; Jeon, H. J.; Yoo, J. H.; Yu, W. R.; Youk, J. H. Synthesis and characterization of biodegradable poly(ε-caprolactone-co-β-butyrolactone)-based polyurethane. *Polym. Degrad. Stab.,* **2007,** *92,* 1186–1192. (c) Rezayana, A. H.; Firoozia, N.; Kheirjoua, S.; Rezaeib, S. J. T.; Nabidc, M. R. Synthesis and characterization of

---

biodegradable semi-interpenetrating polymer networks based on star-shaped copolymers of ε-Caprolactone and lactide. *Iran J. Pharm. Res.,* **2017**, *16*, 63–73

27. Rieth, L. R.; Moore, D. R.; Lobkovsky, E. B.; Coates, G. W. Single-Site β-diiminate zinc catalysts for the ring-opening polymerization of β-Butyrolactone and β-valerolactone to poly(3-hydroxyalkanoates). *J. Am. Chem. Soc.*, **2002,** *124*, 15239–15248.

28. Brown, H. A.; Waymouth, R. M. (2013). Zwitterionic ring-opening polymerization for the synthesis of high molecular weight cyclic polymers. *Acc. Chem. Res.,* **2013,** *46*, 2585–2596.

29. (a) Xia, Y.; Boydston, A. J.; Yao, Y. F.; Kornfield, J. A.; Gorodetskaya, I. A.; Spiess, H. W.; Grubbs, R. H. Ring-expansion metathesis polymerization: Catalyst-dependent polymerization profiles. *J. Am. Chem. Soc.*, **2009**, *131*, 2670–2677. (b) Weil, J.; Mathers, R. T.; Getzler, Y. D. Lactide cyclopolymerization by an alumatrane-inspired catalyst. *Macromolecules*, **2012,** *45*, 1118–1121. (c) Chang, Y. A.; Waymouth, R. M. Recent progress on the synthesis of cyclic polymers via ring-expansion strategies. *J. Polym. Sci. A Polym. Chem.*, **2017,** *55*, 2892–2902.

30. Abbina, S.; Du, G. Chiral amido-oxazolinate zinc complexes for asymmetric alternating copolymerization of CO_2 and cyclohexene oxide. *Organometallics,* **2012***, 31,* 7394–7403.

31. (a) Piedra-Arroni, E.; Ladaviere, C.; Amgoune, A.; Bourissou, D. Ring-opening polymerization with $Zn(C_6F_5)_2$-based lewis pairs: Original and efficient approach to cyclic polyesters. *J. Am. Chem. Soc.,* **2013**, *135,* 13306–13309. (b) Li, X.-Q.; Wang, B.; Jia, H.-Y.; Li, Y. S. Insights into the mechanism for ring-opening polymerization of lactide catalyzed by $Zn(C_6F_5)_2$/organic superbase Lewis pairs. *Catal. Sci. Technol.,* **2016,** *6*, 7763–7772. (c) Li, X.;

Chen, C.; Wu, J. Lewis pair Catalysts in the polymerization of lactide and related cyclic esters. *Molecules,* **2018,** *23*, 189–202. (d) Wang, B.; Pan, L.; Ma, Z.; Li, Y. Ring-Opening Polymerization with Lewis Pairs and Subsequent Nucleophilic Substitution: A Promising Strategy to Well-Defined Polyethylene-like Polyesters without Transesterification. *Macromolecules*, **2018**, *51*, 836−845.