Chemistry of Bismuth, Chromium and Magnesium Complexes and Their Applications in the Ring-Opening Polymerization of Cyclic Esters and Epoxides

DISSERTATION

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By

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Abstract

Over the counter oral relief aids and dietary supplements were investigated as a catalyst for the ring opening polymerization, ROP, of lactide (LA) and ε-caprolactone (ε-CL). Among these catalysts, the activity of the Pepto-Bismol® (the active ingredient bismuth subsalicylate) for ROP is comparable to the industrial ROP catalyst, Sn(Oct)₂. A series of bismuth complexes in the form of SalenBiX, where X = alkoxides, halides, etc., were synthesized and employed for the ROP of LA and these are more reactive than the related Al complexes. Further studies of porphyrin-Bi-alkoxides lead to the discovery of the shortest Bi-Li bond containing complexes.

The reaction of propylene oxide, PO, and rac-LA, by TPPMX/PPN⁺Cl⁻ catalyst, where M = Cr or Al, and X = chloride or alkoxide, produces isotactic polylactide, PLA, at room temperature and at higher temperature favors the formation of small molecules of 3,6-dimethyl-1,4-dioxan-2-one. The mechanistic pathway for the formation of PLA and 3,6-dimethyl-1,4-dioxan-2-one were investigated by GCMS, NMR and MALDI studies.

Several modified β-diketiminate ligands containing Mg complexes were synthesized and employed for the ROP of LA, ε-CL and epoxides (propylene oxide, cyclohexene oxide and styrene oxide). All the Mg complexes are active for the polymerization of LA, ε-CL and epoxides. Among these catalysts, BDI(Ph)Mg⁶Bu(THF) is the fastest catalyst ( \( k_p = 14.47 \text{ M}^{-1}\text{s}^{-1} \) ) for the ROP of LA for the magnesium complexes.
Dedication

This document is dedicated to my parents Mr A. Balasanthiran, Mrs. B. Elagadevy and my uncle Mr. P. Sothinathan.
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substituted acetylenes, aryl–alkyl ethers, 2-alkene-4-ynoates and nitriles using


Fields of Study

Major Field: Chemistry
Table of Contents

Abstract ........................................................................................................................................... ii

Dedication ........................................................................................................................................ iii

Acknowledgments .......................................................................................................................... iv

Vita .................................................................................................................................................... v

List of Abbreviations ....................................................................................................................... xiv

List of Tables .................................................................................................................................... xvi

List of Diagrams .............................................................................................................................. xix

List of Schemes ............................................................................................................................... xx

Chapter 1  Introduction ...................................................................................................................... 1

1.1 Introduction ............................................................................................................................... 1

1.2 Biodegradable polymers .......................................................................................................... 2

1.2.1 Polylactide .......................................................................................................................... 2

1.2.2 Polycaprolactone ............................................................................................................... 4

1.2.3 Polyether and polycarbonates ........................................................................................... 5

1.2.4 Copolymers of epoxides and esters ................................................................................. 7
1.2.5 Copolymers of esters, ethers and carbon dioxide ............................................. 8
1.3 Catalyst development ................................................................................................. 9
  1.3.1 Choice of metal center ......................................................................................... 11
  1.3.2 Tin(II) octanoate .............................................................................................. 11
  1.3.3 Reactivity of other metal catalysts ...................................................................... 12
  1.3.4 Magnesium catalysts ......................................................................................... 13
  1.3.5 Bismuth catalysts .............................................................................................. 18
  1.3.6 Chromium catalyst ........................................................................................... 20
1.4 Polymerization mechanism ......................................................................................... 21
1.5 Stereochemistry of polylactide and polycarbonates .................................................. 24
  1.5.1 Stereo sequence of polylactide ......................................................................... 24
  1.5.2 Stereo sequence of polyethers and polycarbonates .......................................... 30
1.6 Kinetics of lactide polymerization ............................................................................. 34
1.7 Summary .................................................................................................................... 35

Chapter 2 Chemistry of Bi catalysts and their applications for the ROP of PO, LA and ε-CL 37
  2.1 Introduction .............................................................................................................. 37
  2.2 Results and discussion ............................................................................................ 40
    2.2.1 Heterogeneous Bi catalysts .............................................................................. 40
2.2.2 Synthesis of single-site Bi catalysts .......................................................... 48
2.2.3 Ring-opening polymerization of lactide ...................................................... 58
2.3 Reactivity of ε-caprolactone/ propylene oxide with ph-salenBiO’Bu ............. 60
2.4 Polymerization of epoxides with CO₂ by TPPBiI......................................... 60
2.5 Concluding remarks ...................................................................................... 61
2.6 Experimental and general conditions ............................................................ 62
  2.6.1 Measurements .......................................................................................... 63
  2.6.2 General procedure for bulk lactide polymerization .............................. 64
  2.6.3 General procedure for microwave assisted LA polymerization ........... 64
  2.6.4 General procedure for kinetic studies of bulk rac-LA polymerization...... 64
  2.6.5 General procedure for bulk ε-CL polymerization ................................. 65
  2.6.6 General procedure for bulk rac-LA and ε-CL co-polymerization .......... 65
  2.6.7 General procedure for LA polymerization .............................................. 66
  2.6.8 General procedures for kinetics studies of rac-LA polymerization ....... 66
  2.6.9 General procedure for the synthesis of salen ligands and catalysts ....... 67
  2.6.10 Crystallographic Studies ......................................................................... 74

Chapter 3 Interesting Molecular Structure and Bonding in a Bismuth-Lithium Bond in the Ion Pairs: LiBiL₂, Where L = a Porphyrin or a Salen Ligand ...................... 76
  3.1 Introduction .................................................................................................. 76
3.2 Synthesis........................................................................................................... 77

3.3 Results and discussion...................................................................................... 78

3.3.1 Solid state structure of LiBi(TPP)₂................................................................ 78

3.3.2 Computational studies and nature of Bi-Li bond in I .............................. 82

3.3.3 NMR studies of LiBi(TPP)_2........................................................................ 83

3.3.4 MALDI studies ............................................................................................ 88

3.3.5 UV-Vis studies ............................................................................................. 89

3.3.6 Solid-state and molecular structures of IIIA, IIIB and IV .................... 91

3.3.7 Mass spectrometry of compounds II-IV.................................................. 96

3.3.8 NMR spectrometry III and IV ................................................................. 96

3.3.9 ⁷Li NMR spectra ....................................................................................... 98

3.4 Concluding remarks ....................................................................................... 102

3.5 Experimental section...................................................................................... 104

3.5.1 General considerations .............................................................................. 104

3.5.2 Measurements ........................................................................................... 105

3.5.3 Crystallographic information .................................................................. 105

3.5.4 Electronic structure calculations ............................................................... 107

3.5.5 Synthesis .................................................................................................. 107

xi
Chapter 4  Stereochemical Lactide Polymerization and the Coupling of Propylene Oxide and Lactide at a Porphyrin Chromium (III) Center

4.1 Introduction ........................................................................................................................................ 112

4.2 Results and discussions ...................................................................................................................... 114

4.3 Proposed mechanistic investigations of polymerizations ................................................................. 131

4.4 Conclusion ......................................................................................................................................... 142

4.5 Experimental section ......................................................................................................................... 143

4.5.1 General considerations .................................................................................................................. 143

4.5.2 Polymerization of LA by TPPCrCl/PPN+Cl− catalyst .................................................................. 144

4.5.3 General procedure for the kinetics studies of LA catalyzed by TPPCrCl/PPN+Cl− ......................... 144

4.5.4 Synthesis of 3,6-dimethyl-1,4-dioxan-2-one from PO and LA catalyzed by TPPCrCl/PPN+Cl− ........................................... 145

4.5.5 Synthesis of 3,6-dimethyl-1,4-dioxan-2-one ............................................................................. 146

Chapter 5  Ring Opening Polymerization of Lactide, ε-Caprolactone and Propyleneoxide by Modified β-Dikitiminate Magnesium Catalysts

5.1 Introduction ......................................................................................................................................... 147

5.2 Synthesis ........................................................................................................................................... 151

5.3 Results and discussions .................................................................................................................... 154
5.3.1 Solid state studies ................................................................. 154

5.4 Ring opening polymerization of LA and CL .................................. 165

5.5 Solvent effect in the ROP rac-LA by BDIMg\textsuperscript{\textit{n}}Bu(THF) and BDI*\textsuperscript{\textit{n}}Mg\textsuperscript{\textit{n}}Bu(THF) 177

5.6 ROP of PO by \textit{β}-dikitiminate magnesium catalysts .......................... 182

5.7 Variable temperature studies ....................................................... 186

5.8 Conclusions ............................................................................ 192

5.9 Experimental and general considerations ...................................... 193

5.9.1 Measurements ...................................................................... 193

5.9.2 Synthesis ............................................................................. 194

5.9.3 General procedure for the kinetics of LA ROP ............................... 198

5.9.4 Single crystal X-ray crystallography .......................................... 198

References ..................................................................................... 200
List of Abbreviations

LA Lactide
PLA Polylactide
ε-CL ε-Caprolactone
PCL Polycaprolactone
PO Propylene oxide
PPO Polypropylene oxide
PC Propylene carbonate
PPC Polypropylene carbonate
ROP Ring opening polymerization
BSS Bismuth subsalicylate
TPP Tetraphenyl porphyrin
OEP Octaethyl porphyrin
DMAP Dimethylamino pyridine
PPN⁺Cl⁻ Bis(triphenyl phosphine)iminium chloride
MALDI TOF Matrix assisted laser desorption/ionization
ESI Electrospray ionisation
PET Polyethylene terephthalate
$M_n$ Number average molecular weight
$M_w$ Weight average molecular weight
PDI Polydispersity index
HH Head-head junction
HT Head-tail junction
TT Tail-tail junction
List of Tables

Table 1: The activity and selectivity of selected BDI type magnesium catalysts .......... 17
Table 2: Summary of Bismuth initiators investigated for the LA polymerization in the literature ........................................................................................................................................... 19
Table 3: Physical and mechanical properties of different tactility containing polymers.. 25
Table 4: Summary of initial screenings for the melt ROP of L-LA at 130 °C for 65h ..... 41
Table 5: Comparative ROP data for LA employing Pepto-Bismol®, PB (Kroger) and Sn(Oct)₂........................................................................................................................................................................... 42
Table 6: ROP data for PLA formation employing bismuth subsalicylate (BSS) ......... 46
Table 7: Selected crystallographic information for en-salenBiCl(1), [cy-salenBiCl]₂(2), cy-salenBiOC₆H₃-2,6-Bu' (3), and salenBiOCMe₂CO₂Et (4).................................................................................................................. 54
Table 8: Selected bond distances (Å) and bond angles (deg.) for cy-salenBiCl.......... 55
Table 9: Selected bond distances (Å) and bond angles (deg.) for cy-salenBiOC₆H₃-2,6-Bu'₂................................................................. 57
Table 10: Copolymerization of epoxides and CO₂ by TPPBiI .................................. 61
Table 11: Crystallographic data for compound I ..................................................... 81
Table 12: Data Collection Parameters for IIIA, IIIB, and IV ................................ 95
Table 13: The percentage of 3,6-dimethyl-1,4-dioxan-2-one isomers obtained with different combinations of LA and PO ............................................................................... 122
Table 14: Ring opening polymerization data for PLA obtained rac-LA/L-LA catalyzed by TPPCrCl/PPN+Cl− in rac-PO at 0 ºC. ................................................................. 129

Table 15: Summary of catalysts employed in this work for the ROP ......................... 154

Table 16: Selected bond distances and angles of BDI*Mg°Bu, BDI*Mg°Bu(PO) and BDI*Mg°Bu(THF). ........................................................................................................ 156

Table 17: Crystallographic Data Collection Parameters for BDI*Mg°Bu and BDI*Mg°Bu(PO). ........................................................................................................ 158

Table 18: Selected bond distances and angles of [BDI(Ph)MgO°Bu]2 and of [BDIMgO°Bu]2. ........................................................................................................ 160

Table 19: The crystallographic data for the BDI(Ph)MgO°Bu and BDI(CH2Ph)Mg°Bu(THF)........................................................................................................ 162

Table 20: Selected bond distances and bond angle of BDIMg°Bu, BDIMg°Bu(THF) and BDI(CH2Ph)Mg°Bu(THF). ........................................................................ 163

Table 21: Selected bond distances and angles of BDI*Mg°Bu(THF) and BDI(CF3)Mg°Bu(THF). ........................................................................................................ 165

Table 22: k_{app} values for the 7 BDI catalysts for the ROP of rac-LA in DCM at room temperature ................................................................................................. 167

Table 23: Summary of kp values for the rac-LA and ε-CL polymerization by selected β-diketiminate catalysts. ................................................................................. 177

Table 24: Molecular weight and PDI values of polymers obtained from BDI*Mg°Bu(THF) in THF, DCM and rac-PO. ................................................................. 180
Table 25: The $M_w$ and PDI values for the polyethers obtained from the $\beta$-diketiminate catalysts are summarized .......................................................... 184

Table 26: $T_c$ for the apparent aryl group rotation for the BDIMg complexes with the addition of THF ........................................................................................................ 186
List of Diagrams

Diagram 1: Sketch of the locations and influence of the stereochemically active lone-pairs in [cy-salenBiCl]₂................................................................. 53

Diagram 2: β-Hyogens distances form the Mg for BDI*Mg⁷Bu, BDI*Mg⁷Bu(PO) and BDI*Mg⁷Bu(THF).................................................................. 159
List of Schemes

Scheme 1. Life cycle of PLA ................................................................. 3
Scheme 2: Synthesis of PLA by (I) poly condensation of lactic acid and (II) ring opening polymerization of LA ........................................................................... 3
Scheme 3: Synthesis of $\varepsilon$-CL from (I) petroleum resources and (II) biomass ............. 5
Scheme 4: Industrial synthesis of BPA-polycarbonate .................................................. 6
Scheme 5: Synthesis of PCs and cyclic carbonates from epoxides and carbon dioxide ...... 7
Scheme 6: Copolymerization of epoxide with dihydrocoumarin by salenCrCl/PPN$^+$Cl$^-$ system ....................................................................................... 8
Scheme 7: Synthesis of copolymer of CO$_2$ and $\varepsilon$-CL in neat PO ............................... 8
Scheme 8: Industrial production of Tin(II) octanoate .................................................... 12
Scheme 9: Schlenk type equilibrium BDI catalysts .......................................................... 14
Scheme 10: Mechanistic pathway for the formation of PC, PPC and polyethers .......... 23
Scheme 11: Chain transfer of PLA (I) between two growing chain and (II), external addition of alcohol where L = ligands, M,M' = metal centers, P, P’- growing polymer chain, and ROH is alcohol ................................................................. 30
Scheme 12: Possible regio-attacks by the initiating group on methine and methylene region ........................................................................................................ 30
Scheme 13: Mechanism for the ROP of LA by Sn(Oct)$_2$ [P = polymer chain] ............ 37
Scheme 14: Reaction scheme for the general synthesis of salenBiOR.......................... 49

Scheme 15: Mechanisms of olefin polymerization, ring opening polymerization of lactide and copolymerization of propylene oxide with CO$_2$ at a single site metal center. ........ 113

Scheme 16: Possible mechanistic pathway for the formation of small molecules A and B. ......................................................................................................................................................... 120

Scheme 17: Synthetic scheme for the synthesis of 3,6-dimethyl-1,4-dioxan-2-one from ethyl-$L$-lactate and allyl bromide. ............................................................................................................................................ 120

Scheme 18: Possible mechanism for the racemization at the chiral center of the lactide unit in the polymer chain .................................................................................................................................................. 123

Scheme 19: Proposed mechanism for the formation of PLA and 3,6-dimethyl-1,4-dioxan-2-one by the single site catalyst. .................................................................................................................................................. 141

Scheme 20: Reaction scheme for the synthesis of BDIH and BDI(CF$_3$)H ligands by direct condensation method. .................................................................................................................................................. 151

Scheme 21: Reaction scheme for the synthesis of BDI(Ph)H and BDI*H. ................. 152

Scheme 22: Synthesis of BDI(CH$_2$Ph)H from BDIH .................................................. 152

Scheme 23: General scheme for the synthesis of $\beta$-dikimate Mg catalysts .......... 153

Scheme 24: Synthesis of BDI*Mg$^\eta$Bu(PO) ............................................................ 154

Scheme 25: Possible initiation steps of PO by magnesium catalyst. ....................... 183

Scheme 26: The possible products of the reaction of BDI*Mg$^\eta$Bu: PO = 1:1 in toluene $d_8$ after 6h in the J-Young tube experiment .............................................................................................................................................. 183

xxi
List of Figures

Figure 1: Simple pictorial representation of a single-site molecular catalyst .................. 10

Figure 2: Single site catalysts of TPB(I) and BDI(II) based single site magnesium catalysts ........................................................................................................................................................................ 15

Figure 3: Selected BDI based catalysts for the ROP of LA ........................................ 16

Figure 4: Possible chiral backbone containing BDI ligands ......................................... 17

Figure 5: The structures of porphyrin/salen based catalysts and co-catalyst ................. 21

Figure 6: Coordination insertion mechanism of LA by metal alkoxide catalyst .......... 22

Figure 7: Isomers of LA .......................................................................................................................... 24

Figure 8: Tacticites of PLA obtained from L-, D-, rac- or meso- LA ....................... 25

Figure 9: Powder X-ray pattern of stereocomplex PLA ......................................................... 26

Figure 10: Chemical shifts values (ppm) for the PLA tetrads (a) homo decoupled $^1$HMR of PLA obtained from rac-LA (b) $^{13}$C NMR of PLA obtained from the PLA obtained from rac-LA (c) homodecoupled $^1$H-NMR of PLA obtained from meso-LA and (d) $^{13}$C-NMR of PLA obtained from meso-LA. 73 ................................................................. 27

Figure 11: Selected aluminum catalyst for ROP of LA ..................................................... 28

Figure 12: Inter-chain and intra-chain trans-esterification of PLA .............................. 29

Figure 13: Regioregular and regioirregular polypropylene oxide sequence .......................... 31

Figure 14: Tacticites of polypropylene oxide ........................................................................ 31
Figure 15: $^{13}$C NMR of PPO synthesized by TPPCrCl/PPN$^+$Cl$^-$ from $R$-PO and rac-PO.

Figure 16: Microstructure of polypropylene carbonate.

Figure 17: $^{13}$C NMR spectra of carbonyl region of PPC obtained from PO with CO$_2$.

Figure 18: Possible diads of PPC of different regio sequence.

Figure 19: Conversion of LA as a function of time for the polymerization of L-LA initiated by (a) Sn(Oct)$_2$ and (b) Pepto-Bismol®. The comparative reaction was carried out for the ratio L-LA: Catalyst=100:1 at 110 °C.

Figure 20: Linear plots of ln{$[\text{LA}]_0/[\text{LA}]_t$} versus time (min) for the melt polymerization of L-LA initiated by (a) Sn(Oct)$_2$ and (b) Pepto-Bismol®. The comparative reaction was carried out for the ratio L-LA: Catalyst=100:1 at 110 °C.

Figure 21: $^1$H NMR spectra (CDCl$_3$, 400 MHz) of the homodecoupled CH resonance of poly(rac-lactide) processed in CH$_2$Cl$_2$ using (a)Sn(Oct)$_2$, (b) Pepto-Bismol(Kroger), (c) BSS, and (d) Pepto-Bismol® as initiators.

Figure 22: $^{13}$C NMR (75 MHz) spectra of commercial BSS recorded at 25 °C.

Figure 23: $^1$H NMR spectra (CDCl$_3$, 400 MHz) of the homo polymers of poly-rac-lactide, poly-$\varepsilon$-caprolactone, and the copolymer of rac-LA with CL prepared with Pepto-Bismol® in the methane and methylene proton regions.

Figure 24: Free salen ligands with different backbones employed in this work.

Figure 25: The central core of the tetranuclear en-salenBiCl molecule (left) and its central [BiCl]$_4$ core (right).
Figure 26: ORTEP representations of [cy-salenBiCl]$_2$ (Orange = Bismuth, Green = Chlorine, Scarlet = Oxygen, Blue = Nitrogen, Gray = Carbon) drawn at 50% probability. Hydrogen atoms, solvent molecules and tert-butyl groups are excluded for clarity. 

Figure 27: (Left) ORTEP representation of cy-salenBiOC$_6$H$_3$-2,6-i-Bu (Orange = Bismuth, Scarlet = Oxygen, Blue = Nitrogen, Gray = Carbon) drawn at 50% probability. Hydrogen atoms excluded for clarity. (Right) ORTEP representation of cy-salenBiOC$_6$H$_3$-2,6-Bu$'$ (with tert-butyl groups removed for clarity) and emphasizing the nature of the BiO$_3$N$_2$ core. 

Figure 28: Minimization of lone pair –lone pair interactions. 

Figure 29: (Left) ORTEP representation of cy-salenBiOCMe$_2$CO$_2$Et (Orange = Bismuth, Scarlet = Oxygen, Blue = Nitrogen, Gray = Carbon) drawn at 50% probability. Hydrogen atoms excluded for clarity. (Right) ORTEP representation of cy-salenBiOCMe$_2$CO$_2$Et (with tert-butyl groups removed for clarity) and emphasizing the nature of the BiO$_4$N$_2$ core. 

Figure 30: $^1$H NMR spectra (CDCl$_3$, 400 MHz) of the homodecoupled CH resonance of poly(rac-lactide) obtained by cy-salenBiOBu$'$ as initiator. For details of assignments see reference. 

Figure 31: Linear plots of ln{[LA]$_0$/[LA]$_i$} versus time (min) for the polymerization of rac-LA initiated by cy-salenBiOC$_6$H$_3$-2,6-Bu$'_2$ in CH$_2$Cl$_2$ at room temperature. 

Figure 32: Plot of $-\ln(k_{app})$ versus $-\ln[Cat]$ for the rac-LA initiated by cy-salenBiOC$_6$H$_3$-2,6-Bu$'_2$ in CH$_2$Cl$_2$ at room temperature.
Figure 33: ORTEP representation of I viewed parallel (a) and perpendicular (b) to the Li-Bi bond. Figures drawn at 50% probability. (Gray = Carbon, Dark Blue = Nitrogen, Light Blue = Lithium, Orange = Bismuth) Phenyl groups, hydrogens and solvent excluded for clarity. .......................................................................................................................... 78

Figure 34: Bond distances in Å surrounding the Bi-Li core.................................................................................. 80

Figure 35: Packing diagram of I shown along the a-axis (left) and c-axis (right) of the unit cell............................................................................................................................................. 80

Figure 36: The filled frontier orbital HOMO-7 of model compound I from a side-on (left) and top-down (right) view. ............................................................................................................................................. 82

Figure 37: Variable temperature $^1$H NMR (500 MHz) of I in CDCl$_3$ ......................................................... 84

Figure 38: Variable temperature $^1$H-NMR (500 MHz) spectra of LiBi(TPP)$_2$ in THF-$d_8$. ..................................................................................................................................................... 85

Figure 39: DOSY profile of LiBi(TPP)$_2$ in CDCl$_3$ ......................................................................................... 86

Figure 40: $^7$Li-NMR profile of LiBi(TPP)$_2$, LiN(SiMe$_3$)$_2$ and LiCl.............................................................. 87

Figure 41: 2D-NMR: COSY spectra of LiBi(TPP)$_2$ in CDCl$_3$ at -50 °C ................................................... 88

Figure 42: UV-Visible spectra of TPPH$_2$ and BiLi(TPP)$_2$ at room temperature in CH$_2$Cl$_2$ ............................................................................................................................................. 89

Figure 43: UV-Visible spectra of BiLi(TPP)$_2$ in various solvents normalized to the ring-to-ring charge transfer ............................................................................................................................................. 90

Figure 44: UV-Visible spectra of BiLi(TPP)$_2$ diluted to multiple concentrations in CH$_2$Cl$_2$ ............................................................................................................................................. 91
Figure 45: Two ORTEP representations of IIIB drawn at 50% probability, A) parallel and B) perpendicular to the Li – Bi bond. Disorder, solvent, hydrogens and tBu groups removed for clarity. Dark Blue = Nitrogen, Light Blue = Lithium, Orange = Bismuth, Scarlet = Oxygen, Gray = Carbon. ................................................................. 92

Figure 46: Two ORTEP representations of IIIA drawn at 50% probability, A) parallel and B) perpendicular to the Li – Bi axis. Solvent, hydrogens and tBu groups removed for clarity. Dark Blue = Nitrogen, Light Blue = Lithium, Orange = Bismuth, Scarlet = Oxygen, Gray = Carbon. ................................................................. 93

Figure 47: Packing of IIIA illustrating the Ph – Li interactions in the unit cell. Solvent, hydrogen and tBu groups removed for clarity. ................................................................. 93

Figure 48: ORTEP representations of IV drawn at 50% probability. Solvent, hydrogens and tBu groups removed for clarity. Dark Blue = Nitrogen, Light Blue = Lithium, Scarlet = Oxygen, Gray = Carbon. ................................................................. 94

Figure 49: 1H NMR(CD2Cl2; 500MHz) Spectrum of LiBi(phsalen)2. ................................................................. 97

Figure 50: Variable temperature 7Li-NMR of [phsalen]2BiLi.THF (IIIB) in toluene d8. 98

Figure 51: Variable temperature 7Li-NMR of [phsalen]2BiLi (IIIA) in toluene d8. 100

Figure 52: 7Li-NMR of compound IIIA, IIIA+THF and IIIB. ................................................................. 101

Figure 53: 7Li-NMR of ph-salenLi2 in toluene d8 at different temperatures. ................................. 102

Figure 54: (a) Homodecoupled 1H-NMR and (b) 13C-NMR CH resonance of polylactide obtained from the reaction of rac-LA catalyzed by TPPCrCl/PPN+Cl in rac-PO at room temperature. ................................................................. 115
Figure 55: MALDI spectrum of polylactide obtained from the reaction of rac-LA catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\) in rac-PO at room temperature........................................... 116

Figure 56: \(^1\)H NMR spectrum (500 MHz, CDCl\(_3\)) of the crude product rac-PO and rac-LA catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\).[A1 and A2: 3,6-dimethyl-1,4-dioxan-2-one, P: Oligomers of H(\(1/2\)LA)\(_n\)(PO)\(_m\)Cl]............................................................................................................. 117

Figure 57: ESI spectrum of hexane insoluble component from the reaction of rac-LA, rac-PO (rac-LA:rac-PO:TPPCrCl/PPN\(^+\)Cl\(^-\)=100:200:1) catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\) at 60 °C.................................................................................................................................................... 118

Figure 58: GC/MS trace of the products from the hexane soluble component obtained from reaction of PO and LA catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\)......................................................... 119

Figure 59: \(^1\)H NMR (500 MHz, CDCl\(_3\)) spectrum of 3,6-dimethyl-1,4-dioxan-2-one obtained from the reaction of rac-PO and rac-LA (rac-LA:rac-PO:TPPCrCl/PPN\(^+\)Cl\(^-\)=100:200:1) catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\) at 60 °C................................................................. 121

Figure 60: \(^1\)H NMR spectrum (400 MHz, CDCl\(_3\)) of the hexane soluble product obtained from the reaction of A: rac-PO and rac-LA at 60 °C, B: R(+)PO and L-LA at 0 °C and C: S-PO and L-LA at 0 °C catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\). ................................................................................... 123

Figure 61: The isomers of 3,6-dimethyl-1,4-dioxan-2-one ................................................................. 124

Figure 62: COSY NMR (400 MHz, CDCl\(_3\)) spectrum of 3,6-dimethyl-1,4-dioxan-2-one obtained from the reaction of L-LA and R(+)PO (L-LA:R(+)PO:TPPCrCl/PPN\(^+\)Cl\(^-\)=100:200:1) catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\) at 0 °C................................................................. 125

Figure 63: MALDI spectrum of polylactide obtained from the reaction of rac-LA catalyzed by TPPCrCl/PPN\(^+\)Cl\(^-\) in rac-PO at 0 °C................................................................. 126
Figure 64: Homodecoupled $^1$H-NMR (left) and the $^{13}$C-NMR (right) $CH$ resonance of the PLA obtained from the reaction of $rac$-LA in $rac$-PO by TPPCrCl/PPN$^+$Cl at 0 °C. ...

Figure 65: Powder XRD pattern of polylactide obtained from the reaction of $rac$-LA catalyzed by TPPCrCl/PPN$^+$Cl$^-$ in $rac$-PO at 0 °C. ................................................................. 127

Figure 66: Linear plots of $\ln\{[LA]_0/[LA]_t]\}$ versus time (min) for the polymerization of $rac$-LA ($[rac$-LA$]=0.5$ M) initiated by TPPCrCl/PPN$^+$Cl$^-$ in $rac$-PO at 0 °C. ................................................................. 130

Figure 67: Plot of $-\ln(k_{app})$ versus $-\ln\{Cat\}$ for the $rac$-LA initiated by TPPCrCl/PPN$^+$Cl$^-$ in $rac$-PO at 0 °C. ............................................................................................................. 130

Figure 68: The alkoxide resulted by the initiation step of PO by methine [TPPAI(OCH$_a$H$_b$CH$_c$Me$'$Cl)] and methylene [TPPAI(OCH$_c$MeCH$_a$H$_b$Cl)] attack by the Cl$^-$ ........................................................................................................................................... 131

Figure 69: The MALDI spectra of PPO obtained from the reaction of PO and TPPAlCl at room temperature.[$H(PO)_nCl.Na^+]$ ............................................................................................................ 132

Figure 70: MALDI spectrum of the PLA obtained by TPPAlO$^{i}$Pr /PPN$^+$Cl$^-$/PO/LA system in 20 minutes. [$^{i}$PrO(PO)(1/2LA)$_n$H$]$.............................................................. 134

Figure 71: MALDI spectrum of the PLA obtained by TPPAlCl/PPN$^+$Cl$^-$/PO/LA system in 10 minutes. [$H(PO)(LA)_nCl.Na^+]$ ............................................................................................................ 135

Figure 72: MALDI spectrum of the PLA obtained by TPPAlCl/PPN$^+$Cl$^-$/PO/LA system in 20 minutes. [$H(PO)(LA)_nCl.Na^+]$ ............................................................................................................ 136

Figure 73: MALDI spectrum of the PLA obtained by TPPAlCl/PPN$^+$Cl$^-$/PO/LA system in 75 min. [$H(PO)(LA)_nCl.Na^+$, $H(PO)(LA)_nOH.Na^+$, (PO)$_2$(LA)$_nNa^+$, (PO)$_1$(LA)$_nNa^+$] ................................................................................................................................. 137
Figure 74: Possible mechanistic pathway for the formation of (PO)_{2(1/2LA)}_n........... 138
Figure 75: Possible differences in the basicity of alkoxides in the polymer chain........ 138
Figure 76: The MALDI spectra obtained from the reaction of LA, PO and TPPAlOEt at room temperature................................................................. 139
Figure 77: The MALDI spectra obtained for the copolymer of PPO-PLA by the reaction of LA, PO and TPPAlOEt and the later addition of PPN^+Cl^- at room temperature. ...... 140
Figure 78: Schlenk equilibrium ........................................................................... 147
Figure 79: One-step concerted alkyl transfer and β-hydrogen transfer transitions states of Grignard reagent in their reaction with ketone. ....................................................... 148
Figure 80: General schematic diagram of β-dikitimino ligand.............................. 148
Figure 81: Possible equilibrium products of β-dikimate Mg complexes............. 149
Figure 82: Schematic representation for the influence of the EWG and EDG in the M-X bond ........................................................................................................ 149
Figure 83: ORTEP drawing of the Tp^{*}BuCa(O-2,6-iPr_2C_6H_3).PO molecule with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity. ..... 150
Figure 84: BDI ligand systems investigated in this study for the ROP ................. 151
Figure 85: General structure of the BDI catalysts investigated in this study.......... 153
Figure 86: Molecular Structure of BDI*Mg^''Bu drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity. ................................................................. 155
Figure 87: Model of BDI*Mg^''Bu(THF). Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens, and disorder omitted for clarity. ......................... 156
Figure 88: ORTEP drawing of the BDI*Mg^Bu(PO) molecule with thermal ellipsoids drawn at 50% probability level, where Green = Magnesium, Blue = Nitrogen, Oxygen = Red, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity. .......................... 157

Figure 89: Molecular Structure of [BDI(Ph)MgO^Bu]_2 drawn at 50% probability, where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.................................................. 160

Figure 90: Molecular Structure of BDI(CH_2Ph)Mg^Bu(THF) drawn at 50% probability. Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.......................................................... 161

Figure 91: Best superposition of the molecular structures of BDI*Mg^Bu(THF) in green and BDI(CH_2Ph)Mg^Bu(THF) in red showing the relative disposition of the aryl ligands and both contain similar steric pressure on the pocket of the n-butyl group ............... 163

Figure 92: Molecular Structure of BDI(CF_3)Mg^Bu(THF) drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity. .................................................. 164

Figure 93: Linear plots of ln{[LA]_0/[LA]_t} versus time (sec.) for the polymerization of rac-LA initiated by BDI catalysts in CH_2Cl_2 at room temperature. ......................... 166

Figure 94: Linear plots of ln{[LA]_0/[LA]_t} versus time (sec.) for the polymerization of rac-LA initiated by BDI(Ph)Mg^Bu(THF) in CH_2Cl_2 at room temperature. ............... 169

Figure 95: Plot of –ln(k_{app}) versus -ln[Cat] for the rac-LA initiated by BDI(Ph)Mg^Bu(THF) in CH_2Cl_2 at room temperature. ........................................... 169

xxx
Figure 96: Linear plots of \(\ln\left[\frac{[LA]_0}{[LA]_t}\right]\) versus time (sec.) for the polymerization of \(L\)-LA \((L\text{-LA} : \text{Catalyst} = 100:1)\), \(rac\text{-LA} \((rac\text{-LA} : \text{Catalyst} = 100:1)\) and \(rac\text{-LA}\) with \(CL\text{(rac-LA} : \text{CL} : \text{Catalyst} = 100:100:1)\) initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.

Figure 97: Linear plots of \(\ln\left[\frac{[LA]_0}{[LA]_t}\right]\) versus time (sec.) for the polymerization of \(rac\text{-LA}\) initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in THF at room temperature.

Figure 98: Plot of \(-\ln(k_{app})\) versus \(-\ln[Cat]\) for the \(rac\text{-LA}\) initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in THF at room temperature.

Figure 99: Linear plots of \(\ln\left[\frac{[\varepsilon\text{-CL}]_0}{[\varepsilon\text{-CL}]_t}\right]\) versus time (sec.) for the polymerization of \(\varepsilon\text{-CL}\) initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.

Figure 100: Plot of \(-\ln(k_{app})\) versus \(-\ln[Cat]\) for the \(\varepsilon\text{-CL}\) initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.

Figure 101: Linear plots of \(\ln\left[\frac{[LA]_0}{[LA]_t}\right]\) versus time (sec.) for the polymerization of \(rac\text{-LA}\) initiated by BDI(CH\(_2\)Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.

Figure 102: Plot of \(-\ln(k_{app})\) versus \(-\ln[Cat]\) for the \(rac\text{-LA}\) initiated by BDI(CH\(_2\)Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.

Figure 103: Linear plots of \(\ln\left[\frac{[LA]_0}{[LA]_t}\right]\) versus time (sec.) for the polymerization of \(rac\text{-LA}\) initiated by BDI(CH\(_2\)Ph)Mg\(^{\alpha}\)Bu(THF) in THF at room temperature.

Figure 104: Plot of \(-\ln(k_{app})\) versus \(-\ln[Cat]\) for the \(rac\text{-LA}\) initiated by BDI(CH\(_2\)Ph)Mg\(^{\alpha}\)Bu(THF) in THF at room temperature.
Figure 105: Homodecoupled $^1$H NMR (500 MHz, CDCl$_3$) spectrum of the methine proton of polylactide obtained from the reaction of rac-LA catalyzed by BDIMg$^n$Bu(THF) in rac-PO solvent at room temperature in 15 min ($P_r = 0.83$) ........................................ 178

Figure 106: Homodecoupled $^1$H NMR (400 MHz, CDCl$_3$) [left] and $^{13}$C NMR (100 MHz, CDCl$_3$) [right] spectra of the methine proton of polylactide obtained from the reaction of rac-LA catalyzed by BDI*Mg$^n$Bu(THF) in rac-PO solvent at room temperature in 10 min ($P_r = 0.89$). ........................................................................................................ 179

Figure 107: $^1$H NMR spectra (CDCl$_3$, 500 MHz) of the homodecoupled CH resonance of poly(rac-lactide) obtained by BDI*Mg$^n$Bu(THF) in (a) rac-PO ($P_r = 0.89$), (b) DCM ($P_r = 0.56$) and (c) THF ($P_r = 0.65$). ........................................................................................................ 180

Figure 108: MALDI spectrum of the of the PLA obtained from the reaction of BDI(CF$_3$)Mg$^n$Bu(THF) and rac-LA. ........................................................................................................ 181

Figure 109: $^1$H NMR (500 MHz, CDCl$_3$) spectra of BDI*Mg$^n$Bu: $R(+)$-PO = 1: 2 after 12h........................................................................................................ 184

Figure 110: MALDI spectrum of polyether obtained from the reaction of rac-PO catalyzed by BDIMg$^n$Bu(THF) at room temperature. ................................................. 185

Figure 111: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(CF$_3$)Mg$^n$Bu(THF) in toluene d$_8$. The isopropyl methine is shown with a star, *... 187

Figure 112: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(Ph)Mg$^n$Bu(THF) in toluene d$_8$......................................................................................... 188

Figure 113: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(CF$_3$)Mg$^n$Bu(THF) in toluene d$_8$ and 1.5 equiv. THF............................................... 189
Figure 114: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(CF$_3$)Mg$^n$Bu(THF) in THF d$_8$................................................................. 190

Figure 115: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(Ph)Mg$^n$Bu(THF) in toluene d$_8$ +4 equiv. THF................................................................. 191
Chapter 1   Introduction

1.1 Introduction

Polymers play a major role in daily life. Living organisms in the nature are composed of natural polymers; animal kingdom is composed of several polymers such as proteins, enzymes, etc., and plants are mainly made of polymers such as cellulose, polysaccharides and lignin. These polymers are classified as natural polymers where as many of the currently used plastics, rubbers, fibers, etc. are classified into synthetic polymers which are mainly derived from the petroleum resources. However, the production of petroleum resources is predicted to be diminishing in the near future. Furthermore, the increasing amount of carbon dioxide concentration and the improper disposal of petrochemical based polymers are major environmental threats. At the same time, many people have been skeptical and concerned with the health issues associated with these synthetic polymers. These are the major concerns about the sustainable materials. The development of sustainable materials is expected to be one of the most important objectives in terms of both future environmental safety and health concern. In this respect, biodegradable polymers are the suitable replacement of currently available synthetic polymers.
1.2 Biodegradable polymers

Synthetic polymers are found in several applications in agricultural, food, packaging, automobile, pharmaceutical, and medical sectors. These polymers are non-renewable and non-degradable, or taking long time for degradation and resulting accumulation in the landfills, which is a major environmental threat. Biodegradable polymers are degraded mainly by nature and end up as harmless material to the environment. These harmless materials are also renewable and helpful to maintain the ecological balance. Biomass, mainly carbohydrates/cellulose which is obtained from plants, appears to hold the key for supplying renewable materials without affecting the ecological balance. Converting biomass into useful material through the application of chemical catalysts is one of the key approaches which can produce cheap, clean and sustainable materials for the future needs. In this respect, there are several biomass derived polymers such as polyesters, polycarbonates and polyethers which are abundantly needed both in industries and academia. Thus, in this study polylactide, polycaprolactone, polyethers and their copolymers with carbon dioxide will be focused.

1.2.1 Polylactide

Polylactide (PLA), a biodegradable, biocompatible and renewable polyester, can be synthesized by the ring opening polymerization (ROP) of lactide (LA) (Scheme 1) and widely used in several applications.

PLA is the second largest consumed bioplastic in the world. LA is a 6 memberd cyclic diester which is primarily obtained from the plant resources such as corn, beets,
etc.\textsuperscript{4} PLA might have been known from 1680s and the latter part of 17\textsuperscript{th} century the isolation of lactic acid from milk and its self-esterification process were reported.\textsuperscript{5}

Scheme 1: Life cycle of PLA

Currently lactic acid is mainly synthesized by the fermentation process for the industrial production of PLA. Recently, there are several ongoing studies are focused on the synthesis of lactic acid from carbohydrates/biomass by chemical route.

\[ n \text{HO-}\text{O} + n\text{H}_2\text{O} \rightarrow \text{Polylactide} \]  
\[ n \text{O} + 2n\text{H}_2\text{O} \rightarrow \text{Polylactide} \]

Scheme 2: Synthesis of PLA by (I) poly condensation of lactic acid and (II) ring opening polymerization of LA
There are two methods available for the production of PLA: (I) the condensation of LA acid and (II) the ROP of LA as shown in the Scheme 2. The condensation process requires higher energy to favor the forward equilibrium to form PLA by removing the water molecules. The ROP is an alternative route for the production of polycarbonates, polyesters, and polyethers which overcome the drawbacks of traditional polycondensation process including long reaction time, amount/number of side products and high reaction temperature. Furthermore, ROP provides narrow PDIs and well-defined molecular weight ($M_n$). The first ROP of LA was reported in 1932 and the major advancements have been made in the recent decades.

1.2.2 Polycaprolactone

Polycaprolactone (PCL) is one of the other biodegradable aliphatic polyester and has the melting point $\sim 60^\circ$C with the glass transition temperature of $-60^\circ$C. PCL is FDA approved material and found in several applications including drug delivery, tissue engineering, etc. The PCL can degrade by hydrolysis at physiological conditions makes it as a useful biomaterial for the medical implantation. The amphiphilic block copolymers of PCL are used in the form of vesicle membrane of polymersomes. Industrial production of PCL leaving minor impurities of toluene from the raw material and tin from the catalyst residue could be concerns for the medical applications. The monomer, $\varepsilon$-caprolactone ($\varepsilon$-CL), for the industrial production, is mainly obtained from the petroleum resources by the hydrogenation and followed by oxidation reactions of benzene as shown
in Scheme 3(I). In the recent years, there are several studies focused on the process of synthesis of ε-CL from biomass as shown in Scheme 3(II)\(^9\):

![Scheme 3: Synthesis of ε-CL from (I) petroleum resources and (II) biomass](image)

Making PCL and their copolymers from biomass derived ε-CL monomers with biocompatible metal containing catalyst would be the suitable solutions to current CL production for the medical applications as well as towards the sustainable environment.

### 1.2.3 Polyether and polycarbonates

Polyethers are mainly used in coatings and adhesives. The major aliphatic polyethers are found in different brand names by the different producers; polyoxymethylene (Delrin-Dupont), polyethyleneoxide (Carbowax-Dow), polypropyleneoxide and polytetrahydrofuran (Terathane-BASF/Invista). The aromatic polyethers polyphenylether and poly(p-phenyleneoxide) are used in optical devices and aerospace applications.

Polycarbonates, PCs, are another class of biodegradable polymer which can be produced from the copolymerization of epoxides with carbon dioxide. Industries are interested in making polymers from biomass derived epoxides and the copolymers of
epoxides with the C\textsubscript{1} feedstock of CO\textsubscript{2}. The depletion of petrochemical based currently available epoxide raw materials for the production of polyethers and PCs is one of the factors, which made us focus on biomass derived epoxides. Additionally, CO\textsubscript{2} is nontoxic and most abundant material, the utilization of greenhouse gas CO\textsubscript{2} would help to reduce the global warming.

Bisphenol-A polycarbonate (BPA-PC) is one of the major commodity polymers in the current market and is mainly synthesized from bisphenol-A and phosgene or diphenylcarbonate as shown in Scheme 4. Bisphenol-A, phosgene and phenol from the BPA-PC production are certainly considered to be hazardous for both environment and health. There are several in vitro and in vivo studies indicating that BPA shows endocrinic, mutagenic and carcinogenic effects, and also some risk of obesity, diabetes and heart disease.\textsuperscript{10}

Scheme 4: Industrial synthesis of BPA-polycarbonate

Nowadays, most of the leading industries are focusing the phosgene free biodegradable PC synthesis by the copolymerization of epoxides with carbon dioxide\textsuperscript{11}(Scheme 5).
Furthermore, the recent interest is focused on the synthesis of polyethers/PCs from biomass derived monomers or incorporating biomass derived monomers (cyclic esters, ethers, anhydrides, etc.) with epoxides by copolymerization. There are few studies have been found on the utilization of natural product with CO$_2$ for the production of PCs. Coates and co-workers reported the synthesis of polycarbonate by the copolymerization of limonene oxide and CO$_2$ using β-diketiminate Zn based catalysts.$^{12}$

### 1.2.4 Copolymers of epoxides and esters

Synthesis of copolymers of epoxides with esters is another way to tune the physical and mechanical properties. There are few studies available on the synthesis of block copolymer of ethers and esters. Unfortunately, the synthesis of alternating polymer of ether and ester is rare and still be a challenging research area. Recently, Coates and co-workers reported the synthesis of alternating copolymer of epoxide with dihydrocoumarin using salenCrCl/PPN$^+$Cl$^-$ system as shown in Scheme 6.
Scheme 6: Copolymerization of epoxide with dihydrocoumarin by salenCrCl/PPN⁺Cl⁻ system

Synthesis of alternating copolymer of epoxides and anhydrides is another way to making ether-ester containing polymer.¹³

1.2.5 Copolymers of esters, ethers and carbon dioxide

There are few examples of copolymerization of esters, ethers with CO₂ available in the literature. Synthesis of multi-block copolymers, by incorporating two or more homopolymers with a covalent bond, is one of the major strategies to modify the mechanical and thermal properties. Lee and co-workers reported a well-controlled synthesis of triblock polymers by the addition of polymers like PEG during CO₂-PO polymerization.¹⁴ Williams and co-workers synthesized poly(cyclohexeneoxide)-b-polylactide by the two step process using dizinc catalyst for the polycyclohexene carbonate synthesis followed by yttrium catalyst for the PLA synthesis.¹⁵

\[
\text{Scheme 7: Synthesis of copolymer of CO}_2 \text{ and } \varepsilon \text{-CL in neat PO}
\]
The terpolymerization of CO$_2$ and CL in neat PO in one pot synthesis (Scheme 7) was investigated by Ree et.al.$^{16}$ The feedstock ratio is influencing the copolymerization, where 50:50 = PO:CL feed stock mainly produces block copolymers of PC-PCL and the other ratios leave considerable amount of PPO, PPC, PC and PCL in the product.

A few polyester block polycarbonate syntheses have been done in the past. The block polymers of cyclohexeneoxide, anhydride (succinic anhydride, maleic anhydride, etc.) and CO$_2$ are possible whereas the anhydride copolymerizes faster than epoxide with CO$_2$.\textsuperscript{17,18,19} Recently Darensbourg et. al. reported the one pot synthesis of tri block copolymer of PO, CO$_2$ and LA. Herein the PO and CO$_2$ polymerized first by SalenCo catalyst and followed by LA polymerized by DBU (1,8-diazabicyclo[5.4.0]-undec-7-ene) to make the block polymer.\textsuperscript{20} But the reaction with LA, epoxides and CO$_2$ together in the reaction mixture produce a random copolymer of LA, epoxides and CO$_2$.\textsuperscript{21} Making alternating regular/ block copolymer of LA, epoxides with CO$_2$ by one catalyst in a one pot still remains a synthetic challenge.

1.3 Catalyst development

Developing and understanding the structural activity relationship of the ROP is a major goal of the current catalyst development towards the industrial production of biodegradable polymers.\textsuperscript{22} Both ROP of cyclic esters/ethers or the copolymerization and poly condensation of acids-alcohols for the polymer synthesis require a catalyst. Catalyst performance usage can be determined by the following factors:

High reactivity/productivity (can be measured by the TON/TOF)
Controlled polymerization (Catalyst: reactant ratio to control $M_w$)

Reusability/immortality of the catalyst

Narrow PDI values

Better stereo-selectivity /regio-selectivity

Susceptible for the production of different architectures (copolymers)

Toxicity/biodegradability

Cost and availability of catalyst components, and

Suppress the side reactions (*trans*-esterification/epimerization)

The above factors have to be considered for the industrial production of polymers.

The catalysts systems can be classified into homogeneous and heterogeneous. The homogeneous catalysts are particularly important in polymer synthesis. The single site molecular catalysts can be viewed as homogeneous catalysts.

The single-site catalysts can be classified into three components: 1- $\mathbf{M} =$ metal center (Na, Mg, Al, Bi, etc.), 2- $\mathbf{L} =$ bulky ancillary organic ligand (porphyrin, $\beta$-diketiminate, salen, etc.) and 3- $\mathbf{X} =$ initiating/activating group (alkoxides, alkyls, amides, etc.) are represented in the Figure 1.

Figure 1: Simple pictorial representation of a single-site molecular catalyst
These three components determine the stability of the catalysts as well as the reactivity and stereo/regio selectivity of the reaction. The selection of catalysts for the polymer synthesis is the major consideration for the applications in medicine and as well as the disposal/degradation of these residues in the environment. There are several elements in the periodic table have been investigated for the ROP. Mg and lanthanide catalysts are the fastest catalysts for the ROP of LA. Al catalyst provides better stereo selectivity for the ROP of LA.\textsuperscript{23,24} The low polymerization efficiency of dimeric aluminum alkoxide catalysts was attributed to the monomer-dimer equilibrium.\textsuperscript{25}

1.3.1 Choice of metal center

The choice of metal for the catalyst development is one of the major criteria in the industries, which could influence in the activity, toxicity and the production cost. Among the elements in the periodic table, Na, K, Mg,\textsuperscript{26} Zn\textsuperscript{27}, Bi\textsuperscript{28}, Mn\textsuperscript{29}, Al\textsuperscript{29} and Fe\textsuperscript{30,31,32,33} ions may be considered as lowest toxic metal ions since they are taking part in human metabolism. Some of the metals are also found in relatively high concentration than other metal ions in human body. These metal ion containing catalysts can be considered as an alternative to the Sn(Oct)\textsubscript{2} for the production of polyesters.

1.3.2 Tin(II) octanoate

Tin(II) octanoate, Sn(Oct)\textsubscript{2}, is the industrial catalyst for the production of polyurthenes, polyesters, polyethers, silicone, etc. Sn(Oct)\textsubscript{2} is also known as
METATIN™ catalysts S-26, which is produced 4000 metric ton/year by Dow chemical [Product Safety Assessment – METATIN™ Catalyst S-26 DOW]. The industrial production route for the Sn(Oct)$_2$ is shown below (Scheme 8).

Scheme 8: Industrial production of Tin(II) octanoate

Sn(Oct)$_2$ causes the mutagenic, teratogenic, or birth defects. Octanoic acid can be completely biodegradable and the Sn(II) can oxidize in to Sn(IV) in the environment. Sn(IV) is toxic to aquatic organisms, and can lead to a long term effect in aquatic environment. It is necessary to investigate the possible substitute catalyst for the Sn(Oct)$_2$ for the industrial production of polymers in the future.

1.3.3 Reactivity of other metal catalysts

Sodium and pottasium containing salts as well as their alkoxides are active for the ROP of LA and result in racemization even at room temperature. Calcium and magnesium containing catalysts are the highest active catalysts among the other elements, they undergo racemization and trans-esterification mainly in bulk polymerization. Additionally, these catalysts do not favor the stereo selectivity for the synthesis of isotactic PLA from rac-LA. Iron and manganese containing catalysts are less active than
the alkaline and alkaline earth metals. On the other hand, Al favors the isotactic PLA from rac-LA in solution at or above 70°C in benzene/toluene, but there is a concern regarding the health issues such as Alzheimer disease. Bismuth salts have been active for the bulk polymerization of LA, but the synthesis of single-site catalysts remain a challenge. Importantly, Bi ions do not play a role in human body, and they can completely excrete from the body by urine or feces. Bismuth complexes, in the form of Peptobismon®, have been used for several medications more than a century and they have been proven to be nontoxic. Chromium and cobalt catalysts are the most active catalyst for the homo/copolymerization of epoxides with carbon dioxide. Herein, we have chosen Mg, Bi and Cr as a metal center towards the development of single site catalyst to study the reactivity and stereo selectivity for the ROP of cyclic esters and epoxides.

1.3.4 Magnesium catalysts

β-Dikitiminato based ligands are one of the attractive ligand system towards the synthesis of single site Mg initiators for the ROP of cyclic esters. This ligand framework provides several scopes by modification of R, R1, R2 and R3 groups to tune the steric and electronic properties. These steric and electronic properties are mainly influenced the stability and the reactivity of the catalyst system. Furthermore, the steric influence restricts the Schlenk equilibrium towards the stabilization and the formation of single site magnesium catalysts (Scheme 9II).
Grignard reagents or the dialkyl magnesium complexes have been investigated for the ROP of LAs since 1995 and found to be less active below 60°C.\textsuperscript{35} At higher temperatures, above 80°C in both bulk and solution, it is active for the ROP of LA and suffers from the polymerization control by undesired side-reactions such as trans-esterification/epimerization. In 1996, Chisholm and co-workers\textsuperscript{36} reported the early magnesium single-site catalyst, tris(pyrazoyl)borateMgOEt (TPBMgOEt, Figure 2, I), later several Mg based catalysts were well-developed. These catalysts were active and well behaved when compared with dialkyl magnesium catalyst and produced atactic and heterotactic polymer from rac-LA in DCM and THF respectively.

Following by TPB based ligands, Coates and co-workers investigated β-dikittiminate (BDI, Figure 2, II), (2-[(2,6-diisopropylphenyl)amino]-4-[(2,6-isopropylphenyl)imino]pent-2-ene), based dimeric magnesium alkoxide single site catalysts for the ROP of LA. This system is more active than TPB based magnesium catalyst. Then the monomeric single site magnesium alkoxide was reported by Chisholm and co-workers in 2002 and found to be more active than the related dimeric alkoxide catalyst.
Figure 2: Single site catalysts of TPB(I) and BDI(II) based single site magnesium catalysts

The substitution of alkoxide instead of an alkyl group reduces the activity whereas the substitution of alkoxide by BH$_4^-$ shows similar activity. Most of the BDIMg catalysts produce atactic PLA in non-coordinating solvent such as DCM/toluene and heterotactic PLA in coordinating solvents such as THF. The influence of solvent effect and its mechanistic insight were further investigated by Chisholm and co-workers.$^{37}$ Further, the modification of BDI ligand by using different substitution on the phenyl arm was investigated for the ROP of LA. The substitution of alkoxy groups on the phenyl ring suppresses the activity and improves the selectivity for the rac-LA polymerization. The extension of carbon spacing between the N and phenyl arm has no improvement in the activity or selectivity of rac-LA ROP. The above discussed complexes (Figure 3) and their activities are summarized in the Table 1.
Figure 3: Selected BDI based catalysts for the ROP of LA

The electron withdrawing and donating effects in the phenyl arm were investigated for the similar type of zinc complexes (VIII, Figure 3). The electron donating substituents in the phenyl ring decrease the electrophilicity at the Zn center and weakening the Zn-O bond, which favor the coordination insertion of LA. However, the electronic influence of the substitution on α /β-position in the BDI type ligands was not clearly investigated. This could be one of the significant areas for further development of single site BDI type magnesium catalysts.
Table 1: The activity and selectivity of selected BDI type magnesium catalysts

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>Solvent</th>
<th>time</th>
<th>%conversion</th>
<th>LA:Cat:ROH</th>
<th>PDI/P&lt;sub&gt;r&lt;/sub&gt;</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>TPB I</td>
<td>DCM</td>
<td>60m</td>
<td>90%</td>
<td>100:01:00</td>
<td>1.1-1.3</td>
<td>36</td>
</tr>
<tr>
<td>I</td>
<td>DCM</td>
<td>2m</td>
<td>97%</td>
<td>100:01:01</td>
<td>1.28</td>
<td>38</td>
</tr>
<tr>
<td>II</td>
<td>DCM</td>
<td>2m</td>
<td>97%</td>
<td>100:01:00</td>
<td>1.49</td>
<td>39</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>5m</td>
<td>95%</td>
<td>100:01:00</td>
<td>1.47</td>
<td>39</td>
</tr>
<tr>
<td>III</td>
<td>DCM</td>
<td>1.5m</td>
<td>92%</td>
<td>100:01:00</td>
<td>1.45/0.56</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>1.5m</td>
<td>60%</td>
<td>100:01:00</td>
<td>1.30/0.96</td>
<td>40</td>
</tr>
<tr>
<td>IV</td>
<td>THF</td>
<td>5m</td>
<td>94%</td>
<td>100:01:00</td>
<td>1.6</td>
<td>39</td>
</tr>
<tr>
<td>V</td>
<td>THF</td>
<td>5m</td>
<td>85-90%</td>
<td>20-300:1:0</td>
<td>1.4-1.8</td>
<td>41</td>
</tr>
<tr>
<td>VI</td>
<td>C&lt;sub&gt;6&lt;/sub&gt;H&lt;sub&gt;6&lt;/sub&gt;</td>
<td>5m</td>
<td>72%</td>
<td>100:01:00</td>
<td>1.6</td>
<td>42</td>
</tr>
<tr>
<td>VII</td>
<td>DCM</td>
<td>20m</td>
<td>91%</td>
<td>100:01:00</td>
<td>2.23</td>
<td>40</td>
</tr>
<tr>
<td></td>
<td>THF</td>
<td>90m</td>
<td>90%</td>
<td>100:01:00</td>
<td>1.12</td>
<td>40</td>
</tr>
<tr>
<td>IX</td>
<td>CDCl&lt;sub&gt;3&lt;/sub&gt;</td>
<td>2h</td>
<td>100%</td>
<td>100:01:00</td>
<td>1.74</td>
<td>43</td>
</tr>
<tr>
<td>X</td>
<td>DCM</td>
<td>2m</td>
<td>90%</td>
<td>200:01:00</td>
<td>-</td>
<td>44</td>
</tr>
</tbody>
</table>

*All the polymerization reactions were carried out at room temperature.

Additionally introducing chirality to the α and β positions in BDI type ligands as indicated in Figure 4 (I and II) or chiral alkoxide (Figure 4, III) could favor for the isotactic PLA synthesis by ROP of rac-LA by enatiomorphic site control or chain end control mechanism respectively.

Figure 4: Possible chiral backbone containing BDI ligands
1.3.5 Bismuth catalysts

The history of bismuth begins from 1450s and their compounds are important materials for catalysts for organic synthesis\(^45,46\) and industrial applications including metallurgical use, electronics, plastics, chemicals, pigments, cosmetic, and pharmaceutical applications.\(^47\) Bismuth (Bi) is a non-toxic, relatively cheap, non-bio-accumulative and non-radioactive main group element. These properties make Bi as useful component in medicinal, cosmetic and pharmaceutical applications. Regrettably, bismuth complexes favor the formation of high and variable coordination numbers which provide the unpredictable structural arrangements like polymeric inorganic compounds.\(^48\) Most of the bismuth salts and compounds have low solubility.\(^49\) Bismuth amides [Bi(N(SiMe\(_3\))\(_2\)] and Bi(NMe\(_2\))\(_3\)] are extremely air sensitive, volatile, photosensitive and have low melting points.\(^50\) Bismuth alkoxides are extremely sensitive to UV- and X-ray irradiation. Attempts to study the structural behavior of Bi(OEt)\(_3\) darkened and formed amorphous materials during the experiments.\(^51\) Diphenyl bismuth methoxide and ethoxide are the only known single site alkoxides and stable up to approximately 100 °C.\(^52\) Synthesis of porphyrin based bismuth complexes indicates the lack of stability and the demetalations occurs rapidly during the purification process.\(^53\)

Furthermore, synthesis of single site bismuth complexes is difficult and there is no known literature evidence for the conversion of single site Bi-Cl bond into a Bi alkoxide group.\(^34\) Even though there are several drawbacks for the synthesis of bismuth
based catalysts, the low toxicity made them as interesting candidates as a polymerization catalysts.

Very few Bi-based initiators have been investigated for the ROP of LA and their co-polymers/blends. The summary of Bi catalysts for the ROP of LA is given in Table 2. All of these polymerization reactions are carried out in high temperature (120-180 °C) and in long reaction times. The resulting polymers exhibit low molecular weight and they also lack of stereo selectivity.

Table 2: Summary of Bismuth initiators investigated for the LA polymerization in the literature

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>LA:I</th>
<th>Temp. (°C)</th>
<th>Time(h)</th>
<th>Yield %</th>
<th>Ref.</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi Octanoate</td>
<td>100:1</td>
<td>120</td>
<td>48</td>
<td>98</td>
<td>28</td>
</tr>
<tr>
<td>Bi Octanoate</td>
<td>100:1</td>
<td>180</td>
<td>12</td>
<td>96</td>
<td>28</td>
</tr>
<tr>
<td>Bi(OAc)₃/Pentaerythritol</td>
<td>1000:1</td>
<td>120</td>
<td>3</td>
<td>80-95</td>
<td>54</td>
</tr>
<tr>
<td>Bi(OAc)₃/1,1,1-Tris(hydroxymethyl)propane</td>
<td>1000:1</td>
<td>120</td>
<td>3</td>
<td>80-95</td>
<td>54</td>
</tr>
<tr>
<td>Bi(OAc)₃/TEG</td>
<td>1000:1</td>
<td>120</td>
<td>3</td>
<td>80-95</td>
<td>54</td>
</tr>
<tr>
<td>Goldline® Pink Bismuth</td>
<td>100:1</td>
<td>130</td>
<td>65</td>
<td>98.3</td>
<td>55</td>
</tr>
<tr>
<td>Bi(OAc)₃/EG</td>
<td>1000:1</td>
<td>120-140</td>
<td>5</td>
<td>99.7</td>
<td>56</td>
</tr>
<tr>
<td>Bi(Hex)₃</td>
<td>1000:1</td>
<td>120</td>
<td>5</td>
<td>90-92</td>
<td>57</td>
</tr>
<tr>
<td>Bi(III) 2-Ethylhexanoate</td>
<td>100:1</td>
<td>120</td>
<td>2~24</td>
<td>47-90</td>
<td>58</td>
</tr>
</tbody>
</table>

Most of these solvent polymerizations were carried out in chlorobenzene which is considered as a carcinogen. Additionally, Kricheldorf et. al. synthesized multiblock copolymers of LA, ε-CL and trimethylene carbonate using Bi hexanoate as a catalyst. The above studies indicate the possibility of exploring Bi catalysts for the biodegradable polymer synthesis. It is worthwhile to explore single site Bi- based initiators for the synthesis of polymers towards the medicinal applications.
1.3.6 Chromium catalyst

Chromium(III) compounds are nontoxic according to EPA and the chromium(VI) compounds are genotoxic and carcinogens.\textsuperscript{60,61} Considerable amount of Cr(III) compounds are used by general public and industries. For example, chromium(III) picolinate is used as a vitamin supplement.\textsuperscript{62} Chromium catalysts are found in several applications in industries as well as in organic synthesis.\textsuperscript{63} Phillips catalyst, a heterogeneous catalyst (Cr(VI)O$_3$/SiO$_2$), is mainly used in industries for the production of polyethylene.\textsuperscript{64} Furthermore, many chromium based catalysts have been employed as a polymerization catalysts including polycarbonate synthesis from epoxides and CO$_2$.

The history of co-polymerization of epoxides with carbon dioxide began with the discovery of alternating copolymerization of propylene oxide with carbon dioxide using ZnEt$_2$/water catalyst system by Inoue and co-workers in 1969.\textsuperscript{65} In 1995, Kruperan and Deller reported the chromium porphyrin catalyst for the synthesis of cyclic carbonates from epoxides and carbon dioxide.\textsuperscript{66} Later, Holmes and co-workers developed fluorinated porphyrins/co-catalyst system for the alternating co-polymer of cyclohexene oxide with carbon dioxide.\textsuperscript{67} Chisholm and co-workers investigated the electronic influences of porphyrin systems for the co-polymerization of PO and CO$_2$. Here, the activity TPPCrCl > OEPCrCl > TFPPCrCl was noted in the presence of 0.5 equiv. of PPN$^+$Cl$^-$ with respect to catalyst (Figure 5).

The homopolymerization of PO was also investigated with different metal containing porphyrin system and the reactivity of which is found in the order of TPPCr(III) > TPPAl(III) ~ TPPCo(III). TPPCrCl catalyst is very active under the ambient
conditions with higher turnover frequency (TOF ~ 2000 h⁻¹) with the formation of regioregular-isotactic PPO. Rieger and co-workers reported that the slaenCrCl/DMAP system (Figure 5) is active for the copolymerization of PO and CO₂. According to this study, DMAP strongly bound to the Cr metal center and activated the Cr-OR bond. The excess amount of DMAP favors the formation of propylenecarbonate by the backbiting mechanism.⁶⁸

![Diagram of catalyst structures](image)

Figure 5: The structures of porphyrin/salen based catalysts and co-catalyst

Most of these polymers obtained by the co-polymerization of PO with CO₂ produce low molecular weight polymers, which could be attributed to chain transfer or backbiting reaction to form cyclic carbonates/macro cycles.

### 1.4 Polymerization mechanism

There are two main mechanisms, (1) coordination insertion mechanism and (2) activated monomer mechanism, which have been accepted for the LA polymerization.
The activated monomer mechanism is mainly involved with cationic or organo catalysts. The widely accepted coordination insertion mechanism for the LA polymerization has been supported by theoretical studies as well as by experimental studies, such as end group analysis/NMR studies. In this mechanism, the Lewis acidic metal center coordinates with LA and activates to attack by the metal alkoxide. Thus, favor the acyl bond cleavage of the LA to generate a new alkoxide which will undergo further chain propagation reaction to yield PLA as shown in Figure 6.

![Coordination Insertion Mechanism of LA by Metal Alkoxide Catalyst](image_url)

Figure 6: Coordination insertion mechanism of LA by metal alkoxide catalyst
The mechanistic pathway for the formation of PCs by the copolymerization of epoxides with carbon dioxide is shown in Scheme 9. Usually the metal center of the catalyst is a Lewis acid, which coordinates and activates the epoxide to form alkoxide intermediate by ring opening. The metal alkoxide activates the carbon dioxide and inserts between M-O bond to produce metal carbonate bond. Then it can intake another epoxide to form PC (II) or can form cyclic carbonate by backbiting mechanism (Scheme 10-III). The backbiting mechanism is thermodynamically favored for the production of 5 membered cyclic carbonate. Furthermore, metal alkoxide consecutively ring opens epoxide towards the formation of polyethers (Scheme 10-I). The alternating copolymer of epoxide with carbon dioxide can be achieved by related reactivity of metal alkoxide-metal carbonate.

Scheme 10: Mechanistic pathway for the formation of PC, PPC and polyethers
1.5 Stereochemistry of polylactide and polycarbonates

Stereochemistry of the polymer backbone mainly controls the physical and chemical properties of polymers.

1.5.1 Stereo sequence of polylactide

$L_-, D_-, and meso-$-LAs$ are the three isomers of LA (Figure 7). The racemic mixture of LA, rac-LA, contain 50:50 $L-$ and $D-$LA. $L-$LA, the most available enatiopure form of LA mainly obtained from biomass by enzymatic process, polymerizes to produces poly-$L-$LA. Poly-$L-$LA is the major commodity PLA produced by the Cargill and the Nature products.

![Figure 7: Isomers of LA](image)

Polymerization of rac-LA and meso-LA produces various stereo random or stereo regular tacticites are shown in .
Figure 8: Tacticites of PLA obtained from L-, D-, rac- or meso- LA

Chemical, mechanical and physical properties of PLA mainly arise from the stereo chemical arrangement of chiral centers of polymer chain. The physical and mechanical properties are summarized in Table 3.

Table 3: Physical and mechanical properties of different tactility containing polymers

<table>
<thead>
<tr>
<th>Polymer-PLA</th>
<th>T&lt;sub&gt;m&lt;/sub&gt;(°C)</th>
<th>T&lt;sub&gt;g&lt;/sub&gt;(°C)</th>
<th>Modulus(Gpa)</th>
<th>Degradation time(months)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Isotactic</td>
<td>170</td>
<td>60</td>
<td>2.7</td>
<td>&gt;24</td>
</tr>
<tr>
<td>Syndiotatic</td>
<td>153</td>
<td>45</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Heterotactic</td>
<td>amorphous</td>
<td>49</td>
<td>n/a</td>
<td>n/a</td>
</tr>
<tr>
<td>Atactic</td>
<td>amorphous</td>
<td>55</td>
<td>1.9</td>
<td>12~16</td>
</tr>
<tr>
<td>Stereoblock</td>
<td>&gt;200</td>
<td></td>
<td></td>
<td></td>
</tr>
<tr>
<td>Stereoplex</td>
<td>&gt;230</td>
<td>65-72</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Furthermore, blend or mixture of different stereochemical PLAs or PLA with other polymers enhance the properties of resulting polymers. For example, stereocomplex PLA, 1:1 mixture chains of poly-L-LA and poly-D-LA, exhibit higher meting point > 235 °C than either poly-L-LA or poly-D-LA by ~ 50 °C. This property is more important in several industrial applications.
The first synthesis of stereo complex PLA was reported by Idaka et al. by mixing the separate chains of poly-L-LA and poly-D-LA. In 2002, the synthesis of stereocomplex PLA using single site aluminum from rac-LA was reported by Baker and Smith. Later Coates and co-workers re-investigated this catalytic system and found that also produces stereoblock PLA. There are several studies have been available on the synthesis of stereo complex PLA by mechanical mixing poly-L-LA and poly-D-LA. Recently, Akashi et al. reported the synthesis of stereo complex PLA by layer-by-layer assembly of poly-L-LA and poly-D-LA. The stereocomplex assignment can be made by NMR and the distinct powder-X-ray pattern. The typical powder-X-ray pattern of stereocomplex PLA obtained from the layer by layer assembly is shown in the Figure 9.

![Figure 9: Powder X-ray pattern of stereocomplex PLA](image)

The tacticity of PLA can be determined by $^{13}$C NMR of methine region or proton decoupled $^1$H NMR methine resonance as shown in the Figure 10:
Steroselectivity of the LA polymerization can be explained by (1) metal site control and (2) chain end control mechanism.

(1) **The metal site control mechanism**

In this mechanism, mainly the metal site/ligands chirality with the metal controls the selectivity of monomer. This type of mechanism is well documented for the chiral Al based catalysts for the synthesis of isotactic PLA from rac-LA. Chiral \((R)\text{SalBinapAlOMe (C1,)}\)

Figure 11) preferentially polymerizes \(D\)-LA from \(rac\)-LA.\(^{23}\) The selectivity was determined by the optical activity of residual monomer in the reaction mixture and the
estimated rate constant for \( L \)-LA and \( D \)-LA, \( k_D:k_L \sim 20:1 \). Feijen \textit{et.al.} reports that \((R,R\text{-salen})\text{Al-O}'\text{Pr}\) (C2, \ref{fig:11}) preferentially polymerizes \( L \)-LA with the rate constant \( k_L:k_D \sim 14:1 \).\textsuperscript{58}

Coates and co-workers reported the synthesis of syndiotactic and heterotactic PLA from \textit{meso}-LA by \((R,R)-(\text{SalBinap})\text{AlO}'\text{Pr}\) and \textit{rac-} (SalBinap)\text{AlO}'\text{Pr} (C1, where \( R = \text{O}'\text{Pr} \), \ref{fig:11}) catalyst respectively.\textsuperscript{74}

\begin{center}
\includegraphics[width=0.8\textwidth]{fig11.png}
\end{center}

\textbf{Figure 11: Selected aluminum catalyst for ROP of LA}

\subsection*{(2) The chain end control mechanism}

Here the selectivity of the monomer is mainly influenced by the last enchained monomer of the growing polymer chain. For example, \textit{LiO}'\text{Bu} preferentially produced heterotactic PLA from \textit{rac}-LA. Herein, the initial ring-opening of \( L \)-or \( D \)-LA produces an alkoxide, with \( S \) or \( R \) chiral center, which influences the selection of the incoming monomer towards the formation of PLA chains.
The tacticity of the PLA is influenced by the side reactions. These side reactions are mainly classified into two groups as \textit{trans}-esterification and epimerization. The \textit{trans}-esterification is further classified into inter-chain and intra-chain \textit{trans}-esterification as shown in the Figure 12. Inter-chain \textit{trans}-esterification is less prominent in the initial monomer enchainment and it is noticeable when the LA concentration decreases during the polymerization process which leads to the broader molecular weight distributions (PDI). Intra-chain \textit{trans}-esterification mainly forms cyclic oligomers, which reduces the polymer molecular weight. Both these processes cause for the stereo irregularity of the polymer chains, which influencing the polydispersity index ($P_r$) of polymer.

![Figure 12: Inter-chain and intra-chain \textit{trans}-esterification of PLA](image)

Additionally, chain transfer process also influences the molecular weight and the PDI values of polymers that can be take place between two growing chains or an external addition of alcohol as depicted in the Scheme 11.
LM—OP + LM'—OP' → LM—OP' + LM'—OP \hspace{1cm} (I)

LMOP + ROH ⇌ LMOR + POH \hspace{1cm} (II)

Scheme 11: Chain transfer of PLA (I) between two growing chain and (II), external addition of alcohol where L = ligands, M,M' = metal centers, P, P' - growing polymer chain, and ROH is alcohol.

1.5.2 Stereo sequence of polyethers and polycarbonates

The choice of metal, the ancillary ligand and the initiating group/polymer chain (X) influence the regio- and stereo- selectivity of epoxide polymerization. There are two possibilities for the enchainment of propylene oxide (asymmetric epoxide) by the catalyst: (i) the initiating group attacks the methylene carbon with retention of configuration to form a secondary alkoxide and (ii) the initiating group attacks the methine carbon with the inversion of configuration to form a primary alkoxide as shown in Scheme 12.

Scheme 12: Possible regio-attacks by the initiating group on methine and methylene region

These types of the ring opening process of PO can lead to two types of regio polymers such as regioregular and regioirregular polypropylene oxide as depicted below:
Furthermore, depending on the stereo chemical arrangements of chiral centers, PPO can be classified into isotactic, syndiotactic and atactic PPO as shown below (Figure 14): These tacticites can be determined by the NMR studies (Figure 15).

Stereo selectivity of the incoming monomer enchainment can be explained by the enatiomorphic site control or chain end control mechanism as similar to LA polymerization.
Microstructure of the polypropylene carbonate is assigned according to the regiosequence of carbonate junction and substituted methylene carbon (Figure 16). The HH, HT, TH and TT junctions (Figure 17) can be assigned by the NMR spectroscopy (Figure 18).

Figure 15: $^{13}$C NMR of PPO synthesized by TPPCrCl/PPN$^+$Cl$^-$ from $R$-PO and $rac$-PO
Figure 16: Microstructure of polypropylene carbonate

Figure 17: $^{13}$C NMR spectra of carbonyl region of PPC obtained from PO with CO$_2$. 
Figure 18: Possible diads of PPC of different regio sequence

1.6 Kinetics of lactide polymerization

Kinetics study is one of the most useful criteria to evaluate the rate of polymerization and it helps to understand the mechanistic insight of polymerization. General form of LA polymerization can be represented according to the following equation: Most of the ROP of LA follows the first order with respect to LA and catalyst with the overall 2\textsuperscript{nd} order rate constant.

\[-d[\text{LA}]/dt = k_p[\text{LA}]^x[\text{Cat.}]^y\]

Where, \(k_p\) = rate constant, \(x\) and \(y\) are the order of the reaction with respect to LA and catalyst respectively. For experimental purpose, this equation reduces to the pseudo-first order equation as shown below and the LA concentration maintains the same concentration against with different catalyst concentration for the constant volume reaction mixture.
-d[LA]/dt = k_{app}[LA]^x

Where \( k_{app} = k_p[Cat.]^y \)

The activity of polymerization is usually expressed in terms of \( k_p \). In some cases, \( k_{app} \) values are also used to compare the rate of the polymerization. In terms of the rate constant, for a well-controlled polymerization, the rate of initiation must be greater than the rate of propagation. Furthermore, the rate of propagation also must be faster than the chain transfer or the termination reactions.

1.7 Summary

There are significant achievements that have been made in the past two decades towards the development of single-site catalysts for the synthesis of biodegradable polymers. Among these biodegradable polymers, industries are interested in PLAs, PCs, polyethers and their copolymers for several applications. Making new polymers from biomass is one of the major approaches for the sustainable environment. Replacement of currently available industrial catalyst, \( \text{Sn(Oct)}_2 \), is another one of the major goal in polyester synthesis due to the health and environmental concern. Additionally, synthesis of stereoselective catalysts and isotactic polymers are essential to enhance the physical and chemical properties of polymers towards the industrial applications, which could reduce the production cost of currently available biodegradable polymers.

In this study, we have designed and synthesized several bismuth, magnesium and chromium containing single site catalysts using different ligand systems to study the
activity and stereo selectivity of homo and co-polymerization of esters, ethers and carbon
dioxide. These studies are broadly divided into three areas;

**Chapter 2 & 3**: Chemistry of Bi catalysts and their bonding properties as well as
applications for the ROP of PO, LA, ε-CL and their copolymerization.

**Chapter 4**: Chemistry of Cr catalysts and their applications for the ROP of LA and
copolymerizations of LA with epoxides and carbon dioxide, and

**Chapter 5**: Mechanistic insight of β-diketiminate catalysts and their applications for the
ROP of LA, PO and ε-CL. The detailed studies of these three areas will be discussed in
the following chapters.
Chapter 2  Chemistry of Bi catalysts and their applications for the ROP of PO, LA and \( \varepsilon \)-CL

2.1 Introduction

PLAs and their blends have already been recognized and employed in packaging, drug delivery and in medical implants as well as components in the construction of automobiles, carpeting and clothing.\textsuperscript{75} The ROP of LAs to produce the biodegradable and biocompatible polymers PLAs, has been shown to be accomplished by both organic,\textsuperscript{76} and coordinate catalysis\textsuperscript{77}. The coordinate metal catalyst reactivity is involved with nucleophilic initiator ligands such as alkyls, alkoxides, amides, and hydroxides. Tin(II) octanoate, Sn(Oct)\(_2\), where Oct = 2-ethyl hexanoate, is employed in industries as a catalyst for melt polymerization of lactones. The catalytic activity of Sn(Oct)\(_2\) involves the reversible reaction with water, as shown in eq. 1, Scheme 13.

\[
\text{Sn(Oct)}_2 + \text{H}_2\text{O} \quad \rightleftharpoons \quad \text{Sn(Oct)(OH)} + \text{HOOct} \quad (1)
\]

\[
\text{Sn(Oct)(OH)} + \text{n} \quad \rightleftharpoons \quad \text{(Oct)}\text{Sn} \quad (2)
\]

\[
\text{Sn(Oct)(OP)} + \text{HOOct} \quad \rightleftharpoons \quad \text{Sn(Oct)}_2 + \text{POH} \quad (3)
\]

Scheme 13: Mechanism for the ROP of LA by Sn(Oct)\(_2\) [P = polymer chain]
The Sn-OH group acts as an initiator in the ring opening of a LA molecule to generate a tin(II) alkoxide bond which can further undergo the ring-opening and enchainment of LA monomers as depicted in eq. 2. The liberated octanoic acid can back react/displace the growing polymer as a long chain polyester with terminal OH and COOH groups in a reversible manner akin to eq. 1., i.e. as depicted in eq. 3, where POHs represent the hydroxyl terminated oligomers. These equilibria are dynamic and each water molecule acts as a chain transfer catalyst with the Sn-OH group initiating the growth of a new chain.

The current production of PLA leaves the residues of Sn metal ions in the polymer. The standard industrial procedure employs Sn(Oct)$_2$ of concentration levels between 140 and 281 ppm.$^{78}$ Although tin(II) is not considered as a toxic heavy metal and its daily use as stannous fluoride in toothpaste$^{79}$ has been practiced for decades, there are studies showing that tin(II) octanoate inhibits cell growth within the range of 26-125 ppm.$^{80}$ Moreover, it is well known that organotin(IV) compounds are extremely toxic and the handling of compounds such as trimethyltin chloride in the lab requires considerable care.$^{81}$

People have been skeptical and concern regarding the health issues associated with these polymers. While much of these may be considered due to the lack of a scientific education, it also has to be recognized that we are continuously evaluating the hazards associated with products that are introduced to the market place. Thus numerous chemical processes or chemical additives are not currently in use though they were for several decades. Some common examples are the former use of carbon tetrachloride as a
dry cleaning agent; the use of lead pigments in household paints; the use of tetraethyl lead in gasoline as an antiknock additive; fluorocarbons as household refrigerants and in academic laboratories the use of chromic acid baths for the cleaning of glassware. Our world increasingly uses plastics for everything from packaging and construction materials to medical implants. This has raised concern regarding their environmental impact ranging from littering, waste disposal to leaching of monomers such as bisphenol-A. This is leading to an increase in the general awareness that polymers derived from renewable resources, and particularly those that are also bio-degradable represent attractive alternatives to many petrochemical derived materials. This prompted us to consider whether alternatives to tin(II) octanoate, alternatives that are known to be biocompatible and are commonly employed by the public as “health aids” might be equally effective in the melt polymerization of LA.

This living or immortal system has an essential requirement that the M-OH bond be chemically persistent during the reaction conditions. It should not react to form an inert oxo metal derivative nor react with other species present such as CO₂ to form an inert carbonate. This led us to question whether alternative M-OH bonds (but not those of alkali metals that effect epimerization) might be similarly active in melt polymerizations. We subsequently investigated the reactivity of a number of biocompatible metal containing oral relief aids and dietary supplements that contain hydroxyl groups, and found that the most active of the bismuth containing species was bismuth subsalicylate (BSS) which is the active ingredient in Peptobismol®. Both Bi(III) and Sn(II) can support M-OH bonds that will reversibly react to form an oxo species as shown in eq.1.
This chapter mainly focuses on the usage of Bi catalysts for the ROP of LA and \(\varepsilon\)-CL. Furthermore, the preliminary results for the copolymerization epoxides and CO\(_2\) also will be discussed.

### 2.2 Results and discussion

#### 2.2.1 Heterogeneous Bi catalysts

The melt ROPs of LA, typically \(L\)-LA or \(rac\)-LA, and \(\varepsilon\)-CL, were carried out in sealed glass ampoules. Catalyst and monomer were mixed in ratios ranging from 25:1 to > 1000:1. The over the counter substances and other non-air sensitive catalysts were ground with a mortar and pestle to make sure good mixing with the LA. Mainly the catalyst to monomer ratio was determined based on the formula mass of the active ingredient. The ampoules were heated in a preheated oil bath at 110-130 °C and subsequently opened and the residual matter dissolved in chloroform/ dichloromethane, extracted and quickly quenched with acidic (HCl) methanol. The resulting product was dried under vacuum and the percentage conversion of monomer to polymer was determined by \(^1\)H NMR. For \(\varepsilon\)-CL, a portion of reaction mixture was used to find the percentage conversion. The crude polymer was purified by methanol and dried for the GPC and further NMR analysis. The micro structure of the polymer was determined by homo-decoupled \(^1\)H-NMR spectroscopy and the molecular weight distribution was analyzed by gel permeation chromatography in THF solution. The molecular weights were determined with respect to polystyrene standards and the correction factor (0.58) for
PLA was applied. The initial screening polymerizations results using biocompatible substances are shown in Table 4. This result shows that calcium hydroxyapatite is very poor initiator for the ROP of \textit{L-LA}. CaO and MgO showed the evidence for the epimerization. Among these initiators Goldline Pink Pepto-Bismol® and Pepto-Bismol® tablets were found to be more active and further comparison was carried out with Sn(Oct)$_2$. Interestingly Pepto-Bismol® (Kroger) shows the evidence for the \textit{trans}-etherification and epimerization, which could be the results from the other additives in the tablet.

The detailed comparison of the activity of Pepto-Bismol® and Sn(Oct)$_2$ were summarized in Table 5 which reveals their similar activity.

\textbf{Table 4: Summary of initial screenings for the melt ROP of \textit{L-LA} at 130 °C for 65h}

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>ratio$^a$</th>
<th>% conversion$^b$</th>
<th>$M_n$ $^c$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>Sn(Oct)$_2$</td>
<td>50:1</td>
<td>96</td>
<td>12000</td>
<td>2.47</td>
</tr>
<tr>
<td>CaO</td>
<td>50:1</td>
<td>94</td>
<td>11000</td>
<td>1.70</td>
</tr>
<tr>
<td>BaO</td>
<td>25:1</td>
<td>95</td>
<td>3000</td>
<td>1.44</td>
</tr>
<tr>
<td>MgO</td>
<td>25:1</td>
<td>92</td>
<td>7100</td>
<td>2.23</td>
</tr>
<tr>
<td>ZnO</td>
<td>50:1</td>
<td>63</td>
<td>14200</td>
<td>2.94</td>
</tr>
<tr>
<td>CaCO$_3$</td>
<td>50:1</td>
<td>79</td>
<td>3600</td>
<td>1.33</td>
</tr>
<tr>
<td>MgCO$_3$</td>
<td>50:1</td>
<td>88</td>
<td>5200</td>
<td>1.89</td>
</tr>
<tr>
<td>TUMS®</td>
<td>50:1</td>
<td>76</td>
<td>2100</td>
<td>1.21</td>
</tr>
<tr>
<td>Ca$_{10}$(PO$<em>4$</em>)$_6$(OH)$_2$</td>
<td>25:1</td>
<td>29</td>
<td>3400</td>
<td>1.42</td>
</tr>
<tr>
<td>Rolaids®</td>
<td>50:1</td>
<td>76</td>
<td>2100</td>
<td>1.21</td>
</tr>
<tr>
<td>Goldline® Pink</td>
<td>100:1</td>
<td>98</td>
<td>14700</td>
<td>1.27</td>
</tr>
<tr>
<td>Pepto-Bismol®</td>
<td>100:1</td>
<td>100</td>
<td>23700</td>
<td>1.30</td>
</tr>
<tr>
<td>Pepto-Bismol® (Kroger)</td>
<td>100:1</td>
<td>98</td>
<td>4800</td>
<td>1.72</td>
</tr>
</tbody>
</table>

$^a [L-$LA$_{10}$]:[initiator]$_0$ ratio, all the polymerization reactions were carried out for 65 hours at 130°C. $^b$ Percentage conversion was obtained by \textit{\textsuperscript{1}H NMR spectroscopy.} $^c$ Determined by GPC relative to polystyrene standards in THF. The experimental M$_n$ was calculated considering Mark-Houwink’s corrections for M$_n$ (M$_n$(obsd) = 0.56[M$_n$(GPC)]).
Table 5: Comparative ROP data for LA employing Pepto-Bismol®, PB (Kroger) and Sn(Oct)$_2$

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ratio$^a$</th>
<th>Time</th>
<th>% Conversion$^b$</th>
<th>$M_n$$^c$</th>
<th>PDI</th>
<th>Pr$^d$</th>
</tr>
</thead>
<tbody>
<tr>
<td>PB-L-LA</td>
<td>100:1</td>
<td>1.5 h</td>
<td>~100</td>
<td>25648</td>
<td>1.39</td>
<td>-</td>
</tr>
<tr>
<td>PB-rac-LA</td>
<td>100:1</td>
<td>1.5 h</td>
<td>~100</td>
<td>21392</td>
<td>1.35</td>
<td>0.76</td>
</tr>
<tr>
<td>PB-rac-LA</td>
<td>1000:1</td>
<td>4 h</td>
<td>78</td>
<td>87340</td>
<td>1.63</td>
<td>0.75</td>
</tr>
<tr>
<td>PB-L-LA</td>
<td>1000:1</td>
<td>4 h</td>
<td>86</td>
<td>112000</td>
<td>1.61</td>
<td>-</td>
</tr>
<tr>
<td>PB(K)-L-LA</td>
<td>100:1</td>
<td>1.5 h</td>
<td>&gt;98</td>
<td>4300</td>
<td>1.67</td>
<td>-</td>
</tr>
<tr>
<td>Sn(Oct)$_2$-L-LA</td>
<td>100:1</td>
<td>1.5 h</td>
<td>~100</td>
<td>65880</td>
<td>1.71</td>
<td>-</td>
</tr>
<tr>
<td>PB(K)-rac-LA</td>
<td>100:1</td>
<td>1.5 h</td>
<td>99</td>
<td>6510</td>
<td>1.37</td>
<td>0.74</td>
</tr>
<tr>
<td>Sn(Oct)$_2$-rac-LA</td>
<td>100:1</td>
<td>1.5 h</td>
<td>~100</td>
<td>32140</td>
<td>1.63</td>
<td>0.74</td>
</tr>
<tr>
<td>MW-PB-L-LA$^e$</td>
<td>100:1</td>
<td>10 min</td>
<td>80</td>
<td>37520</td>
<td>1.37</td>
<td>-</td>
</tr>
<tr>
<td>MW Sn(Oct)$_2$-L-LA$^e$</td>
<td>100:1</td>
<td>10 min</td>
<td>84</td>
<td>33600</td>
<td>1.28</td>
<td>-</td>
</tr>
<tr>
<td>MW-PB-K-L-LA$^e$</td>
<td>100:1</td>
<td>10 min</td>
<td>86</td>
<td>5100</td>
<td>1.64</td>
<td>-</td>
</tr>
</tbody>
</table>

$^a$ [L-lactide]$_0$:[initiator]$_0$ ratio, all the polymerization reactions were carried out at 110°C.
$^b$ Percentage conversion was obtained by $^1$H NMR spectroscopy.
$^c$ Determined by GPC relative to polystyrene standards in tetrahydrofuran. The experimental $M_n$ was calculated considering Mark-Houwink’s corrections for $M_n$(obsd) = 0.56[$M_n$(GPC)].
$^d$ Determined from decoupled $^1$H NMR by Pr = 2$I_1$/($I_1$ + $I_2$), with $I_1$ = 5.20-5.25 ppm (rmm, mm/m, rmm, mrm), $I_2$ = 5.13-5.20 ppm (mm/m, mm/m, mrm, mrm). e. Polymerization reactions were carried out for 10 minutes in a microwave oven. Where PB- Pepto-Bismol®, PB-K-Kroger brand Pepto-Bismol® and MW- microwave assisted polymerization.

The plots in Figure 19 and Figure 20 show the living polymerization of LA and that the rate of polymerization is two fold faster for [Sn] relative to [Bi]. One notable difference is that the polymers derived from Pepto-Bismol® have a bimodal molecular weight distribution. The active ingredient in Pepto-Bismol® is BSS [C$_7$H$_5$BiO$_4$] and the empirical structure is depicted below:

![Empirical Structure](image-url)
Figure 19: Conversion of LA as a function of time for the polymerization of $L$-LA initiated by (a) Sn(Oct)$_2$ and (b) Pepto-Bismol$^\text{®}$. The comparative reaction was carried out for the ratio $L$-LA: Catalyst=100:1 at 110 $^\circ$C.

Figure 20: Linear plots of $\ln([LA]_0/[LA]_t)$ versus time (min) for the melt polymerization of $L$-LA initiated by (a) Sn(Oct)$_2$ and (b) Pepto-Bismol$^\text{®}$. The comparative reaction was carried out for the ratio $L$-LA: Catalyst=100:1 at 110 $^\circ$C.
Given the large size of Bi(3+), 117 pm, it is likely that the active species is not mononuclear and the structure of BSS is not known. However, there are a number of other additives present in Pepto-Bismol®, namely calcium, sodium, salicylate, sugar free, calcium carbonate, magnesium stearate, mannitol, microcrystalline cellulose, polysorbate 80, povidone, red 27 aluminum-lake, silicon dioxide, and sodium starch glycolate. Also Kroger sells an equivalent antacid to Kroger brand Pepto-Bismol® (PB-Kroger) based on BSS that has higher relative calcium content and this yielded lower molecular weight polymers relative to Pepto-Bismol®. For these reasons we believed that the additives were improving to polymerization reaction and we examined the use of commercially available BSS.

The results of employing a commercial source BSS are shown in Table 6, which can be compared with the use of tin(II) octanoate shown in Table 5. Furthermore, microwave assisted polymerization employing Pepto-Bismol® and Sn(Oct)₂ were successful within few minutes, yielding ~75% conversion of 100 equivalent of LA. Pepto-Bismol® or BSS generates heterotactic enriched PLA from rac-LA. A comparison of the homo-decoupled methine resonances for the PLA produced from rac-LA with BSS, Pepto-Bismol®, Pepto-Bismol® (Kroger) and Sn(Oct)₂ is shown in Figure 21. Pepto-Bismol® and BSS clearly yield a heterotactic PLA compared with Sn(Oct)₂ or Kroger brand Pepto-Bismol®.
Figure 21: $^1$H NMR spectra (CDCl$_3$, 400 MHz) of the homodecoupled CH resonance of poly(rac-lactide) processed in CH$_2$Cl$_2$ using (a) Sn(Oct)$_2$, (b) Pepto-Bismol(Kroger), (c) BSS, and (d) Pepto-Bismol® as initiators.

As a melt polymerization catalyst BSS was just slightly less active than Sn(Oct)$_2$ based on its empirical formula. Since BSS is a polymeric material of unknown structure, based on the fact that only a few active sites were present when the BSS powder was employed. Interestingly, no well-defined bismuth alkoxide has been employed in the ROP of LAs, though Kricheldorf$^{84,85}$ has reported that bismuth alkanoates Bi(O$_2$CR)$_3$ may be used as initiators. Here presumably the reactions proceed similar to Sn(Oct)$_2$ due to adventitious water (Scheme 13). We report the use of counter oral aids/ dietary supplements and the single site Bi(III) alkoxide complexes for the ROP. The Bi catalysts were more active than the Sn(Oct)$_2$ and related Al catalysts for the ROP of LA in the comparable conditions.
Table 6: ROP data for PLA formation employing bismuth subsalicylate (BSS)

<table>
<thead>
<tr>
<th>Entry</th>
<th>Ratio(^a)</th>
<th>Time(h)</th>
<th>%Conversion(^b)</th>
<th>(M_n)(^c)</th>
<th>PDI</th>
<th>(P_r)(^d)</th>
</tr>
</thead>
<tbody>
<tr>
<td>BSS-L-LA</td>
<td>100:1</td>
<td>1.5</td>
<td>98</td>
<td>27980</td>
<td>1.52</td>
<td>-</td>
</tr>
<tr>
<td>BSS-rac-LA</td>
<td>100:1</td>
<td>1.5</td>
<td>93</td>
<td>18600</td>
<td>1.35</td>
<td>0.78</td>
</tr>
<tr>
<td>BSS-L-LA</td>
<td>1000:1</td>
<td>4</td>
<td>92</td>
<td>63390</td>
<td>1.54</td>
<td>-</td>
</tr>
<tr>
<td>BSS-rac-LA</td>
<td>1000:1</td>
<td>4</td>
<td>97</td>
<td>56400</td>
<td>1.41</td>
<td>0.82</td>
</tr>
</tbody>
</table>

\(^a\) \([L\text{-lactide}]_0:[\text{initiator}]_0\) ratio, all the polymerization reactions were carried out at 110 °C.

\(^b\) Percentage conversion was obtained by \(^1\)H NMR spectroscopy.

\(^c\) Determined by GPC relative to polystyrene standards in tetrahydrofuran. The experimental Mn was calculated considering Mark_Houwink’s corrections for \(M_n\) (\(M_n\)(obsd) = 0.56[\(M_n\)(GPC)]).

\(^d\) Determined from decoupled \(^1\)H NMR by \(P_r = 2I_1/(I_1 + I_2)\), with \(I_1 = 5.20\text{-}5.25\) ppm (rmm, mmr/rmm), \(I_2 = 5.13\text{-}5.20\) ppm (mmr/mm, mmm, mrm).

The enhanced heterotacticity in the polymerization of rac-LA certainly reflects the presence of steric crowding around the active site. Additionally, the molecular weight of the resulting polymer is higher than the calculated \(M_w\), which indicates that BSS clusters or oligomeric forms allows only certain active sites for the ROP. Solid state \(^{13}\)C NMR of BSS exhibits (Figure 22) broad peaks clearly show that aromatic carbons of salicylic acid component are in different chemical environment, which could be an indication of oligomeric nature of BSS.
Additionally, Pepto-Bismol® and BSS are active for the homo polymerization ε-CL, to yield PCL, as well as the co-polymerization of rac-LA and L-LA with CL. The resulting polymers indicate the presence of homo-polymer of PCL, PLA and random co-polymer of PLA/PCL (See Figure 23 for the $^1$H NMR spectra of the random copolymer of PLA PCL and the co-polymer of PCL/PLA).

The activity of the BSS and Pepto-Bismol® for the ROP of LA and ε-CL motivated us to synthesize the single site Bi catalysts.
Figure 23: $^1$H NMR spectra (CDCl$_3$, 400 MHz) of the homo polymers of poly-rac-lactide, poly-$\varepsilon$-caprolactone, and the copolymer of rac-LA with CL prepared with Pepto-Bismol$^\circledR$ in the methane and methylene proton regions.

### 2.2.2 Synthesis of single-site Bi catalysts

Salen based and porphyrin based ligands were employed towards the synthesis of single-site bismuth complexes. The salen-type ligands with different back-bone employed in this study are shown in Figure 24. The ligands were synthesized by the condensation reaction employing 3,5-di-tert-butylsalisaldehyde and their corresponded diamines namely ethylene diamine, 1,2-cyclohexyldiamine or otho-phenyl diamine. The resulting ligands were abbreviated as en-salen, cy-salen and ph-salen, respectively.
Two synthetic procedures have been employed toward the synthesis of the salenBi(OR). The first synthesis involves with reactions of Bi[N(SiMe₃)₂]₃ with the free salen-H₂ ligands to yield salenBiN(SiMe₃)₂. Then, the resulting salenBiN(SiMe₃)₂ was allowed to react with the appropriate alcohol, acids, or phenol to produce their corresponded salenBi(OR). The second synthetic procedure involves with the synthesis of salenBiCl by the direct reaction between BiCl₃ and Na₂salen or via the reaction between Bi[N(SiMe₃)₂]₂Cl and the free salen-H₂ ligand according to the Scheme 14. Then the corresponded salenBi(OR) was synthesized by a metathetic reaction involving KOR.

Scheme 14: Reaction scheme for the general synthesis of salenBiOR
Most of the complexes were soluble in toluene, hexane, pentane, THF and dichloromethane. However, chloroform was often found to be reactive with alkoxides with time. Presumably, the decomposition occurs similar to well-known reaction between bases and CDCl₃ via elimination of HCl. Ph-salenBiCl and ph-salenBiOCOPh were found to be less soluble compared with their corresponded alkoxides or phenoxides. The solubility of several of these alkoxides were often found to be a problem for obtaining suitable crystals for single crystal X-ray diffraction studies.

2.2.2.1 Single crystal X-ray studies

Several attempts were made to obtain a full structural determination of various tert-butoxides but with no success. In all cases we observed sample decomposition in the X-ray beam or upon placing the sample within the oil employed for air-sensitive work. Decomposition in the oil may be due to either solvent of crystallization loss or fast sample decomposition. We were, however, able to obtain crystals of a phenoxide derivative and note that the molecular structure of the homoleptic phenoxides Bi(OC₆H₃-2,6-R₂)₃ where R = Ph, Pr₈₆ or Me₈₇ are known to be monomeric while that of the pentafluoro-phenoxide complex is dimeric.₈₈,₈₉ Other alkoxides of the form Bi(OR)₃ are polymeric and the ethoxide has been shown to have a cyclic octameric structure[Bi(OEt)₃]₈·(7+x)EtOH.₉₀ As a structural model for a salenBi(OR) compound, where R = Me or Et, we have examined the molecular structure of a salenBiCl. For a
bulky alkoxide or aryloxide we might anticipate a monomeric salenBi(OR) structure but for a lesser steric demanding group we anticipate a higher degree of aggregation.

2.2.2.2 SalenBiCl structure

En-salenBiCl(1) and cy-salenBiCl(2) were synthesized and characterized in this study including single X-ray crystallography. The crystallographic data for these compounds are summarized in Table 7. The en-salenBiCl was a twinned data set and it also suffered from disorder of various types of solvent molecules. As a result, it was necessary to use many restraints in the refinement of the model, and the final results are less than optimal. However, the structure clearly indicates an arrangement of tetranuclear \([\text{BiCl}]_4\) units, which indicate the ability of the Bi(III) ions to establish six-coordination by formation of a tetranuclear aggregate as opposed to a more simple dimeric structure.

The central \([\text{BiCl}]_4\) core is shown in Figure 25 where the \(\kappa^4\)-en-salen ligands have been omitted. This 8 membered ring contains a non-crystallographic two-fold rotation axis through its center and a boat conformation.
The molecular structure of the cy-salenBiCl was more successfully determined and its dimeric chloride bridged structure is shown in Figure 26. There is a planar [BiCl]₂ unit supported by κ⁴-cy-salen ligands. Also we see that the N₂O₂ unit of the cy-salen ligand is planar or near planar and as such the central N₂O₂BiCl₂ core can simply be described as being derived from an octahedral geometry. The view in Figure 26 which is almost parallel to the Bi₂Cl₂ plane emphasizes the tilt of the two cy-salen ligands which allows one to speculate that this distortion arises from what can be termed a stereochemically active lone-pair. The present structure is seemingly most closely related to that of tpClppBiCl (tpClpp=5,10,15,20-tetra-p-chlorophenylporphyrin)⁰¹ except that the latter structure does not clearly implicate a stereochemically active lone pair.
Figure 26: ORTEP representations of [cy-salenBiCl]$_2$ (Orange = Bismuth, Green = Chlorine, Scarlet = Oxygen, Blue = Nitrogen, Gray = Carbon) drawn at 50% probability. Hydrogen atoms, solvent molecules and tert-butyl groups are excluded for clarity.

In the view shown in Figure 26, the two “lone pairs” would be mutually anti as indicated in the simple representation shown below in diagram I.

Diagram 1: Sketch of the locations and influence of the stereochemically active lone-pairs in [cy-salenBiCl]$_2$. 
Table 7: Selected crystallographic information for en-salenBiCl(1), [cy-salenBiCl]_2(2), cy-salenBiOC_6H_3-2,6-Bu(3), and salenBiOCMe_2CO_2Et (4)

<table>
<thead>
<tr>
<th>Compound</th>
<th>3</th>
<th>2</th>
<th>1</th>
<th>4</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{30}H_{73}BiN_2O_3</td>
<td>C_{30}H_{12}Bi_2Cl_4N_2O_4</td>
<td>C_{128}H_{184}Bi_4Cl_4N_8O_8</td>
<td>C_{44}H_{68}BiN_2O_5</td>
</tr>
<tr>
<td>Formula weight</td>
<td>959.08</td>
<td>1918.16</td>
<td>3124.01</td>
<td>917.49</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2) K</td>
</tr>
<tr>
<td>Space group</td>
<td>Triclinic, P-1</td>
<td>Monoclinic, P2_1/n</td>
<td>Orthorhombic, P2_1_2_1_2_1</td>
<td>Triclinic</td>
</tr>
<tr>
<td>a (Å)</td>
<td>12.4091(1)</td>
<td>15.2904(5)</td>
<td>17.4471(3)</td>
<td>9.2610(3)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>14.7848(2)</td>
<td>10.4994(3)</td>
<td>17.4510(3)</td>
<td>14.6556(4)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>14.9983(1)</td>
<td>27.3011(8)</td>
<td>58.3860(11)</td>
<td>33.9761(10)</td>
</tr>
<tr>
<td>α (°)</td>
<td>110.801(1)</td>
<td>110.801(1)</td>
<td>110.801(1)</td>
<td>110.801(1)</td>
</tr>
<tr>
<td>β (°)</td>
<td>102.945(1)</td>
<td>102.945(1)</td>
<td>102.945(1)</td>
<td>102.945(1)</td>
</tr>
<tr>
<td>γ (°)</td>
<td>100.046(1)</td>
<td>100.046(1)</td>
<td>100.046(1)</td>
<td>100.046(1)</td>
</tr>
<tr>
<td>V (Å³)</td>
<td>2407.55(4)</td>
<td>4257.2(2)</td>
<td>17776.7(5)</td>
<td>4524.7(2)</td>
</tr>
<tr>
<td>Z</td>
<td>2</td>
<td>2</td>
<td>4</td>
<td>4</td>
</tr>
<tr>
<td>Dcalcd (Mg/m³)</td>
<td>1.323</td>
<td>1.496</td>
<td>1.167</td>
<td>1.347</td>
</tr>
<tr>
<td>Crystal Size (mm)</td>
<td>0.19 X 0.12 X 0.12</td>
<td>0.12 X 0.10 X 0.08</td>
<td>0.19 x 0.19 x 0.35</td>
<td>0.360 x 0.360 x 0.310</td>
</tr>
<tr>
<td>Theta range for data collection</td>
<td>1.66 to 27.48°</td>
<td>1.72 to 25.03°</td>
<td>1.05 to 25.19°</td>
<td>1.221 to 27.658°</td>
</tr>
<tr>
<td>μ(Mo, Kα) (mm⁻¹)</td>
<td>3.701</td>
<td>4.888</td>
<td>4.06</td>
<td>3.939</td>
</tr>
<tr>
<td>F(000)</td>
<td>988</td>
<td>1928</td>
<td>6297</td>
<td>1884</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>51970</td>
<td>63237</td>
<td>214449</td>
<td>135703</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>11011 [R(int) = 0.040]</td>
<td>7490 [R(int) = 0.112]</td>
<td>31482, [R(int) = 0.085]</td>
<td>20812 [R(int) = 0.0821]</td>
</tr>
<tr>
<td>Completeness to θmax</td>
<td>99.90%</td>
<td>99.60%</td>
<td>98.70%</td>
<td>100%</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>51970 / 0 / 542</td>
<td>63237 / 0 / 433</td>
<td>214449 / 206/1426</td>
<td>135703 / 5 / 923</td>
</tr>
<tr>
<td>R1 (%) (all data)</td>
<td>2.40 (6.08)</td>
<td>6.92 (9.95)</td>
<td>5.43 (7.86)</td>
<td>0.0464</td>
</tr>
<tr>
<td>wR2 (°) (all data)</td>
<td>3.31 (8.33)</td>
<td>18.44 (20.20)</td>
<td>13.25 (14.39)</td>
<td>10.62</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.198</td>
<td>1.046</td>
<td>1.047</td>
<td>1.21</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>2.154 and -0.941</td>
<td>5.126 and -2.851</td>
<td>1.748 and -0.851</td>
<td>1.886 and -1.581</td>
</tr>
</tbody>
</table>

\[ aR1 = \frac{\sum |F_o| - |F_c|}{\sum |F_o|} \times 100 \]

\[ bW(R2) = \frac{\sum w(F_o^2 - F_c^2)^2}{\sum (wF_o^2)^2} \times 100 \]

54
Selected bond distances and angles for \([\text{cy-salenBiCl}_2]\) are given in Table 8.

<table>
<thead>
<tr>
<th>Compound 2</th>
<th>Bi(1)-O(2)</th>
<th>2.154(7)</th>
<th>Bi(1)-Cl(1)</th>
<th>2.932(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Bi(1)-O(1)</td>
<td>2.233(7)</td>
<td>Bi(1)-N(2)</td>
<td>2.404(8)</td>
<td></td>
</tr>
<tr>
<td>Bi(1)-N(1)</td>
<td>2.325(8)</td>
<td></td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

<table>
<thead>
<tr>
<th></th>
<th>O(2)-Bi(1)-O(1)</th>
<th>74.6(3)</th>
<th>O(2)-Bi(1)-N(1)</th>
<th>79.3(3)</th>
</tr>
</thead>
<tbody>
<tr>
<td>O(1)-Bi(1)-N(1)</td>
<td>115.9(3)</td>
<td></td>
<td>O(2)-Bi(1)-N(2)</td>
<td>118.6(3)</td>
</tr>
<tr>
<td>O(1)-Bi(1)-N(2)</td>
<td>74.7(3)</td>
<td></td>
<td>N(1)-Bi(1)-N(2)</td>
<td>68.7(3)</td>
</tr>
<tr>
<td>O(2)-Bi(1)-Cl(1)</td>
<td>82.50(19)</td>
<td></td>
<td>O(1)-Bi(1)-Cl(1)</td>
<td>147.7(2)</td>
</tr>
<tr>
<td>N(1)-Bi(1)-Cl(1)</td>
<td>80.9(2)</td>
<td></td>
<td>N(2)-Bi(1)-Cl(1)</td>
<td>137.3(2)</td>
</tr>
<tr>
<td>C(22)-N(1)-Bi(1)</td>
<td>125.7(7)</td>
<td></td>
<td>C(21)-N(1)-Bi(1)</td>
<td>110.4(6)</td>
</tr>
<tr>
<td>C(15)-N(2)-Bi(1)</td>
<td>121.7(7)</td>
<td></td>
<td>C(16)-N(2)-Bi(1)</td>
<td>116.3(6)</td>
</tr>
</tbody>
</table>

### 2.2.2.3 SalenBi-phenoxide structure

The molecular structure of cy-salenBiOC₆H₆·2,6-Bu’₂ (3) is shown in Figure 27. This structure can easily be described as that of a distorted square based pyramid. The view shown in Figure 28 emphasizes again the presence of the “stereochemically active lone pair”. Not only does this influence the N₂O₂BiO geometry but also it influences the Bi-O-C angle which is 130.7°. Typically in terminal metal-phenoxide bonds we see linear M-O-C angles. This is favored by the oxygen lone pair interaction with the π-system of the aryl ring and often in transition metal complexes by Mdπ-Opπ bonding. In the present case if we assume a linear M-O-C moiety one of the oxygen pπ orbitals would be forced into a filled-filled orbital interaction with the Bi lone-pair. By rehybridization toward sp² this interaction is minimized as schematically represented below in Figure 28.
Figure 27: (Left) ORTEP representation of cy-salenBiOC₆H₃-2,6-′Bu (Orange = Bismuth, Scarlet = Oxygen, Blue = Nitrogen, Gray = Carbon) drawn at 50% probability. Hydrogen atoms excluded for clarity. (Right) ORTEP representation of cy-salenBiOC₆H₃-2,6-′Bu' (with tert-butyl groups removed for clarity) and emphasizing the nature of the BiO₃N₂ core.

Figure 28: Minimization of lone pair – lone pair interactions

A summary of crystallographic data for the three molecules described above is given in Table 7 and selected bond distances for cy-salenBiOC₆H₃-2,6-′Bu'₂ and bond angles are given in Table 9.
Table 9: Selected bond distances (Å) and bond angles (deg.) for cy-salenBiOC₆H₅-2,6-Bu′₂.

<table>
<thead>
<tr>
<th>Compound 1</th>
<th></th>
<th></th>
<th></th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1)-Bi</td>
<td>2.335(3)</td>
<td>N(2)-Bi</td>
<td>2.343(3)</td>
</tr>
<tr>
<td>O(1)-Bi</td>
<td>2.237(3)</td>
<td>O(2)-Bi</td>
<td>2.260(2)</td>
</tr>
<tr>
<td>O(3)-Bi</td>
<td>2.324(2)</td>
<td>N(1)-C(16B)</td>
<td>1.478(9)</td>
</tr>
<tr>
<td>N(1)-C(16A)</td>
<td>1.569(7)</td>
<td>N(2)-C(21A)</td>
<td>1.506(6)</td>
</tr>
<tr>
<td>N(2)-C(21B)</td>
<td>1.554(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>C(37)-O(3)-Bi</td>
<td>130.7(2)</td>
<td>C(24)-O(2)-Bi</td>
<td>117.5(2)</td>
</tr>
<tr>
<td>C(1)-O(1)-Bi</td>
<td>132.7(2)</td>
<td>O(1)-Bi-O(2)</td>
<td>83.54(9)</td>
</tr>
<tr>
<td>O(1)-Bi-O(3)</td>
<td>133.96(9)</td>
<td>O(2)-Bi-O(3)</td>
<td>142.05(9)</td>
</tr>
<tr>
<td>O(1)-Bi-N(1)</td>
<td>77.66(10)</td>
<td>O(2)-Bi-N(1)</td>
<td>111.38(11)</td>
</tr>
<tr>
<td>O(3)-Bi-N(1)</td>
<td>67.72(10)</td>
<td>O(1)-Bi-N(2)</td>
<td>128.87(12)</td>
</tr>
<tr>
<td>O(2)-Bi-N(2)</td>
<td>74.73(11)</td>
<td>O(3)-Bi-N(2)</td>
<td>82.11(11)</td>
</tr>
<tr>
<td>N(1)-Bi-N(2)</td>
<td>68.72(11)</td>
<td>C(22)-N(2)-Bi</td>
<td>123.8(3)</td>
</tr>
</tbody>
</table>

2.2.2.4 SalenBiOCMe₂CO₂Et (4) structure

The molecular structure of SalenBiOCMe₂CO₂Et (4) is shown in Figure 29. The crystallographic data is summarized in Table 7.

Figure 29: (Left) ORTEP representation of cy-salenBiOCMe₂CO₂Et (Orange = Bismuth, Scarlet = Oxygen, Blue = Nitrogen, Gray = Carbon) drawn at 50% probability. Hydrogen atoms excluded for clarity. (Right) ORTEP representation of cy-salenBi OCMeeCO₂Et (with tert-butyl groups removed for clarity) and emphasizing the nature of the BiO₄N₂ core.
The BiN$_2$O$_4$ core can easily be described as an octahedral geometry. The ligand OCMe$_2$COOEt is cheated by the carbonyl group of the ester group and it is present in the solid and solution state.

2.2.3 Ring-opening polymerization of lactide

Both the tert-butoxide and the phenoxide complexes with the cy-salen supporting ligands are active in the ROP of L- and rac-lactide in either toluene or dichloromethane solutions at room temperature. Interestingly, the polymerization of rac-LA proceeds to give predominantly heterotactic PLA with isi and sis tetrads. The preference for the alternating ring-opening of L and D lactides is given by $P_r \sim 0.9$ when reactions are carried out to 80% completion. The spectrum of a sample of heterotactic PLA is given in Figure 30.

Figure 30: $^1$H NMR spectra (CDCl$_3$, 400 MHz) of the homodecoupled CH resonance of poly(rac-lactide) obtained by cy-salenBiOBu' as initiator. For details of assignments see reference.\textsuperscript{92}

58
We have also studied the kinetics of these polymerizations involving the initiator cy-salenBiOC₆H₃-2,6-Bu′₂ at room temperature in dichloromethane. Plots of \(\ln([\text{LA}]_0/[\text{LA}]_t)\) versus time are shown in Figure 31 and reveal the living polymerization by the catalyst system and moreover, that the order of polymerization is the first order in [Bi]. The plot of \(-\ln k_{\text{app}} \text{ versus } -\ln[\text{cat}]\) is shown in Figure 32. The \(k_p\) value of \(5 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}\) is notably faster than any salenAl(OR) system and just a little slower than the most active Zn based catalyst systems. The \(k_p\) value for the polymerization of rac-LA by cy-salenBiOBu′ is \(9.2 \times 10^{-2} \text{ M}^{-1}\text{s}^{-1}\) in toluene at room temperature. For a direct comparison with cy-salenAlOPr which has \(k_p = 9.02 \times 10^{-3} \text{ M}^{-1}\text{s}^{-1}\) at 70°C in toluene, we note that the bismuth complex is \(\sim 10\) times faster at room temperature.

Figure 31: Linear plots of \(\ln([\text{LA}]_0/[\text{LA}]_t)\) versus time (min) for the polymerization of rac-LA initiated by cy-salenBiOC₆H₃-2,6-Bu′₂ in CH₂Cl₂ at room temperature.
2.3 Reactivity of \( \varepsilon \)-caprolactone/ propylene oxide with ph-salenBiO'Bu

The homopolymerization reactions of \( \varepsilon \)-caprolactone and propylene oxide were unsuccessful in neat or in DCM at room temperature by ph-salenBiO'Bu. We have not seen any indication for the polycaprolactone or polypropyleneoxide formation even in 2 days.

2.4 Polymerization of epoxides with CO\(_2\) by TPPBiI

The preliminarily reactions of epoxides with CO\(_2\) at 50 bar at room temperature produce cyclic carbonate. There is no observation for the formation of ethers or
polycarbonates. Additionally, the addition of co-catalyst found to enhance the reactivity. The initial results for the copolymerization of epoxides with CO₂ by TPPBiI are summarized in Table 10.

Table 10: Copolymerization of epoxides and CO₂ by TPPBiI

<table>
<thead>
<tr>
<th>Entry</th>
<th>Epoxide</th>
<th>% of cyclic carbonate</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>Propyleneoxide</td>
<td>26</td>
</tr>
<tr>
<td>2</td>
<td>Cyclohexeneoxide</td>
<td>17</td>
</tr>
<tr>
<td>3</td>
<td>Styreneoxide</td>
<td>9</td>
</tr>
<tr>
<td>4</td>
<td>Propyleneoxide + PPN⁺Cl⁻</td>
<td>32</td>
</tr>
</tbody>
</table>

0.05 mmol TPPBiI reacted with 2 mL rac-PO in a stainless steel Vessel at 50 bar CO₂ for 24 h at room temperature. After 24 h, the reaction mixture was quenched with 0.5 M acidic MeOH and the conversion was monitored by ¹H-NMR. In addition, PPN⁺Cl⁻ also added as a co-catalyst for some of the reactions.

The above preliminary results show that the bismuth catalysts have the potential towards the cyclic carbonate synthesis using bismuth catalysts.

2.5 Concluding remarks

From the above studies it is apparent that Pepto-Bismol® is an effective initiator for the polymerization of lactide and in many ways similar to that of tin(II) octanoate. A feature common to both Sn(Oct)₂ and bismuth(III) subsalicylate is the living nature of the equilibrium involving the hydroxyl group. Neither system is “poisoned” by the presence of trace quantities of water and indeed for Sn(Oct)₂ this is required for the initiation of the reaction. Both systems yield polymers that are hydroxyl terminated and this is clearly seen in the MALDI-TOF mass spectrum. Both systems also participate in trans-esterifications yielding PDI values of 1.3 to 2.0. We also note that Kricheldorf, in his proceeding work on the ring-opening of lactide and cyclic ester employed bismuth(III)
alkanoates (acetates, octanoates, and hexanoates) in melt or solution phase polymerizations and noted that Bi(III) alkanoates were similar in action to Sn(Oct)$_2$. The polymers also had hydroxyl end groups implicating a reversible reaction:

$$\text{Bi-alkanoate} + H_2O \leftrightarrow \text{Bi-OH} + \text{alkanoic acid}$$

The latter work describes the synthesis of the first Bi containing single-site catalyst and their applications for the ROP of lactide at room temperature. The reactivity of Bi-OR bond is greater than that of aluminum alkoxides of related formula and notably much more active than Sn(Oct)$_2$ at room temperature. The compounds of formula salenBiOR are, however, regrettably not tolerant to water which is clearly a limiting feature when compared to Sn(Oct)$_2$ or bismuth subsalicylate. The reaction with water is believed to lead to ligand scrambling and crystals of a bismuth salen complex of formula (en-salen)Bi(en-salenH) have been obtained.

### 2.6 Experimental and general conditions

Calcium hydroxyapatite, Pepto-Bismol$^\text{®}$, TUMS, and Rolaids$^\text{®}$ were purchased from local grocery stores and used as received. BaO, CaO, CaCO$_3$, MgO, MgCO$_3$, ZnO, Sn(Oct)$_2$, BiCl$_3$, LiN(SiMe$_3$)$_2$, 1,2-cyclohexanediaine, ethylenediamine, ortho-aminoaniline, anhydrous Bu$'$OH, anhydrous Pr$'$OH, 2,6-di-Bu$'$C$_6$H$_3$OH, chloroform, methanol, ethanol, hydrochloric acid, dicholoro methane, ε-caprolactone, and bismuth subsalicylate(BSS) were purchased from Sigma Aldrich and used without further purification. $L$-Lactide ($L$-LA), and rac-Lactide ($rac$-LA) were purchased from Sigma Aldrich, and purified by sublimation, followed by recrystallization in dry toluene. Then
the lactides were dried under reduced pressure at 40°C overnight. Chloroform-$d$, toluene-$d_8$, THF-$d_8$ and benzene–$d_6$ were purchased from Cambridge Isotopes and distilled under nitrogen over CaH$_2$. Pentane, hexane, $\varepsilon$-caprolactone, THF, toluene, and dichloromethane were distilled under nitrogen over CaH$_2$. 3,5-Di-tert-butylsalicylaldehyde was purchased from Alfa Aesar. All the air moisture sensitive experiments were carried out under a rigorously dried nitrogen atmosphere either using Schlenk techniques or a glove box. Bi[N(SiMe$_3$)$_3$]$_3$ and TPPBiI was prepared according to the literature procedure. Tetraphenylporphyrin(TPPH$_2$) and Octaethyl porphyrin(OEPH$_2$) were purchased from Frontier Scientific.

2.6.1 Measurements

$^1$H and $^{13}$C NMR spectra were recorded in CDCl$_3$ ($\delta$: 7.26), C$_7$D$_8$($\delta$: 2.08) , THF ($\delta$: 3.58) or C$_6$D$_6$ ($\delta$: 7.15) and $^{13}$C$_6$D$_6$ ($\delta$: 128.06) on Bruker DPX-400 NMR or DRX-500 NMR spectrometers and referenced against the $^1$H or $^{13}$C signal quoted. Gel permeation chromatography (GPC) measurements were carried out using a Waters 1525 binary HPLC pump and Waters 1525 differential refractometer equipped with styrageal HR 2 and 4 columns (100 to 1000 Å). THF was used as an eluent at 1 mL/min at 40 °C and the calibration was done with polystyrene standards. MALDI-TOF mass spectra were collected on a Bruker Microflex mass spectrometer 28 kV.
2.6.2 General procedure for bulk lactide polymerization

A mixture of 0.500 g (3.47 mmol) of L-LA/ rac-LA and appropriate amount of finely powdered initiator (0.037 mmol initiator for [LA]/[Initiator] = 100 and 3.7×10⁻³ mmol initiator for [LA]/[Initiator]=1000) were loaded in 5 mL glass ampoules and sealed under vacuum. Then the ampoules were immersed in a thermo stated oil bath at 120 °C for appropriate time. The resultant polymer was purified by dissolving in CHCl₃/CH₂Cl₂ (initiator was settled on the bottom of the vial). The supernatant liquid was transferred into another flask. The polymerization was quenched in excess acidic methanol and dried under high vacuum and the conversion was estimated by ¹H NMR spectroscopy.

2.6.3 General procedure for microwave assisted LA polymerization

A mixture of 0.500 g (3.47 mmol) of L-LA and an appropriate amount of finely powdered initiator (0.037 mmol initiator for [LA]/[Initiator]=100) were loaded in 5 mL glass ampoules and sealed under vacuum. Then the ampoules were placed in a microwave for appropriate time (2-10 minutes) and the polymers were processed according to the general procedure for bulk lactide polymerization.

2.6.4 General procedure for kinetic studies of bulk rac-LA polymerization

A mixture of 0.500 g (3.47 mmol) of L-LA and 35 mg of finely powdered Pepto-Bismol® (or 14 mg of Sn(Oct)₂) initiator (0.037 mmol initiator for [L-
LA]/[Initiator]=100) were loaded in 5 mL glass ampoules and sealed under vacuum. Then the ampoules were immersed in a thermo stated oil bath at 110 °C for an appropriate time. At appropriate time intervals vials the polymers were processed similar to the general procedure for lactide polymerization.

2.6.5 General procedure for bulk ε-CL polymerization

A mixture of 0.400 g (3.47 mmol) of ε-caprolactone and 35 mg of finely powdered Pepto-Bismol® initiator (0.037 mmol initiator for [ε-caprolactone]/[Initiator]=100) were loaded in 5 mL glass ampoules and sealed under vacuum. Then the ampoules were immersed in a thermo stated oil bath at 120 °C for 90 minutes. The resultant polymer was purified by dissolving in CHCl₃/CH₂Cl₂ (Initiator was settled on the bottom of the vial). The supernatant liquid was quickly transferred into another flask. The polymerization was quenched in excess acidic methanol and dried under high vacuum and the conversion was estimated by ¹H NMR spectroscopy.

2.6.6 General procedure for bulk rac-LA and ε-CL co-polymerization

A mixture of 0.500 g (3.47 mmol) rac-LA, 0.400 g (3.47 mmol) of ε-caprolactone and 70 mg of finely powdered Pepto-Bismol® initiator (0.074 mmol initiator for [ε-caprolactone]: [rac-LA]:[Initiator]=100:100:1) were loaded in 5 mL glass ampoules and sealed under vacuum. Then the ampoules were immersed in a thermostated oil bath at 120 °C for 90 minutes. The resultant polymer was purified by dissolving in
CHCl₃/CH₂Cl₂ (Initiator was settled on the bottom of the vial). The supernatant liquid was quickly transferred into another flask. The polymerization was quenched in excess acidic methanol and dried under high vacuum and the conversion was estimated by ¹H NMR spectroscopy.

2.6.7 General procedure for LA polymerization

*L*-LA/*rac*- LA (0.500 g, 3.47 mmol) was loaded into a Schlenk flask containing a magnetic bar and dissolved in 10 mL CH₂Cl₂ in the glove box. An appropriate amount of initiator (0.0347 mmol initiator for [LA]/[Initiator]=100 and 3.47×10⁻³ mmol initiator for [LA]/[Initiator]=1000) was loaded into another flask and dissolved in 10 mL CH₂Cl₂ in the glove box. Both flasks were taken out from the glove box and attached to the Schlenk line. The initiator solution was quickly added to the LA containing flask using a cannula and stirred at room temperature. The polymerization was quenched in 5N acidic methanol. The polymer was precipitated in excess methanol and dried under high vacuum. The conversion of LA was estimated by ¹H NMR spectroscopy and the molecular weights and PDI were determined by GPC.

2.6.8 General procedures for kinetics studies of *rac*-LA polymerization

*rac*-LA (0.500 g, 3.47 mmol) was loaded in the Schlenk flask containing a magnetic bar and dissolved in 10 mL CH₂Cl₂ in the glove box. 33.0 mg of cy-salenBiOC₆H₃-2,6-OBu₂ initiator (0.0347 mmol initiator for [rac-LA]/[Initiator]=100) was loaded in another Schlenk flask and dissolved in 10 mL CH₂Cl₂ in the glove box.
Both flasks were taken out from the glove box and attached to the Schlenk line. The initiator solution was quickly transferred by cannula into the lactide solution and stirred at room temperature. Then ~ 0.5 mL aliquots were removed at appropriate time intervals and quenched with 5N acidic MeOH. The aliquots were dried under vacuum and the % conversions were obtained by $^1$H-NMR spectroscopy. Similar procedures were followed for the kinetics studies of cy-salenBiOBu’ in toluene at room temperature.

2.6.9 General procedure for the synthesis of salen ligands and catalysts

All the salen ligands were prepared by the condensation reaction of 3,5-di-tert-butyl-2-hydroxybenzaldehyde with the appropriate diamine (2:1 ratio) in ethanol under reflux for 3h. The desired product was precipitated in ice bath and collected by filtration. Then the ligands were dried under vacuum at 60 °C overnight.

**Synthesis of cy-salenBiN(SiMe$_3$)$_2$**

The solution of cy-salenH$_2$ (1.0 g, 1.8 mmol) in 15 mL of THF and the solution of Bi[N(SiMe$_3$)$_2$]$_3$ (1.2 g, 1.8 mmol) in 15 mL of THF were prepared in a glove box. Then the cy-salenH$_2$ solution was transferred to the Bi[N(SiMe$_3$)$_2$]$_3$ solution via cannula and the solution was stirred at room temperature for 12 h in a Schlenk flask under a N$_2$ atmosphere. All the volatile components were removed under vacuum. The completion of the reaction was monitored by $^1$H-NMR. Orange microcrystalline product was obtained
with 95% yield. The resulting product was employed in the synthesis below without further purification.

**Synthesis of cy-salenBiOBu′**

Cy-salenBiN(SiMe$_3$)$_2$ (1.0 g, 1.1 mmol) was dissolved in THF and 0.15 mL (1.6 mmol) of Bu′OH was added and stirred for 6h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at -25°C for 2 days. An orange precipitate (product) was obtained in 70 % yield by filtration. $^1$H NMR (C$_6$D$_6$, δ, ppm, 500 MHz) 1.41 (s, 18 H, C(CH$_3$)$_3$), 1.76 (s, 18 H, C(CH$_3$)$_3$), 0.63, 0.80, 1.42, 1.44, 2.52, 3.59 (cyclohexyl), 1.46 (s, 9H, O C(CH$_3$)$_3$), 7.03 (s, 1H, ArH), 7.07 (s, 1H, ArH), 7.80 (s, 2H, ArH), 7.82 (s, 1H, N=CH), 7.88 (s, 1H, N=CH). $^{13}$CNMR (C$_6$D$_6$, δ, ppm, 125 MHz) 24.84, 25.05, 30.15, 30.24, 30.63, 31.48, 31.77, 31.79 (′Bu), 33.96, 34.25, 34.39, 35.73 (′Bu), 66.27, 69.77(HC-N), 121.93, 122.02, 129.19, 129.43, 130.57, 130.85, 135.16, 135.26, 142.01, 142.08, 164.93, 166.23 (phenyl), 166.83, 167.23 (HC=N). MS(MALDI-TOF): m/z M$^+$ calculated 826.45; found 826.14.

**Synthesis of cy-salenBiOC$_6$H$_3$-2,6Bu′$_2$**

Cy-salenBiN(SiMe$_3$)$_2$ (1.0 g, 1.1 mmol) was dissolved in THF and 0.25 mL (1.1 mmol) of OH-C$_6$H$_3$-2,6Bu′$_2$ was added and stirred for 6h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at 0°C for 2 days. A yellow precipitate (product) was obtained in 75 % yield. Crystals suitable for single-crystal X-ray crystallography were
obtained by placing a concentrated hexane solution in freezer at -25°C for a week. \( ^1H \) NMR (C\(_6\)D\(_6\), δ, ppm, 500 MHz) 1.32, 1.34 (18 H, C(CH\(_3\))\(_3\)), 1.43 (s, 18H, C(CH\(_3\))\(_3\)), 1.61, 1.64 (18 H, C(CH\(_3\))\(_3\)), 0.87, 1.23, 1.47, 1.71, 2.39, 5.51 (cyclohexyl), 6.69 (t, 1H, ArH), 6.98 (d, 1H, ArH), 7.24(d, 1H, ArH), 7.39(d, 2H, ArH), 7.83 (d, 1H, ArH), 7.87 (d, 1H, ArH), 8.21(s, 1H, N=CH), 8.26(s, 1H, N=CH) \(^{13}C\)NMR (C\(_6\)D\(_6\), δ, ppm, 125 MHz) 24.52, 25.65, 25.83, 27.78, (CH\(_2\) in cyclohexyl) 30.10, 30.43, 31.59, 31.70 (C(CH\(_3\))\(_3\)), 32.18, 32.25, 34.05, 34.08(C(CH\(_3\))\(_3\)), 34.40, 34.98, 35.63, 35.76 (C(CH\(_3\))\(_3\)), 65.28, 69.93(CH-N), 115.70, 121.69, 122.61, 124.95, 125.41, 128.56, 128.86, 130.89, 132.29, 137.93, 138.29, 140.63, 142.57, 142.91, 162.12, 165.29 (phenyl), 164.71, 169.94(HC=N). MS(MALDI-TOF): m/z M\(^+\) calculated 958.54; found 958.42.

**Synthesis of cy-salenBiOPr\(^i\)**

A mixture of 1.0 g (1.1 mmol) of cy-salenBiN(SiMe\(_3\))\(_2\) and 0.15 mL, (2.0 mmol) of Pr\(^i\)OH were dissolved in THF and stirred for 6h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at -25°C for 2 days. An orange precipitate (product) was obtained in 65 % yield. \( ^1H \) NMR (C\(_6\)D\(_6\), δ, ppm, 500 MHz) 1.03 (bs, 6H, \(^1\)CH(CH\(_3\))\(_2\)), 1.39 (s, 18 H, C(CH\(_3\))\(_3\)), 1.77 (s, 18 H, C(CH\(_3\))\(_3\)), 0.68, 0.74, 1.15, 1.45, 2.59, 3.17 (cyclohexyl), 4.17 (m, 1H, \(^1\)CH(CH\(_3\))\(_2\)), 7.06 (s, 1H, ArH), 7.09 (s, 1H, ArH), 7.82(2, 2H, ArH), 7.82(s, 1H, N=CH), 8.04(s, 1H, N=CH). \(^{13}C\)NMR (C\(_6\)D\(_6\), δ, ppm, 125 MHz) 24.90, 24.99, 25.97, 27.15, 29.66, 30.05, 30.13, 31.77, 31.90, 34.00, 35.76, 35.82, 68.11, 68.23, 122.21, 129.40, 129.54, 130.85, 130.88, 135.40, 135.64, 141.89, 142.02, 164.22, 166.89, 166.99. MS(MALDI-TOF): m/z M\(^+\) calculated 812.43; found 812.81.
Synthesis of ph-salenBiOBu'.

A solution of ph-salenH₂ (1.0 g, 1.8 mmol) in 15 mL of THF and a solution of Bi[N(SiMe₃)₂]₃ (1.2 g, 1.8 mmol) in 15 mL of THF were prepared in a glove box. Then the cy-salenH₂ solution was transferred to the Bi[N(SiMe₃)₂]₃ solution via cannula and the solution was stirred at room temperature for 12 h. The volatile components were removed under vacuum. The completion of the reaction was monitored by ¹H-NMR. The resultant product was re dissolved in THF and 0.20 mL (2.1 mmol) Bu'OH was added and stirred for another 6 h. All the volatile components were removed under vacuum. The residue was re dissolved in pentane and placed in a freezer at -25°C for two days. A deep orange precipitate was obtained in 80% yield. ¹H NMR (C₆D₆, δ, ppm, 500 MHz) 1.05 (bs, 9 H, C(CH₃)₃), 1.34 (bs, 18 H, C(CH₃)₃), 1.75(bs, 18 H, C(CH₃)₃),  6.51 (s, 2H, ArH), 6.90 (s, 2H, ArH), 7.03 (s, 2H, ArH), 7.84 (s, 2H, ArH), 8.18 (s, 2H, N-C=H). ¹³CNMR (C₆D₆, δ, ppm, 125 MHz) 30.30, 31.44, 33.89, 35.69 (C(CH₃)₃), 120.17, 122.78, 127.34, 129.64, 131.91, 136.19, 141.95, 144.0 (phenyl), 162.77, 170.50 (HC=N). MS(MALDI-TOF): m/z M⁺ calculated 820.40; found 820.94.

Synthesis of ph-salenBiCl

A solution of 1.08 g of ph-salenH₂ ( 2.0 mmol) was prepared in THF. 0.12 g ( 5.0 mmol) of NaH were charged in Schlenk flasks in the glove box. The flasks were taken out from the glove box and attached to the Schlenk line. The ph-salenH₂ solution was cooled in an ice bath and transferred to the NaH containing Schlenk flask via cannula and stirred overnight. The conversion was monitored by the disappearance of the OH
peak by $^1$H-NMR. To the resultant mixture 0.64 g (2.0 mmol) of BiCl$_3$ was added and stirred for overnight. All the volatile components were removed under vacuum and the crude product was dissolved in pentane and centrifuged. The resulting solution was transferred to another flask and placed in a freezer at -25°C for one week. Orange colored crystals were obtained with a yield of 85%.

$^1$H NMR (C$_6$D$_6$,δ, ppm, 500 MHz) 1.31(bs, 18 H, C(CH$_3$)$_3$), 1.74 (bs, 18 H, C(CH$_3$)$_3$), 6.57 (s, 2H, ArH), 6.95 (s, 2H, ArH), 7.01 (s, 2H, ArH), 7.89 (s, 2H, ArH), 8.13 (s, 2H, N=C=CH).

**Synthesis of cy-salenBiOCOPh**

A solution of cy-salenBiN(SiMe$_3$)$_2$ (1.0 g, 1.1 mmol) was prepared in THF and (1.34 g, 1.1 mmol) benzoic acid was added and stirred for 6h at room temperature. The volatile components were removed under vacuum and the crude product was dissolved in pentane and placed in a freezer at -25°C for 2 days. Yellow precipitate was obtained in 70 % yield by filtration.

$^1$H NMR (C$_6$D$_6$,δ, ppm, 500 MHz) 1.05 (bs, 9 H, C(CH$_3$)$_3$), 1.34 (bs, 18 H, C(CH$_3$)$_3$), 1.75(bs, 18 H, C(CH$_3$)$_3$), 6.51 (s, 2H, ArH), 6.90 (s, 2H, ArH), 7.03 (s, 2H, ArH), 7.84 (s, 2H, ArH), 8.18 (s, 2H, N=C=CH).

**Synthesis of cy-salenBi[OCMe$_2$COCH$_2$CH$_3$]**

A solution of (1.0 g, 1.1 mmol) of cy-salenBiN(SiMe$_3$)$_2$ was prepared in THF and 0.15 g (1.1 mmol) of ethyl 2-hydroxy-2-methylpropanoate was added and stirred for 6h at room temperature. The volatile components were removed under vacuum and the
crude product was dissolved in pentane and placed in a freezer at -25°C for 2 days. Orange precipitate was obtained in 70% yield by filtration.

\[^1\text{H} \text{NMR} (\text{C}_7\text{D}_8, \delta, \text{ppm}, 500 \text{ MHz}): 1.00 \text{ (t, 3H, OCH}_2\text{CH}_3), 1.06 \text{ (s, 3H, CH}_3), 1.09 \text{(s, 3H, CH}_3), 1.40 \text{ (s, 9H, C(CH}_3)_3), 1.41 \text{ (s, 9H, C(CH}_3)_3), 1.67 \text{ (s, 9H, C(CH}_3)_3), 1.72 \text{ (s, 9H, C(CH}_3)_3), 0.85, 1.45, 2.74, 3.16, \text{(cyclohexyl), 4.15 (q, 2H, OCH}_2\text{CH}_3), 7.05-7.13 \text{ (m, 2H, ArH), 7.70-7.73 \text{ (m, 2H, ArH), 7.87 \text{ (s, 1H, N=CH), 7.99 (s, 1H, N=CH).}}\]

\[^{13}\text{CNMR} (\text{C}_7\text{D}_8, \delta, \text{ppm}, 125 \text{ MHz}, -30^\circ\text{C}): 13.59, 25.08, 25.18, 29.29, 29.45, 30.01, 30.09, 30.27, 31.29, 31.50, 33.67, 33.87, 35.61, 35.64, 62.69, 67.38, 68.74, 74.09, 100.2, 122.96, 123.00, 134.18, 134.30, 140.87, 140.94, 163.07, 166.16, 167.28, 167.82, 191.59.\]

**Synthesis of en-salenBiCl**

Method 1:

A solution of en-salenH\(_2\) (1.0 g, 2.0 mmol) dissolved in THF and 0.12 g (5.0 mmol) of NaH were charged in Schlenk flasks in the glove box. The flasks were taken out from the glove box and attached to the Schlenk line. The en-salenH\(_2\) solution was cooled in an ice bath and transferred to the NaH containing Schlenk flask \textit{via} cannula and stirred overnight. The conversion was monitored by the disappearance of the OH peak by \[^1\text{H}-\text{NMR}.\] To the resultant mixture 0.64 g (2.0 mmol) of BiCl\(_3\) was added and stirred for overnight. All the volatile components were removed under vacuum and the crude product was dissolved in pentane and centrifuged. The resulting solution was
transferred to another flask and placed in a freezer at -25°C for three months. Yellow
colored crystals were obtained with a yield of 85%.

Method 2:

\[ \text{Bi}[\text{N(SiMe}_3\text{)}_2]\text{Cl} \] was prepared by adding 2 equivalents of \( \text{LiN(SiMe}_3\text{)}_2 \) to 1 equivalent of \( \text{BiCl}_3 \) in THF at 0°C. 1.0 g (2.0 mmol); en-salenH\(_2\) dissolved in THF was then added to the solution of 1.1 g (2.0 mmol) \( \text{Bi}[\text{N(SiMe}_3\text{)}_2]\text{Cl} \) in THF. The resulting solution was stirred overnight and all volatile components were removed under vacuum. The crude product was dissolved in pentane and placed in a freezer at -25°C for one month. Yellow colored crystals were obtained in 70 % yield.

\(^{1}\text{H NMR (C}_6\text{D}_6,\delta, \text{ppm, 500 MHz)}\) 1.33 (bs, 18 H, \( \text{C(CH}_3\text{)}_3 \)), 1.71(bs, 18 H, \( \text{C(CH}_3\text{)}_3 \)), 3.00 (bs, 2H, \( \text{CH}_2 \)), 4.16 (bs, 2H, \( \text{CH}_2 \)), 6.89 (bs, 2H, \( \text{ArH} \)), 7.28 (bs, 2H, \( \text{N=CH} \)), 7.82(bs, \( \text{ArH} \)). MS(MALDI-TOF): \( \text{m/z M}^+ \) calculated 734.30; found 734.94.

**Synthesis of cy-salenBiCl**

A solution of cy-salenH\(_2\) (1.0 g, 1.8 mmol) in THF was prepared. 0.12 g (5.0 mmol) of NaH was charged separately in Schlenk flasks in the glove box. The cy-salenH\(_2\) solution was cooled in an ice bath and transferred to the NaH containing Schelenk flask via cannula and stirred overnight. The conversion was monitored by the disappearance of OH the peak by \(^{1}\text{H-NMR}. To the resultant mixture 0.58 g (1.8 mmol) of \( \text{BiCl}_3 \) was added and stirred overnight. All the volatile components were removed under vacuum and the crude product was dissolved in pentane and centrifuged. The resulting solution was
transferred to another flask and placed in a freezer at \(-25^\circ\text{C}\) for one month. Yellow colored crystals were obtained in 65\% yield.

\(^1\text{H} \text{NMR (C}_6\text{D}_6, \delta, \text{ppm, 400 MHz}) 0.65, 1.10, 1.35, 1.45, 2.14, 5.15 (\text{cyclohexyl}), 1.30, 1.34, 1.68, 1.75 (\text{C(CH}_3)_3), 6.89 (\text{s, 1H, ArH}), 7.08 (\text{bs, 1H, ArH}), 7.46 (\text{bs, 1H, ArH}), 7.77 (\text{s, 1H, N=CH}), 7.79 (\text{s, 1H, N=CH}), 7.88 (\text{s, 1H, ArH}). \text{MS(MALDI-TOF): m/z M}^+ \text{calculated 788.35; found 788.24.}

\textbf{2.6.10 Crystallographic Studies}

Single crystals of 1-4 were isolated under a pool of fluorinated oil and were found to be quite reactive. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo K\(\alpha\) radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with SADABS for 3 and Scalepack for 1 and 2. The structures were solved by the direct methods program in SHELXS-97.\(^{96}\) Full-matrix least-squares refinements based on \(F^2\) were performed in SHELXL-97, as incorporated in the WinGX package.\(^{92}\)

For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with \(U(H) = 1.5U_{\text{eq}}\) (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with \(U(H) = 1.2U_{\text{eq}}\) (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.\(^{97}\)
Structure 1 contains a disordered cyclohexane backbone which crystallized in two conformations. The two orientations were found in the difference map and their occupancy was allowed to refine to 0.55/0.45. The pivot carbon atoms C17A/C17B and C20A/C20B were restrained with EXYZ and EADP commands.

Structure 3 consists of an en-salen[Bi-Cl] tetramer plus three different solvent molecules: fully occupied THF, (CH$_3$)$_3$Si-NH-Si(CH$_3$)$_3$ with a refined occupancy factor of 0.598(9), and diethyl ether with an occupancy factor set to 0.2. There are other regions of lower electron density, which are most likely very disordered solvent molecules, and these were not modeled. Pseudo-merohedral twinning is present and the following twin law was applied to the data (0 -1 0 / -1 0 0 / 0 0 1) with a twin fraction of 0.3633(8). It was necessary to use many restraints (SADI, DFIX, and FLAT) during the refinement for both the Bi tetramer and the solvent molecules.

CCDC 928067 - 928069 contains the supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Centre via www.ccdc.cam.ac.uk/data_request/cif
Chapter 3  Interesting Molecular Structure and Bonding in a Bismuth-Lithium Bond in the Ion Pairs: LiBiL$_2$, Where L = a Porphyrin or a Salen Ligand

3.1 Introduction

ROP of LA by coordination complexes is a topic of considerable current interest with regard to stereocontrol by the metal center with its attending set of ligands. A limitation of the majority of these catalyst systems lies in their immortality due to side reactions with minor impurities such as water, oxygen and carbon dioxide and ligand scrambling. In earlier work we noted that bismuth compounds, namely bismuth subsalicylate, Peptobismol$^{98}$ and salenBiOR$^{99}$ compounds were effective in the ROP of lactides. While the former represented as a heterogeneous system the latter was molecular and single-site. Both yielded a preference for formation of heterotactic poly lactide from rac-LA. The salenBiOR systems were, however, limited by side reactions involving ligand scrambling and the formation of Bi(salen)(salenH) was observed as one such product.$^{100}$ We reasoned that a porphyrin ligand would be less susceptible to this type of ligand scrambling and thus attempted the preparation of TPPBiOR compound, where TPP = 5,10,15,20-tetraphenylporphyrin. This prompted us to investigate the reactions of porphyrin bismuth alkoxides thinking that the porphyrin ligand would be more
chemically inert compared to the Schiff base salen ligands. During the synthesis of porphyrin/salen Bi alkoxides, we discovered the interesting crystalline Bi-Li bond containing complexes that can be formed in high yield according to the reaction shown in eq. 1.

\[
\text{BiCl}_3 + 4\text{LiN(SiMe}_3\text{)}_2 + 2\text{LH}_2 \xrightarrow{25 \, ^\circ \text{C}} \text{LiBiL}_2 + 3\text{LiCl} + 4\text{HN(SiMe}_3\text{)}_2 \quad \text{THF}
\]

We describe here our full details of these and related work that reveal the propensity of bismuth-lithium bond formation in the ion pairs [BiL]+[LiL] where L = TPP, octaethylporphyrin, OEP and 6,6’- (1,2 phenylenebis(azanylylidene)bis(methanlylidene)bis(2,4-di-tert-butyphenol), phsalen. We also report the Li₂phsalen.2THF and its THF exchange by NMR studies.

3.2 Synthesis

The new compounds LiBiL₂, where L = TPP, I, L = OEP, II and L = phsalen, III, were prepared in a one pot synthesis as indicated in equation 1. The Li₂(phsalen).2THF, IV, complex prepared from the reaction of LiN(SiMe₃)₂ (2equiv) with phsalenH₂ in THF as shown in eq.2. This compound IV was also structurally characterized.

\[
\text{phsalenH}_2 + 2\text{LiN(SiMe}_3\text{)}_2 \xrightarrow{25 \, ^\circ \text{C}} \text{Li}_2\text{phsalen} + 2\text{HN(Si Me}_3\text{)}_2 \quad \text{THF}
\]

The new compounds are soluble in benzene, toluene, THF, CH₂Cl₂ and CHCl₃. Crystallization from CH₂Cl₂/ hexane yielded crystals suitable for single X-ray studies for
I and III. The compounds are colored, I (green), II (red purple) and III (red-orange) and air-sensitive. Thus their preparation and handling involved the use of rigorously dried and deoxygenated solvents under an atmosphere of purified N₂ via standard Schlenk and dry-box techniques. Compound III crystallizes in two forms; compound IIIA involves the loss of THF and can be prepared from the reaction involving IIB, LiBiphsalen₂·THF by the removal of THF.

3.3 Results and discussion

3.3.1 Solid state structure of LiBi(TPP)₂

The solid state structure of compound I crystallized in the space group C2/c there is one unique LiBi(TPP)₂ ion pair and CH₂Cl₂ disordered molecules of solvent within the unit cell. A view of the molecular structure looking down the Li-Bi axis, and a view of the central portion of the molecule (lacking phenyl substituents for clarity) looking perpendicular to the Li-Bi axis can be seen in Figure 33A and B, respectively.

Figure 33: ORTEP representation of I viewed parallel (a) and perpendicular (b) to the Li-Bi bond. Figures drawn at 50% probability. (Gray = Carbon, Dark Blue = Nitrogen, Light Blue = Lithium, Orange = Bismuth) Phenyl groups, hydrogens and solvent excluded for clarity.
The former view of the molecule emphasizes the staggered nature of the porphyrin LiBi-N$_8$ core which minimizes steric hindrance of the eight phenyl groups. Figure 33 B more clearly demonstrates the close porphyrin-porphyrin ring separation of ~3.5 Å. This is not surprising given the formal nature of the molecule as an ion pair involving [Li(TPP)]$^-$ and [Bi(TPP)]$^+$. The Bi atom lies significantly out of the N$_4$ plane of its porphyrin by 1.12 Å. Given the ionic radius of Bi$^{3+}$ this is hardly surprising and is commonly seen for the heavier elements of the d-block and the lanthanides. It is also immediately obvious from Figure 33B that the Li atom is also slightly out of the N$_4$ plane of its porphyrin by 0.58 Å. Bond distances around the Bi-Li core can be seen in Figure 34 and the packing pattern is shown in Figure 35.

Given that Bi$^{3+}$ commonly has a stereochemically active lone pair arising from its 6s$^2$ orbital, this Bi sp hybrid is directed toward the Li$^+$ cation. This distance is comparable to those seen in LiBiR$_2$ compounds that are analogous to related LiER$_2$ compounds where E = N, P, As. In these we may anticipate a Li$^+$ to Bi sp$^2$ lone pair bonding interaction. In the present case the Li$^+$ cation lies above the plane of its attendant porphyrin which might be taken to imply a potential repulsion from the Bi$^+$ cation. However, the Bi to Li distance of 2.87 Å would surely seem to imply a bonding distance as predicted by Pyykkö. Moreover, it is plausible to consider that this short Li$^+$ to Bi$^{3+}$ distance could have been avoided by the slippage of the two porphyrin or salen ligands.
Figure 34: Bond distances in Å surrounding the Bi-Li core

Figure 35: Packing diagram of 1 shown along the a-axis (left) and c-axis (right) of the unit cell
An immediate interest is the Bi-Li distance of 2.874(8) Å. Given that both Li and Bi are cations with formal charge of +1 and +3 respectively, one has to question whether this distance is imposed by the ionic nature of the ions Li(TPP)\(^-\) and Bi(TPP)\(^+\) or there is a dative Bi \(\rightarrow\) Li bond involving the non-bonding Bi 6s\(^2\) orbital. In order to gain insight into this matter we undertook electronic structure calculations employing the commercial programs provided by Guassian 09.

Table 11: Crystallographic data for compound I

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<th>Compound</th>
<th>I</th>
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<tr>
<td>Chemical Formula</td>
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</tr>
<tr>
<td>Formula Weight</td>
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</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space Group</td>
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<tr>
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<td>(b) (Å)</td>
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<tr>
<td>(c) (Å)</td>
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</tr>
<tr>
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<td>90.800(2)</td>
</tr>
<tr>
<td>(\beta) (°)</td>
<td>90.800(2)</td>
</tr>
<tr>
<td>(\gamma) (°)</td>
<td>90.800(2)</td>
</tr>
<tr>
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<td>(Z)</td>
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<td>R1(^a) (%) (all data)</td>
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<tr>
<td>wR2(^b) (%) (all data)</td>
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<tr>
<td>Largest diff. peak and hole (e Å(^{-3}))</td>
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</tr>
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</table>

\(^aR1\) = \(\Sigma |F_o|-|F_c|| / \Sigma F_o\times100\)

\(^b\text{wR2}\) = \(\Sigma w (F_o^2-F_c^2)^2 / \Sigma (w|F_o|^2)^1/2 \times 100\)
3.3.2 Computational studies and nature of Bi-Li bond in I

Employing the density functional theory (DFT) calculations were carried out on the model compound involving the porphyrin lacking phenyl substituents to save on computational time and resources. The highest energy occupied orbitals are associated with the Li(porphyrin)⁻ ion not surprisingly given its negative charge and below these lie the frontier Bi(porphyrin)⁺ orbitals. These sets of orbitals arise from the filled π-systems of the porphyrins. The HOMO-7 contains a polarized Bi 6s filled orbital with some 6p mixing and is clearly directed to the Li⁺ ion (See Figure 36).

![Figure 36](image_url)

Figure 36: The filled frontier orbital HOMO-7 of model compound I from a side-on (left) and top-down (right) view.

This can be viewed as the dative Bi → Li bond which is primarily a Li⁺ polarized Bi lone pair. The calculated Bi-Li distance of 2.81 Å is close to the value which is obtained from the crystal structure. The phenyl groups on the porphyrin were omitted in the calculation. The calculated structure still indicate that the Li⁺ ion is out of the N₄ plane of the porphyrin and one may ask whether there is a Bi-Li bond. The answer lies in the porphyrin-porphyrin attraction is more sustained than the Bi→Li dative bond. The repulsive energy curve of a bond rises much more steeply upon compression due to core-
core repulsion than the attractive potential energy curve rises with extension of the bond length. This is why the WW quadruple bond is nearly 0.1 Å longer than the MoMo quadruple bond. Otherwise in the identical molecules the atomic radii for Mo and W atoms are essentially identical due to the lanthanide contraction. So the Li$^+$ ion is pushed slightly out of the plane of its porphyrin by the repulsive core force of the Bi$^{3+}$ ion. This notwithstanding the Bi-Li distance is remarkably short. We know of no other immediately relevant comparison that is available from crystallographic data banks. We do, however, recognize that there are lithium bismuthide complexes of formula LiBiR$_2$ where R is a bulk organic ligand. Here bismuth is formally Bi$^{2+}$. It is quite reasonable to envisage the bonding between Bi$^{2+}$ and the Li$^+$ ions involve the use of a lone pair from bismuth sp$^2$ orbital with the BiR$_2$ group. The related similar bonding its lighter congeners NR$_2$, PR$_2$ and AsR$_2$ are well known to form bonds to lithium. The Li-Bi distances in these complexes range from 2.90 to 3.19 Å$^{104,105}$. Certainly, we would consider these as bonding distances and so in the case of the complex LiBi(TPP)$_2$ with a comparable distance it seems fair to invoke the presence of a Bi$\rightarrow$Li bond though this may well not be the driving force for the formation of the complex.

3.3.3 NMR studies of LiBi(TPP)$_2$

The proton NMR spectra of compound I in CDCl$_3$ and THF-d$_8$ in different temperatures are shown in Figure 37 and Figure 38 respectively. Both of these NMR spectra clearly show that the compound behaves the same in both of coordinating and non-coordinating solvent.
The low temperature spectrum is consistent with two different porphyrins and restricted rotation about the phenyl porphyrin carbon bonds as might be expected due to steric factors. There are 12 sets of aromatic peaks in the 6.5-9.5 ppm range. The two sharp peaks in the 8.3-8.7 ppm are corresponded to pyrrole hydrogen of the porphyrin core. Out of other 10 peaks, 5 are Bi coordinated porphyrin ring phenyl hydrogens and the other belongs to the Li coordinated porphyrin ring phenyl hydrogens. Li ion bound porphyrin ring is in more fluxional compare with Bi due to the size. Thus might be seen that one set of aromatic hydrogens are more fluxional than other. These two sets of aromatic rings can be verified by the 2D-COSY NMR (Figure 41).

Figure 37: Variable temperature $^1$H NMR (500 MHz) of I in CDCl$_3$
Figure 38: Variable temperature $^1$H-NMR (500 MHz) spectra of LiBi(TPP)$_2$ in THF-$d_8$.

DOSY (Figure 39) spectra results a single diffusion coefficient for the compound I. This is also consistent with the LiTPP$^-$ and BiTPP$^+$ being associated in solution as a dinuclear species.
Figure 39: DOSY profile of LiBi(TPP)$_2$ in CDCl$_3$

$^7$Li NMR spectroscopy (Figure 40) reveals a sharp signal at $\delta$ -14.3 ppm, which is one of the indication that the compound I has the Li ion. The high field signal reveals that the Li coordinates/binds to the aromatic ring, which results from the ring current effect.
Figure 40: $^7$Li-NMR profile of LiBi(TPP)$_2$, LiN(SiMe$_3$)$_2$ and LiCl.

2D-COSY NMR (Figure 41) shows the correlation to the two sets of aromatic regions, which also consistent with the LiTPP$^-$ and BiTPP$^+$ being associated in solution as a dinuclear species.
Figure 41: 2D-NMR: COSY spectra of LiBi(TPP)₂ in CDCl₃ at -50 °C

3.3.4 MALDI studies

In the MALDI mass spectrum the parent ion LiBi(TPP)₂ ion is seen in both the positive and negative ion modes along with BiTPP⁺ and LiTPP⁻ in the positive and negative ion modes, respectively. The latter constitute the most intense ions. The complete MALDI data is given in the experimental section.
3.3.5 UV-Vis studies

Electronic structure calculations on the model compound I indicate an expected absorption due to LiTPP- to Bi TPP+ charge transfer. The electronic absorption spectrum of I and free porphyrin are shown Figure 42.

![UV-Visible spectra of TPPH₂ and BiLi(TPP)₂ at room temperature in CH₂Cl₂](image)

Figure 42: UV-Visible spectra of TPPH₂ and BiLi(TPP)₂ at room temperature in CH₂Cl₂

The electronic absorption spectra of I in different solvents are shown in Figure 43, here the big shift in the lower energy band indicates the decomposition of I in methanol. The same behavior also observed with the dilution in DCM (See Figure 44).
There is some solvent dependence of the lower energy absorption at ~450 nm which red shifts and decreases in intensity upon dilution in CH₂Cl₂ (Figure 44). This may reflect dissociation of the ion pair.
3.3.6 Solid-state and molecular structures of IIIA, IIIB and IV

Compound IIIB crystallized in the space group P2₁/c. The unit cell contains four THF\(\text{LiBiL}_2\) units where the THF is bound to \(\text{Li}^+\). The structural determination suffered from two disorder problems: (i) a disorder of the bound THF and (ii) a disorder of the LiBi unit. The latter was particularly problematic with the presence of an extremely light atom in close proximity to the heavy Bi atom. However, there is little or no uncertainty about the fundamental nature of the structure and the LiBi disorder was modeled as 3:1 and the major species are shown in Figure 45. The essential features of the structure are that the Bi is raised above the \(\text{N}_2\text{O}_2\) unit of its phsalen ligand and in addition there are longer Bi – O distances to the lithiated salen ligand. The shorter Bi – O distances are 2.25 and 2.13 Å while the longer distances are 2.76 and 2.61 Å. The \(\text{Li}^+\) cation is also slightly
raised above the $N_2O_2$ plane of its phsalen ligand and the Li – O THF distance is approximately 1.9 Å. The Bi – Li distance is 2.93 Å which is comparable to that seen in I. The central $(N_2O_2)_2$ unit is staggered and notably the $O_4$ unit of the square antiprism adopts one face as does the $N_4$ unit.

Figure 45: Two ORTEP representations of IIIB drawn at 50% probability, A) parallel and B) perpendicular to the Li – Bi bond. Disorder, solvent, hydrogens and 'Bu groups removed for clarity. Dark Blue = Nitrogen, Light Blue = Lithium, Orange = Bismuth, Scarlet = Oxygen, Gray = Carbon.

With the application of a vacuum, compound IIIB loses its THF molecule and is converted to a “slipped form”, IIIA, where one ring has been disposed to reveal two short Li to O distances of 1.95 Å and a Li – Bi distance of 3.1 Å. In the unit cell P-1 there are two molecules in close contact with a phenyl C-H...Li bond distance of 2.7 Å. Compound IIIA is shown in a molecular structure diagram in Figure 46 and Figure 47 shows the molecular packing.
Figure 46: Two ORTEP representations of IIIA drawn at 50% probability, A) parallel and B) perpendicular to the Li – Bi axis. Solvent, hydrogens and 'Bu groups removed for clarity. Dark Blue = Nitrogen, Light Blue = Lithium, Orange = Bismuth, Scarlet = Oxygen, Gray = Carbon.

Figure 47: Packing of IIIA illustrating the Ph – Li interactions in the unit cell. Solvent, hydrogen and 'Bu groups removed for clarity.
The molecular structure of IV is given in Figure 48. Here there are two Li atoms, one which is five coordinate, \( \text{Li}^+\text{N}_2\text{O}_2\text{THF} \) and the other is three coordinate \( \text{Li}^+\text{O}_2\text{THF} \). The notable distance between the two \( \text{Li}^+ \) atoms is 2.47 Å. If the difference between \( \text{Li}^+ \) and \( \text{Bi}^{3+} \) is 0.30 Å then the distance of \( \text{Li}^+ - \text{Bi}^{3+} \) remains at 2.76 Å, which is the distance seen in the structures of I and IIIB.

Figure 48: ORTEP representations of IV drawn at 50% probability. Solvent, hydrogens and \(^7\text{Bu} \) groups removed for clarity. Dark Blue = Nitrogen, Light Blue = Lithium, Scarlet = Oxygen, Gray = Carbon.

A summary of crystallographic parameters for IIIA, IIIB and IV are given in Table 12.
Table 12: Data Collection Parameters for IIIA, IIIB, and IV

<table>
<thead>
<tr>
<th>Compound</th>
<th>IIIA</th>
<th>IIIB</th>
<th>IV</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>$C_{73}H_{94}BiCl_2LiN_4O_4$</td>
<td>$C_{80}H_{108}BiLiN_4O_6$</td>
<td>$C_{51}H_{70}Li_2N_2O_4$</td>
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<tr>
<td>Formula Weight</td>
<td>1378.4</td>
<td>1437.62</td>
<td>788.97</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space Group</td>
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<td>Monoclinic, P2$_1$/c</td>
<td>Monoclinic, P2$_1$</td>
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<td>$a$ (Å)</td>
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<td>11.8047(2)</td>
<td>15.1780(2)</td>
</tr>
<tr>
<td>$b$ (Å)</td>
<td>14.8193(1)</td>
<td>24.8364(3)</td>
<td>12.9818(2)</td>
</tr>
<tr>
<td>$c$ (Å)</td>
<td>19.3492(3)</td>
<td>25.4195(3)</td>
<td>25.0542(5)</td>
</tr>
<tr>
<td>$\alpha$ (°)</td>
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<td>105.150(1)</td>
<td>101.166(1)</td>
</tr>
<tr>
<td>$\beta$ (°)</td>
<td>25.4195(3)</td>
<td>97.922(1)</td>
<td>92.700(1)</td>
</tr>
<tr>
<td>$\gamma$ (°)</td>
<td>105.150(1)</td>
<td>101.166(1)</td>
<td>101.166(1)</td>
</tr>
<tr>
<td>$V$ (Å$^3$)</td>
<td>3600.47(8)</td>
<td>7381.52(18)</td>
<td>4931.14</td>
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<td>$Z$</td>
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<td>4</td>
<td>4</td>
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<tr>
<td>Dcalcd (Mg/m$^3$)</td>
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<td>1.294</td>
<td>1.063</td>
</tr>
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<td>Crystal Size (mm)</td>
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<td>0.23 X 0.19 X 0.15</td>
<td>0.35 X 0.31 X 0.23</td>
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<tr>
<td>Theta range for data collection</td>
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<td>$\theta$ (mm$^{-1}$) [Mo, Kα]</td>
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<td>2.442 3000</td>
<td>0.065 1712</td>
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<tr>
<td>F(000)</td>
<td>93296</td>
<td>100173</td>
<td>51344</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>16482 [R(int)= 0.051]</td>
<td>13058 [R(int)= 0.052]</td>
<td>17225 [R(int)= 0.048]</td>
</tr>
<tr>
<td>Unique reflections</td>
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<td>100% [25.000]</td>
<td>99.9% [25.000]</td>
</tr>
<tr>
<td>Data Completeness to [θ ]</td>
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<td>13058 / 210 / 926</td>
<td>17225 / 371 / 1189</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>R1$^a$ (%) (all data)</td>
<td>3.45 (4.96)</td>
<td>3.69 (5.84)</td>
</tr>
<tr>
<td>wR2$^b$ (%) (all data)</td>
<td>8.57 (10.64)</td>
<td>8.24 (8.93)</td>
<td>21.79 (24.49)</td>
</tr>
<tr>
<td>Goodness-of-fit on $F^2$</td>
<td>1.148</td>
<td>1.034</td>
<td>1.039</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å$^{-3}$)</td>
<td>1.463 and -1.260</td>
<td>0.795 and -0.682</td>
<td>0.552 and -0.335</td>
</tr>
</tbody>
</table>

$^a$R1 = $\Sigma | |F_{o}| - |F_{c}| |/ \Sigma |F_{o}| x 100$

$^b$wR2 = $[\Sigma w ( F_{o}^2 - F_{c}^2 )^2 / \Sigma (w|F_{o}|^2)^{1/2}] x 100$
3.3.7 Mass spectrometry of compounds II-IV

The compounds were examined by MALDI-TOF mass spectrometry in both the positive and negative mode. All the MALDI data are given in the experimental section. Compound IIIA /IIIB showed molecular ions corresponding to LiBiL$_2^{+/–}$ in the positive and negative modes and LiL$^–$ in the negative and more BiL$^+$ in the positive modes. The porphyrin complexes showed only weak molecular ions but intensive BiL$^+$ and LiL$^–$ in the positive and negative modes, respectively. The compound IV shows the peak LLi$_2^+$ for the parent ion and LiL$^–$ in the negative and more LiL$^+$ in the positive modes.

3.3.8 NMR spectrometry III and IV

Compound I has been described previously and shows two types of TPP ligands in the ratio 1:1. At low temperatures two sets of rings were observed due to the conversion of inner and outer rings. Compound IIIB shows four sets of tert-Bu ligands consistent with a C$_2$ symmetry of each ligand LiL$^–$, BiL$^+$ along with one THF. By $^{13}$C NMR we observe 20 aromatic signals which indicate a C$_2$ symmetry. Compound IIIA, which does not contain THF, also shows four tert-Bu resonances and a similar set of 10 CH resonances supporting the structure.
Figure 49: $^1$H NMR($\text{CD}_2\text{Cl}_2$; 500MHz) Spectrum of LiBi(phsalen)$_2$.

We note that in IIIA the aromatic $^1$H signals fall in the ratio of sharp 1:1:1:1:1 and then a broad signals set of 1:1:1:1:1. The former set we assigned to phsalenBi$^+$ and the latter to Liphsalen$. The integral of 4H is a supposition of two sets of compounds. A similar set of sharp and weaker broadened set of CH resonance are seen for compound IIB.
3.3.9 $^7$Li NMR spectra

Compound IIIB shows three signals in the $^7$Li NMR spectrum at around 1-2 ppm at room temperature and below these are in the ratio 13:6:1. Upon raising the temperature these become one resonance at 90°C (Figure 50).

Figure 50: Variable temperature $^7$Li-NMR of [phsalen]$_2$BiLi.THF (IIIB) in toluene $d_8$. 

98
Three of these could be due to stacking of the rings as shown below where BiL⁺ and LiL⁻
stack as shown in the following diagram.

![Diagram of stacked rings]

Compound IIIA shows two major signals, one at ~2 ppm and one at ~ -1ppm (See
Figure 51). The low field signal shows a minor peak at 1.8ppm. The signals at 2 ppm are
very close to those involving IIIB and upon addition of THF we see the increase of the
signals at 2ppm and the decrease of that at corresponds -1ppm (See Figure 52). So we are
inclined to the view that the low field signals, -1 ppm, to the slipped isomer. In solution
there is a significant amount of compound IIIA observed with the lacking THF signal.
Upon the addition of THF the signal at ~2ppm appears very similar to that shown in
Figure 52.
Figure 51: Variable temperature $^7$Li-NMR of [phsalen]$_2$BiLi (IIIA) in toluene $d_8$. 
The spectrum of IIIA recorded in toluene d₈ at various temperatures shown in Figure 51 and that of IIIA +THF is shown in Figure 52.

Figure 52: $^7$Li-NMR of compound IIIA, IIIA+THF and IIIB.

The $^7$Li NMR spectrum of compound IV showed only one signal at +1.65 ppm. This was temperature independent (see Figure 53) and thus the THF was labile and would exchange rapidly. Otherwise we could see the inequivalent Li sites, namely the 5 and 3 coordinate sites.
Figure 53: $^7$Li-NMR of ph-salenLi$_2$ in toluene d$_8$ at different temperatures.

3.4 Concluding remarks

From the reaction between BiCl$_3$ (1 equiv.) and LiN(SiMe$_3$)$_2$ (4 equiv.) and LH$_2$ (2 equiv.), where L= a tetraphenylporphyrin, TPP, an octaethylporphyrin, OEP and phsalen in THF the title compounds have been obtained I LiBiTPP$_2$, II LiBiOEP$_2$, and IIIA LiBi(phsalen)$_2$ and IIIB LiBi(phsalen)$_2$.THF. Crystals grown from CH$_2$Cl$_2$/hexanes are colored; I (green), II (red-purple) and IIIA and IIIB (red-orange). The molecular structures of compound I, IIIA and IIIB were determined by single-crystal X-ray
crystallography and are shown to have short Li…Bi bonds of distance 2.8 Å involving the LiL⁺BiL⁻. Compound IIIA shows a slipped structure involving Li to two oxygens and a Li…Bi distance of 3.1 Å. Compounds IIIA and IIIB undergo a rapid reversible exchange in toluene-d₈ at 90°C. The short Li⁺ to Bi³⁺ distances are comparable to those seen in Li…Bi compounds, such as LiBiR₂, and are comparable to those seen in Pyykkö¹⁰⁶,¹⁰⁷ for Li-Bi bonds. These can be seen to be involving Bi6s6p hybrid lone-pairs to Li⁺ atoms. The compound IV contains two Li⁺ atoms, one coordinated to five atoms LiO₂N₂. THF. and the other being coordinated to three atoms, LiO₂ THF. By ⁷Li and ¹H NMR both lithium atoms share an equivalent environment.

The complex LiBi(TPP)₂ which may be considered as a tight ion pair [Bi(TPP)]⁺[Li(TPP)]⁻ is present both in the solid state and in solution. The solid-state structure has a staggered porphyrin structure with virtual C₄ symmetry which affords the favorable packing of the phenyl groups. The variable temperature ¹H NMR spectra indicate a dynamic process at room temperature which is frozen out on the NMR time scale below 0 °C in CDCl₃. The short Li-Bi distance of 2.874(8) Å can be considered as a dative bond from the Bi³⁺ 6s² lone pair to the Li⁺ ion. The bond distance of 2.87 Å is close to that predicted for a Bi-Li bond as seen in the structures of LiBiR₂ and as suggested by Pyykkö. Whether this is a result of the TPP-TPP ion pair formation or contributes significantly to the assembly of the structure as observed is a matter of conjecture at this time. However, attempts to prepare a related complex NaBi(TPP)₂ based on a reaction involving NaN(SiMe₃)₂ in place of LiN(SiMe₃)₂ failed to yield a related complex. The Na⁺ ion is roughly 0.2 Å larger than the Li⁺ ion and notably less
electrophilic and polarizing as is well seen in their respective coordination chemistry with alkyl groups. Thus a Bi→Na bond would be expected not only to be longer but also weaker. We have not pursued the possible nature of the species that might be formed in the reaction mixture involving NaN(SiMe₃)₂, BiCl₃ and TPPH₂. This possibly forms the species of the form Na⁺(solvent) Bi(TPP)_2⁻. We have, however, obtained a similar structure to that of I for the compound LiBi(ph-salen)_2 which is prepared in a related manner to III. This also has a similarly short Bi-Li distance and this result would seem to discount the view that the short Bi-Li distance in I is due to the favorable π-π stacking of the porphyrin ligands. However, as can be seen here the bond is not worth a great deal in its enthalpy. As seen in a composition of the structures IIIA and IIIB the loss of a THF molecule can cause slippage of this bond and the formation of stronger Bi…O distances. It is, however, a realistic bond based on the Bi 6s6p hybridization and its polarity to the small cation Li⁺.

3.5 Experimental section

3.5.1 General considerations

All the experiments were carried out under a rigorously dried nitrogen atmosphere using Schlenk techniques. Pentane, benzene, tetrahydrofuran, toluene, and dichloromethane were distilled under nitrogen over CaH₂. BiCl₃, and LiN(SiMe₃)₂ were purchased from Sigma Aldrich. Tetrphenylporphyrin(TPPH₂) and octaethylporphyrin(OEPH₂) were purchased from Frontier Scientific. Phsalen ligand was synthesized similar to literature procedure.¹ All of the above chemicals were used without
further purification. Chloroform-$d$, tetrahydrofuran-$d_8$, and benzene-$d_6$ were purchased from Cambridge Isotopes and distilled under nitrogen over CaH$_2$.

3.5.2 Measurements

$^1$H, $^7$Li, COSY, and DOSY spectra were recorded in C$_7$D$_8$ ($\delta$: 2.08) CDCl$_3$ ($\delta$: 7.24) or C$_6$D$_6$ ($\delta$: 7.15) and THF-$d_8$ ($\delta$: 3.58) on a Bruker DRX-500 NMR spectrometer. MALDI-TOF mass spectra were collected on a Bruker Microflex mass spectrometer. The UV-Vis spectra of BiLiTPP$_2$ were recorded at room temperature with a Perkin-Elmer Lambda 900 spectrometer using a 1cm quartz cuvette.

3.5.3 Crystallographic information

Single crystals of I, III and IV were isolated and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo K$\alpha$ radiation. The data collection was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack.$^{108}$ The structures were solved by the direct methods program in SHELXS-13.$^{109}$ Full-matrix least-squares refinements based on $F^2$ were performed in SHELXL-13$^{109}$, as incorporated in the WinGX package.$^{110}$ For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with U(H) = 1.5Ueq (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model
with $U(H) = 1.2U_{eq}$ (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.\textsuperscript{111}

Compound \textbf{IIIB} had several different areas of disorder. The Bi-Li core was disordered over two locations. The two bismuth atoms were found in the difference map and allowed to refine on a free variable. Coordinated to the resulting lithium atoms were THF molecules which were also highly disordered. These THF molecules were also modeled in two locations leading to a ~69\% major component and a 31\% minor component. The modeling of this disorder was made difficult by the fact that Bi is very electron rich and resides quite closely to lithium which is electron poor. To ensure a stable refinement and reasonable bond distances and thermal parameters, ridged bond restraints and thermal constraints were employed.

Compound \textbf{IV} also showed disorder in the coordinated THF. All four THF molecules were found to be disordered over two locations. The two parts were allowed to refine on a free variable and were modeled using similarity restraints and ridged bond restraints. It is also important to note that there is an apparent pseudo-symmetry between the two molecules in the asymmetric unit corresponding to a translation that is roughly $[1/2, 0, 1/2]$.

CCDC 955214 and 1044021 - 1044023 contain the supplementary crystallographic data can be obtained free of charge from The Cambridge Crystallographic Data Center via \url{www.ccdc.cam.ac.uk/data_request/cif}. 

106
3.5.4 Electronic structure calculations

The model complex was optimized in the gas-phase using density functional theory (DFT) utilizing the Gaussian09 suite of programs. The SDD energy consistent pseudopotential and the SDD energy consistent basis set were used for bismuth. The geometry was not constrained to a specific point group. An optimized structure was confirmed to be at a local minimum on the potential energy surface using the frequency analysis. Visualizations of the orbitals were obtained with Gaussview 5.0 using an iso value of 0.20\textsuperscript{112}. Electronic absorption spectra were calculated using the time dependent DFT (TD-DFT) method.

3.5.5 Synthesis

Synthesis of BiLi(TPP)\textsubscript{2}

A mixture of (0.500 g (1.59 mmol) of BiCl\textsubscript{3}, 1.06 g (6.34 mmol) LiN(SiMe\textsubscript{3})\textsubscript{2}, and 1.95 g (3.17 mmol) of tetraphenylporphyrin(TPPH\textsubscript{2}) were dissolved in 30.0 mL of tetrahydrofuran and stirred at room temperature for 12h. All the volatile components were removed under vacuum and the crude product was dissolved in benzene. The supernatant liquid was transferred to another Schlenk flask by cannula and the solvent was removed by vacuum. The resultant crude product was dissolved in a minimum amount of CH\textsubscript{2}Cl\textsubscript{2} and placed in a freezer at -25°C. Green crystals were obtained in 70% yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated CH\textsubscript{2}Cl\textsubscript{2} solution in a freezer at -25°C for one month.
^1^H NMR (CDCl$_3$, $\delta$, ppm, 500 MHz, room temperature) 7.01 (bs, 4H, ArH), 7.33 (d, 4H, ArH), 7.42 (bs, 4H, ArH), 7.46 (t, 4H, ArH), 7.70 (t, 4H, ArH), 7.77 (t, 4H, ArH), 7.88 (t, 4H, ArH), 7.96(bs,4H,ArH), 8.40(s, 8H, pyrroleH), 8.57(s, 8H, pyrroleH), 7.78 (d, 4H, ArH), 9.05 (bs, 4H, ArH). ^7^Li NMR (CDCl$_3$, ppm) -14.3.

MS(MALDI-TOF): Positive ion mode; m/z [TPPBi]$^+$ calculated 821.21; found 821.41 and [BiLiTPP$_2$]$^+$ calculated 1440.46; found 1440.43. Negative ion mode; m/z [TPPLi]$^-$ calculated 619.25; found 621.88 and [BiLiTPP$_2$]$^-$. calculated 1440.46; found 1439.83.

**Synthesis of BiLi(phsalen)$_2$.THF**

A mixture of 0.540 g (1.00 mmol) of phsalenH$_2$, 0.158 g (0.50 mmol) BiCl$_3$ and 0.340 g (2.00 mmol) of LiN(SiMe$_3$)$_2$ were dissolved in 15.0 mL of tetrahydrofuran and stirred at room temperature for 6h. All the volatile components were removed under vacuum and the crude product was dissolved in pentane. The supernatant liquid was transferred to another Schlenk flask by cannula and the solvent was removed by vacuum. The resultant crude product was dissolved in a minimum amount of CH$_2$Cl$_2$/toluene and placed in a freezer at -25°C red brown crystals were obtained in 60% yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated CH$_2$Cl$_2$/toluene solution in a freezer at -25°C for three days.

^1^H NMR (C$_6$D$_6$, $\delta$, ppm, 500 MHz, room temperature) 8.43 (s, 2H, N=CH), 8.43 (bs, 2H, N=CH), 7.91 (s, 2H, ArH), 7.91 (s, 2H, ArH), 7.76 (s, 2H, ArH), 7.27 (s, 2H, ArH), 7.26 (s, 2H, ArH), 7.24 (s, 2H, ArH), 7.16 (s, 2H, ArH), 6.98(m, 2H, ArH), 108.
6.63 (m, 2H, ArH), 3.12 (m, 4H, THF), 1.84 (s, 18H, ‘Bu), 1.71 (s, 18H, ’Bu), 1.61 (s, 18H, ’Bu), 1.48 (s, 18H, ’Bu), 1.00 (m, 4H, THF)

$^{13}$C NMR (C$_6$D$_6$, δ, ppm, 125 MHz, room temperature): 172.83, 166.87, 163.44, 161.09, 144.44, 144.18, 142.48, 139.74, 136.16, 134.81, 132.69, 129.77, 129.46, 128.57, 127.22, 126.27, 124.28, 122.96, 120.34, 116.14, 68.12, 35.76, 35.46, 34.16, 34.04, 32.06, 31.47, 31.20, 30.63, 24.99.

$^7$Li NMR (CDCl$_3$, ppm): 1.95, 1.63, 1.33 (1.95:1.63:1.33 = 13:6:1

MS(MALDI-TOF): Positive ion mode; m/z [phsalenBiLi]$^+$ calculated 1292.7; found 1292.7 and [phsalenBi]$^+$ calculated 747.3; found 747.3, Negative ion mode; m/z [phsalenBiLi]$^-$ calculated 1292.7; found 1292.7 and [phsalenLi]$^-$ calculated 545.3; found 545.3.

**Synthesis of BiLi(phsalen)$_2$**

A mixture of 0.540 g (1.00 mmol) of phsalenH$_2$, 0.158 g (0.50 mmol) BiCl$_3$ and 0.340 g (2.00 mmol) of LiN(SiMe$_3$)$_2$ were dissolved in 15.0 mL of toluene and stirred at room temperature for 6h. All the volatile components were removed under vacuum and the crude product was dissolved in pentane. The supernatant liquid was transferred to another Schlenk flask by cannula and the solvent was removed by vacuum. The resultant crude product was dissolved in a minimum amount of toluene and placed in a freezer at -25°C. Red orange crystals were obtained in 60% yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated toluene solution in a freezer at -25°C for three days.
\(^1\)H NMR (CD\(_2\)Cl\(_2\), \(\delta\), ppm, 500 MHz, room temperature) 7.97 (s, 2H, N=CH), 7.86 (bs, 2H, N=CH), 7.56 (s, 4H, ArH), 7.36 (bs, 2H, ArH), 7.26 (s, 2H, ArH), 7.13 (bs, 2H, ArH), 6.81 (s, 2H, ArH), 6.64 (bs, 2H, ArH), 6.54 (s, 2H, ArH), 1.73 (s, 18H, \('\text{Bu}\)), 1.49 (s, 18H, \('\text{Bu}\)), 1.44 (s, 18H, \('\text{Bu}\)), 1.34 (s, 18H, \('\text{Bu}\)).

\(^1\)H NMR (C\(_6\)D\(_6\), \(\delta\), ppm, 500 MHz, room temperature) 7.93 (s, 2H, N=CH), 7.81 (s, 2H, N=CH), 7.56 (s, 2H, ArH), 7.45 (s, 2H, ArH), 7.32 (s, 2H, ArH), 7.10 (s, 2H, ArH), 6.60 (s, 6H, ArH), 6.27(s, 2H, ArH), 1.80 (s, 18H, \('\text{Bu}\)), 1.56 (s, 18H, \('\text{Bu}\)), 1.46 (s, 18H, \('\text{Bu}\)), 1.36 (s, 18H, \('\text{Bu}\)).

\(^7\)Li NMR (toluene, ppm): 2.12, 1.37, -0.70. (2.12:1.37:-0.70= 10:2:5)

**Synthesis of BiLi(OEP)\(_2\)**

A mixture of 0.500 g (1.59 mmol) of BiCl\(_3\), 1.06 g (6.34 mmol) LiN(SiMe\(_3\))\(_2\), and 1.70 g (3.17 mmol) of octathylporphyrin (OEPH\(_2\)) were dissolved in 20.0 mL of tetrahydrofuran and stirred at room temperature for 12h. All the volatile components were removed under vacuum and the crude product was dissolved in benzene. The supernatant liquid was transferred to another Schlenk flask by cannula and the solvent was removed by vacuum. The resultant crude product was washed four times with pentane and purple powder was obtained in 45% yield.

\(^1\)H NMR (CDCl\(_3\),\(\delta\), ppm, 500 MHz, room temperature) 9.14 (bs, 4H, pyH), 8.76 (bs, 4H, pyH), 7.33 (d, 4H, ArH), 4.21 (m, 16H, CH\(_2\)CH\(_3\)), 3.96 (m, 16H, CH\(_2\)CH\(_3\)), 1.83 (t, 24H, CH\(_2\)CH\(_3\)), 1.58 (t, 24H, CH\(_2\)CH\(_3\)).

\(^7\)Li NMR (CDCl\(_3\), ppm) : -15.64
SYNTHESIS OF Li₂(phsalen)

A mixture of 0.540 g (1.00 mmol) of phsalenH₂ and 0.336 g (2.00 mmol) LiN(SiMe₃)₂ were dissolved in 10.0 mL of tetrahydrofuran and stirred at room temperature for 12h. All the volatile components were removed under vacuum and the crude product was dissolved in toluene. The supernatant liquid was transferred to another Schlenk flask by cannula and placed in a freezer at -25°C. Yellow crystals were obtained in 75% yield. Crystals suitable for single-crystal X-ray crystallography were obtained by placing a concentrated toluene solution in a freezer at -25°C for one week.

¹H NMR (C₆D₆, δ, ppm, 500 MHz, room temperature): 8.77 (s, 2H, N=CH), 7.73 (s, 2H, ArH), 7.38 (s, 2H, ArH), 7.36 (s, 2H, ArH), 7.06 (s, 2H, ArH), 3.25 (m, 8H, THF), 1.77 (s, 18H, tBu), 1.47 (s, 18H, tBu), 1.02 (m, 8H, THF)

¹³C NMR (C₆D₆, δ, ppm, 125 MHz, room temperature): 168.26, 161.00, 145.35, 139.78, 133.82, 129.95, 126.47, 123.47, 115.84, 68.02, 35.45, 34.16, 32.07, 30.93, 25.70.

¹⁷Li NMR (C₆D₆, ppm): 1.81 ppm

MS(MALDI-TOF): Positive ion mode; m/z [OEP₂BiLi]⁺ calculated 1280.7; found 1281.9.

MS(MALDI-TOF): Positive ion mode; m/z [phsalenLi₁]⁺ calculated 545.4; found 546.1, [phsalenLi₂]⁺ calculated 552.4; found 552.1 and [phsalenLi₃]⁺ calculated 559.4; found 559.1, Negative ion mode; m/|phsalenLi₁|⁻ calculated 546.3; found 546.1.
Chapter 4  Stereoselective Lactide Polymerization and the Coupling of Propylene Oxide and Lactide at a Porphyrin Chromium (III) Center

4.1 Introduction

Ring-opening of PO by a metal coordinate mechanism can occur by a bimetallic pathway as demonstrated by Jacobsen in the stereoselective ring-opening of rac-PO by chiral Schiff base chromium and cobalt complexes. In this mechanism one metal serves as a Lewis acid to activate PO toward nucleophilic attack by a ligand, typically a halide or alkoxide that is delivered from the other metal center. This type of mechanism may also work efficiently in the copolymerization of PO and CO$_2$ to form polypropylene carbonates. However, the ROP of PO can also occur at a single metal center and has been well documented by Darenbourg and others. In the recent studies, Chisholm et.al. reported that the reactivity PO with porphyrin metal (III) catalysis can be involved with the single site mechanism in both the homopolymerization of PO and in its copolymerization with CO$_2$. The rate of homopolymerization of PO follows the order $M = Cr > Al \sim Co$. For the TPPCr(III), the enchainment of PO at ambient conditions is quite rapid with a turnover frequency (TOF) of $\sim 2000 \text{ h}^{-1}$ yielding
regioregular (HT)\textsubscript{n} polypropylene oxide (PPO). The reaction of \textit{rac}-PO with the TPPCrCl significantly produces isotactic junctions.

The enchainment of PO at a single metal center can be considered to occur by a mechanism akin to a 1,2-migratory addition of the type common for the insertion of alkenes into metal-alkyl bonds in olefin polymerization.

\begin{itemize}
  \item Olefin Polymerization
  \item Ring-opening Polymerization of Lactide
  \item Ring-opening polymerization of propylene oxide and CO\textsubscript{2}
\end{itemize}

Scheme 15: Mechanisms of olefin polymerization, ring opening polymerization of lactide and copolymerization of propylene oxide with CO\textsubscript{2} at a single site metal center.

Although this may not be a commonly accepted view for the homopolymerization of PO certainly there are some similarities with olefin polymerization. The metal needs to be coordinatively unsaturated, and provide an electrophilic site for activation of the
substrate. This results a polar metal –alkyl or –alkoxide bond. Similar requirements pertain to the ROP of cyclic esters such as rac-, L-, D-, and meso lactides. Lanthanides and Group 2 metals Mg and Ca are the most active coordinate catalysts for the ROP of LAs. The commonly accepted mechanism for the ROP of LA is also shown in Scheme 15. Rather interestingly though metal single-site catalysis is well established for the ROP of LA, these sites are not typically active for the ROP of PO despite the ability of PO to bind to these centers. This is nicely seen in the molecular structure of Tp*Ca(OAr)(PO) where the OAr and PO occupy adjacent sites at the 5-coordinate Ca(2+) ion (Tp* = tris-tert-butylpyrazolyl borate).

Chisholm and co-workers recently reasoned that the greater reactivity of TPPCr(III) toward the homopolymerization of PO was due to its more polar Cr-OR bond relative to Al-OR and Co-OR. This prompted us to investigate the TPPCr(III) system with PO and LA and herein we report our initial findings. Additionally we have investigated the reactivity of Al catalyst for the coupling of PO and LA. Furthermore, Al compounds have been used to investigate the mechanistic insight by NMR studies.

4.2 Results and discussions

The reaction between TPPCrCl, PPN+Cl−, LA and PO at room temperature for an hour, produces initially an isotactic enriched PLA (Figure 54) with the end group of OCHMeCH2Cl as shown in Figure 55. The resulting polymer was characterized by 1H-NMR, 13C-NMR, MALDI and GPC. In longer reaction time/ elevated temperature, the
system favors the formation of PLA oligomers and some small molecules. The homodecoupled $^1$H-NMR and the $^{13}$C-NMR of the PLA obtained from rac-LA, rac-PO with TPPCrCl/PPN$^+$Cl$^-$ at room temperature are shown in Figure 54.

![Figure 54](image)

Figure 54: (a) Homodecoupled $^1$H-NMR and (b) $^{13}$C-NMR CH resonance of polylactide obtained from the reaction of rac-LA catalyzed by TPPCrCl/PPN$^+$Cl$^-$ in rac-PO at room temperature.

NMR studies and the MALDI peak separation by 72 Daltons reveal that the polymer undergoes transesterification or chain transfer process at room temperature. Furthermore, the MALDI (See Figure 55) spectra shows that the resulting polymer is PLA with the end group of - OCHMeCH$_2$Cl (POCl) with sodiated or protonated form of H(1/2 LA)$_n$POCl.
Figure 55: MALDI spectrum of polylactide obtained from the reaction of rac-LA catalyzed by TPPCrCl/PPN^+Cl^- in rac-PO at room temperature.

To study the temperature effect we have studied this reaction at different temperatures 0°C, 60°C and 100°C. The same reaction, with rac-LA and rac-PO, was carried out at 60°C and the crude $^1$H-NMR (Figure 56) product clearly indicates the presence of some polymers and some distinct peaks for small molecules.
Figure 56: $^1$H NMR spectrum (500 MHz, CDCl$_3$) of the crude product rac-PO and rac-LA catalyzed by TPPCrCl/PPN$^+$Cl.$^*$[A1 and A2: 3,6-dimethyl-1,4-dioxan-2-one, P: Oligomers of H(½LA)$_n$(PO)$_m$Cl]

The oligomers and small molecules were separated by hexane extraction. Oligomers were hexane insoluble component and this is analyzed by ESI-MS (Figure 57). The oligomers have the PO and ½LA unit with OH/Cl end group, which can be assigned as H(½LA)$_n$(PO)$_m$Cl.Na$^+/H^+$ or H(½LA)$_n$(PO)$_m$OH.Na$^+/H^+$. 

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117
Figure 57: ESI spectrum of hexane insoluble component from the reaction of rac-LA, rac-PO (rac-LA:rac-PO:TPPCrCl/PPN⁺Cl⁻=100:200:1) catalyzed by TPPCrCl/PPN⁺Cl⁻ at 60 °C.

Further, the hexane soluble component was analyzed by NMR and GC-MS. The peak corresponded to the molecular weight of 130.1 Daltons with the closest two retention time (8.484 and 8.681 min.) reveal the presence of two types of molecules.
Figure 58: GC/MS trace of the products from the hexane soluble component obtained from reaction of PO and LA catalyzed by TPPCrCl/PPN$^+$Cl$^-$. The formation of these two types of possible small molecules can be expected by the back biting mechanism as shown in Scheme 16.
Scheme 16: Possible mechanistic pathway for the formation of small molecules A and B.

But, the PPO formation by the ring opening process of PO by Lewis acid catalyst mainly occurs via methylene attack, which could result in the preference in the formation of molecule A. This prompted us to synthesize the molecule A from ethyl lactate and allyl bromide according to Scheme 17.

Scheme 17: Synthetic scheme for the synthesis of 3,6-dimethyl-1,4-dioxan-2-one from ethyl-L-lactate and allyl bromide.

The $^1$H-NMR, $^{13}$C-NMR and GC-MS studies are in match with the product obtained by catalytic reaction. For the synthesized molecules 4 and 2 peaks were
observed from the chiral and achiral GC respectively. The reaction between ethyl-\textit{L}-LA and allyl bromide expected to give two isomers, but the chiral GC 4 peaks clearly indicate the epimerization on the ethyl-\textit{L}-LA chiral center. This promoted us to investigate the different combinations of LA and PO to understand the mechanistic pathway for the formation of these small molecules. All these combinations at room temperature reactions yield the similar NMR spectra (Figure 59). The summary of chiral GC data for the small molecule with different combination of LA and PO is given in Table 13.

Figure 59: $^1$H NMR (500 MHz, CDCl$_3$) spectrum of 3,6-dimethyl-1,4-dioxan-2-one obtained from the reaction of \textit{rac}-PO and \textit{rac}-LA (\textit{rac}-LA: \textit{rac}-PO:TPPCrCl/PPN$^\text{+}$Cl$^-$ \textit{=100:200:1}) catalyzed by TPPCrCl/PPN$^\text{+}$Cl$^-$ at 60 °C.
Table 13: The percentage of 3,6-dimethyl-1,4-dioxan-2-one isomers obtained with different combinations of LA and PO.

<table>
<thead>
<tr>
<th>Entry</th>
<th>3,6-dimethyl-1,4-dioxan-2-one</th>
<th>Retention time (Rt, in min.)</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td></td>
<td>14.71 (3R,6S)</td>
</tr>
<tr>
<td>rac-LA + rac-PO</td>
<td>28%</td>
<td>28%</td>
</tr>
<tr>
<td>rac-LA + R(+)-PO</td>
<td>-</td>
<td>58%</td>
</tr>
<tr>
<td>L-LA + rac-PO</td>
<td>26%</td>
<td>29%</td>
</tr>
<tr>
<td>L-LA + R(+)-PO</td>
<td>-</td>
<td>58%</td>
</tr>
<tr>
<td>L-LA + S-PO*</td>
<td>-</td>
<td>100%</td>
</tr>
<tr>
<td>3,6-dimethyl-1,4-dioxan-2-one **</td>
<td>18%</td>
<td>39%</td>
</tr>
</tbody>
</table>

*reactions were carried out at 0 °C. **3,6-dimethyl-1,4-dioxan-2-one is obtained from the reaction of ethyl-L-lactate and allyl bromide according to Scheme 16.

At 0 °C, the reaction between L-LA [(3S,6S)-3,6-dimethyl-1,4-dioxane-2,5-dione] and S- or R(+)-PO yielded one product, namely I [(3S,6S)-3,6-dimethyl-1,4-dioxan-2-one] and II [(3S,6R)-3,6-dimethyl-1,4-dioxan-2-one], respectively, as the major product. This indicates that the stereocenter of the R(+)- and S-PO remains the same. However, when the reactions were repeated at elevated temperature then the reaction between L-LA and S- or R(+)-PO yield two isomers I, III and II, IV, respectively. Here each compound at 60 °C produces a mixture of PO-LA oligomers and cycles as shown in Figure 59. The $^1$H-NMR of the enantiopure form of the 3,6-dimethyl-1,4-dioxan-2-one and the diasteriomic pair were shown in Figure 60.
Figure 60: $^1$H NMR spectrum (400 MHz, CDCl$_3$) of the hexane soluble product obtained from the reaction of A: rac-PO and rac-LA at 60 °C, B: $R$ (+)-PO and $L$-LA at 0 °C and C: $S$-PO and $L$-LA at 0 °C catalyzed by TPPCrCl/PPN$^+$Cl$^-$. While at 0 °C the reaction to form one form of each enantiomer following the reaction between $R$ (+)/$S$-PO and $L$-LA, at higher temperatures the formation of two isomers arises because of the stereo sequence shown in Scheme 18.

![Scheme 18: Possible mechanism for the racemization at the chiral center of the lactide unit in the polymer chain](image-url)
At 25°C the ratio of the two isomers is smaller than that produced at 60°C and above where the 3:2 pattern emerges as shown in Figure 60(A).

These products were assigned by $^1$H-NMR, achiral and chiral GC and the four isomers are shown in Figure 61.

![Diagrams of isomers](image_url)

Figure 61: The isomers of 3,6-dimethyl-1,4-dioxan-2-one

Both of I [(3S,6S)-3,6-dimethyl-1,4-dioxan-2-one] and II [(3S,6R)-3,6-dimethyl-1,4-dioxan-2-one] were also investigated by 2D-COSY and the representative spectrum for the II is shown in Figure 62.
Figure 62: COSY NMR (400 MHz, CDCl₃) spectrum of 3,6-dimethyl-1,4-dioxan-2-one obtained from the reaction of L-LA and R(+)PO (L-LA:R(+)PO:TPPCrCl/PPN⁺Cl⁻ = 100:200:1) catalyzed by TPPCrCl/PPN⁺Cl⁻ at 0 °C.

The reaction between TPPCrCl, PPN⁺Cl⁻, LA and PO at 0°C for an hour to produce mainly an isotactic enriched PLA with the end group of OCHMeCH₂Cl and with trace amount of OCHMeCH₂OH as determined by mass spectrometry (Figure 63). This polymerization reaction was carried out in atmospheric conditions, where the
moisture/water in the environment may hydrolyze TPPCrCl to produce TPPCrOH. The TPPCrOH should cause for the OCHMeCH₂OH end group.

Figure 63: MALDI spectrum of polylactide obtained from the reaction of rac-LA catalyzed by TPPCrCl/PPN⁺Cl⁻ in rac-PO at 0 °C.

With rac-LA the formation of isotactic PLA was determined by \(^1\)H-NMR spectroscopy and by powder X-ray diffraction studies. The homodecoupled \(^1\)H-NMR, \(^1^\)C-NMR and XRD pattern are shown below.
Figure 64: Homodecoupled $^1$H-NMR (left) and the $^{13}$C-NMR (right) CH resonance of the PLA obtained from the reaction of rac-LA in rac-PO by TPPCrCl/PPN$^+$Cl at 0 °C.

Homodecoupled $^1$H-NMR and the $^{13}$C-NMR of the resulting PLA indicate the formation of isotactic PLA. Further, the isotactic can be classified as stereoplex PLA according to powder XRD pattern (Figure 65). The absence of iis/ssi/sis tetrads also supports that the resulting PLA belongs to stereoplex.
Figure 65: Powder XRD pattern of polylactide obtained from the reaction of *rac*-LA catalyzed by TPPCrCl/PPN+Cl' in *rac*-PO at 0 ºC.

In the formation of isotactic PLA at 0 ºC we encounter a factor that limits high $M_w$. Typically in (TPPCrCl+PPNCl): LA = 1:80 equivalent we obtain a $M_w$ of 3500-5000 Daltons. With higher ratio of catalyst: substrate eg. 1:400 we obtain a $M_w$ of ~10,400 Daltons. The molecular weight and the PDI values for the selected polymer samples are given in Table 14. We find that in addition to the formation of the six-membered ring we also see observations of [(PO)$_m$(1/2LA)$_n$] where $m = 2$ and $n$ = a large number . Thus the formation of [Cr]OCHMeCH$_2$-(ring)-OCHMeCH$_2$Cl by attacking at the terminal chain may prevent the formation of long chains. Herein, all the reactions were carried out in neat PO and the PO concentration is very high comparing with LA during the PLA formation. The higher concentration of PO could favor the insertion of PO during the
PLA formation and consequently back attack to form \((\text{PO})_n(1/2 \text{ LA})_n\), which could be reduced by the addition of some other solvent with PO. Assignment of the stereoplex polymer \((P-L\text{-LA}+P-D\text{-LA})\) is expected due to the chiral end group as in the formation of poly-\textit{iii} PPO from \textit{rac}-PO.

Table 14: Ring opening polymerization data for PLA obtained \textit{rac}-LA/L-LA catalyzed by TPPCrCl/PPN\(+\text{Cl}^-\) in \textit{rac}-PO at 0 °C.

<table>
<thead>
<tr>
<th>Entry</th>
<th>ratio\textsuperscript{a}</th>
<th>Time(h)</th>
<th>% Conversion\textsuperscript{b}</th>
<th>Mn\textsuperscript{c}</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>\textit{rac}-LA</td>
<td>80</td>
<td>1</td>
<td>72</td>
<td>3480</td>
<td>1.06</td>
</tr>
<tr>
<td>\textit{L}-LA</td>
<td>80</td>
<td>1</td>
<td>92</td>
<td>4779</td>
<td>1.07</td>
</tr>
<tr>
<td>\textit{rac}-LA</td>
<td>400</td>
<td>8</td>
<td>70</td>
<td>10,400</td>
<td>1.02</td>
</tr>
<tr>
<td>\textit{rac}-LA\textsuperscript{d}</td>
<td>80</td>
<td>1</td>
<td>98</td>
<td>3005</td>
<td>1.14</td>
</tr>
</tbody>
</table>

\textsuperscript{a} \([\text{lactide}]_0/[\text{initiator}]_0\) ratio , All the polymerization reactions were carried out at 0 °C. \textsuperscript{b} Percentage conversion was obtained by \(^1\)H NMR spectroscopy. \textsuperscript{c} Determined by GPC relative to polystyrene standards in tetrahydrofuran. The experimental \(M_n\) was calculated considering Mark_Houwink’s corrections for \(M_n (M_n(\text{obsd}) = 0.58[M_n(\text{GPC})]. \textsuperscript{d} \) Reaction carried out at room temperature.

The kinetics studies indicate the living nature of the polymerization process and this follows the \(1^{\text{st}}\) order with respect to monomer and 1.5 order with respect to TPPCrCl/PPN+Cl- as shown in Figure 66 and Figure 67.
Figure 66: Linear plots of $\ln([\text{LA}]_0/\text{[LA]})$ versus time (min) for the polymerization of rac-LA([rac-LA]=0.5 M) initiated by TPPCrCl/PPN$^+$Cl$^-$ in rac-PO at 0 °C.

Figure 67: Plot of $-\ln(k_{\text{app}})$ versus $-\ln[\text{Cat}]$ for the rac-LA initiated by TPPCrCl/PPN$^+$Cl$^-$ in rac-PO at 0 °C.
4.3 Proposed mechanistic investigations of polymerizations

The diamagnetic nature of Al complexes provide NMR spectra to study the mechanistic insight of coupling reaction of PO and LA compared with related paramagnetic Cr/Co complexes. We have used TPPAlCl as a model catalyst to study the mechanistic insight into this catalytic process.

Initially we have investigated the interaction of each component of LA, PO and PPN$^+$Cl$^-$ with TPPAlCl in CDCl$_3$. The NMR clearly shows that each of these components coordinate/interact with TPPAlCl. Interestingly, the addition of PO and LA together to the TPPAlCl favors the coordination of PO compared with LA. The addition of PO to the TPPAlCl ring opens PO with the preference of methylene attack as shown in Figure 68 to form Cl$^-$ end group. The addition of PPN$^+$Cl$^-$ to the TPPAlCl/PO system increases the rate of PPO formation. The MALDI spectrum of the resulting PPO from the above reaction shows the Cl$^-$ end group as shown in Figure 69.

![Figure 68](image_url)

Figure 68: The alkoxide resulted by the initiation step of PO by methine [TPPAl(OCH$_a$H$_b$CH$_c$Me$'$Cl)] and methylene [TPPAl(OCH$_a$MeCH$_b$H$_c$Cl)] attack by the Cl$^-$.
Figure 69: The MALDI spectra of PPO obtained from the reaction of PO and TPPAlCl at room temperature. \([\text{H(PO)}_n\text{Cl.Na}^+]\)

The polymer series can be assigned as \(\text{H(PO)}_n\text{Cl.Na}^+\). The reaction between PO and LA with TPPAlCl preferentially polymerizes PO to form PPO at room temperature. On the other hand, the addition of \(\text{PPN}^+\text{Cl}^-\) to the above system preferentially polymerizes LA. The reaction of LA with TPPAlCl and \(\text{PPN}^+\text{Cl}^-\) in DCM/THF is too slow and takes more than a week to complete 20% PLA formation. While the addition of LA, PO and \(\text{PPN}^+\text{Cl}^-\) to TPPAlCl polymerizes LA within a few minutes. Herein, one of the PO inserts between Al and Cl to form \(\text{AlOCH(Me)CH}_2\text{Cl}\) follows the ROP of LA,
which yields the PLA with OCH(Me)CH₂Cl end group. The similar reactivity also has been seen in Cr systems.

This led a question whether the TPPAlOR complexes can produce PLA in the presence of PPN \(^+\)Cl\(^-\). This motivated us to investigate the reactivity of TPPAlOEt and TPPAlO\(^i\)Pr for the LA polymerization. We have synthesized TPPAlOEt and TPPAlO\(^i\)Pr to understand the mechanistic insight of this polymerization. The previous studies showed that the TPPAlOR polymerizes rac-LA at 70°C in toluene to produce isotactic enriched PLA. The reaction of TPPAlOEt or TPPAlO\(^i\)Pr with LA in DCM/THF/acetone/DMF is found to be inactive or very slow. The addition of PO to the above reaction systems produces PLA within an hour for the 100 equiv. of LA. The resulting polymer has the OEt/O\(^i\)Pr end group as determined by MALDI (See Figure 70 for O\(^i\)Pr end group containing polymer; the polymer series can be assigned as \(^i\)PrO(PO)(1/2LA)\(_n\)H).
Unfortunately, the TPAIOr/PO/LA/PPN+Cl system also restricted with the 3000-5000 Daltons molecular weight polymers (for any Catalyst :monomer ratio) similar to the Cr. We have monitored the reaction progress by MALDI studies for the TPAIcI/PPN+Cl/PO/LA system, which produces PLA mainly in the form of H(PO)(LA)nCl.Na+ in the early stage. For example, in 10 minutes we see the polymers in the molecular weight in the range of 1200-2000 Daltons (Figure 71) and in 20 min the
molecular weight range of 1500-3000 Daltons (Figure 72). This clearly indicates the living nature of polymerization during the propagation step. In longer time we see more than two series of polymers as shown in Figure 73.

Figure 71: MALDI spectrum of the PLA obtained by TPPAlCl/PPN⁺Cl⁻/PO/LA system in 10 minutes. [H(PO)(LA)ₙCl.Na⁺]
Figure 72: MALDI spectrum of the PLA obtained by TPPAlCl/PPN⁺Cl⁻/PO/LA system in 20 minutes. [H(PO)(LA)$_n$Cl.Na$^+$]
The decaying shape of polymer series can be assigned as \( \text{H(PO)(1/2LA)}_n \text{Cl} \) and the bell shape series can be assigned as \( \text{(PO)}_2(1/2\text{LA})_n \). The bell shape series can be reasoned by the back biting reaction of the polymer chain as shown in Figure 74. The increasing amount of LA: Al ratio also yields the PLA in the molecular weight range of 3000-5000 Daltons (similar behavior also observed in Cr catalysts – see Table 14). This is consistent that only of the PO react with TPPAlCl to form TPPAlOCHMeCH\(_2\)Cl and activate the PLA formation. While the concentration of LA reduces in the system, the PO
inserts between PLA and Al as shown in Figure 74 and undergoes back-biting reaction to form the macrocycles.

Figure 74: Possible mechanistic pathway for the formation of \((PO)_2(1/2LA)_n\).

If we have a closer look on the catalyst growing chain end for the following cases, where the LA is the coordinated end (Figure 75A), these can be undergo keto-enol tautomerism, while the PO coordinated end cannot have such an equilibration. Therefore, the alkoxide in the case B is more basic than A, which could favor the back biting reaction than A.

Figure 75: Possible differences in the basicity of alkoxides in the polymer chain
The reaction of LA, PO and TPPAlOEt at room temperature produces PPO with the –OEt end group as shown in the Figure 76. The resulting polymer can be assigned as sodiated PPO series of H(PO)$_n$OEt.Na$^+$. The addition of PPN$^+$Cl$^{-}$ after the formation of PPO to the same system produces a block polymer of PPO and PLA. The polymer series can be assigned as OEt (PPO)(PLA)H. Na$^+$ as shown in Figure 76 (The mass unit differs by 1-2 unit for higher molecular weight). The reaction of PO, PPN$^+$Cl$^{-}$ and TPPAlOEt at room temperature produces PPO with the –OEt end group and the addition of LA forming the block polymer of PPO and PLA.

![Figure 76: The MALDI spectra obtained from the reaction of LA, PO and TPPAlOEt at room temperature.](image-url)
Figure 77: The MALDI spectra obtained for the copolymer of PPO-PLA by the reaction of LA, PO and TPPAlOEt and the later addition of PPN$^+$Cl$^-$ at room temperature.

This clearly shows that we need the presence of PPN$^+$Cl$^-$ and PO to enhance the LA polymerization process, which implies that PO, PPN$^+$Cl$^-$ and TPPAlCl are involved in the polymerization. Furthermore, after the completion of LA, the PO inserts and yields a 6 membered ring by the back biting mechanism as shown in Scheme 19. The reactivity for the PLA formation for both of Al and Cr are similar. But the six member ring formation by the Al catalyst is slower than the Cr catalyst at room temperature.
Scheme 19: Proposed mechanism for the formation of PLA and 3,6-dimethyl-1,4-dioxan-2-one by the single site catalyst.

Finally it is worth noting that most coordinate catalysts that are achiral, such as β-diiminates of Mg and Zn favor the formation of heterotatic PLA in the ROP of rac-LA. The conversion of rac-LA to isotactic chains having iii tetrads is much rarer and generally has involved chiral metal centers as in the original report by Baker and Smith, employing rac-salen aluminum alkoxide initiators. An exception of this is seen in the work of Williams employing penta-dentate N₃O₂ ligand even though here the introduction of chiral alkoxide could introduce chirality in the binding of the N₃O₃ ligand.
In the present case of TPPCr the porphyrin is relatively inflexible and so any stereoselectivity must be due to the alkoxide bound to the metal. Presumably this end-group control will lead to a blocky polymer involving alternating section of -(L-LA)n(D-LA)m \(^{128,129,130,131,132}\) and this needs to be determined. Also in the development of an understanding of the reaction profile we noted that in the reaction between TPPCrCl and PO+ LA at room temperature only the formation of PPO is favored. Presumably here [Cr] center acts in a bimetallic manner to form PPO and the [Cr]-OR bonds do not react with LA which is present in solution. In our studies with the 1:1 ratio of TPPCrCl/PPN\(^+\)Cl\(^-\) we see that the formation of H-(LA)\(_n\)-OCHMeCH\(_2\)Cl is formed at low temperatures, 0\(^\circ\)C, with small amounts of the six-membered ring as the inversion starts to compete as the [LA] concentration gets less. In our studies we find that the rate of formation is proportional to the ratio of [TPPCrCl/PPN\(^+\)Cl\(^-\)] where n=1.5. Clearly we need to learn more about the mechanism that adding PPN\(^+\)Cl\(^-\) to the catalytically active system means.

4.4 Conclusion

5,10,15,20-Tetraphenylporphyrin chromium chloride, TPPCrCl with added [Ph\(_2\)P=N=NPh\(_2\)]\(^+\)Cl\(^-\), PPN\(^+\)Cl\(^-\), will selectively polymerize lactide (\(L\) and \(rac\)) dissolved in neat propylene oxide, PO, to yield polylactide PLA terminated by the OCHMeCH\(_2\)Cl group. At room temperature and below \(rac\)-LA yields polymers highly enriched in isotactic tetrads, \(iii\). At 25\(^\circ\)C, the stereo selectivity is lost as trans-esterification becomes significant. At 60\(^\circ\)C and above the enchainment of PO leads to the formation of 3,6-dimethyl-1,4-dioxan-2-one by a back-biting mechanism. At 0\(^\circ\)C after the enchainment of
L-(S,S)-LA in neat $R(+)$-PO, the formation of $(3S,6R)$-3,6-dimethyl-1,4-dioxan-2-one occurs while at higher temperatures the ratio of $(3S,6R)$-3,6-dimethyl-1,4-dioxan-2-one and $(3R,6R)$-3,6-dimethyl-1,4-dioxan-2-one falls 3:2. Furthermore, we see some similar reactivity for the Al catalysts. Further studies must be carried out to get the higher molecular weight isotactic PLA by optimizing the reaction conditions.

4.5 Experimental section

4.5.1 General considerations

Hexane, THF, toluene, and dichloromethane were distilled under nitrogen over CaH$_2$. 5,10,15,20-tetraphenylporphyrin (Fisher), CrCl$_2$ (Strem), and PPN$^+$Cl$^-$, NaH, NaOH, H$_2$SO$_4$, allyl bromide, ethyl-L-lactate, CaH$_2$ (Sigma Aldrich) were purchased and used as received. (TPP)CrCl was prepared according to the literature. L-Lactide (L-LA), and rac-Lactide (rac-LA) were purchased from Sigma Aldrich, and purified by sublimation, followed by recrystallization in dry toluene. Then the lactides were dried under reduced pressure at room temperature overnight. Chloroform-$d$ and benzene –$d_6$ were purchased from Cambridge Isotopes and distilled under nitrogen over CaH$_2$. Rac-PO, S(-)PO and $R(+)$ PO were distilled over CaH$_2$ under a nitrogen environment. $^1$H and $^{13}$C spectra were recorded in CDCl$_3$ ($\delta$: 7.26 and $^{13}$CDCl$_3$ $\delta$: 77.16) on Bruker DPX-400 MHz NMR or DRX-500 MHz NMR spectrometers and referenced against the $^1$H or $^{13}$C signal quoted. MALDI-TOF mass spectra were collected on a Bruker ultrafleXtreme mass spectrometer. GC-mass spectra were recorded on a Thermo Scientific Focus DSQII system. Gas chromatography analyses were carried out by an Agilent using a HP-1
Methylsilicone column and FID detector. Chiral compounds were analyzed by chiral stationary phase chromatography (CSP GC).

4.5.2 Polymerization of LA by TPPCrCl/PPN\(^{+}\)Cl\(^{-}\) catalyst

24.3 mg (0.0347 mmol) TPPCrCl, 20.0 mg (0.0347 mmol) PPN\(^{+}\)Cl\(^{-}\), 0.500 g (3.47 mmol \(L\) or \(r\)-rac-\(\) LA and 5 mL \(r\)-rac-PO were loaded into a vial. The vial was sealed with a Teflon cap and stirred for appropriate time at room temperature. The reaction mixture was quenched with 5N HCl and the PO was evaporated under vacuum. The percentage conversion was obtained by \(^1\)H NMR. The resulting product was washed with methanol several times and the resulting polymer was used for the further analysis (GPC, MALDI, and NMR). For the reaction at 0\(^\circ\)C, 24.3 mg (0.0347 mmol) TPPCrCl, 20.0 mg (0.0347 mmol) PPN\(^{+}\)Cl\(^{-}\) and 0.500 g (3.47 mmol, \(L\)- or \(r\)-rac-\(\) LA were loaded in to a Teflon caped vial and 5 mL \(r\)-rac-PO was loaded into a Teflon caped vial separately. Both vials were placed in the ice bath for 1h before introducing PO in to the LA containing vial. Other procedures were carried out at room temperature reaction.

4.5.3 General procedure for the kinetics studies of LA catalyzed by TPPCrCl/PPN\(^{+}\)Cl\(^{-}\)

A mixture of 10 mg (0.014 mmol) TPPCrCl, 8.0 mg (0.014 mmol) PPN\(^{+}\)Cl\(^{-}\), 0.500 g (3.47 mmol) \(r\)-rac-LA and 7 mL \(r\)-rac-PO were loaded into a vial. The vial was sealed with a Teflon cap and stirred at 0\(^\circ\)C. Then \(\sim\)0.5 mL aliquots were removed at
appropriate time intervals and quenched with 5N acidic methanol. The aliquots were dried under vacuum and the % conversions were obtained by $^1$H-NMR spectroscopy

4.5.4 Synthesis of 3,6-dimethyl-1,4-dioxan-2-one from PO and LA catalyzed by TPPCrCl/PPN$^+$Cl$^-$

A mixture of 24.3 mg (0.0347 mmol) TPPCrCl, 20.0 mg (0.0347 mmol) PPN$^+$Cl$^-$, 0.500 g (3.47 mmol L- or rac-) LA and 0.490 mL (6.94 mmol L- or R(+) or rac-) PO were loaded into a sealable ampule. The ampule was immersed in a 60 °C preheated oil bath for 6h. The reaction mixture was poured into hexane and the hexane soluble component was collected. Hexane was removed under vacuum yielding products (A1 and A2, Figure 56) with 60-70% yield and the products were analyzed by NMR and GC/MS. A1 and A2 are the diastereomeric pairs of 3,6-dimethyl-1,4-dioxan-2-one, $^1$H NMR assignments were made by the independent synthesis of diastereomers. Oligomers were analyzed by ESI.

3,6-dimethyl-1,4-dioxan-2-one (A1): $^1$H NMR (500 MHz, CDCl$_3$) δ 1.33 (d, 3H, CH$_3$), 1.56 (d, 3H, CH$_3$), 3.44-3.50 (dd, 1H, CH$_3$H$_b$), 3.94-3.98 (dd, 1H, CH$_3$H$_b$), 4.27 (q, 1H, CHMe), 4.74 (m, 1H, CHMe). $^{13}$C NMR (125.72 MHz, CDCl$_3$): 17.20, 18.07, 68.57, 72.62, 76.30, 170.24. GC/MS (EI): Calcd for C$_6$H$_{10}$O$_3$ M$^+$:130.1, Found: 130.1

3,6-dimethyl-1,4-dioxan-2-one (A2): $^1$H NMR (500 MHz, CDCl$_3$) δ 1.45(d, 3H, CH$_3$), 1.55(d, 3H, CH$_3$), 3.65-3.70 (dd, 1H, CH$_3$H$_b$), 3.87-3.90 (dd, 1H, CH$_3$H$_b$), 4.41 (q, 1H, CHMe)
1H, CHMe), 4.70 (m, 1H, CHMe). $^{13}$C NMR (125.72 MHz, CDCl$_3$): 17.83, 18.35, 65.83, 71.73, 75.42, 170.57. GC/MS (EI): Calcd for C$_6$H$_{10}$O$_3$ M$:130.1$, Found: 130.1

CSP GC (cyclosil B, 85 °C): RT 14.89, 15.5, 17.3 and 18.6 min.

### 4.5.5 Synthesis of 3,6-dimethyl-1,4-dioxan-2-one

NaH (10.0 g, 60% dispersion in mineral oil) was washed with hexane and dispersed in 60 mL of THF. Then 10.0 mL (87.0 mmol) of ethyl-L-lactate was added drop wise and stirred overnight at room temperature. Into the resulting mixture 8.0 mL (93.0 mmol) allyl bromide was added drop wise and stirred for 4h. The reaction was quenched with water and the organic compound was extracted with DCM ethyl 2-(allyloxy) propanoate was confirmed by $^1$H-NMR. The organic layer was evaporated and redissolved in KOH/ ethanol and refluxed for 6 hours. Then the resulting mixture was neutralized with diluted HCl and the organic compounds were extracted in DCM. DCM was evaporated and 2-(allyloxy)propanoic acid was obtained with (6.81 g) 60% yield. The resulting 2-(allyloxy) propanoic acid was refluxed with 35% H$_2$SO$_4$ for 8h to obtain the 3,6-dimethyl-1,4-dioxan-2-one as a mixture of ($R$,$R$), ($R$,$S$), ($S$,$R$) and ($S$,$S$) isomers.

**2-(allyloxy)propanoic acid:** $^1$H NMR (400 MHz, CDCl$_3$) δ 1.44 (d, 3H, CH$_3$), 3.95-4.17 (m, 2H, CH$_2$), 4.05 (q, 1H, CHMe), 5.18-5.32 (m, 2H, CH$_a$H$_b$), 5.83-5.95 (m, 1H, CH=CH$_2$), 10.74 (bs, 1H, COOH). $^{13}$C NMR (100.62 MHz, CDCl$_3$): 18.41, 71.30, 73.60, 118.35, 133.77, 178.05. GC/MS (EI): Calcd for C$_6$H$_{10}$O$_3$ M$:130.1$, Found: 130.1.
Chapter 5  Ring Opening Polymerization of Lactide, ε-Caprolactone and Propyleneoxide by Modified β-Dikitiminate Magnesium Catalysts

5.1 Introduction

Grignard reagent, in the form of RMgX (R = alkyl and X = halides), was discovered in 1900 and consequently awarded Nobel Prize in 1912, which is one of the most used organometallic reagents in the synthetic chemistry. Grignard reagents are synthesized by refluxing alkyl /aryl halides with magnesium turnings in ethereal solvents using standard air-moisture free conditions. The reactivity and stability of the Grignard reagent is mainly influenced by the choice of solvent. The existence of equilibrium for the Grignard reagent was suggested by Abegg and further extensive studies have done by Schlenk, later the equilibrium is referred as the Schlenk equilibrium (See Figure 78).

\[
2\text{RMgX} \rightleftharpoons \text{R}_2\text{Mg} + \text{MgX}_2
\]

Figure 78: Schlenk equilibrium
The mechanism for the reactivity of the RMgX with ketones is still inconclusive and it is still under investigation. The experimental evidence suggests that the mechanisms proceed by both of radical pathway as well as one step concerted pathway. The one step concerted mechanism usually undergoes via the alkyl transfer or β-hydrogen transfer. The alkyl group transfer proceeds via the four-membered ring transitions state, whereas the β-hydrogen transfer proceeds via six-membered transition state as depicted in Figure 79.

![Figure 79: One-step concerted alkyl transfer and β-hydrogen transfer transitions states of Grignard reagent in their reaction with ketone.](image)

β-Dikiminato based ligands are one of the attractive ligand systems towards the synthesis of single site Mg initiators for the ROP of cyclic esters. This ligand framework provides several scopes for the variation of R, R1, R2 and R3 groups (See Figure 81) to
tune the steric and electronic properties. These steric and electronic properties mainly influenced in the stability and the reactivity of the catalyst system. Furthermore, the steric influence restricts the Schlenk equilibrium towards the stabilization and the formation of single site magnesium catalysts (Figure 81, II) is shown below.

![Figure 81: Possible equilibrium products of β-dikitimate Mg complexes.](image)

The EDG in the phenyl groups decreases the electrophilicity of the metal center, which will decrease the M…X bond strength and favor for the bond dissociation as shown in Figure 82. This will favor the coordination insertion of the monomer and increase the rate of polymerization. Similarly, the EWG decrease the rate of polymerization.136

![Figure 82: Schematic representation for the influence of the EWG and EDG in the M-X bond.](image)
Well controlled and selective reactions of aldehydes, ketones, CO$_2$, LA and $\varepsilon$-CL with BDIMg$^n$Bu(THF) catalysts were documented by Chisholm and co-workers.$^{137}$ Similarly we could expect that epoxides can be selectively reacted with BDIMg$^n$Bu(THF) to form alcohols or polyethers. Mg($^{n}$Bu)$_2$ and RMgX compounds were investigated for the ROP of PO in toluene and were found to show slow polymerization rates, *ie.* 6-days to complete 100 equivalent of PO at room temperature.$^{138,139}$ Calcium containing single site catalysts also do not react with PO, and the product of Tp$^*$Ca(OAr)(PO) was isolated by Chisholm and co-workers (Tp$^*$ = tris-tert-butylpyrazolyl borate).$^{140}$ The crystal structure of the Tp$^*$Ca(OAr)(PO) is shown in Figure 83. This clearly indicates that PO bound to Ca (Ca-O$_{PO}$ = 2.454 Å) and not favor the subsequent nucleophilic attack by the bulky OAr group. This prompted us to investigate further reactions of PO with bulky $\beta$-diketiminate Mg catalysts.

![Figure 83: ORTEP drawing of the Tp$^*$BuCa(O-2,6-$^t$Pr$_2$C$_6$H$_3$).PO molecule with thermal ellipsoids drawn at 50% probability level. Hydrogen atoms are omitted for clarity.](image)
This chapter is mainly focused on the synthesis of modified β-diketimate ligand systems and their application towards the synthesis of polyesters, polyethers and polycaprlactone.

5.2 Synthesis

The following ligands were studied towards the development of single-site Mg catalysts for the ROP of LAs and ε-CL. The schematic representation of the ligands systems are shown in Figure 84.

Figure 84: BDI ligand systems investigated in this study for the ROP

BDIH and BDI(CF₃)H ligands were synthesized by the condensation reactions as shown below in Scheme 20.

Scheme 20: Reaction scheme for the synthesis of BDIH and BDI(CF₃)H ligands by direct condensation method.
BDI*H and BDI(Ph)H ligands were synthesized according to the literature and the general reaction scheme is shown below in Scheme 21.

Scheme 21: Reaction scheme for the synthesis of BDI(Ph)H and BDI*H.

BDI(CH₂Ph)H was synthesized according to the following Scheme 22.

Scheme 22: Synthesis of BDI(CH₂Ph)H from BDIH

152
All the Mg containing catalyst synthesis were carried out according to the following general procedure (Scheme 23) and employed for the polymerization studies.

\[
\text{BDIH} + \text{Mg}^\pi \text{Bu}_2 \xrightarrow{\text{pentane-reflux}} \text{BDIMg}^\pi \text{Bu} + n\text{-butane}
\]

\[
\text{BDIH} + \text{Mg}^\pi \text{Bu}_2 \xrightarrow{\text{pentane + THF-reflux}} \text{BDIMg}^\pi \text{Bu(THF)} + n\text{-butane}
\]

Scheme 23: General scheme for the synthesis of $\beta$-dikimate Mg catalysts

The resulted catalyst structures are shown by a general structure in the Figure 86 and the summary of the catalysts are given in the following Table 15.

Figure 85: General structure of the BDI catalysts investigated in this study
Table 15: Summary of catalysts employed in this work for the ROP

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>(R_1)</th>
<th>(R_2)</th>
<th>Sol</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Me</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>B</td>
<td>Me</td>
<td>H</td>
<td>THF</td>
</tr>
<tr>
<td>C</td>
<td>'Bu</td>
<td>H</td>
<td>-</td>
</tr>
<tr>
<td>D</td>
<td>'Bu</td>
<td>H</td>
<td>THF</td>
</tr>
<tr>
<td>E</td>
<td>CF₃</td>
<td>H</td>
<td>THF</td>
</tr>
<tr>
<td>F</td>
<td>Ph</td>
<td>H</td>
<td>THF</td>
</tr>
<tr>
<td>G</td>
<td>Me</td>
<td>CH₂Ph</td>
<td>THF</td>
</tr>
</tbody>
</table>

- Where \(R = \text{"Butyl}"\.

BDI*Mg*Bu(PO) was synthesized by the stochiometric addition of BDI*Mg*Bu with PO in DCM/pentane as shown below in Scheme 24.

![Scheme 24: Synthesis of BDI*Mg*Bu(PO)](image)

5.3 Results and discussions

5.3.1 Solid state studies

The crystallographic data for BDI*Mg*Bu structure is given in Table 17 and a summary of notable bond distances and angles can be seen in Table 16. BDI*Mg*Bu crystallized in the orthorhombic space group Fdd2 where there are two independent molecules found in the asymmetric unit, one of which has a disorder in the "Bu group. One of these is shown in Figure 86.
The N-Mg-N angle is 94.2° and the N-Mg-C angles fall in the range 130-135 °C and so each N₂MgC unit is trigonal planer. In contrast to the BDI structure the ’Bu groups impart greater stereo regularity and the angle of the aryl ring with respect to N₂MgC plane is around 85°. When comparing the structures seen in Figure 86 and Figure 87, we note that the Mg is 0.67 Å out of the N₂C plane and that the distances are notably longer as a result of forming the Mg-O bond distance 2.09 Å for the THF structure (Figure 87).

Figure 86: Molecular Structure of BDI*Mg°Bu drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.
Figure 87: Model of BDI*Mg/Bu(THF). Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens, and disorder omitted for clarity.

Table 16: Selected bond distances and angles of BDI*Mg/Bu, BDI*Mg/Bu(PO) and BDI*Mg/Bu(THF).

<table>
<thead>
<tr>
<th></th>
<th>BDI*Mg/Bu</th>
<th>BDI*Mg/Bu(PO)</th>
<th>BDI*Mg/Bu(THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg – N(1)</td>
<td>2.010(4)</td>
<td>2.068(2)</td>
<td>2.067(2)</td>
</tr>
<tr>
<td>Mg – N(2)</td>
<td>2.026(4)</td>
<td>2.087(2)</td>
<td>2.087(2)</td>
</tr>
<tr>
<td>Mg – O</td>
<td>2.092(2)</td>
<td>2.091(1)</td>
<td></td>
</tr>
<tr>
<td>Mg – C</td>
<td>2.117(5)</td>
<td>2.135(3)</td>
<td>2.122(2)</td>
</tr>
</tbody>
</table>

Angles in degrees

<table>
<thead>
<tr>
<th></th>
<th>BDI*Mg/Bu</th>
<th>BDI*Mg/Bu(PO)</th>
<th>BDI*Mg/Bu(THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1) – Mg – N(2)</td>
<td>94.2(2)</td>
<td>92.65(7)</td>
<td>93.19(6)</td>
</tr>
<tr>
<td>N(2) – Mg – C(α-nBu)</td>
<td>130.0(2)</td>
<td>132.29(9)</td>
<td>119.12(8)</td>
</tr>
<tr>
<td>C(α-nBu) – Mg – N(1)</td>
<td>135.8(2)</td>
<td>116.30(9)</td>
<td>125.66(8)</td>
</tr>
<tr>
<td>C(α-nBu) – Mg – O</td>
<td>107.52(9)</td>
<td>107.65(8)</td>
<td></td>
</tr>
<tr>
<td>N(2) – Mg – O</td>
<td>101.10(7)</td>
<td>104.25(6)</td>
<td></td>
</tr>
<tr>
<td>N(1) – Mg – O</td>
<td>102.90(7)</td>
<td>104.33(6)</td>
<td></td>
</tr>
</tbody>
</table>

The crystal structure of the BDI*Mg/Bu(PO) is shown in Figure 88.
Figure 88: ORTEP drawing of the BDI*Mg*Bu(PO) molecule with thermal ellipsoids drawn at 50% probability level, where Green = Magnesium, Blue = Nitrogen, Oxygen = Red, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.

Selected bond distances and the angles are summarized in Table 16 and the crystallographic data collection parameters are summarized in Table 17. This clearly indicates that PO bound to Mg (Mg-PO = 2.092 Å). The Mg-PO distance in the BDI*Mg*Bu(PO) is same as the Mg-O_{THF} bond in BDI*Mg*Bu(THF). Intrestingly the Mg-C_{(α-nBu)} of the BDI*Mg*Bu(PO) > BDI*Mg*Bu(THF) by 0.012 Å. At the same time the β-hydrogens of the BDI*Mg*Bu(PO) is closer to the Mg than BDI*Mg*Bu(THF) as shown in the Diagram 2, which will favor the β-hydrogen elimination reaction for BDI*Mg*Bu(PO).
Table 17: Crystallographic Data Collection Parameters for BDI*Mg°Bu and BDI*Mg°Bu(PO).

<table>
<thead>
<tr>
<th>Compound</th>
<th>BDI*Mg°Bu</th>
<th>BDI*Mg°Bu(PO)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical Formula</td>
<td>C_{39}H_{62}MgN_{2}</td>
<td>C_{42}H_{68}MgN_{2}O</td>
</tr>
<tr>
<td>Formula Weight</td>
<td>583.21</td>
<td>641.29</td>
</tr>
<tr>
<td>Temperature (K)</td>
<td>150(2)</td>
<td>150(2)</td>
</tr>
<tr>
<td>Space Group</td>
<td>Orthorhombic, Fdd2</td>
<td>Monoclinic, P2_{1}/n</td>
</tr>
<tr>
<td>a (Å)</td>
<td>32.347(7)</td>
<td>11.8794(4)</td>
</tr>
<tr>
<td>b (Å)</td>
<td>43.499(9)</td>
<td>26.2797(11)</td>
</tr>
<tr>
<td>c (Å)</td>
<td>21.529(4)</td>
<td>13.3750(5)</td>
</tr>
<tr>
<td>α (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>β (°)</td>
<td></td>
<td>104.787(2)</td>
</tr>
<tr>
<td>γ (°)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>V (Å³)</td>
<td>30293(11)</td>
<td>40037.2(3)</td>
</tr>
<tr>
<td>Z</td>
<td>32</td>
<td>4</td>
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<tr>
<td>D_{calcld} (Mg/m³)</td>
<td>1.023</td>
<td>1.055</td>
</tr>
<tr>
<td>Crystal Size (mm)</td>
<td>0.42 X 0.35 X 0.27</td>
<td>0.38 X 0.27 X 0.11</td>
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<tr>
<td>Theta range for data collection</td>
<td>1.229 to 24.982°</td>
<td>1.550 to 25.022°</td>
</tr>
<tr>
<td>μ (mm⁻¹) [Mo, Kα]</td>
<td>0.073</td>
<td>0.076</td>
</tr>
<tr>
<td>F(000)</td>
<td>10304</td>
<td>1416</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>55253</td>
<td>44602</td>
</tr>
<tr>
<td>Unique reflections</td>
<td>13053[R(int)=0.065]</td>
<td>7095 [R(int)=0.040]</td>
</tr>
<tr>
<td>Data Completeness to [ θ ]</td>
<td>99.6% [25.000]</td>
<td>99.7% [25.000]</td>
</tr>
<tr>
<td>Data/restraints/parameters</td>
<td>13053 / 64 / 801</td>
<td>7095 / 19 / 451</td>
</tr>
<tr>
<td>R1[^a] (%) (all data)</td>
<td>7.55 (12.12)</td>
<td>5.65(8.80)</td>
</tr>
<tr>
<td>wR2[^b](%)(all data)</td>
<td>17.45 (20.04)</td>
<td>13.10(14.57)</td>
</tr>
<tr>
<td>Goodness-of-fit on F²</td>
<td>1.044</td>
<td>1.035</td>
</tr>
<tr>
<td>Largest diff. peak and hole (e Å⁻³)</td>
<td>0.613 and -0.271</td>
<td>0.358 and -0.279</td>
</tr>
</tbody>
</table>

\[^a\] R1 = Σ |F_o| - |F_c| / Σ |F_o| x 100

\[^b\] wR2 = Σ w (F_o²-F_c²)² / Σ (w |F_o|²)²]¹/² x 100

These might be the reasons for that BDI*Mg°Bu(PO) is more reactive than BDI*Mg°Bu(THF). This results that the BDI*Mg°Bu(PO) in solution with the time ring opens the PO. Similarly, 3 coordinated BDI*Mg°Bu also relatively less stable than the BDI*Mg°Bu(THF).
Diagram 2: β-Hyogens distances form the Mg for BDI*Mc "Bu, BDI*Mg"Bu(PO) and BDI*Mg"Bu(THF).

The compound BDI(Ph)Mg"Bu(THF), not yielding the X-ray suitable crystals, in hydrocarbon solvents readily reacts with oxygen to form alkoxides. The X-ray quality BDI(Ph)MgO"Bu crystals were grown in toluene and the crystal structure is shown in Figure 89. The crystallographic data for the BDI(Ph)MgO"Bu is given in Table 19. This is an oxygen bridged dimeric structure and has the similar structural features to BDIMgO"Bu.137

The N-Mg-N angle for the [BDI(Ph)MgO"Bu]_2 is 0.33° smaller than [BDIMgO"Bu]_2 which clearly results from the steric hindrance of the Ph group in the back bone (See Table 18).
Figure 89: Molecular Structure of [BDI(Ph)MgO\textsuperscript{Bu}]\textsubscript{2} drawn at 50\% probability, where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.

Table 18: Selected bond distances and angles of [BDI(Ph)MgO\textsuperscript{Bu}]\textsubscript{2} and of [BDIMgO\textsuperscript{Bu}]\textsubscript{2}.

<table>
<thead>
<tr>
<th>Distances in Å</th>
<th>[BDI(Ph)MgO\textsuperscript{Bu}]\textsubscript{2}</th>
<th>[BDIMgO\textsuperscript{Bu}]\textsubscript{2} \textsuperscript{13/}</th>
<th>Angles in degrees</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg – N(1)</td>
<td>2.102(2)</td>
<td>2.0883(15)</td>
<td>N(1) – Mg – N(2)</td>
</tr>
<tr>
<td>Mg – N(2)</td>
<td>2.1010(19)</td>
<td>2.0883(15)</td>
<td>N(2) – Mg – O</td>
</tr>
<tr>
<td>Mg – O</td>
<td>1.9693(18)</td>
<td>2.026(2)</td>
<td>N(2) – Mg – O*</td>
</tr>
<tr>
<td>Mg-O*(bridged)</td>
<td>1.9736(18)</td>
<td>2.026(2)</td>
<td>N(1) – Mg – O</td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>3.0039(15)</td>
<td>2.968(16)</td>
<td>N(1) – Mg – O*</td>
</tr>
<tr>
<td>Mg-O-Mg</td>
<td></td>
<td></td>
<td>O-Mg-O*</td>
</tr>
</tbody>
</table>

160
The compound BDI(CH$_2$Ph)Mg"Bu(THF) crystals were obtained in pentane and the molecular structure is shown in Figure 90. The crystallographic data for the BDI(CH$_2$Ph)Mg"Bu(THF) is given in Table 19. The Mg-O$_{\text{THF}}$ and the Mg-C$_{\text{(α-nBu)}}$ bond lengths for the BDI(CH$_2$Ph)Mg"Bu(THF) were longer than BDIMg"Bu(THF) by 0.02 Å (See Table 20). Additionally the N-Mg-N angle is 3.5˚ smaller than BDIMg"Bu(THF), which clearly shows again the steric influence of CH$_2$Ph. The benzyl group in the backbone bends by 118.2˚ and the Ph ring of the benzyl group is anti to the THF to reduce the steric effect. The Figure 91 clearly shows that the BDI(CH$_2$Ph)Mg"Bu(THF) has the nearly same pocket size compare with BDIMg"Bu(THF).

![Molecular Structure of BDI(CH$_2$Ph)Mg"Bu(THF) drawn at 50% probability. Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.](image-url)
Table 19: The crystallographic data for the BDI(Ph)MgO^Bu and BDI(CH_2Ph)Mg^Bu(THF)

<table>
<thead>
<tr>
<th>Compound</th>
<th>BDI(CH_2Ph)Mg^Bu(THF)</th>
<th>[BDI(Ph)MgO^Bu]_2</th>
</tr>
</thead>
<tbody>
<tr>
<td>Chemical formula</td>
<td>C_{44}H_{64}MgN_2O</td>
<td>C_{100}H_{124}Mg_2N_4O_2</td>
</tr>
<tr>
<td>Formula weight</td>
<td>661.28</td>
<td>1462.64</td>
</tr>
<tr>
<td>Temperature</td>
<td>150(2) K</td>
<td>150(2) K</td>
</tr>
<tr>
<td>space group</td>
<td>Monoclinic, C 2/c</td>
<td>Triclinic, P -1</td>
</tr>
<tr>
<td>Unit cell dimensions</td>
<td></td>
<td></td>
</tr>
<tr>
<td>a (Å)</td>
<td>23.6489(7)</td>
<td>14.0161(2)</td>
</tr>
<tr>
<td>b(Å)</td>
<td>23.7766(7)</td>
<td>14.0441(3)</td>
</tr>
<tr>
<td>c(Å)</td>
<td>15.8289(5)</td>
<td>4.7562(2)</td>
</tr>
<tr>
<td>α(°)</td>
<td>90</td>
<td>86.7400(10)</td>
</tr>
<tr>
<td>β(°)</td>
<td>100.31</td>
<td>62.4160(10)</td>
</tr>
<tr>
<td>γ(°)</td>
<td>90</td>
<td>89.6470(10)</td>
</tr>
<tr>
<td>V(Å)^3</td>
<td>8756.8(5)</td>
<td>2569.66(8)</td>
</tr>
<tr>
<td>Z</td>
<td>8</td>
<td>1</td>
</tr>
<tr>
<td>Calculated density Mg/mÅ^3</td>
<td>1.003</td>
<td>0.945</td>
</tr>
<tr>
<td>Crystal size  mm</td>
<td>0.350 x 0.350 x 0.310</td>
<td>0.380 x 0.150 x 0.150</td>
</tr>
<tr>
<td>Θ range for data collection</td>
<td>1.224 to 24.982</td>
<td>2.066 to 25.023</td>
</tr>
<tr>
<td>Reflections collected</td>
<td>55229</td>
<td>63812</td>
</tr>
<tr>
<td>unique reflections</td>
<td>7683 [R(int) = 0.038]</td>
<td>9077 [R(int) = 0.042*]</td>
</tr>
<tr>
<td>Completeness to Θ_{max}</td>
<td>96.90%</td>
<td>97.60%</td>
</tr>
<tr>
<td>Data / restraints / parameters</td>
<td>7683 / 0 / 444</td>
<td>9077 / 0 / 497</td>
</tr>
<tr>
<td>Goodness-of-fit on F^2</td>
<td>1.038</td>
<td>1.061</td>
</tr>
<tr>
<td>R_{1a}(%)(all data)</td>
<td>0.0841</td>
<td>0.0856</td>
</tr>
<tr>
<td>wR_{2a}(%)(alldata)</td>
<td>0.1748</td>
<td>0.1958</td>
</tr>
<tr>
<td>Largest diff. peak and hole</td>
<td>e.A^3</td>
<td>0.532 and -0.416</td>
</tr>
</tbody>
</table>

a R1 = \sum |F_o|-|F_c| / \sum |F_o| \times 100

b wR2 = [\sum w (F_o^2-F_c^2)^2 / \sum (w |F_o|^2)^{1/2}] \times 100
Figure 91: Best superposition of the molecular structures of BDIMgBu'(THF) in green and BDI(CH$_2$Ph)MgBu'(THF) in red showing the relative disposition of the aryl ligands and both contain similar steric pressure on the pocket of the n-butyl group.

Table 20: Selected bond distances and bond angle of BDIMg'Bu, BDIMg'Bu(THF) and BDI(CH$_2$Ph)Mg'Bu(THF).

<table>
<thead>
<tr>
<th>Distances in Å</th>
<th>BDIMg'Bu</th>
<th>BDIMg'Bu(THF)</th>
<th>BDI(CH$_2$Ph)Mg'Bu(THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg – N(1)</td>
<td>2.054(9)</td>
<td>2.063(1)</td>
<td>2.0562(18)</td>
</tr>
<tr>
<td>Mg – N(2)</td>
<td>2.046(10)</td>
<td>2.071(1)</td>
<td>2.0639(19)</td>
</tr>
<tr>
<td>Mg – O</td>
<td>2.058(1)</td>
<td>2.0750(17)</td>
<td></td>
</tr>
<tr>
<td>Mg – C</td>
<td>2.251(3)</td>
<td>2.127(2)</td>
<td>2.145(2)</td>
</tr>
<tr>
<td>Mg-C*(bridged)</td>
<td>2.253(3)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>Mg-Mg</td>
<td>2.7248(16)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>

Angles in degrees

<table>
<thead>
<tr>
<th>Angles in degrees</th>
<th>BDIMg'Bu</th>
<th>BDIMg'Bu(THF)</th>
<th>BDI(CH$_2$Ph)Mg'Bu(THF)</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1) – Mg – N(2)</td>
<td>93.52(9)</td>
<td>93.00(5)</td>
<td>89.40(7)</td>
</tr>
<tr>
<td>N(2) – Mg – C</td>
<td>111.47(10)</td>
<td>126.40(7)</td>
<td>129.01(10)</td>
</tr>
<tr>
<td>C– Mg – N(1)</td>
<td>112.58(10)</td>
<td>119.20(7)</td>
<td>119.59(9)</td>
</tr>
<tr>
<td>C – Mg – O</td>
<td>110.56(7)</td>
<td>109.68(10)</td>
<td></td>
</tr>
<tr>
<td>N(2) – Mg – O</td>
<td>101.31(5)</td>
<td>101.38(7)</td>
<td></td>
</tr>
<tr>
<td>N(1) – Mg – O</td>
<td>102.56(5)</td>
<td>103.77(7)</td>
<td></td>
</tr>
<tr>
<td>C – Mg – C*</td>
<td>105.56(9)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(2) – Mg – C*</td>
<td>114.94(10)</td>
<td></td>
<td></td>
</tr>
<tr>
<td>N(1) – Mg – C*</td>
<td>118.70(10)</td>
<td></td>
<td></td>
</tr>
</tbody>
</table>
The X-ray quality crystals of BDI(CF$_3$)Mg$^n$Bu(THF) were obtained in pentane and the crystal structure is shown in Figure 92. The Mg-O$_{THF}$ bond length for the BDI(CF$_3$)Mg$^n$Bu(THF) is 2.06 Å, which is 0.05 Å smaller than the Mg-O$_{THF}$ bond length of BDI*Mg$^n$Bu(THF). Additionally the N-Mg-N angle is 2.2 deg. smaller than BDI*Mg$^n$Bu(THF), which clearly shows again the steric influence of CF$_3$.

Figure 92: Molecular Structure of BDI(CF$_3$)Mg$^n$Bu(THF) drawn at 50% probability. Where Green = Magnesium, Blue = Nitrogen, and Gray = Carbon. Hydrogens and isopropyl groups omitted for clarity.
Table 21: Selected bond distances and angles of BDI*Mg^nBu(THF) and BDI(CF$_3$)Mg^nBu(THF).

<table>
<thead>
<tr>
<th></th>
<th>Distances in Å</th>
<th>BDI*Mg^nBu(THF)$^{111}$</th>
<th>BDI(CF$_3$)Mg^nBu(THF).</th>
</tr>
</thead>
<tbody>
<tr>
<td>Mg – N(1)</td>
<td>2.067(2)</td>
<td>2.098(3)</td>
<td></td>
</tr>
<tr>
<td>Mg – N(2)</td>
<td>2.087(2)</td>
<td>2.112(3)</td>
<td></td>
</tr>
<tr>
<td>Mg – O</td>
<td>2.091(1)</td>
<td>2.062(2)</td>
<td></td>
</tr>
<tr>
<td>Mg – C$_{\alpha$-nBu}</td>
<td>2.122(2)</td>
<td>2.16(3)*</td>
<td></td>
</tr>
</tbody>
</table>

Angles in degrees

<table>
<thead>
<tr>
<th></th>
<th>BDI*Mg^nBu(THF)$^{111}$</th>
<th>BDI(CF$_3$)Mg^nBu(THF).</th>
</tr>
</thead>
<tbody>
<tr>
<td>N(1) – Mg – N(2)</td>
<td>93.19(6)</td>
<td>90.4(1)</td>
</tr>
<tr>
<td>N(2) – Mg – C$_{\alpha$-nBu}</td>
<td>119.12(8)</td>
<td>123.5(8)</td>
</tr>
<tr>
<td>C$_{\alpha$-nBu}– Mg – N(1)</td>
<td>125.66(8)</td>
<td>130.2(8)</td>
</tr>
<tr>
<td>C$_{\alpha$-nBu}– Mg – O</td>
<td>107.65(8)</td>
<td>107.1(8)</td>
</tr>
<tr>
<td>N(2) – Mg – O</td>
<td>104.25(6)</td>
<td>99.7(1)</td>
</tr>
<tr>
<td>N(1) – Mg – O</td>
<td>104.33(6)</td>
<td>100.4(1)</td>
</tr>
</tbody>
</table>

5.4 Ring opening polymerization of LA and CL

All the seven synthesized complexes were employed for the ROP of LAs and CLs. The rate of LA polymerization for the four coordinated (THF) Mg complexes is faster than the three coordinated complexes.
The rate for the four coordinated complexes follows the following order:

$$\text{BDI(Ph)Mg}^{n}\text{Bu(THF)} > \text{BDI(CH}_2\text{Ph})\text{Mg}^{n}\text{Bu(THF)} > \text{BDIMg}^{n}\text{Bu(THF)} > \text{BDI(CF}_3\text{)}\text{Mg}^{n}\text{Bu(THF)} > \text{BDI*Mg}^{n}\text{Bu(THF)}.$$  

The rate for the four coordinated complexes follows the following order: BDI(Ph)Mg"Bu(THF) > BDI(CH2Ph)Mg"Bu(THF) > BDIMg"Bu(THF) > BDI(CF3)Mg"Bu(THF) > BDI*Mg"Bu(THF). The ln{[LA]0/[LA]t} versus time (sec.) plots for all 7 complexes are shown in Figure 93 and the $k_{app}$ values are summarized in Table 22. All these polymerization process follow the first order with respect to catalyst and monomer. BDI(Ph)Mg"Bu(THF) is the fastest catalyst for the for the ROP of LA and it is higher than the previously reported highest active Mg catalyst, BDIMg"Bu(THF). The initiation step is same for both of BDI(Ph)Mg"Bu(THF) and BDIMg"Bu(THF) while the propagation step is slightly faster for the BDI(Ph)Mg"Bu(THF). This might be
influenced by the electron donating or inductive effect of Ph substitution in the BDI backbone ligand. The rate of polymerization of BDI(CH$_2$Ph)Mg"Bu(THF) is slightly faster than BDIMg"Bu(THF). The rate initiation step of the rac-LA polymerization for BDI(CH$_2$Ph)Mg"Bu(THF) is lesser than BDIMg"Bu(THF). The rate of propagation is for BDI(CH$_2$Ph)Mg"Bu(THF) higher than BDIMg"Bu(THF). This might results from the electron donating effect of the CH$_2$Ph group.

Table 22: $k_{app}$ values for the 7 BDI catalysts for the ROP of rac-LA in DCM at room temperature

<table>
<thead>
<tr>
<th>Catalyst</th>
<th>R$_1$</th>
<th>R$_2$</th>
<th>Sol</th>
<th>$k_{app}$</th>
</tr>
</thead>
<tbody>
<tr>
<td>A</td>
<td>Me</td>
<td>H</td>
<td>-</td>
<td>0.032</td>
</tr>
<tr>
<td>B</td>
<td>Me</td>
<td>H</td>
<td>THF</td>
<td>0.045</td>
</tr>
<tr>
<td>C</td>
<td>'Bu</td>
<td>H</td>
<td>-</td>
<td>0.0052</td>
</tr>
<tr>
<td>D</td>
<td>'Bu</td>
<td>H</td>
<td>THF</td>
<td>0.0088</td>
</tr>
<tr>
<td>E</td>
<td>CF$_3$</td>
<td>H</td>
<td>THF</td>
<td>0.031</td>
</tr>
<tr>
<td>F</td>
<td>Ph</td>
<td>H</td>
<td>THF</td>
<td>0.064</td>
</tr>
<tr>
<td>G</td>
<td>Me</td>
<td>CH$_2$Ph</td>
<td>THF</td>
<td>0.051</td>
</tr>
</tbody>
</table>

If we compare the EWG containing catalyst, BDI(CF$_3$)Mg"Bu(THF), and the EDG containing catalyst, BDI*Mg"Bu(THF), the rate of polymerization is faster for the BDI(CF$_3$)Mg"Bu(THF).

Now if we consider the 3-coordinated and 4-coordinated compounds of BDI* or BDI backbone containing analogs, the four coordinated compounds reactivity is higher than the 3-coordinated complex in DCM. The lower reactivity in the 3-coordinated
compounds could be attributed to the competing reaction of monomer in the initiation step at the metal center as shown below.

On the other hand, the electron donating ability of the oxygen by THF is greater than the ketonic oxygen on LA. The THF coordinated compound could increase the electron density at the metal center and consequently weaken the Mg-C bond or corresponding Mg-O bond of the propagating species. This could explain the lower reactivity of the 3-coordinated compound.

The polymerization of LA by BDI(Ph)Mg"Bu(THF) in CH₂Cl₂ at room temperature follows the 1ˢᵗ order with respect to LA and catalyst. The ln(A₀/A) vs time and the ln(cat) vs ln(kₓ) were shown in Figure 94 and Figure 95 respectively. This catalyst is the fastest magnesium catalyst among the currently reported catalysts with the kₓ value of 14.5 M⁻¹s⁻¹, where the previous reported highest active Mg catalyst [BDIMg"Bu(THF)] has the kₓ = 10.7 M⁻¹s⁻¹.
Figure 94: Linear plots of $\ln([\text{LA}]_0/\text{LA})$ versus time (sec.) for the polymerization of rac-LA initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.

Figure 95: Plot of $-\ln(k_{\text{app}})$ versus $-\ln(\text{Cat})$ for the rac-LA initiated by BDI(Ph)Mg\(^{\alpha}\)Bu(THF) in CH\(_2\)Cl\(_2\) at room temperature.
The reaction of \textit{L-LA} and \textit{rac-LA} in DCM was investigated by the BDI(Ph)Mg\textsuperscript{n}Bu(THF) catalyst. The reactivity of \textit{L-LA} is faster than the \textit{rac-LA}, which implies that the metal center has some selectivity towards the chiral centers of the monomer. The competing reactions of \textit{L-LA} and \textit{D-LA} in the \textit{rac-LA} with the metal center could reduce the reactivity. The reaction of \textit{rac-LA} in the presence of \textit{ɛ-CL} in DCM is slower than the reaction of \textit{rac-LA} in DCM. Thus again indicates the competing reaction of \textit{ɛ-CL} and \textit{rac-LA} with the Mg center. Furthermore the addition of \textit{ɛ-CL} increases the heterotacticity for \textit{LA} polymerization. Overall, the rate of polymerization by BDI(Ph)Mg\textsuperscript{n}Bu(THF) follows \textit{L-LA} > \textit{rac-LA} > \textit{rac-LA : ɛ-CL} (1:1)* as shown in Figure 96.* \textit{rac-LA} and \textit{ɛ-CL} were added together in 1:1 ratio instead of LA.

![Graph](image)

Figure 96: Linear plots of $\ln\{[LA]_0/[LA]_t\}$ *versus* time (sec.) for the polymerization of \textit{L-LA} ($L$-LA : Catalyst = 100:1), \textit{rac-LA} ($rac$-LA : Catalyst = 100:1) and \textit{rac-LA} with \textit{CL} ($rac$-LA : CL: Catalyst = 100:100:1) initiated by BDI(Ph)Mg\textsuperscript{n}Bu(THF) in CH\textsubscript{2}Cl\textsubscript{2} at room temperature.
The kinetics data for the polymerization of rac-LA by BDI(Ph)Mg\textsuperscript{II}Bu(THF) in THF is shown in Figure 97 and Figure 98. The rate of polymerization of lactide in THF is $kp = 3.1 \text{ M}^{-1}\text{S}^{-1}$. This shows that the rate of polymerization in the coordinating solvents (THF) is slower than the non-coordinating solvents (DCM).

Figure 97: Linear plots of $\ln([LA]_0/[LA]_t)$ versus time (sec.) for the polymerization of rac-LA initiated by BDI(Ph)Mg\textsuperscript{II}Bu(THF) in THF at room temperature.
Figure 98: Plot of $-\ln(k_{\text{app}})$ versus $-\ln[\text{Cat}]$ for the rac-LA initiated by BDI(Ph)Mg\textsuperscript{\textit{n}}Bu(THF) in THF at room temperature.

The kinetics studies for the $\epsilon$-CL also carried out in DCM using BDI(Ph)Mg\textsuperscript{\textit{n}}Bu(THF). The plots of $\ln(A_0/A)$ vs time and the $\ln(k_{\text{app}})$ vs $\ln([\text{catalyst}])$ were shown in Figure 99 and Figure 100 respectively. The $k_p$ values for the $\epsilon$-CL polymerization by BDI(Ph)Mg\textsuperscript{\textit{n}}Bu(THF) is $k_p = 81.4 \text{ M}^{-1}\text{s}^{-1}$. 

\[
y = 0.9933x - 1.0583 \\
R^2 = 0.9882
\]
Figure 99: Linear plots of $\ln\left[\frac{[\varepsilon-\text{CL}]_0}{[\varepsilon-\text{CL}]_t}\right]$ versus time (sec.) for the polymerization of $\varepsilon$-CL initiated by BDI(Ph)Mg$^+$Bu(THF) in CH$_2$Cl$_2$ at room temperature.

Figure 100: Plot of $-\ln(k_{\text{app}})$ versus $-\ln[\text{Cat}]$ for the $\varepsilon$-CL initiated by BDI(Ph)Mg$^+$Bu(THF) in CH$_2$Cl$_2$ at room temperature.
The kinetics data for the *rac*-LA polymerization by BDI(CH$_2$Ph)Mg''Bu(THF) in CH$_2$Cl$_2$ is shown in Figure 101 and Figure 102. The kp for the *rac*-LA polymerization in CH$_2$Cl$_2$ by BDI(CH$_2$Ph)Mg''Bu(THF) is 11.7 M$^{-1}$s$^{-1}$.

**Figure 101**: Linear plots of ln([LA]$_0$/[LA]$_t$) versus time (sec.) for the polymerization of *rac*-LA initiated by BDI(CH$_2$Ph)Mg''Bu(THF) in CH$_2$Cl$_2$ at room temperature.
Figure 102: Plot of $-\ln(k_{\text{app}})$ versus $-\ln([\text{Cat}])$ for the rac-LA initiated by BDI(CH$_2$Ph)Mg$^\alpha$Bu(THF) in CH$_2$Cl$_2$ at room temperature.

The kinetics data for the rac-LA polymerization by BDI(CH$_2$Ph)Mg$^\alpha$Bu(THF) in THF is shown in Figure 103 and Figure 104. The kp for the rac-LA polymerization in THF by BDI(CH$_2$Ph)Mg$^\alpha$Bu(THF) is 1.75 M$^{-1}$s$^{-1}$. 

$$y = 1.0945x + 2.4622$$  
$$R^2 = 0.9982$$
Figure 103: Linear plots of ln([LA]₀/[LA]ₜ) versus time (sec.) for the polymerization of rac-LA initiated by BDI(CH₂Ph)MgBu(THF) in THF at room temperature.

Figure 104: Plot of $-\ln(k_{app})$ versus $-\ln(Cat)$ for the rac-LA initiated by BDI(CH₂Ph)MgBu(THF) in THF at room temperature.
Table 23: Summary of kp values for the rac-LA and ε-CL polymerization by selected β-dikitiminate catalysts.

<table>
<thead>
<tr>
<th>Entry</th>
<th>Initiator</th>
<th>Monomer</th>
<th>Solvent</th>
<th>kp (M⁻¹s⁻¹)</th>
</tr>
</thead>
<tbody>
<tr>
<td>1</td>
<td>BDI(Ph)Mg&quot;Bu(THF)</td>
<td>rac-LA</td>
<td>DCM</td>
<td>14.5</td>
</tr>
<tr>
<td>2</td>
<td>BDI(Ph)Mg&quot;Bu(THF)</td>
<td>rac-LA</td>
<td>THF</td>
<td>3.1</td>
</tr>
<tr>
<td>3</td>
<td>BDI(Ph)Mg&quot;Bu(THF)</td>
<td>ε-CL</td>
<td>DCM</td>
<td>81.4</td>
</tr>
<tr>
<td>4</td>
<td>BDIMg&quot;Bu(THF)#</td>
<td>rac-LA</td>
<td>DCM</td>
<td>10.7</td>
</tr>
<tr>
<td>5</td>
<td>BDIMg&quot;Bu(THF)#</td>
<td>rac-LA</td>
<td>THF</td>
<td>3.0</td>
</tr>
<tr>
<td>6</td>
<td>BDIMg&quot;Bu(THF)#</td>
<td>ε-CL</td>
<td>DCM</td>
<td>110</td>
</tr>
<tr>
<td>7</td>
<td>BDI(CH₂Ph)Mg&quot;Bu(THF)</td>
<td>rac-LA</td>
<td>DCM</td>
<td>11.7</td>
</tr>
<tr>
<td>8</td>
<td>BDI(CH₂Ph)Mg&quot;Bu(THF)</td>
<td>rac-LA</td>
<td>THF</td>
<td>1.7</td>
</tr>
<tr>
<td>9</td>
<td>BDI*Mg&quot;Bu(THF)#</td>
<td>rac-LA</td>
<td>DCM</td>
<td>6.12</td>
</tr>
<tr>
<td>10</td>
<td>BDI*Mg&quot;Bu(THF)#</td>
<td>rac-LA</td>
<td>THF</td>
<td>0.24</td>
</tr>
<tr>
<td>11</td>
<td>TMPMg&quot;Bu(THF)#</td>
<td>rac-LA</td>
<td>DCM</td>
<td>5.11</td>
</tr>
<tr>
<td>12</td>
<td>TMPMg&quot;Bu(THF)#</td>
<td>rac-LA</td>
<td>THF</td>
<td>0.71</td>
</tr>
</tbody>
</table>

#reported by our group previously TMP = 1,5,9-trimesityldipyromethene

The above table clearly shows that BDI(Ph)Mg"Bu(THF) is the highest active catalyst for the ROP of rac-LA in both of DCM and THF. For all the catalysts, the rate of ROP of LA in DCM is greater than THF. The EDG substitution in the BDI backbone increasing the rate of polymerization and the EWG reduces the rate of polymerization.

5.5 Solvent effect in the ROP rac-LA by BDIMg"Bu(THF) and BDI*Mg"Bu(THF)

Herein, we have investigated the influence of PO as a solvent for the ROP of rac-LA and the results were compared with DCM/THF. The rac-LA polymerization by the BDIMg"Bu(THF) in DCM and THF produces atactic (Pᵣ = 0.55) and heterotactic (Pᵣ = 0.95) PLA, respectively. The selectivity of rac-LA polymerization and the previous low temperature studies suggest that THF is involved in the transition state of the
polymerization. Similarly, *rac*-LA polymerization in *rac*-PO solvent by BDIMg\textsuperscript{n}Bu(THF) produces heterotactic enriched PLA with $P_r > 0.83$. The homodecoupled $^1$H-NMR is shown below (Figure 105). This is an indirect evidence for that the PO reversibly coordinates with Mg center similar to THF.

![Homodecoupled $^1$H NMR spectrum](image)

Figure 105: Homodecoupled $^1$H NMR (500 MHz, CDCl$_3$) spectrum of the methine proton of polylactide obtained from the reaction of *rac*-LA catalyzed by BDIMg\textsuperscript{n}Bu(THF) in *rac*-PO solvent at room temperature in 15min ($P_r = 0.83$).

The polymerization of *rac*-LA with BDI*Mg\textsuperscript{n}Bu(THF) in both of DCM ($P_r = 0.5$) and THF($P_r = 0.65$) produces almost atactic PLA\textsuperscript{143}. The selectivity of *rac*-LA polymerization and the previous low temperature studies suggest that THF does not take part in the transition state of the polymerization. Interestingly, the *rac*-LA polymerization in *rac*-PO solvent by BDI*Mg\textsuperscript{n}Bu(THF) produces heterotactic enriched...
PLA with \( P_r > 0.89 \). The homodecoupled \(^1\text{H}-\text{NMR}\) and the \(^{13}\text{C}-\text{NMR}\) (Figure 106) spectra are shown below.

![Homodecoupled 
\(^1\text{H}-\text{NMR}\) (400 MHz, CDCl\(_3\)) [left] and 
\(^{13}\text{C}-\text{NMR}\) (100 MHz, CDCl\(_3\)) [right] spectra of the methine proton of polylactide obtained from the reaction of \( \text{rac-LA} \) catalyzed by BDI*Mg\(^{n}\)Bu(THF) in \( \text{rac-PO} \) solvent at room temperature in 10 min ( \( P_r = 0.89 \)).](#)

The polymerization reactions of \( \text{rac-LA} \) using BDI*Mg\(^{n}\)Bu(THF) in THF, \( \text{rac-PO} \) and DCM solvents were carried out to compare the solvent influence in polymerization. The homodecoupled \(^1\text{H}-\text{NMR}\) spectra of the \( \text{CH} \) resonance of resulted poly(\( \text{rac-lactide} \)) are shown in Figure 107. This clearly shows that the PO increases the \textit{is}i/sis selectivity compare with THF/DCM for \( \text{rac-LA} \) polymerization by BDI*Mg\(^{n}\)Bu(THF).
Figure 107: $^1$H NMR spectra (CDCl$_3$, 500 MHz) of the homodecoupled CH resonance of poly(rac-lactide) obtained by BDI$^*$Mg$^*$Bu(THF) in (a) rac-PO ($P_r = 0.89$) , (b) DCM ($P_r = 0.56$) and (c) THF ($P_r = 0.65$).

The molecular weight, PDI and the $P_r$ values are summarized in Table 24 and this clearly shows the well-controlled polymerization process by the catalyst in all three different solvent systems. This clearly shows that the PO can be used as a solvent for the synthesis of heterotactic PLA from rac-LA by BDI$^*$Mg$^*$Bu(THF).

Table 24: Molecular weight and PDI values of polymers obtained from BDI$^*$Mg$^*$Bu(THF) in THF, DCM and rac-PO.

<table>
<thead>
<tr>
<th>Solvent</th>
<th>ratio$^a$</th>
<th>% conversion$^b$</th>
<th>$M_n$$^c$</th>
<th>PDI</th>
<th>$P_r$</th>
</tr>
</thead>
<tbody>
<tr>
<td>THF</td>
<td>125:1</td>
<td>96</td>
<td>19775</td>
<td>1.10</td>
<td>0.65</td>
</tr>
<tr>
<td>DCM</td>
<td>125:1</td>
<td>97</td>
<td>19051</td>
<td>1.21</td>
<td>0.56</td>
</tr>
<tr>
<td>rac-PO</td>
<td>100:1</td>
<td>98</td>
<td>12590</td>
<td>1.20</td>
<td>0.89</td>
</tr>
</tbody>
</table>

$^a$ [rac-lactide]$_0$:[initiator]$_0$ ratio. $^b$ Percentage conversion was obtained by $^1$H NMR spectroscopy. $^c$ Determined by GPC relative to polystyrene standards in THF. The experimental $M_n$ was calculated considering Mark-Houwink’s corrections for $M_n$ ($M_n$(obsd) = 0.58[$M_n$(GPC)]).

All the LA ROPs by the $\beta$-dikitimate Mg complexes proceed through the $\beta$-hydride transfer, which is observed by $^1$H-NMR and MALDI end group analysis.
Representative MALDI spectrum of the PLA obtained from the reaction of BDI(CF$_3$)Mg$^\text{II}$Bu(THF) and rac-LA is shown below (Figure 108). The polymer series can be assigned as $B_n = \text{H(LA)}_n\text{H.Na}^+$ and $A_{n+1/2} = \text{H(LA)}_n(\text{LA})_{1/2}\text{H.Na}^+$. 

Figure 108: MALDI spectrum of the PLA obtained from the reaction of BDI(CF$_3$)Mg$^\text{II}$Bu(THF) and rac-LA.
5.6 ROP of PO by β-dikitminate magnesium catalysts

Only a few examples of polyether synthesis have been seen in the literature by magnesium complexes. Polyethers are used for several medical and cosmetic applications and the magnesium metal has been considered as a least toxic metal ion. The usage of magnesium catalysts will be an advantage in terms of health concerns. The initial studies on the polyether synthesis by Mg catalyst are discussed below.

The reactions of PO with BDIMg"Bu(THF) catalyst in any solvents (THF/DCM/toluene) were unsuccessful. Interestingly, the reaction of neat PO with BDIMg"Bu(THF) produces polyethers at room temperature in 6h. The same reaction of 3 coordinated BDIMg"Bu with PO is faster than BDIMg"Bu(THF). This suggests that binding ability of THF is greater than PO, which reduces the coordination/exchange of PO with the Mg center.

The immediate point of our interest is to find the mechanistic pathway for the formation of the polymer. During this study, we have isolated PO coordinated BDI*Mg"Bu and the crystal structure was discussed before. The initiation step of the polymerization can occur by alkyl transfer or β-hydride transfer (Scheme 25) via methylene or methine attack and the subsequent step will result in -^Bu and –H end group in the polymer. The ring opening of the PO with BDI*Mg"Bu (PO: BDI*Mg"Bu=1:1) proceeds through β-hydride elimination and we can also see some unreacted BDI*Mg"Bu (See Figure 109). The addition of more PO with BDI*Mg"Bu (PO: BDI*Mg"Bu = 5-10:1) also leaves some unreacted PO and BDI*Mg"Bu. This reveals that the initiation step is slower than the propagation step.
Scheme 25: Possible initiation steps of PO by magnesium catalyst.

$^1$H-NMR studies suggest that the following products [PPO, unreacted PO, unreacted BDI$^\text{Mg}^\text{nBu}$, and $n$-butene] were present in the product of the reaction of BDI$^\text{Mg}^\text{nBu}$ with PO as shown in Scheme 26.

Scheme 26: The possible products of the reaction of BDI$^\text{Mg}^\text{nBu}$: PO = 1:1 in toluene $d_8$ after 6 h in the J-Young tube experiment
Figure 109: $^1$H NMR (500 MHz, CDCl$_3$) spectra of BDI*Mg$^{n}$Bu: R(+)-PO = 1: 2 after 12h.

The ROP data for epoxides by $\beta$-dikitiminate catalysts are summarized in Table 25 and it shows that these systems can be used for the industrial production of polyethers.

Table 25: The $M_w$ and PDI values for the polyethers obtained from the $\beta$-dikitiminate catalysts are summarized

<table>
<thead>
<tr>
<th>Entry</th>
<th>Volume$^a$</th>
<th>Time$^b$</th>
<th>$M_w$ $^c$</th>
<th>PDI</th>
</tr>
</thead>
<tbody>
<tr>
<td>BDI*Mg$^{n}$Bu(THF)</td>
<td>10mL</td>
<td>24h</td>
<td>86,172</td>
<td>1.30</td>
</tr>
<tr>
<td>BDI*Mg$^{n}$Bu(THF)</td>
<td>20 mL</td>
<td>48h</td>
<td>952,622</td>
<td>1.07</td>
</tr>
<tr>
<td>BDI*Mg$^{n}$Bu(THF)</td>
<td>10mL</td>
<td>24h</td>
<td>88,419</td>
<td>1.30</td>
</tr>
<tr>
<td>BDI*Mg$^{n}$Bu</td>
<td>10mL</td>
<td>12h</td>
<td>72,452</td>
<td>1.21</td>
</tr>
<tr>
<td>BDI*Mg$^{n}$Bu$^#$</td>
<td>10mL</td>
<td>48h</td>
<td>76,540</td>
<td>1.20</td>
</tr>
</tbody>
</table>

$^a$Volume of epoxides, all the polymerization reactions were carried out at room temperature in neat PO. $^b$All the reaction was quenched by acidic methanol after the reaction mixture become viscous. $^c$Determined by GPC relative to polystyrene standards in THF. # CHO is used instead of PO. The percentage conversions were not determined by NMR due to the solubility issues of polymers in CDCl$_3$. 

184
Furthermore, the system is also active for the ROP of cyclohexene oxide and styrene oxide. The resulting PPO was analyzed by MALDI spectrometry and the data are shown in Figure 110. The end group analysis by MALDI indicates the presence of hydride end group, which suggests that initiation step proceeds through $\beta$-hydride transfer. The polymer series can be assigned as doubly charged ions of H(PO)$_n$H.Na$^+$.H$^+$. 

Figure 110: MALDI spectrum of polyether obtained from the reaction of rac-PO catalyzed by BDIMg$^+$/Bu(THF) at room temperature.
5.7 Variable temperature studies

BDI(Ph)Mg"Bu(THF) and BDI(CF₃)Mg"Bu(THF) complexes were investigated in toluene d₈ with the addition of THF by ¹H and ¹³C NMR in the range of -90 °C to +60 °C. The apparent aryl group rotation can be monitored by the coalescence point of the methine proton of the isopropyl group. The coalescence temperature, T_c, of the methine region of the isopropyl group is directly correlated with the THF exchange.¹⁴⁴ For the BDI(CH₂Ph)Mg"Bu(THF), the T_c values could not be calculated due to the overlap of isopropyl peaks with CH2 back bone peaks. The T_c values for the above complexes with the addition of THF are summarized in Table 26 and the corresponded plots are shown in Figure 111 - Figure 115.

Table 26: T_c for the apparent aryl group rotation for the BDIMg complexes with the addition of THF

<table>
<thead>
<tr>
<th>Compound</th>
<th>T_c app. Aryl rotation</th>
</tr>
</thead>
<tbody>
<tr>
<td></td>
<td>toluene-d₈</td>
</tr>
<tr>
<td>BDI(Ph)Mg&quot;Bu(THF)</td>
<td>-15</td>
</tr>
<tr>
<td>BDI* Mg&quot;Bu(THF)</td>
<td>-60</td>
</tr>
<tr>
<td>BDI(Ph)Mg&quot;Bu(THF)</td>
<td>~ -15</td>
</tr>
<tr>
<td>BDI(CF₃)Mg&quot;Bu(THF)</td>
<td>~ -5</td>
</tr>
</tbody>
</table>

Chisholm and co-workers have shown that the THF exchange occurs through both of dissociative and associative process for the BDI*Mg^"Bu(THF) and it occurs through the dissociative process alone for the BDI*Mg^"Bu(THF).¹⁴⁴,¹²⁷ This might be the indirect observation that the T_c not changes with the addition of THF for the BDI*Mg^"Bu(THF). While the addition of THF for the BDIMg^"Bu(THF) changes T_c. Similarly we could expect that the THF exchange might occur through the associative and dissociative process for both of BDI(Ph)Mg^"Bu(THF) and BDI(CF₃)Mg^"Bu(THF). 186
Figure 111: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(CF$_3$)Mg$^{i}$Bu(THF) in toluene d$_8$. The isopropyl methine is shown with a star, *.

The isopropyl group peaks for the BDI(CF$_3$)Mg$^{i}$Bu(THF) are within the 2.5-3.5 ppm region. At or above 27 °C we see a sharp septet and while decreasing the temperature the peaks gett broader and later split in to two peaks. Here the peak getting splits between 0 °C and -10 °C and the estimated $T_c$ for the isopropyl group rotation is ~ -5 °C.
The isopropyl group peaks for the BDI(Ph)Mg\textsuperscript{6}Bu(THF) are between 3.0 - 3.7 ppm region. Here the peak getting splits between -10 °C and -20 °C and the T\textsubscript{c} is ~ -15 °C. Additionally the α-CH\textsubscript{2} peaks of the THF falls under 3.5-4 ppm range and when lowering the temperature the peaks are splitting at -85 °C.
When we add the 1.5 equiv. of THF to the BDI(CF$_3$)Mg$^n$Bu(THF) complex, the isopropyl group peaks are within the 3.3 - 3.7 ppm region. Here the peak getting split between -10 °C and -20 °C and the estimated $T_c$ for the isopropyl group rotation is ~ -15 °C.
Figure 114: Variable temperature $^1$H-NMR (500 MHz) stacking of BDI(CF$_3$)Mg$^n$Bu(THF) in THF d$_8$. The isopropyl methine is shown with a star, *.

When we do the experiment in THF-d$_8$ for the BDI(CF$_3$)Mg$^n$Bu(THF) complex, the isopropyl group peaks are within the 3.3 - 3.7 ppm region. Here the peak is not getting split even at -90 °C.
When we add the 4 equiv. of THF to the BDI(Ph)MgBu(THF) complex, the isopropyl group peaks are within the 3.2 - 3.6 ppm region. Here the peak splits between -10 °C and -20 °C and the T_c for the isopropyl group rotation is ~ -15 °C.
5.8 Conclusions

Different back bone modified \(\beta\)-dikitiminate magnesium complexes were synthesized and employed for the ROP of LA and \(\varepsilon\)-CL. BDI(Ph)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF) is the fastest catalyst among the reported magnesium catalysts for the ROP of LA. The following order of reactivity follows: BDI(Ph)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF) > BDI(CH\(2\)Ph)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF) > BDI\(\textsuperscript{\textprime\prime}\)Bu(THF) > BDI\(\textsuperscript{\textprime}\)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF) > BDI\(\textsuperscript{\textprime}\)Mg\(\textsuperscript{\textprime\prime}\)Bu. Four coordinated Mg complexes are more active than the three coordinated complexes, which could be explained by the competitive reactions of LA and THF. Furthermore the THF exchange occurs through the associative and dissociative process for both of BDI(Ph)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF) and BDI\(\textsuperscript{\textprime}\)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF). Herein, the THF is involved in the transition state of the catalytic process. Increasing steric crowding around the metal center may increase stereo selectivity. This results in the enhancement in heterotacticity for the rac-LA polymerization in THF. The rate of polymerization is enhanced by the EDG substitution in the back bone of the BDI ligand. Furthermore, rac-LA polymerization by BDI\(\textsuperscript{\textprime}\)Mg\(\textsuperscript{\textprime\prime}\)Bu(THF) in the PO solvent enhances the heterotacticity. Additionally, we have shown the possibility of the usage of the \(\beta\)-dikitiminate magnesium complexes for the synthesis of polyethers. The polymerization initiation step occurs by the \(\beta\)-hydride transfer and these catalysts are active at room temperature. It is necessary to understand the propagating species of the magnesium catalyst of these polymerizations.
5.9 Experimental and general considerations

All the air moisture sensitive reactions were carried out under nitrogen environment employing standard Schlenk line and dry box techniques. Dichloromethane, toluene, and THF were distilled twice under nitrogen from calcium hydride. ε-caprolactone, rac-LA, benzoil chloride, acetophenone, 2,4,6-trimethyl aniline, 2,4-pentanedione, 2,6-diisopropylaniline and di-n-butyl magnesium were purchased from Sigma-Aldrich. Benzene-d6, toluene-d8 and chloroform-d1 were purchased from Cambridge Isotopes. rac-LA was sublimed three times and crystallized in toluene, then dried under a dynamic vacuum at 50 °C overnight. ε-Caprolactone was stirred over calcium hydride overnight under nitrogen and distilled under reduced pressure at 100 °C prior to use. BDIH, BDI*H, BDI(β-CH2Ph)H, BDI(α-CF3)H, BDI(Mes)H and BDI(α-Ph)H were synthesized according to the literature procedures.

5.9.1 Measurements

1H and 13C NMR spectra were acquired in C6D6, C7H8 and CDCl3 on Bruker DPX-400 and 500 NMR Spectrometers. All chemical shifts were determined using the residual protio impurity peaks; (C6D6, 7.16 ppm, C7H8, 2.08 and CDCl3, 7.26 ppm). Gel-permeation chromatography (GPC) analyses were performed using 1mL/min flow rate of THF eluent at 40°C on a Waters 1525 binary HPLC pump and Waters 2414 refractive index detector equipped with styragel HR 2&4 columns (7.8 x 300 mm). The molecular weights were calibrated using polystyrene standard. High resolution matrix assisted laser
desorption ionization time-of-flight (MALDI-TOF) mass spectrometry experiments were performed in Microflex Brucker MALDI.

5.9.2 Synthesis

Synthesis of BDIMg"Bu

BDIH (0.500 g, 1.19 mmol) was dissolved in 10 mL of pentane and 1.0 M di-n-butylmagnesium solution in heptanes (1.60 mL, 1.6 mmol, 1.34 equiv.) was added to the pentane solution. The resulting solution was stirred at room temperature for 15 minutes. The resulting mixture was placed in a freezer at -25 °C for overnight and the white crystals were obtained with 85% yield. Single X-ray crystals were grown from a concentrated pentane solution at -25 °C.

\(^1\)H NMR (500 MHz, C\(_6\)D\(_6\), 27 °C): 7.10-7.20 (m, 6H, ArH), 4.95(s, 1H, β-CH), 3.17 (m, 4H, CHMeMe'), 1.69 (s, 6H, CMe), 1.32 (m, 2H, β-Bu"), 1.28 (d, 12H, CHMe\(_2\)), 1.18 (d, 12H, CHMe\(_2\)' ), 1.15 (m, 2H, γ-Bu"), 0.85 (t, 3H, δ-Bu"), -0.22 (AA'XX'Y, 2H, α-Bu").

\(^{13}\)H NMR (125 MHz, C\(_6\)D\(_6\), 27 °C): 169.28, 143.86, 141.88, 126.00, 124.07, 95.34, 31.23, 31.08, 28.67, 24.62, 23.57, 23.46, 14.37, 5.61.

Synthesis of BDI*Mg"Bu

BDI*H (0.60 g, 1.19 mmol) was dissolved in 10 mL of pentane and 1.0 M di-n-butylmagnesium solution in heptanes (1.60 mL, 1.6 mmol, 1.34 equiv.) was added to the
pentane solution. The resulting solution was refluxed for 8h. The resulting mixture was placed in a freezer at -25 °C for overnight and the white crystals were obtained with 70% yield. Single X-ray crystals were grown from a concentrated pentane solution at -25 °C.

\(^{1}\)H NMR (500 MHz, C\(_6\)D\(_6\), 27 °C): 6.95-7.10 (m, 6H, ArH), 5.39 (s, 1H, \(\beta\)-CH), 3.27 (m, 4H, CHMe\(_2\)), 1.29 (d, 12H, CHMe\(_2\)), 1.26 (d, 12H, CHMe\(_2\)), 1.19 (s, 18H, (\(\alpha\)-CMe\(_3\))\(_2\)), 1.22 (m, 2H, \(\beta\)-Bu\(^n\)), 0.95 (m, 2H, \(\gamma\)-Bu\(^n\)), 0.81 (t, 3H, \(\delta\)-Bu\(^n\)), -0.62 (AA’XX’Y, 2H, \(\alpha\)-Bu\(^n\)).

\(^{13}\)H NMR (125 MHz, C\(_6\)D\(_6\), 27 °C):176.01, 145.23, 141.37, 125.39, 123.81, 94.84, 94.84, 44.02, 32.96, 30.73, 30.63, 28.44, 25.25, 25.18, 23.16, 14.30, 6.93.

\(^{1}\)H NMR (500 MHz, C\(_7\)D\(_8\), 27 °C): 6.90-7.10 (m, 6H, ArH), 5.34 (s, 1H, \(\beta\)-CH), 3.24 (m, 4H, CHMe\(_2\)), 1.26 (d, 24H, CHMe\(_2\)), 1.16 (s, 18H, (\(\alpha\)-CMe\(_3\))\(_2\)), 0.86 (m, 4H, \(\beta\)/\(\gamma\)-Bu\(^n\)), 0.75 (t, 3H, \(\delta\)-Bu\(^n\)), -0.73 (AA’XX’Y, 2H, \(\alpha\)-Bu\(^n\)).

\(^{13}\)H NMR (125 MHz, C\(_7\)D\(_8\), 27 °C):176.04, 145.27, 141.28, 123.75, 94.92, 44.03, 32.97, 30.58, 30.64, 28.46, 25.21, 23.14, 14.26, 6.82.

**Synthesis of BDI\(^*\)Mg\(^n\)Bu(PO)**

The BDI\(^*\)Mg\(^n\)Bu(PO) was synthesized from the careful stoichiometric addition of BDI\(^*\)Mg\(^n\)Bu and PO in pentane at room temperature. The slow evaporation of pentane yielded X-ray quality crystals.

\(^{1}\)H NMR (500 MHz, C\(_7\)D\(_8\), 27 °C): 6.90 -7.10 (m, 6H, ArH), 5.34 (s, 1H, \(\beta\)-CH), 3.24 (m, 4H, CHMe\(_2\)), 2.60 (m, 1H, CHMe[PO]), 2.34 (m, 1H, CH\(_4\)H\(_8\)[PO]), 1.98 (m,
1H, CH₃H₆ [PO]), 1.20-1.30 (m, 24H, CHMe₂), 1.16 (s, 18H, (α-CMe₃)₂), 0.93 (d, 3H, CHMe[PO]), 0.91 (m, 4H, β/γ -Bu''), 0.76 (t, 3H, δ-Bu''), -0.71 (AA'XX'Y, 2H, α-Bu'').

$^{13}$H NMR (125 MHz, C₇D₈, 27 °C): 176.00, 145.43, 141.32, 123.73, 94.96, 48.48, 47.91, 44.04, 32.93, 30.83, 28.39, 25.47, 23.27, 17.83, 14.30, 6.80.

NMR data for PO in C₇H₈: $^1$H NMR (500 MHz, C₇D₈, 27 °C): 2.54, 2.29, 1.97, 0.96., $^{13}$H NMR (125 MHz, C₇D₈, 27 °C): 47.49, 47.19, 18.03.

**Synthesis of BDI(β-CH₂Ph)Mg''Bu(THF)**

A mixture of BDI(β-CH₂Ph)H (0.600 g, 1.18 mmol) in 10 mL THF and 1.0 M di-n-butylmagnesium solution in heptanes (1.50 mL, 1.50 mmol, 1.27 equiv.) were refluxed for 6 hours and allowed to cool down for at least 1 hour. The resulting mixture was placed in the freezer for overnight and pale yellow crystals were obtained with 75% yield. Single X-ray crystals were grown from a concentrated pentane solution at -25 °C.

$^1$H NMR (500 MHz, C₆D₆, 27 °C): 6.95-7.31 (m, 11H, ArH), 3.64 (s, 1H, CH₂Ph), 3.47 (m, 4H, THF), 3.31 (m, 4H, CHMe₂), 1.65 (s, 6H, CMe), 1.45 (m, 2H, β-Bu''), 1.28 (bd, 12H, CHMe₂), 1.19 (m, 4H, THF), 1.14 (d, 12H, CHMe₂), 1.12 (m, 2H, γ-Bu''), 0.97 (t, 3H, δ-Bu''), -0.43 (AA'XX'Y, 2H, α-Bu'').

**Synthesis of BDI(α-CF₃)Mg''Bu(THF)**

A mixture of BDI(α-CF₃)H (0.530 g, 1.01 mmol) in 10 mL THF and 1.0 M di-n-butylmagnesium solution in heptanes (1.30 ml, 1.3 mmol, ~1.30 equivalence) were
refluxed for 6 hours and cooled for at least an hour. The resulting mixture was placed in freezer for overnight and the yellow color crystals were obtained in quantitative yield.

Single X-ray crystals were grown from a concentrated pentane solution at -25 °C.

$^1$H NMR (500 MHz, C$_6$D$_6$, 27 °C): 7.11 (m, 6H, ArH), 5.97 (s, 1H, β-C$_6$H$_2$), 3.63 (m, 4H, THF), 3.07 (m, 4H, CHMe$_2$), 1.2-1.23 (m, 2H, β-Bu"), 1.2-1.3 (m, 4H, THF), 1.2-1.3 (m, 24H, CHMe$_2$), 1.12 (m, 2H, γ-Bu"), 0.83 (t, 3H, δ-Bu"), -0.45 (AA'XX'Y, 2H, α-Bu").

$^{13}$H NMR (125 MHz, C$_6$D$_6$, 27 °C): 156.62 (q), 142.53, 141.52, 126.38, 124.09, 86.57 (m), 70.51, 32.07, 31.72, 28.78, 25.83, 25.31, 24.15, 14.32, 5.21.

$^{19}$F NMR (400 MHz, C$_6$D$_6$, 27°C): -165.81

**Synthesis of BDI(Ph)Mg"Bu(THF)**

A mixture of BDI(Ph)H (0.500 g, 1.00 mmol) in 10 mL THF and 1.0 M di-n-butylmagnesium solution in heptanes (1.25 ml, 1.25 mmol, ~1.25 equivalent) were refluxed for 6 hours and let cooled for at least an hour. The resulting mixture was placed in freezer for overnight and the yellow precipitate was obtained in near quantitative yield.

$^1$H NMR (500 MHz, C$_6$D$_6$, 27 °C): 7.25 (m, 4H, ArH), 7.10 (m, 6H, ArH), 6.85 (m, 6H, ArH), 5.40 (s, 1H, β-C$_6$H$_2$), 3.93 (m, 4H, THF), 3.44 (m, 4H, CHMe$_2$), 1.48 (m, 2H, β-Bu"), 1.41 (m, 4H, THF), 1.31 (d, 12H, CHMe$_2$), 1.29 (m, 2H, γ-Bu"), 1.06 (d, 12H, CHMe$_2$), 0.97 (t, 3H, δ-Bu"), -0.62 (AA'XX'Y, 2H, α-Bu").
$^{13}$H NMR (125 MHz, C$_6$D$_6$, 27 °C): 169.57, 145.57, 142.46, 142.38, 129.16, 127.42, 125.40, 123.80, 100.28, 70.14, 32.64, 32.10, 28.63, 26.09, 25.53, 23.71, 14.45, 5.5.

5.9.3 General procedure for the kinetics of LA ROP

A Schlenk flask was charged with rac-lactide (0.50 g, 3.47 mmol) in dichloromethane (DCM). To this solution was added dichloromethane to bring the total volume of the reaction to 22.00 mL. ($[rac\text{-LA}]_0 = 0.16$M) The solution was stirred at room temperature under a nitrogen atmosphere. Then, the equivalent amounts of 0.0350 M catalyst initiator in toluene (0.40 – 1.00 mL) was introduced. At appropriate time intervals, 0.5-1.0 mL aliquots were taken out of the stirred solution and immediately quenched with 1 drop of 0.5 M HCl. The aliquots were then dried under a dynamic vacuum and analyzed by $^1$H NMR spectroscopy.

5.9.4 Single crystal X-ray crystallography

All the single crystals were isolated and handled under a pool of fluorinated oil. Examination of the diffraction pattern was done on a Nonius Kappa CCD diffractometer with Mo Kα radiation. All work was done at 150 K using an Oxford Cryosystems Cryostream Cooler. Data integration was done with Denzo, and scaling and merging of the data was done with Scalepack. The structures were solved by the direct methods program in SHELXS-13. Full-matrix least-squares refinements based on F2 were
performed in SHELXL-13, as incorporated in the WinGX package. For each methyl group, the hydrogen atoms were added at calculated positions using a riding model with $U(H) = 1.5U_{eq}$ (bonded carbon atom). The rest of the hydrogen atoms were included in the model at calculated positions using a riding model with $U(H) = 1.2U_{eq}$ (bonded atom). Neutral atom scattering factors were used and include terms for anomalous dispersion.
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