

Synthesis of Metal Complexes and their Catalysis: Polymers for Li-ion Conductivity as Solid Polymer Electrolytes

A Thesis Submitted for the degree of

DOCTOR OF PHILOSOPHY

By

H. Vignesh Babu



**School of Chemistry
University of Hyderabad
Hyderabad - 500 046
INDIA**

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DEDICATED

TO MY

FAMILY

STATEMENT

I hereby declare that the matter embodied in the thesis entitled “**Synthesis of Metal Complexes and their Catalysis: Polymers for Li-ion Conductivity as Solid Polymer Electrolytes**” is the result of investigations carried out by me in the School of Chemistry, University of Hyderabad, Hyderabad, India, under the supervision of **Dr. K. Muralidharan** and it has not been submitted elsewhere for the award of any degree or diploma or membership, etc.

In keeping with the general practice of reporting scientific investigations, due acknowledgements have been made wherever the work described is based on the findings of other investigators. Any omission, which might have occurred by oversight or error, is regretted.

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CERTIFICATE

This is to certify that the work described in this thesis entitled “**Synthesis of Metal Complexes and their Catalysis: Polymers for Li-ion Conductivity as Solid Polymer Electrolytes**” has been carried out by **Mr. H. Vignesh Babu** under my supervision and the same has not been submitted elsewhere for any degree.

Dr. K. Muralidharan
(Thesis Supervisor)

Dean
School of Chemistry

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CONTENTS

Statement		i
Certificate		ii
Acknowledgements		iii
Synopsis		xvi
 Chapter 1	 Introduction	 1-50
	1.1. Conducting polymers	2
	1.2. Batteries	2
	1.3. Batteries with lithium	6
	1.4. Secondary batteries based on lithium	9
	1.4.1. Lithium Anode Battery	9
	1.4.2. Lithium-ion Battery	10
	1.4.3. Lithium-air (Li-O ₂) and lithium-sulfur (Li-S) batteries	12
	1.5. Non-aqueous electrolytes for lithium based batteries	15
	1.5.1. Liquid electrolytes	16
	1.5.2. Gel Electrolytes	17
	1.5.3. Solid Electrolytes	18
	1.6. Solid Polymer Electrolyte	19
	1.7. Polymerization reactions	21
	1.8. Living polymerization	23
	1.8.1. Anionic and cationic living polymerization	24
	1.8.2. Living free radical polymerization	25
	1.9. Ring opening polymerization	28
	1.9.1. Cationic ring opening polymerization	29
	1.9.2. Activated monomer ring opening polymerization	30
	1.9.3. Anionic ROP	30
	1.10. Scope of the thesis	34
	1.10.1. Enhancing battery performances	34
	1.10.2. Improvement on electrolyte	35
	1.10.3. Conduction mechanism	37
	1.10.4. Ways to increase the conductivity of SPE	38
	1.10.5. Focus of the Thesis	39
	1.11. References	42
 Chapter 2	 Zn(II), Cd(II) and Cu(II) Complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole: Syntheses and Structures	 53-77
	2.1. Introduction	55
	2.2. Results and discussion	58
	2.2.1. Synthesis and characterization	58

	2.2.2. Spectroscopic Study	59
	2.2.3. Crystallographic characterization	60
2.3.	Conclusions	68
2.4.	Experimental section	68
	2.4.1. Materials and instrumentation	68
	2.4.2. Experimental procedure	68
2.5.	References	71
Chapter 3	Efficient Cyclic Carbonate Synthesis from Epoxides and Carbon Dioxide at Atmospheric Pressure	80-107
3.1.	Introduction	82
3.2.	Results and discussion	83
3.3.	Conclusions	92
3.4.	Experimental section	93
	3.4.1. Materials and instrumentation	93
	3.4.2. Experimental procedure	93
3.5.	References	100
Chapter 4	Versatile Metal Complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole for Ring Opening Polymerization of ϵ-caprolactone	110-129
4.1.	Introduction	112
4.2.	Results and discussion	113
	4.2.1. Ring opening polymerization	113
	4.2.2. Bulk and solution phase ring opening polymerization	113
	4.2.3. Significance of alcohols as initiator	115
	4.2.4. Effect of BnOH in BP-ROP and SP-ROP	116
	4.2.5. Mechanism of SP-ROP	119
	4.2.6. Solid polymer electrolyte	122
	4.2.7. Thermal studies	123
	4.2.8. Lithium-ion conductivity	125
4.3.	Conclusions	125
4.4.	Experimental section	126
	4.4.1. Materials and instrumentation	126
	4.4.2. Experimental procedure	126
4.5.	References	127
Chapter 5	Polyethers with Phosphate Pendant Groups by Monomer Activated Anionic Ring Opening Polymerization: Syntheses, Characterization and their Lithium-ion Conductivities	132-171
5.1.	Introduction	134
5.2.	Results and discussion	135
	5.2.1. Synthesis of monomers	136

5.2.2. Ring opening polymerization	140	
5.2.3. Branched polymers	143	
5.2.4. Properties of the polymers	146	
5.2.5. Mechanism of polymerization	146	
5.2.6. Lithium-ion conductivity	147	
5.3. Conclusions	153	
5.4. Experimental section	153	
5.4.1. Materials and instrumentation	153	
5.4.2. Experimental procedure	155	
5.5. References	164	
Chapter 6	Intrinsic Porous Polymer Framework: A New Generation of Solid Polymer Electrolyte	174-203
6.1. Introduction		176
6.2. Results and discussion		177
6.3. Conclusions		191
6.4. Experimental section		192
6.4.1. Materials and instrumentation		192
6.4.2. Conductivity studies		193
6.4.3. Experimental section		194
6.5. References		197
Summary and conclusion		206-213
Publications and presentations		216-218

List of Tables

1.1	Electrochemical reactions and energy density properties of various primary aqueous batteries	5
1.2	Electrochemical reactions and energy density properties of various secondary aqueous batteries	6
1.3	Electrochemical reactions and energy parameters of various primary lithium batteries	8
1.4	Properties of lithium secondary batteries	9
1.5	Structures of various polymers based on carbon backbone and their lithium-ion conductivities	20
1.6	Structures of various polysiloxanes and polyphosphazenes and their lithium-ion conductivities	21
1.7	Electrochemical properties of various SPEs	36
2.1	Crystal data and structural refinement details for 1-4	65
3.1	Screening studies for the synthesis of 6	84
3.2	Optimization studies for the synthesis of 9	85
3.3	Scope of catalysts 1 and 4	87
3.4	Screening studies for the synthesis of 14	89
3.5	Progress of diol 10 formation	91
4.1	Optimization studies for BP-ROP of M1	114
4.2	Optimization studies for SP-ROP of M1	115
4.3	SP-ROP of M1 in presence of various initiators	116
4.4	Optimization studies for BP-ROP of M1 in the presence of BnOH	117
4.5	Optimization studies for SP-ROP of M1 in the presence of BnOH	118
4.6	Results of living and immortal SP-ROP of M1	119
4.7	Properties of P1 and SPE1 (10%-40%)	122
5.1	Crystal data and structural refinement details for S9 and M5	139
5.2	Results of optimization studies for ROP ^a of M3 to form P3	141
5.3	Results of syntheses of various phosphorus containing polyethers (P2-P7) and their properties	142
5.4	Properties of SPE2 (10%-40%)	151

5.5	Properties of SPE3 (10%-40%) and SPE5 (10%-40%)	151
5.6	Properties of SPE6 (10%-40%) and SPE7 (10%-40%)	152
6.1	Properties of polymers P8-P11	179
6.2	Conductivity of P10 with various lithium salts at room temperature	181
6.3	Properties of SPE8 (10%-40%)-SPE9 (10%-40%)	184
6.4	Properties of SPE10 (10%-40%)-SPE11 (10%-40%)	184
6.5	Conductivities of SPE8 (40%)-SPE11 (40%) at increasing temperature	186
7.1	Structures of P1-P11 and comparison of room temperature conductivities of SPE1 (10%-40%)-SPE11 (10%-40%)	212

List of Figures

1.1	Basic components of a cell	3
1.2	Classification of batteries based on electrolytes	4
1.3	Schematic diagram showing discharge process of lithium battery	10
1.4	Schematic diagram showing the discharge process of lithium-ion battery	11
1.5	Schematic diagram showing the discharge process of lithium-air battery	13
1.6	Schematic diagram showing the discharge process of lithium-sulfur battery	14
1.7	Comparison of specific energy of primary lithium batteries with various aqueous batteries	15
1.8	Structures of organic solvent used in non-aqueous batteries as electrolyte	17
1.9	Structures of various polymer hosts	18
1.10	Stable free radical and alkoxyamine initiators	26
1.11	Structures of some of the RAFT agents	28
1.12	Structures of various cyclic ethers and cyclic lactones	29
1.13	Structures of some of the metal complexes utilized for the ROP of cyclic monomers	32
1.14	Structures of (a) $\text{PEO}_6\text{:LiPF}_6$, (b) $\text{PEO}_6\text{:LiAsF}_6$, and (c) $\text{PEO}_6\text{:LiSbF}_6$	37
1.15	Structure of polycaprolactone and polycarbonate	39
1.16	Synthetic approach for the syntheses of polymers	41
2.1	ORTEP of the molecular structure of 1	61
2.2	ORTEP of the molecular structure of 2	62
2.3	ORTEP of the molecular structure of 3	63
2.4	ORTEP of the molecular structure of 4	64
2.5	UV visible absorption spectra of $(\text{DIP}_2\text{pyr})\text{H}$ and its complexes 1-4 in hexane	67
2.6	TGA plots of $(\text{DIP}_2\text{pyr})\text{H}$ and its complexes 1-4	67

3.1	Progress of diol 10 formation monitored by ^1H NMR	90
3.2	Possible cyclic carbonate formation mechanism	92
4.1	Plot of $\ln([\text{M1}]_0/[\text{M1}]_t)$ <i>versus</i> time for the polymerization of M1 catalysed by 1 and 4 in presence of BnOH	120
4.2	Plot of molecular weight (M_n) and polydispersity (PDI) <i>versus</i> monomer conversion for the ROP of M1 catalysed by 1 (left) and 4 (right) in presence of BnOH	120
4.3	Plot of molecular weight (M_n) and polydispersity (PDI) <i>versus</i> $[\text{M1}]_0/[\text{C}]_0$ for the ROP of M1 catalysed by 1 (left) and 4 (right) in presence of BnOH	121
4.4	^1H NMR spectrum of P1	121
4.5	TGA plots of P1 and SPE1 (10%-40%)	122
4.6	DSC plots of P1 and SPE1 (10%-40%)	122
4.7	Temperature dependent nyquist plots of SPE1 with a) 10% b) 20% c) 30%	124
4.8	Arrhenius plot of temperature dependent conductivities of SPE1 (10%-30%)	124
5.1	ORTEP of the molecular structure S9 (top) and M5 (down)	138
5.2	Possible branching structures of P6 and P7	143
5.3	^1H , ^{31}P and ^{13}C NMR spectra of P3 (left) and P6 (right)	144
5.4	TGA plots of polyethers P2-P7	145
5.5	DSC plots of polyethers P2-P7	145
5.6	Plot of molecular weight (M_n) and polydispersity (PDI) <i>versus</i> $[\text{M3}]_0/[\text{I}]_0$ for the ROP of M3 catalysed by 1 in presence of TBAB	145
5.7	(a) TGA and (b) DSC plots of SPE2 (10%-40%). Temperature dependent nyquist plots of SPE2 c) 10% d) 20% e) 30% f) 40%.	148
5.8	(a) TGA and (b) DSC plots of SPE3 (10%-40%). Temperature dependent nyquist plots of SPE3 c) 10% d) 20% e) 30% f) 40%.	148
5.9	(a) TGA and (b) DSC plots of SPE5 (10%-40%). Temperature dependent nyquist plots of SPE5 c) 10% d) 20% e) 30% f) 40%.	149
5.10	(a) TGA and (b) DSC plots of SPE6 (10%-40%). Temperature	149

	dependent nyquist plots of SPE6 c) 10% d) 20% e) 30% f) 40% .	
5.11	(a) TGA and (b) DSC plots of SPE7 (10%-40%). Temperature dependent nyquist plots of SPE7 c) 10% d) 20% e) 30% f) 40% .	150
5.12	Arrhenius plot of temperature dependent conductivity of a) SPE2 b) SPE3 c) SPE5 d) SPE6 e) SPE7 .	150
6.1	Schematic representation of a) crystalline porous polymer framework (left). b) amorphous covalent organic framework (right)	176
6.2	TGA plots of polyether P8-P11	180
6.3	DSC plots of P8-P11	180
6.4	Stacked IR spectra of P8 and SPE8 (10%-40%)	182
6.5	TGA plots of SPE8 (10%-40%)- SPE11 (10%-40%)	182
6.6	DSC plots of SPE8 (10%-40%)- SPE11 (10%-40%)	182
6.7	Temperature dependent nyquist plots of SPE8 a) 10% b) 20% c) 30% d) 40%	183
6.8	Temperature dependent nyquist plots of SPE9 a) 10% b) 20% c) 30% d) 40%	184
6.9	Arrhenius plots of temperature dependent conductivities of a) SPE8 b) SPE9 c) SPE10 d) SPE11 e) SPE11 2 nd heating	185
6.10	Schematic representation of a) a fragment of building block polymer chain P8 or P9 b) If the building block grows in 2D c) If the building block grows in 3D (SPE) (Black dots represent lithium-ion). d) FE-SEM image of SPE10 coated on a glass plate from a concentrated solution. e) FE-SEM image of SPE10 coated on a glass plate from a dilute solution.	187
6.11	Space filling molecular model of a fragment of one of the conformation of P9 (2D) (top), P9 (3D) (down) showing the unsymmetrical shape and inefficient packing of polymer chain.	187
6.12	FE-SEM images of a) P8 b) P9 c) P10 d) P11 . Polymer samples dissolved in chloroform (dilute concentration) and coated on glass plate by drop casting.	188
6.13	Schematic representation of an intrinsic porous polymer framework	188

	(2D) produced by a linear polymer (non-network): a) in solid state b) in solution.	
6.14	Nitrogen adsorption (filled triangles)-desorption (empty triangles) isotherm of powdered sample a) P8 b) P9 c) P10 d) P11 .	189
6.15	a) FE-SEM image of coated SPE10 (10%) after heating. b) TEM image of dispersed SPE10 (10%) after heating.	190
6.16	Nitrogen adsorption (filled triangles and squares) – desorption (empty triangles and squares) isotherms of powdered sample SPE10 (10%) (triangles) and pre-heated sample SPE10 (10%) (squares).	191
7.1	The systematic approach followed in the thesis for producing SPEs.	209

SYNOPSIS

The thesis entitled “**Synthesis of Metal Complexes and their Catalysis: Polymers for Li-ion Conductivity as Solid Polymer Electrolytes**” comprises six chapters.

Chapter 1: Introduction

This chapter commences with the brief introduction of primary and secondary batteries and classification of batteries based on electrolytes. The working principles of secondary lithium batteries such as lithium battery, lithium-ion battery, lithium-air and lithium-sulfur battery is described. This chapter also describes various types and mechanisms of living polymerization and ring opening polymerization (ROP). Examples of various catalysts used for ROP to synthesize polycarbonate/cyclic carbonate, polycaprolactone (PCL) and polyether are discussed. The importance of non-aqueous electrolytes, specifications of electrolytes to be used in a battery, advantages of solid polymer electrolyte (SPE) compared to liquid electrolyte, gel electrolyte and inorganic solid electrolyte are discussed in detail. The issues of SPEs are elaborated and our strategies to increase the conductivity of SPEs are also emphasized.

Chapter 2: Zn(II), Cd(II) and Cu(II) Complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole: Syntheses and Structures

This chapter describes the syntheses of Zn(II) **1**, Cd(II) **2-3** and Cu(II) **4** complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H (Figure 1). The Zn(II) **1** and Cd(II) **2** complexes were synthesized from M[N(SiMe₃)₂]₂ (M = Zn or Cd) whereas Cd(II) **3** and Cu(II) **4** were synthesized from anhydrous MCl₂ (M = Cd or Cu) with ligand (DIP₂pyr)H in 1 : 2 ratio. The structures of these complexes were characterized by IR, UV, ¹H, ¹³C NMR and single crystal X-ray diffraction techniques. These complexes were synthesized to use as catalysts for the synthesis of polycarbonate/cyclic carbonate, polycaprolactone and polyethers from their corresponding monomers.

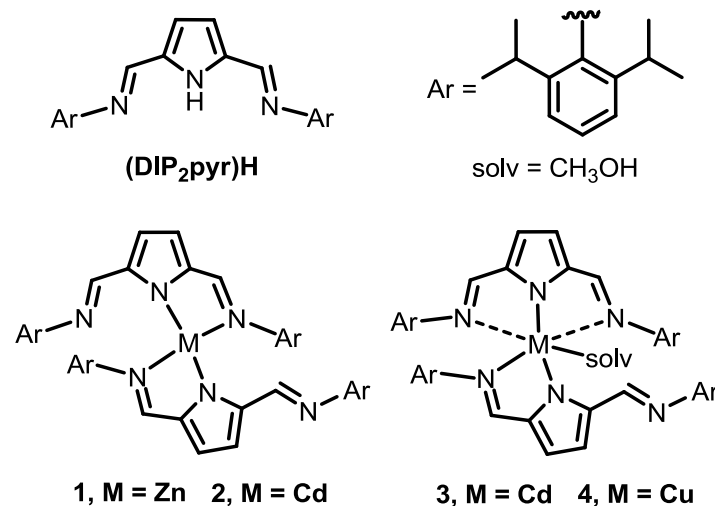
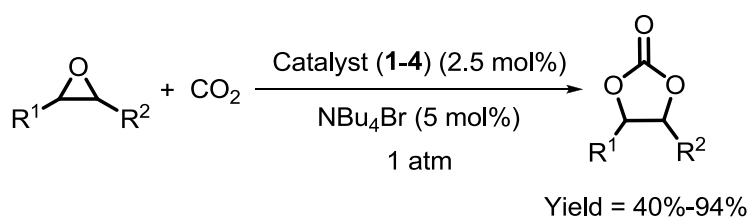


Figure 1. Structure of the ligand (DIP₂pyr)H and its complexes **1-4**.

Chapter 3: Efficient Cyclic Carbonate Synthesis from Epoxides and Carbon Dioxide at Atmospheric Pressure

In this chapter, the catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) for the cycloaddition of CO₂ to an epoxide in the presence of tetrabutylammonium bromide (TBAB) under one atmosphere of pressure and mild temperature conditions to yield cyclic carbonate have been studied (Scheme 1). Among these complexes **1-4**, Zn(II) **1** and Cu(II) **4** complexes were found to be versatile whereas the Cu(II) **4** complex was more selective in the conversion. They were highly effective for the conversion of monosubstituted terminal epoxides, disubstituted terminal, and internal epoxides to their corresponding cyclic carbonates with good to high yields.

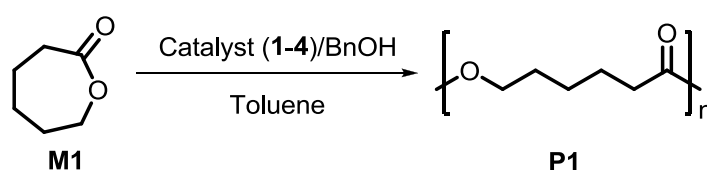


Scheme 1. Synthesis of cyclic carbonates from epoxides and CO₂.

Chapter 4: Versatile Metal Complexes of 2,5-bis{N-(2,6-diisopropylphenyl)imino methyl}pyrrole for Ring Opening Polymerization of ϵ -caprolactone

This chapter describes the catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) for ring opening polymerization (ROP) of ϵ -caprolactone (**M1**) (Scheme 2).

The ROP of **M1** was investigated in the presence and absence of benzyl alcohol (BnOH). All these complexes were active for ROP of **M1** under mild temperature. In particular, the complexes **1** and **4** exhibited remarkable catalytic activity for ROP of **M1** at 25 °C in toluene in the presence of BnOH. The ROP of **M1** catalysed by **1** and **4** complexes, not only proceeded through living polymerization but also immortal. Further, the synthesized polycaprolactone (**P1**) was examined for lithium-ion conductivity by preparing solid polymer electrolyte (**SPE1**) using lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The conductivity of **SPE1** with 30 wt% of LiTFSI was $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $7.2 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C (Figure 2).



Scheme 2. ROP of ϵ -caprolactone (**M1**).

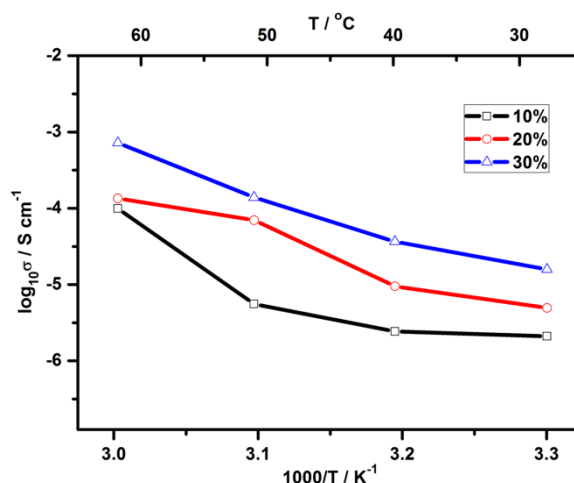
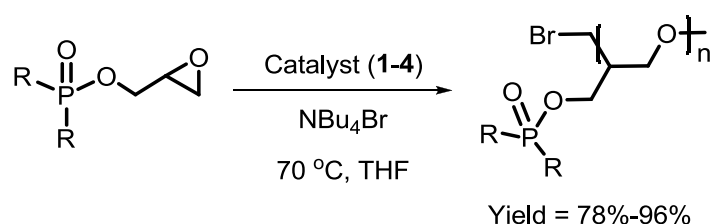


Figure 2. Arrhenius plot of temperature dependent conductivity of **SPE1** (10%-30%).

Chapter 5: Polyethers with Phosphate Pendant Groups by Monomer Activated Anionic Ring Opening Polymerization: Syntheses, Characterization and their Lithium-ion Conductivities

In this chapter, the preparations and lithium-ion conductivities of various solid polymer electrolytes for potential use in high-energy density lithium-ion batteries have been described. The ring opening polymerization of epoxides (**M2-M7**), catalyzed by Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) in the presence of tetrabutylammonium bromide

(TBAB), yielded polyethers (**P2-P7**) in which phosphates are attached as pendant groups (Scheme 3). A reaction condition where Zn(II) catalyst used slightly excess to TBAB increased the polymerization rate remarkably and yielded the polyethers with higher molar masses in short time. These polymerizations proceeded following a “monomer activated anionic ring opening polymerization” mechanism. These living like polymerizations also progressed according to “formation of polymer chain per initiator” model. The solid-state lithium-ion conductivities of these polymers were examined using LiTFSI. The conductivity of one of the solid polymer electrolyte **SPE3** with 40 wt% of LiTFSI was $5.2 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $2.9 \times 10^{-4} \text{ S cm}^{-1}$ at 80 °C (Figure 3).



Scheme 3. Syntheses of phosphorus containing polyethers by ROP of epoxide.

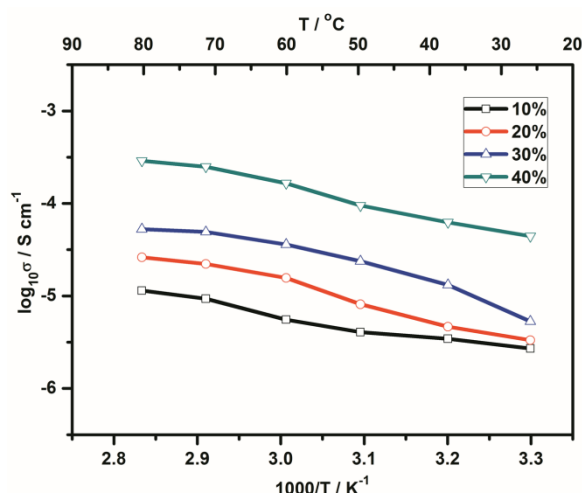
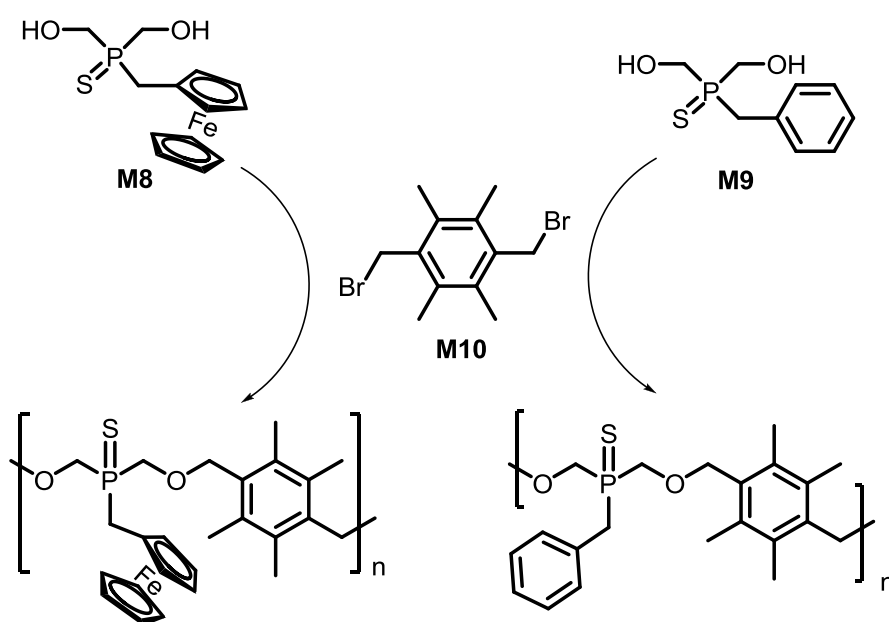


Figure 3. Arrhenius plot of temperature dependent conductivity of **SPE3** (10%-40%).

Chapter 6: Intrinsic Porous Polymer Framework: A New Generation of Solid Polymer Electrolyte

Rechargeable lithium-ion batteries are the major power sources for portable electronics. However, the current technology cannot be promoted to automobile batteries due to the potential fire hazard of organic liquid present in batteries. A better solid polymer electrolyte (SPE) with flame retardance property for high-energy density lithium ion batteries is always

been in demand to replace the organic liquid. In this chapter, syntheses of intrinsic porous polymers for lithium-ion conductivity are described. The copolymerization of substituted bis(hydroxymethyl)phosphine sulfide [RP(S)(CH₂OH)₂ R = ferrocenylmethyl (**M8**), benzyl (**M9**)] with dibromo monomer (**M10**) are successfully carried out to produce novel intrinsic porous polyethers containing phosphorus (Scheme 4). These polymers are obtained by nucleophilic substitution reactions and characterized using ¹H, ³¹P NMR, gel permeation chromatography and BET adsorption and desorption isotherm (Figure 4). The mesoporosity in these polymers is confirmed by nitrogen adsorption and desorption analyses. The porosity is explained by inefficient packing of polymer chains producing interconnected voids throughout the bulk material. This intrinsic porous polymer is examined for lithium-ion conductivity by preparing **SPE** using LiTFSI. The conductivity of **SPE9** with 40 wt% of LiTFSI is 8.9 × 10⁻⁴ S cm⁻¹ at room temperature and 5.3 × 10⁻³ S cm⁻¹ at 80 °C. These all solid-state polymer electrolytes have potential to achieve the conductivity of organic liquid/Li salt (Figure 4).



Scheme 4. Synthesis of phosphorus containing polyethers by condensation polymerization.

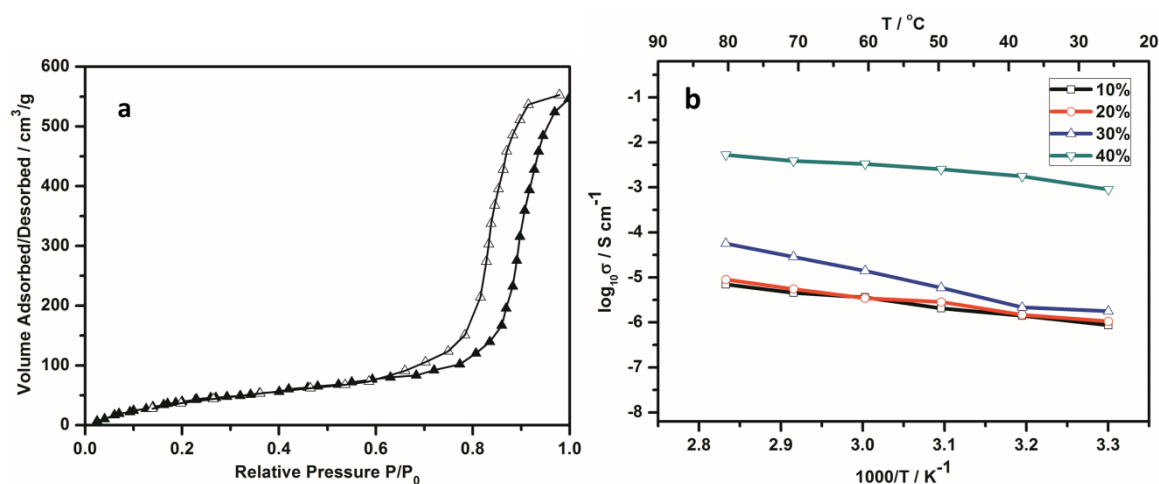


Figure 4. a) Nitrogen adsorption (filled triangles)-desorption (empty triangles) isotherm of powdered polymer sample **P8**. b) Arrhenius plot of temperature dependent conductivity of **SPE9** (10%-40%).

Summary and Conclusion

The multiple catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) was thoroughly studied for the synthesis of cyclic carbonate, polycaprolactone and polyethers. Our catalysts were very efficient to utilize the renewable resources to produce basic valuable materials. The solid polymer electrolytes of different types with different ratios were prepared and characterized. The conductivity behavior of biodegradable, PCL (**P1**) based **SPE1** was studied. Further, we designed and synthesized the polyethers with phosphate pendant groups; and polyethers with phosphorus in main chain, in order to achieve the conformational flexibility and/or to create suitable superstructure for lithium-ion mobility. Our strategy enabled to achieve the conductivity of $8.9 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature in one of the intrinsic porous polyether based **SPE9**. To the best of our knowledge, this is the best conductivity achieved so far in all solid state polymer electrolytes. The SPE with flame retardant property having good lithium-ion conductivity has been achieved. They can be utilized as solid polymer electrolyte in automobile lithium ion batteries.

CHAPTER 1

Introduction

1.1. Conducting polymers

The discovery of electrical conductivity by polymers enriched applications of polymers in various fields [1]. Some of the topical field of technologies are solar cells, organic light emitting diodes, electrochromic devices, biomedical applications, cellular adhesion and imaging, biosensors and energy storage devices. Alan J. Heeger, Alan G. MacDiarmid, Hideki Shirakawa shared the chemistry Nobel Prize in 2000 for the discovery and development of conductive polymers [2]. Two types of conducting polymers viz. electronically conducting and ion conducting polymers are known. The electronic conductive polymers are so different from any other polymeric (plastic) material in their conductivity but are similar to other plastics in their weight, cost, moldability, and general physical properties. The prominent conducting polymers are polyaniline, polypyrrole, polyacetylene, polythiophene, polyphenylene and poly(phenylenevinylene) [3].

Two general types of ion-conducting polymers have been intensively investigated. They are polymer-salt complexes and polyelectrolytes. A typical polymer salt complex consists of a coordinating polymer, usually a polyether, in which a salt, e.g. LiClO_4 , is dissolved [4]. Polyelectrolytes contain charged groups, either cations or anions, covalently attached to the polymer, so only the counter ion is mobile [5]. Among ion-conducting polymers, Li-ion conductivity is well studied but still requires more research for enhancing the conductivity as well as the capacity of Li-ion batteries for portable devices and automobiles. Especially study on solid polymer electrolytes gained considerable attention due to their potential use in larger lithium batteries. A battery technology which provides high specific capacity and high energy density is in demand for rapidly developed miniature electronic products such as watches, calculator, remote controls, video games and energy portability [6].

1.2. Batteries

A battery converts the chemical energy into electrical energy during discharge and vice versa while charging. Important purposes of battery are to store and supply the power over a period. An electrochemical cell consists of a positive electrode and a negative electrode separated by an electrolyte solution. During discharge, the electrode where the oxidation dominates is called negative electrode (anode). The electrode where the reduction dominates is called positive electrode (cathode) [7].

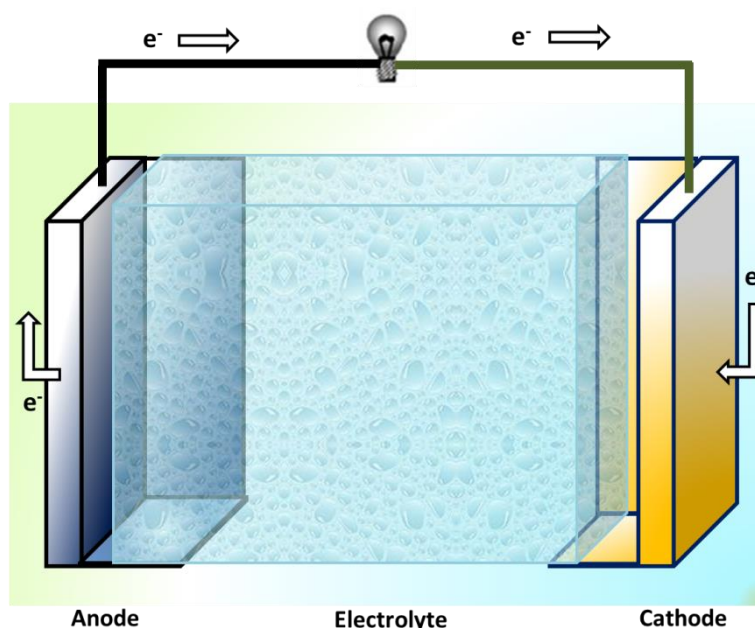


Figure 1.1. Basic components of a cell

An electrolyte sandwiched between the positive and negative electrodes, physically separates them to prevent direct contact (Figure 1.1). Electrolyte is made up of salts dissolved in either water or a non-aqueous media such as organic and inorganic molecules. Role of an electrolyte is serving as medium for the transport of ions between a pair of electrodes. When electrodes are connected externally, a chemical reaction taking place at both electrodes, electrons released from the electrode, thus electricity is produced to power any device connected to it. A battery is composed of one or more electrochemical cells (galvanic cells). These electrochemical cells can be connected either in series to reach a higher voltage or in parallel to achieve higher capacity. Nowadays, various energy storage systems (battery) are available depending on the field of applications. Based on the working principles, it is commonly divided into primary batteries and secondary batteries. They are further classified as shown in Figure 1.2 based on the nature of electrolytes used in a battery [8].

The primary batteries are non-rechargeable batteries in which the electrochemical reaction is irreversible. Once a primary battery is discharged, it would be discarded. The ancient primary aqueous batteries are still commercially important primary batteries for a wide range of practical applications due to their low cost of materials, ease of manufacturing and reliable performance. One of the major factors for their wide applications is that the aqueous electrolyte is swollen by gelling agents or incorporated into microporous separators *i.e.*, the electrolyte is modified into immobilized paste. They are often referred as ‘dry

batteries'. Unlike wet cells, dry cells can be operated in any orientation without spilling. The secondary batteries are rechargeable batteries in which the electrochemical reaction is reversible. Once the battery is discharged, the electrochemical reaction can be reversed by applying the external electrical energy. So the reactants at electrodes return to their original form which can be used again. Compared with primary batteries, secondary batteries save the cost and resources [9]. The electrodes, operating voltage, energy density property and electrochemical reactions of selected important primary and secondary aqueous batteries are listed in Table 1.1 and 1.2 respectively.

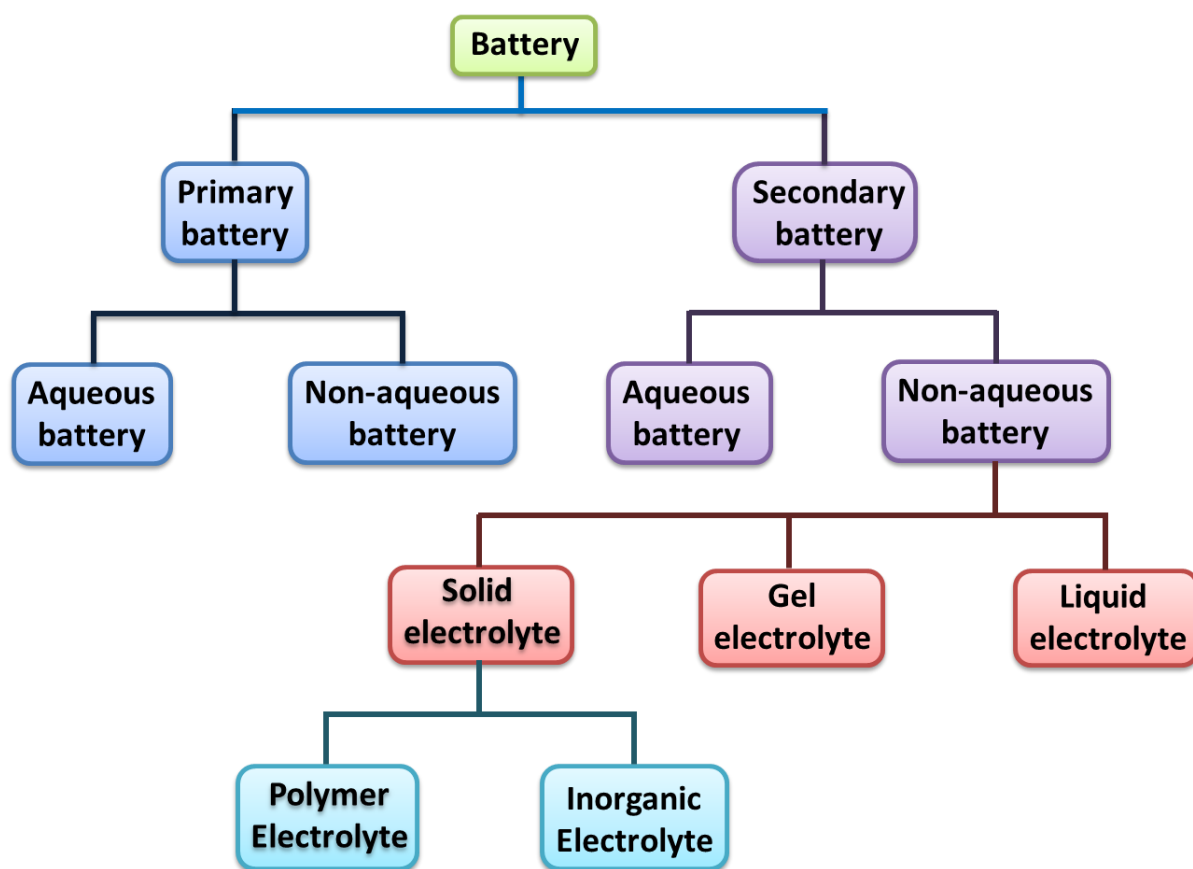


Figure 1.2. Classification of batteries based on electrolytes

Table 1.2. Electrochemical reactions and energy density properties of various secondary aqueous batteries [9-13]

Type of battery/cell reaction	Anode	Cathode	Electrolyte	Operating voltage (V)	Specific energy (Wh/kg)	Energy density (Wh/L)
Pb-acid	Pb	PbO ₂	Sulphuric acid	2.1	22-33	49-83
$\text{PbO}_2 + \text{Pb} + 2 \text{H}_2\text{SO}_4 \xrightleftharpoons[\text{charge}]{\text{discharge}} 2 \text{PbSO}_4 + 2 \text{H}_2\text{O}$ 8						
Ni-Cd	Cd	Ni(OH) ₂	Aq. KOH	1.2	26-37	61-85
$2 \text{NiO.OH} + \text{Cd} + 2 \text{H}_2\text{O} \xrightleftharpoons[\text{charge}]{\text{discharge}} 2 \text{Ni(OH)}_2 + \text{Cd(OH)}_2$ 9						
Ni-MH	Intermetallic compound	Ni(OH) ₂	Aq. KOH	1.2	60-75	150-200
$\text{NiO.OH} + \text{MH} \xrightleftharpoons[\text{charge}]{\text{discharge}} \text{Ni(OH)}_2 + \text{M}$ 10						

1.3. Batteries with lithium

Lithium is the most attractive anode material since it has the highest reduction potential (-3.0 V versus standard hydrogen electrode) and has the lowest density (0.534 g/cm³). Highest reduction potential of lithium anode is able to afford high cell voltage when it is combined with cathodes. Moreover, the light weight, lithium metal provides high specific capacity of about 3.86 Ah/g [6b, 7, 9]. The following features are made the lithium based batteries particularly suitable for electronic applications.

- *High cell voltage:* The high energy density is attributable to the operating voltage of lithium batteries (3-4 V). As a result, compared with aqueous batteries, number of cells in a battery pack can be reduced by a factor of 2 or 3.

- *Low temperature performance:* Lithium batteries can function even at temperatures of around $-40\text{ }^{\circ}\text{C}$ because of low freezing point of non-aqueous solvents. The conductivity of lithium batteries at cold temperature is far better than the previous aqueous batteries.
- *Long shelf life:* The storage limits of lithium batteries are in the range of 5-10 years. The self-discharge is restricted might be due to the formation of solid electrolyte interface (SEI) on lithium.

The lithium metal is both ductile and malleable. Freshly cut shiny surface of lithium rapidly turns greyish-white to grey or black in air. So the assembly of lithium batteries should be done in 'Dry rooms'. Handling of lithium is comparatively safer than other alkali metals. Since lithium readily reduces water due to its electropositive nature, non-aqueous media is only employed as electrolyte in the cells containing lithium anode. So, dissolving lithium salts in aprotic organic solvents proved to be the most suitable electrolytes. The inorganic solvents (thionyl chloride and sulphur dioxide) which are stable with lithium are also used as electrolyte solvent for lithium batteries. Generally, lithium metal is stable in a number of non-aqueous electrolytes due to the formation of passivating layer on lithium which prevents further reaction or corrosion, but the layer allows for cell discharge. This layer is often referred as solid electrolyte interface (SEI). This film formation helps in chemical stability and low self-discharge.

Some of the potential primary non-aqueous batteries using lithium anode are lithium-manganese dioxide battery, lithium-carbon monofluoride battery and lithium-thionyl chloride [14]. Li-MnO₂ cell is made up of a manganese dioxide cathode and a lithium anode. The lithium salt (LiClO₄) dissolved in a mixture of propylene carbonate and dimethoxyethane is utilized as electrolyte. It has the features of high voltage (2.9 V), high energy density, very low self-discharge characteristics, long shelf life, non-corrosive, leak proof, safe and effective low temperature performance. All these facts collectively enhanced the production of Li-MnO₂ primary batteries and it reserves almost 80% of total production of lithium primary batteries. The Li-(CF_x)_n is a 2.8 V battery combining a lithium anode and a carbon monofluoride (CF_x)_n cathode. The (CF_x)_n is prepared by the reaction of carbon powder with fluorine gas at an elevated temperature and pressure [15]. The electrolyte consists of lithium tetrafluoroborate (LiBF₄) dissolved in α -butyrolactone. The Li-SOCl₂ battery consists of a

Table 1.3. Electrochemical reactions^a and energy parameters of various primary lithium batteries [9-13]

Type of battery/cell reaction	Cathode	Electrolyte	Operating voltage (V)	Specific energy (Wh/kg)	Energy density (Wh/L)
Li-MnO ₂	MnO ₂	Organic liquid	2.9	150-350	450-750
Reaction at cathode	$\text{MnO}_2 + \text{Li}^+ + \text{e}^- \longrightarrow \text{MnO}_2^-(\text{Li}^+) \quad \text{.....11}$				
Overall reaction	$\text{MnO}_2 + \text{Li} \longrightarrow \text{MnO}_2^-(\text{Li}^+) \quad \text{.....12}$				
Li-(CF _x) _n	(CF _x) _n	Organic liquid	2.8	235	330-580
Reaction at cathode	$(\text{CF})_n + n \text{e}^- \longrightarrow n \text{C} + n \text{F}^- \quad \text{.....13}$				
Overall reaction	$n \text{Li} + (\text{CF})_n \longrightarrow n \text{C} + n \text{LiF} \quad \text{.....14}$				
Li-SOCl ₂	SOCl ₂	Inorganic liquid	3.6	360	660
Reaction at cathode	$2 \text{SOCl}_2 + 4 \text{Li}^+ + 4 \text{e}^- \longrightarrow 4 \text{LiCl} + \text{S} + \text{SO}_2 \quad \text{.....15}$				
Overall reaction	$4 \text{Li} + 2 \text{SOCl}_2 \longrightarrow 4 \text{LiCl} + \text{S} + \text{SO}_2 \quad \text{.....16}$				

^aIn all the primary lithium batteries, lithium acts as anode and the general discharge reaction at anode is as follows: $n \text{Li} \longrightarrow n \text{Li}^+ + n \text{e}^-$

porous carbon cathode and a lithium anode. This battery have a high operating voltage (3.6 V) and wide operating temperature range (-55 to 85 °C). The electrolyte is prepared by dissolving lithium tetrachloroaluminate (LiAlCl₄) in SOCl₂. The SOCl₂ acts as both the cathode and as electrolyte solvent. The side product formed in the discharge reactions is dissolved in the electrolyte (SO₂) whereas sulphur and LiCl is precipitated on the porous carbon cathode [16]. The electrochemical reactions happening in these kinds of batteries and their energy density parameters are described in Table 1.3.

1.4. Secondary batteries based on lithium

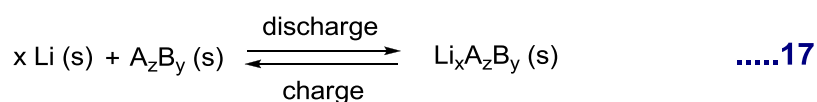
Always secondary batteries are more advantageous than primary batteries because of the usability over a period and portability. They are promising for use in automobiles and utilization of electricity from photovoltaic devices especially in night. Therefore, understanding of their operating principle and the possibilities for further enhancement of their properties are important for discussion [17]. Properties of four important secondary batteries based on lithium are tabulated (Table 1.4) and their operating principles are discussed in following sections.

Table 1.4. Properties of lithium secondary batteries [18]

Type of battery	Operating voltage (V)	Theoretical specific energy (Wh/kg)	Theoretical energy density (Wh/L)
Lithium-ion	3.8	387	1015
Non-aqueous Li-O ₂	3.0	3505	3436
Aqueous Li-O ₂	3.2	3582	2234
Li-S	2.2	2567	2199

1.4.1. Lithium Anode Battery

The batteries using lithium anode is normally referred as lithium batteries. Since lithium metal anode has a very large theoretical capacity of 3860 mAh/g, in contrast to the value of 372 mAh/g for a LiC₆ carbon anode, much effort has been made in developing secondary batteries with metallic lithium anodes [18]. The schematic representation of batteries using lithium as anode is shown in the Figure 1.3 and the electrochemical reaction is given below.



Even though lithium battery is very successful and promising in the case of primary battery, while promoting the lithium anode into rechargeable technology, severe problems have been encountered especially in case of cycle performance and safety issues. These drawbacks were mainly observed due to the dendrite formation of lithium upon recharge. As discussed earlier, lithium metal remain stable under organic solvents due to the formation of SEI on lithium, but the layer formation causes more difficulties when the electrode is cycled

in a secondary battery. When a cell is charged, lithium is deposited on the lithium anode. Sometimes, the deposited lithium is not flat but fiber or needle like crystals (dendrite). When the cell is discharged, the lithium anode dissolves, and sometimes the needle like lithium is cut and becomes isolated from the anode substrate. This isolated lithium is called “dead lithium”, and it is electrochemically inactive but chemically active. Moreover, when dendrite growth pierces the separator, it results in an internal short that leads to thermal runaway and explosion.

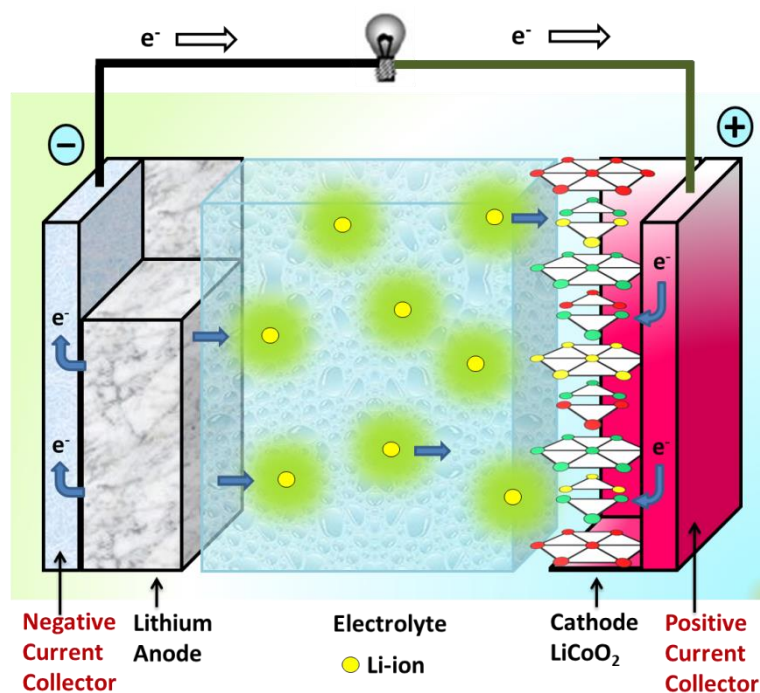


Figure 1.3. Schematic diagram showing discharge process of lithium battery. The battery contains lithium metal as anode and LiCoO_2 as cathode. In the discharge process, lithium-ions (yellow colour circle) dissociate from lithium anode and enter into layered structure of cathode LiCoO_2 by intercalation.

1.4.2. Lithium-ion Battery

The morphological changes (dendrite formation) and passivation reactions at lithium metal negative electrodes in lithium batteries reduce their cycle life and introduce safety hazards. To overcome this, a more recent development involves the replacement of the lithium metal anode by graphite. Lithium-ion battery is the most widely used secondary battery systems for portable electronic devices. Compared with aqueous rechargeable batteries (such as Pb-acid, Ni-Cd and Ni-MH), Li-ion battery possess higher energy density, higher operating voltages,

lower self-discharge and lower maintenance requirements. Due to these properties, Li-ion battery occupies the highest performing available secondary battery [19].

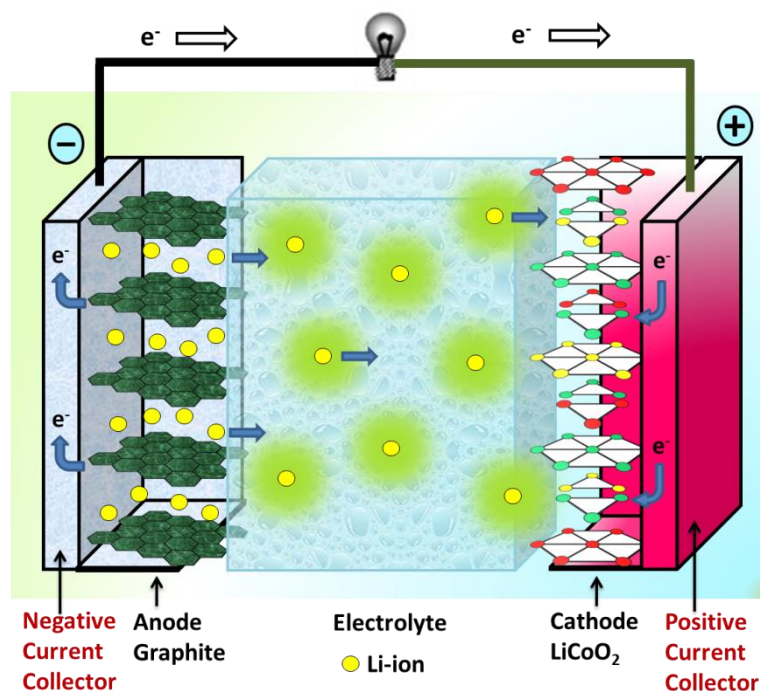


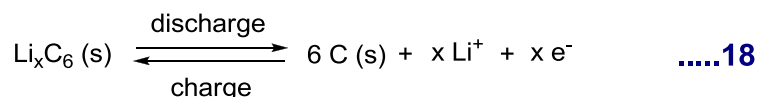
Figure 1.4. Schematic diagram showing the discharge process of lithium-ion battery. The battery contains graphitic carbon as anode and LiCoO_2 as cathode. In the discharge process, lithium-ion (yellow colour circle) underwent deintercalation from the graphite carbon anode and entered into LiCoO_2 layered structure cathode by intercalation.

In this battery, during charging the reaction at negative electrode is uptake of lithium-ions by graphite instead lithium plate anode and release of lithium-ions during discharge (Figure 1.4) [20]. Therefore, during discharge, the negative electrode (Li_xC_6) acts as lithium-ion source whereas the positive electrode (A_zB_y) acts as lithium-ion recipient. It is often referred to as ‘rocking chair battery’. Present-day lithium-ion battery consists of lithium cobalt oxide (LiCoO_2) as positive electrode and graphite as negative electrode. The electrolyte is lithium hexafluorophosphate (LiPF_6) dissolved in a mixture of propylene carbonate and dimethoxyethane solvent.

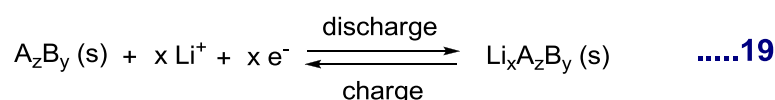
Generally, the conductivity of organic aprotic solvents containing lithium salts is in the range of $10^{-3} \text{ S cm}^{-1}$. Whereas the conductivity of H_2SO_4 in lead-acid batteries and aqueous KOH in Ni-Cd batteries are $8 \times 10^{-1} \text{ S cm}^{-1}$ and $5 \times 10^{-1} \text{ S cm}^{-1}$ respectively. Since the conductivity of organic liquid electrolyte is much lower than that of aqueous electrolyte

solutions, much focus is needed to obtain high ionic conductivity for organic electrolytes [21]. The electrochemical reaction in lithium-ion battery can be represented as follows:

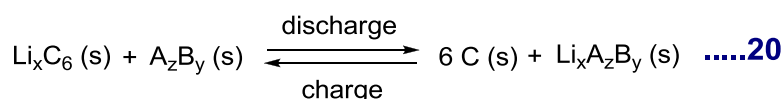
The reaction at anode



The reaction at cathode



The overall reaction of a battery



1.4.3. Lithium-air (Li-O₂) and lithium-sulfur (Li-S) batteries

Since their introduction in 1991, Li-ion batteries have transformed portable electronic devices. New generations of such batteries will play a key role in the electrification of transport [22]. However, the highest energy storage possible for Li-ion batteries is insufficient for long-term needs of society, for example, extended range electric vehicles. To go beyond the horizon of Li-ion batteries is a formidable challenge; there are few options such as non-aqueous and aqueous Li-O₂ and Li-S battery (Table 1.4). But, these technologies are not yet established for commercial product, and both present significant challenges.

The rechargeable non-aqueous Li-O₂ battery was first reported by Abraham and co-workers and the interest has expanded rapidly in recent years [23]. In Li-air battery, intercalation LiCoO₂ cathode of lithium battery is replaced by a porous, electronically conducting substrate, usually carbon, immersed into the electrolyte (LiPF₆ in propylene carbonate). Upon discharge, Li-ions form by oxidation of lithium metal anode and pass across the electrolyte (Figure 1.5). At cathode, oxygen from the atmosphere dissolves in electrolyte is reduced. In the case of non-aqueous Li-air battery, reduced oxygen combines with Li-ions from the electrolyte to form Li₂O₂ and the process is reversed on charging.

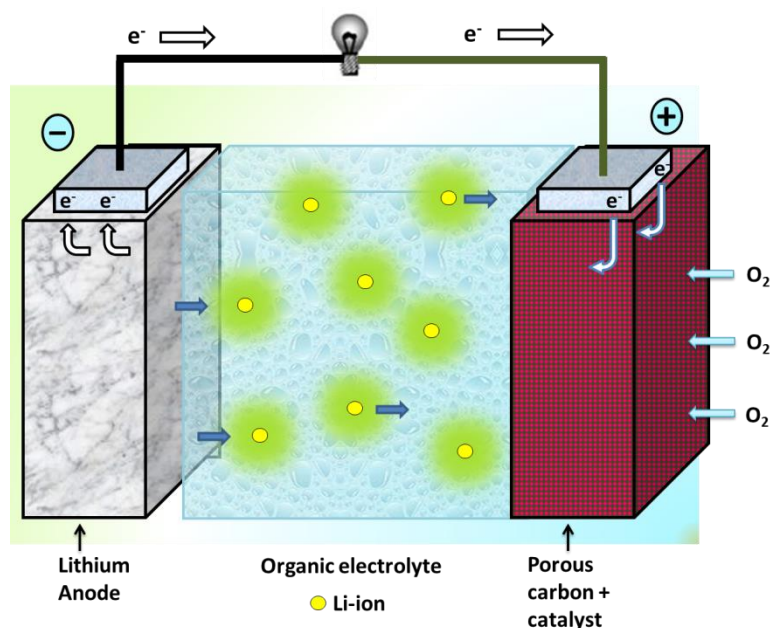
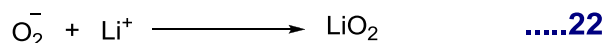
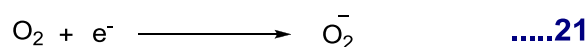
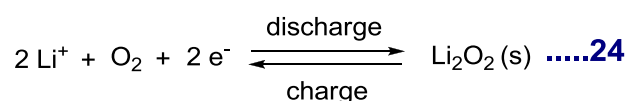


Figure 1.5. Schematic diagram showing the discharge process of non-aqueous lithium-air battery. The battery contains porous carbon as cathode and lithium as anode.

The mechanism of oxygen reduction at cathode on discharge



The overall battery reaction involved in non-aqueous Li-O₂ battery is



The mechanism involved in the oxygen reduction on discharge as well as the oxidation of Li₂O₂ on charging is not well-established. The organic carbonate electrolytes gradually undergo decomposition on reduction process which makes more difficult to find actual mechanism. However, non-aqueous Li-O₂ battery containing solid polymer electrolyte (SPE) has provided evidence for the oxygen reduction mechanism at cathode owing to the electrochemical stability of SPE. It clearly indicated the importance of SPE in a battery [24]. For the aqueous Li-air battery, water is also involved in the discharge reaction to form LiOH and the process is reversed on charging. The overall battery reaction involved in aqueous Li-O₂ battery is

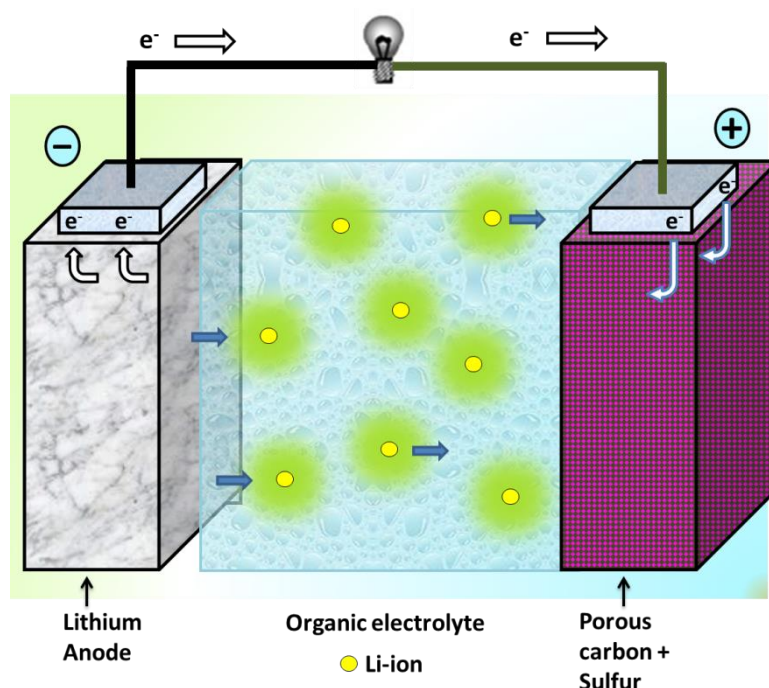
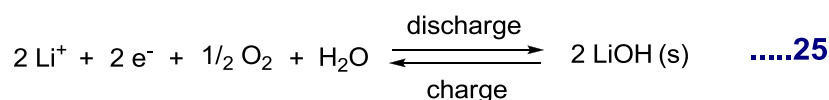
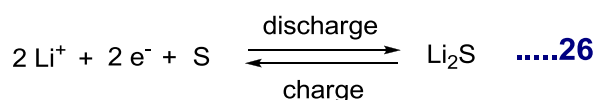


Figure 1.6. Schematic diagram showing the discharge process of lithium-sulfur battery. The battery contains porous carbon containing sulfur as cathode and lithium as anode.

Li-S battery has the following attractive features: (a) the natural abundance and low cost of S; and (b) high theoretical energy storage [25]. Yet the promise of a device with greater energy storage and cycle life than Li-ion has not materialized. In the discharge of the Li-S battery, the sulfur at the cathode is reduced and combines with Li-ion to ultimately form Li_2S . The reaction is reversed on charge (Figure 1.6). Even though Li-air and Li-S batteries possess high theoretical specific energy, it suffers from the dendrite formation, cycling efficiency, safety issues, decomposition of electrolytes, blocking of porous electrodes by produced solid products such as Li_2O_2 , LiOH and Li_2S . Although an important progress has been made by many authors, significant challenges remain. The overall battery reaction involved in Li-S battery is



1.5. Non-aqueous electrolytes for lithium based batteries

Since the electrolytic decomposition voltage of water is 1.23 V, the operating voltage and energy density of primary and secondary aqueous batteries are remained in the limited range. This necessitates for a non-aqueous and non-flammable electrolytes for batteries with improved performance. The following points explain the advantages of batteries with non-aqueous electrolytes.

1. Wide electrochemical stability of non-aqueous electrolytes allows constructing non-aqueous batteries with high cell voltage. Battery voltage of non-aqueous batteries lied in the range of 3-4 V whereas aqueous batteries remain in the range of 0.9-1.5 V.
2. Compared with aqueous batteries, high energy density can be achieved in non-aqueous batteries (Figure 1.7) [9]. The energy properties of a battery pack are either represented by specific energy (Wh/kg) or energy density (Wh/L).
3. The non-aqueous batteries can provide approximately three times the energy of aqueous battery. To explain, consider two batteries both having same capacity 5 Ah (ampere-hour), among which one is aqueous battery while the other is non-aqueous. The watt-hours stored in a battery pack are approximated by multiplying the ampere-hours and battery voltage.

$$\text{Watt-hour (Wh)} = \text{Battery voltage} \times \text{Ampere-hour (Ah)}$$

Now, the aqueous battery having mean voltage 1.2 V can deliver 6 Wh ($1.2 \text{ V} \times 5 \text{ Ah}$), while a $3.6 \text{ V} \times 5 \text{ Ah}$ non-aqueous battery can deliver 18 Wh.

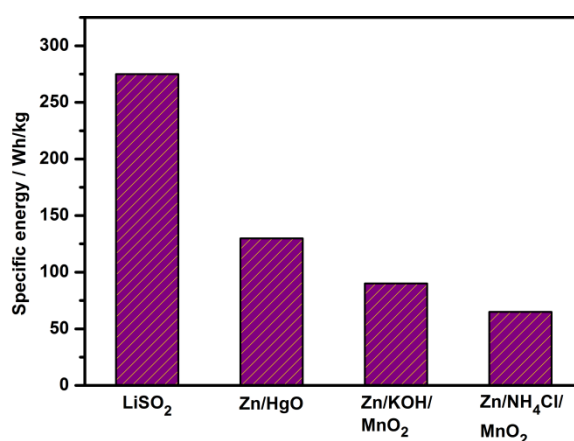


Figure 1.7. Comparison of specific energy of primary lithium battery with various aqueous batteries

Generally, three different kinds of non-aqueous electrolytes are used in the lithium based non-aqueous batteries. Based on the physical nature they are classified into liquid, gel and solid. Since the electrolyte is in close interaction with both the electrodes, it is important to check the compatibility when new electrodes are used [10, 26]. The electrolytes should possess following features for use in these batteries.

- It has to be a good ionic conductor and electronic insulator.
- It should have wide electrochemical window.
- It should be inert to other cell components like electrodes, separator and cell packaging material.
- It should be robust against various abuses such as electrical, mechanical and thermal conditions.
- It should be environmentally friendly.

An ideal lithium salt for non-aqueous batteries should satisfy following requirements [26]:

- Lithium salt has to be completely dissolve and dissociate in non-aqueous media, and the solvated ions should move in the media with high mobility.
- The anion has to be stable against oxidative decomposition at cathode.
- The anion has to be inert to electrolyte solvents.
- Both anion and cation should be inert toward other cell components such as separator, electrodes and cell packaging materials.
- The anion should be nontoxic and stable against thermally induced reactions with electrolyte solvents.

1.5.1. Liquid electrolytes

The most effective electrolyte for non-aqueous battery is liquid electrolyte. It consists of lithium salts dissolved in aprotic organic solvents. Widely used lithium salts are LiPF_6 , LiAsF_6 , LiBF_4 , LiClO_4 and LiAlCl_4 . More recently, a series of salts based on the sulphonate group have been developed, for example, lithium trifluoromethanesulphonate LiCF_3SO_3 (lithium triflate), $\text{LiN}(\text{SO}_2\text{CF}_3)_2$, LiTFSI (lithium imide) and $\text{LiC}(\text{SO}_2\text{CF}_3)_3$ (lithium methide) [26, 27]. The solvent used for electrolyte should have low melting point, high boiling point, low vapour pressure and wide operating temperature range. Further, high permittivity and low viscosity are desirable for the solvent to ensure higher ionic conductivity of electrolyte solution. The commonly used organic solvents include cyclic esters (propylene carbonate,

ethylene carbonate, γ -butyrolactone), linear esters, cyclic ethers (2-methyltetrahydrofuran, 1,3-dioxolane), linear ethers (Figure 1.8), amides and sulphoxides [28]. However, solvents with high dielectric constants have generally high viscosity even at room temperature, resulting in slow transfer of lithium ions, *i.e.*, low ionic conductivity in electrolytes. Hence, the solvents with low viscosity are mixed with the solvents described above in order to lower the viscosity of electrolyte system and to increase ionic conductivity [27, 28]. The common solvents used to decrease the viscosity are tetrahydrofuran, dimethoxyethane, diethyl carbonate (DEC), dimethyl carbonate (DMC) and ethyl methyl carbonate (EMC) (Figure 1.8).

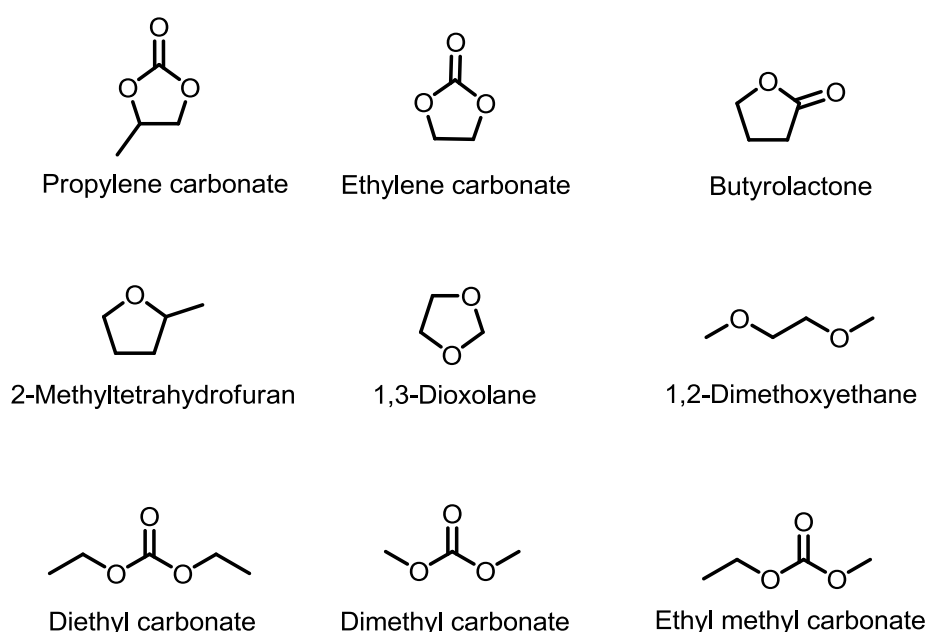


Figure 1.8. Structures of organic solvent used in non-aqueous batteries as electrolyte

1.5.2. Gel Electrolytes

Gel polymer electrolytes were prepared by incorporating liquid electrolytes (organic solvents) into polymer matrices. The polymer matrices play a role as a ‘holder’ of organic solvents. The electrolytes are easily prepared by heating a mixture containing appropriate amounts of polymer, solvents and a lithium salt (LiClO_4 , LiCF_3SO_3) to about 120-150 °C (a temperature above the glass transition temperature of the polymer) to form viscous but clear liquids. These electrolytes have ionic conductivities in between 10^{-4} to $10^{-3} \text{ S cm}^{-1}$ [29]. These systems are expressed in various terms such as plasticized polymer electrolytes, polymer hybrids, gelionics and gel electrolytes. Various polymeric hosts such as, poly(vinylidene fluoride) (PVdF), poly(acrylonitrile) (PAN), poly(vinyl chloride) (PVC) and poly(vinyl

pyrrolidone) (PVP) have been found to immobilize the lithium salt solvates of organic solvents (Figure 1.9). Low vapour pressure solvents, such as ethylene carbonate (EC), propylene carbonate (PC), dimethyl formamide (DMF), diethyl phthalate (DEP), diethyl carbonate (DEC), ethyl methyl carbonate (EMC), dimethyl carbonate (DMC), γ -butyrolactone (BL) have been commonly investigated as ‘plasticizer’ solvents for the gel electrolytes.

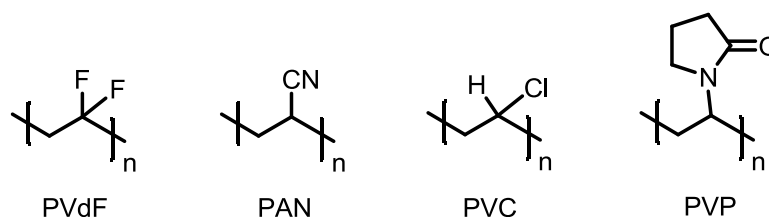


Figure 1.9. Structures of various polymer hosts

1.5.3. Solid Electrolytes

At present, the performance of lithium-ion battery for miniature portable electronic devices is satisfactory. However, the current technology cannot be upgraded to higher version of batteries especially for electric vehicles. Since such batteries have a flammable organic solvent as an electrolyte the considerations become serious. Organic solvents also suffer from volatility, pressure build-up or even explosion, harmful leakage and flammability. Thus, a wide operating temperature range is impractical. The fundamental solution to this problem is substituting the flammable organic electrolyte with non-flammable solid electrolytes, *i.e.*, inorganic solid electrolytes or solid polymer electrolytes.

Inorganic solid electrolyte (ISE) containing batteries have not been widely used because ISEs have not completely satisfied the requirements for practical application. Studies on lithium-ion conductive ISEs started with crystalline materials, such as lithium halides including LiI, Li₃N and their derivatives, oxysalts including LISICON and sulphides [30]. The ionic conductivity of ISEs is generally lower than that of organic liquid electrolytes by a factor of $1/10 - 1/10^5$. However, some of the high ionic conductive ISEs possess less electrochemical stability for the battery application. For example, Li₃N has a high ionic conductivity of $10^{-3} \text{ S cm}^{-1}$. However, the decomposition potential is about 0.45 V. The low decomposition potential limits the cell voltage of the battery containing ISEs. Some oxysalts, *e.g.*, Li_{1+x}M_xTi_{2-x}(PO₄)₃ (M = Al, Sc, Y, La) and Li_{0.5-3x}TiO₃ also show ionic conductivity as

high as $10^{-3} \text{ S cm}^{-1}$. But the transition metal elements are easily reduced electrochemically, because the negative electrode materials in lithium batteries are strong reducing agents [30].

1.6. Solid polymer electrolyte (SPE)

Replacement of the liquid electrolyte with a thin polymer membrane is highly desirable. The all solid state lithium-ion polymer battery is recognized as attractive technology for rechargeable electric vehicles than the lithium-ion battery having organic solvents as electrolyte. So there has been a continuously growing interest to produce SPEs having high ionic conductivity and flame retardant property [26, 31]. Polymer electrolytes consist of a polymer matrix and appropriate amount of lithium salts. Besides the safety considerations, other interesting properties such as flexibility, easy manipulation and high temperature use of SPEs gives possibilities for advanced lithium-ion polymer secondary batteries. In addition, both ion conduction and mechanical separation can be attained in a single solid electrolyte membrane. Furthermore, a battery can be fabricated in any desired shape and size due to the flexibility of polymer membranes. Unlike ISEs, SPE can be cast into thin film that can adhere to the electrode surface. Thus, when the electrodes undergo dimensional changes, thin film of SPEs did not lose the contact with electrode [32].

Wright and co-workers were the first to discover the ability of ether based polymer - poly(ethylene oxide) (PEO) to dissolve inorganic salts and exhibiting ion conduction at room temperature [33]. After this, PEO became the representative polymer matrix for SPEs and so a wide spectrum of polymers has been investigated as electrolyte solvents (Table 1.5 and 1.6) [6, 32, 34]. While dissolving lithium salts, the polymer play a role as a solvent. The atoms with lone pair of electrons (for example, oxygen atom) present in polymer chains act as electron donors thus loosely coordinate to Li-ions. Consequently, the Li^+ of lithium salt was solvated by polymer, and lithium salt no more exist as aggregates. For the solvation of lithium salts by the polymers, the solvation Gibbs energy should be larger than the lattice Gibbs energy of lithium salts. The solvation Gibbs energy depends on the ion-solvent electrostatic interactions.

Molecular design of lithium salts with lower lattice energies is also important to obtain higher ionic conductivity. Attempts have been made to use following lithium salts to prepare SPEs: LiClO_4 , LiCF_3SO_3 , LiPF_6 and LiBF_4 [26]. However, their solubility is not so high in polymer electrolytes because their solvation energy is insufficient to overcome the lattice energies of lithium salts. It was first reported by Armand et al that due to the lower

lattice energy and anion size, lithium bis(trifluoromethanesulfonyl)imide $\text{LiN}(\text{CF}_3\text{SO}_2)_2$ (LiTFSI) has been the most attractive lithium salts. Poorly conducting LiCF_3SO_3 , hazardous LiClO_4 , thermally unstable LiBF_4 and LiPF_6 , and toxic LiAsF_6 would be replaced by LiTFSI in lithium battery applications [26]. LiTFSI is proved to be safe, thermally stable, and highly conducting lithium salt. It melts at 236 °C without decomposition and does not decompose until 360 °C. Later studies presented a new types of lithium salts, with lower lattice energies, such as $\text{LiC}(\text{CF}_3\text{SO}_2)_3$, $\text{LiN}(\text{SO}_2\text{CF}_2\text{CF}_3)_2$, etc.

Table 1.5. Structures of various polymers based on carbon backbone and their lithium-ion conductivities [6, 32, 34].

Entry	Polymer host	Repeat unit	Lithium salt	Conductivity, σ (S cm^{-1}) at RT
1	Poly(oxymethylene)	$\text{-(CH}_2\text{O)-}_n$	LiClO_4	$\sim 10^{-8}$
2	Poly(ethylene oxide)	$\text{-(CH}_2\text{CH}_2\text{O)-}_n$	LiClO_4	$\sim 10^{-7}$
			LiCF_3SO_3	1.1×10^{-6}
3	Poly(propylene oxide)	$\text{-(CH(CH}_3\text{)CH}_2\text{O)-}_n$	LiClO_4	$\sim 10^{-8}$
			LiCF_3SO_3	2.2×10^{-6}
4	Poly(oxymethylene-oligo-oxyethylene)	$\text{-(CH}_2\text{O)(CH}_2\text{CH}_2\text{O)-}_n$	LiCF_3SO_3	3.0×10^{-5}
5	Poly(β -propiolactone)	$\text{-(CH}_2\text{CH}_2\text{CO)-}_n$	LiClO_4	3.5×10^{-6}
6	Poly(ethylene adipate)	$\text{-(CH}_2\text{CH}_2\text{C(=O)(CH}_2\text{)}_4\text{C(=O)-}_n$	LiCF_3SO_3	$\sim 10^{-6}$
7	Poly[(2-methoxy)ethyl glycidyl ether]	$\text{-(CH}_2\text{CHO)-}_n$ $\text{CH}_2(\text{OCH}_2\text{CH}_2)_2\text{OCH}_3$	LiClO_4	$\sim 10^{-5}$
8	Poly(methoxy poly(ethylene glycol)methacrylate)	$\text{-(C(CH}_3\text{)(CO(CH}_2\text{CH}_2\text{O)}_{22}\text{CH}_3\text{)-}_n$	LiCF_3SO_3	2.0×10^{-6}
9	Poly(methoxy ethoxy ethyl methacrylate)	$\text{-(C(CH}_3\text{)(COCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3\text{)-}_n$	LiClO_4	3.3×10^{-6}

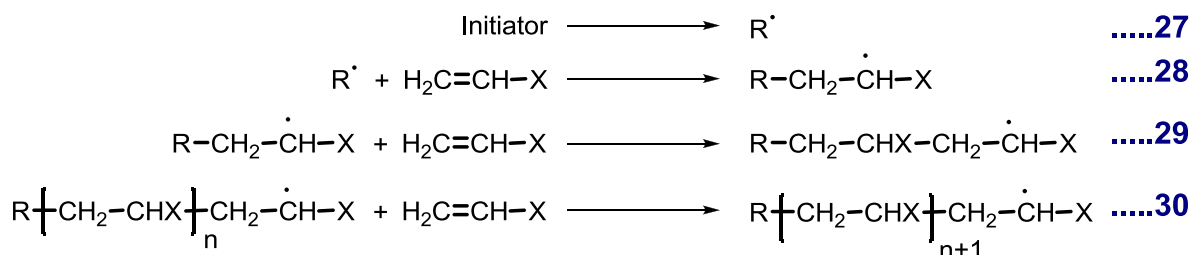
Table 1.6. Structures of various polysiloxanes and polyphosphazenes and their lithium-ion conductivities [6, 32, 34].

Entry	Polymer host	Repeat unit	Lithium salt	Conductivity, σ (S cm ⁻¹) at RT
1	Poly(dimethyl siloxane)	$\text{---} \text{Si}(\text{CH}_3)_2 \text{---}_n$	LiClO ₄	$\sim 10^{-4}$
2	PEO-grafted polysiloxane	$\text{---} \text{Si}(\text{CH}_3)(\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3) \text{---}_n$	LiClO ₄	$\sim 10^{-4}$
3	Double-comb polysiloxane	$\text{---} \text{Si}(\text{CH}_2\text{CH}_2\text{O}(\text{CH}_2\text{CH}_2\text{O})_5\text{CH}_3)_2 \text{---}_n$	LiTFSI	4.5×10^{-4}
4	Poly[(bis-2-(2-methoxyethoxy) ethoxy) phosphazene]	$\text{---} \text{P}(\text{OCH}_2\text{CH}_2\text{OCH}_2\text{CH}_2\text{OCH}_3)_2 \text{---}_n$	LiBF ₄	2.0×10^{-5}
			LiTFSI	5.0×10^{-5}
			LiC(CF ₃ SO ₂) ₃	$\sim 10^{-4}$
			LiCF ₃ SO ₃	2.7×10^{-5}
5	Poly(etheroxy phosphazene)	$\text{---} \text{P}(\text{OCH}_2\text{CH}_2)_7 \text{---}_n$	LiCF ₃ SO ₃	2.4×10^{-5}

1.7. Polymerization reactions

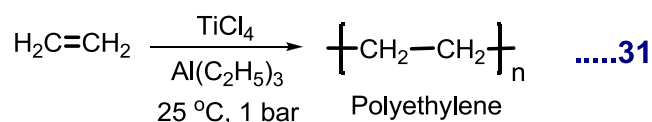
Polymers are classified based on the polymer structure as addition polymers and condensation polymers. It can also be classified based on the nature of chemical reactions employed in the polymerization. *i.e.*, chain polymerization and step polymerization. The polymerization reactions typically consist of three phases, namely initiation, propagation and termination. Various initiators are used to start polymerization reactions. The initiators play a major role in deciding the reaction mechanism such as free radical, anionic or cationic [35]. In a free radical polymerization, the reaction is initiated by molecules which readily undergo fragmentation to free radicals either when heated or when irradiated with electromagnetic radiation. Examples of free radical initiators are 2,2'-azobisisobutyronitrile (AIBN), 1,1'-

azobis(cyclohexanecarbonitrile), benzoyl peroxide, t-butyl peroxide and potassium persulfate. The general steps involved in the free radical polymerization are shown in Scheme 1.1.



Scheme 1.1. Initiation and propagation steps of free radical polymerization.

Ionic polymerizations are initiated either by cations or anions. Cationic polymerization is initiated by addition of a proton from the initiator to monomer. Typical catalysts for the cationic polymerization are protonic acids and Lewis acids. Examples are H_2SO_4 , HClO_4 , AlCl_3 , BF_3 and TiCl_4 . In case of Lewis acids, a protonic co-catalyst is often required usually water or methanol. The optimum proportion of catalyst and co-catalyst varies with the polymerization [35]. In anionic polymerization, initiation and propagation proceed via anionic intermediates. Monomers that are polymerized this way include styrene, methyl methacrylate and butadiene. The monomers which contain electron withdrawing substituents such as nitrile and carboxyl group undergo anionic polymerization. In anionic polymerization, the anionic part of initiator adds across the double bond of the monomer to form the active centre for polymerization. The electron withdrawing group present in the monomer helps to stabilize this anion. Typical examples include sodium in liquid ammonia, alkali metal alkyls and Grignard reagents. The strong electron withdrawing groups like nitrile containing monomers can be polymerized with relatively weak base like hydroxide ion whereas phenyl requires a strong base like amide ion [35].

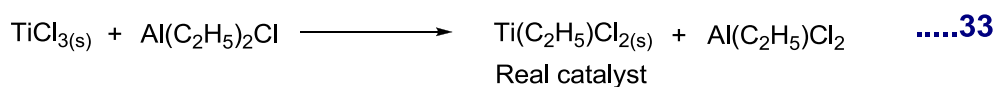


Scheme 1.2. Ziegler-Natta polymerization of ethylene.

The polymerization by coordination catalyst is generally brought about a substantial level of control which is not possible with other polymerization methods [36]. The pioneering Ziegler-Natta polymerization of ethylene for the synthesis of polyethylene is represented in scheme 1.2. The Ziegler-Natta catalysts consist of two components a) Halides of group IVB

to VIIIB transition metal compounds such as TiCl_4 , TiCl_3 , VCl_4 , VCl_3 and ZrCl_4 . b) Group IA to IIIA metal alkyls or hydrides like $(\text{C}_2\text{H}_5)_3\text{Al}$, $(\text{C}_2\text{H}_5)_2\text{Mg}$ and $\text{C}_4\text{H}_9\text{Li}$.

The first step involves the formation of real catalyst where the transition metal compound is alkylated by the metal alkyl reagent (Scheme 1.3). Thus, the real catalyst which has a vacant coordination site on the transition metal to which a molecule of monomer can bond. The addition of monomer to alkyl group (attached with real catalyst) then occurs by the insertion through concerted mechanism. Now, a second molecule of monomer then attaches to vacant coordination site (vacated by first monomer), from which it is able to undergo the addition with the growing chain. This causes the coordination site to become vacant once again, thereby allowing a further molecule of monomer to enter and react with the growing polymer chain. The monomers that can be polymerised using these catalysts are restricted to monomers such as ethylene, propylene, but-1-ene, butadiene, and styrene which do not contain polar functional groups.



Scheme 1.3. Initiation steps of Ziegler-Natta polymerization.

This kind of polymerization can produce the stereoregular polymers in which all repeating units have identical stereochemistry either isotactic or syndiotactic. Isotactic and syndiotactic polymers are crystalline and have better mechanical properties due to the regular arrangement of substituents whereas atactic polymers are amorphous. Depending on catalytic system and polymerization condition, a particular stereoregular polymer can be obtained [37]. The Ziegler-Natta polymerization is free from chain termination whereas it suffers from chain transfer reactions to both monomer and metal alkyls. Ziegler-Natta catalyst encourages for invention of novel metal complexes for polymerization.

1.8. Living polymerization

In case of chain polymerization, a high molecular weight polymer can be obtained at the beginning of polymerization itself. Once the monomer initiated, it undergoes rapid propagation to yield the high molecular weight polymer ($R_p > R_i$). However, in the step

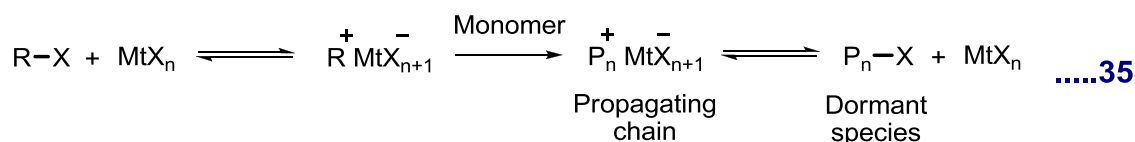
polymerization, the high molecular weight would be obtained only at the near end of the polymerization and only after the maximum conversion; the average molecular weight begins to increase rapidly. Apart from these classifications of polymer by their structure and mechanism, certain polymerizations differ in their mechanism than the above mentioned mechanisms (step and chain polymerization). Some chain polymerizations undergo in a different manner where the molecular weight increases linearly with conversion. This kind of polymerization is called as living polymerization [38]. Unlike the conventional chain polymerization, the initiation step is fast and all the active centres are produced simultaneously that does not undergo either the termination or transfer reactions. Consequently, all the chains have the equal opportunity to grow and all the polymer molecules have nearly the same molecular weight in living polymerization. The living polymerization has been noticed in free radical as well as in ionic (anionic and cationic) chain polymerizations [35]. The living nature of the polymerization may be verified by adding the fresh monomer to a living polymer solution where the polymerization of the previously added monomer is completed. When the two monomers are different, it forms block copolymers.

1.8.1. Anionic and cationic living polymerization

The living anionic polymerization can be obtained when the polymerization is conducted in a well purified system without water. Otherwise, the presence of water terminates the anionic propagating centres by proton transfer. Generally, anionic propagating chains do not terminate by itself under the dry polymerization conditions. So, the polymerization must be performed using strictly purified monomers, solvents, and reagents from which air and moisture have been thoroughly removed. Living cationic polymerizations are relatively difficult to achieve, even in well-purified systems. Cationic propagating centres undergo termination reaction by itself at higher temperature due to the transfer of proton to monomer. In order to achieve the living cationic polymerization, the termination reaction has to be restricted by extending the lifetime of the propagating centres. This can be achieved by introducing the Lewis acid (as co-initiator, SbF_5 , TiCl_4 and BCl_3) along with the initiator (HCl or cumyl chloride) [35, 39].

Generally, the hydrohalogenated monomer is often used as the model initiator. Examples are 1-phenylethyl chloride for styrene, and (2,4,6-trimethylphenyl)-1-ethyl chloride for 2,4,6-trimethylstyrene. The initiator reversibly combined with Lewis acid to form ionic initiator. In propagation, the polymerization is proceeded by the addition of monomer to the

ionic species. At this stage, the propagating chain is in fast equilibrium with dormant species (Scheme 1.4) [35, 40]. Because of this, the life time of propagating chains significantly increases. In addition, the living cationic polymerization is obtained when it is carried out at lower temperature. For example, the living cationic polymerization of isobutyl vinyl ether using HCl as the initiator with SnCl₄ or TiCl₄ in CH₂Cl₂ was observed when the polymerization was performed at -78 °C whereas the living polymerization was not observed when the reaction was conducted at -15 °C [41].



Scheme 1.4. Reaction scheme of living cationic polymerization

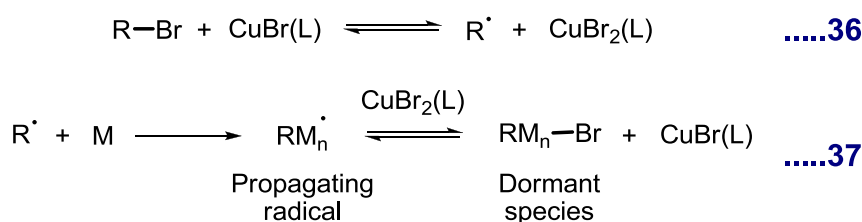
1.8.2. Living free radical polymerization

The living free radical polymerization is the one where irreversible chain termination or chain transfer reactions do not occur. It is also referred as controlled radical polymerization. The reversible chain termination and reversible chain transfer are the solutions to restrict the side reactions which can be attained by the introduction of dormant states for the propagating species. Since the propagating chain spends a considerable amount of time in the dormant condition, free radical termination reactions such as coupling and disproportionation are effectively suppressed. When monomer has been consumed, the chains remain in the dormant capped state and are capable of being re-initiated using different monomers, thus, providing a route to the synthesis of block and multi-block copolymers. Atom transfer radical polymerization, stable free radical polymerization and reversible addition-fragmentation chain transfer has been the effective methods of controlled radical polymerization.

(a) Atom transfer radical polymerization (ATRP)

The well defined polymers with predetermined molecular weights, narrow molecular weight distributions, precisely controlled architecture and suppressed radical termination reactions can be attained by ATRP [35, 42]. This is achieved by utilizing the dynamic equilibrium between propagating radicals and dormant species. ATRP is a multicomponent system, composed of a monomer, an initiator with a transferable halogen, and a copper complex (comprised of a copper(I)halide and nitrogen based ligand). The transfer of a halogen atom from an alkyl halide (RX) to a transition metal halide (Cu(I)X/ligand, CuBr(L)) generates a

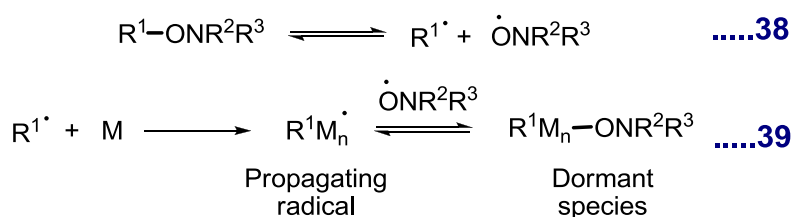
free radical ($R^\bullet$) and increase the oxidation state of the metal by one unit. The radical initiates the polymerization of olefin monomer to form the adduct radical at the end of the polymer chain ($RM_n^\bullet$). It is converted to the adduct halide by reverse transfer of a halogen atom from the oxidized metal halide ($CuBr_2(L)$). At this stage, the metal halide ($CuBr(L)$) is regenerated that starts a new cycle (Scheme 1.5). Thus, in preference to self-termination, the oxidized metal halide terminates the adduct radical.



Scheme 1.5. ATRP mechanism

(b) Stable free radical polymerization (SFRP)

The mechanism is similar to that of ATRP discussed above except that the activation is unimolecular in SFRP but bimolecular in ATRP. SFRP with nitroxides are called as nitroxide-mediated polymerization (NMP). The control in NMP is achieved with dynamic equilibration between dormant alkoxyamines and active propagating radicals (Scheme 1.6). In order to effectively mediate polymerization, stable nitroxide free radicals such as 2,2,6,6-tetramethyl-1-piperidiny-1-oxyl (TEMPO), di-*tert*-butyl nitroxide (DBN) and 2,2,5-trimethyl-4-phenyl-3-azahexane-3-oxyl (TIPNO) can be used (Figure 1.10).



Scheme 1.6. Mechanism involved in SFRP

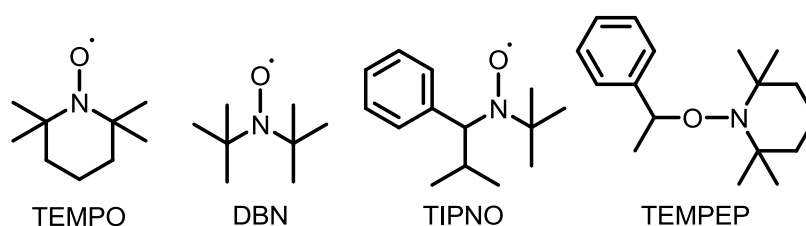
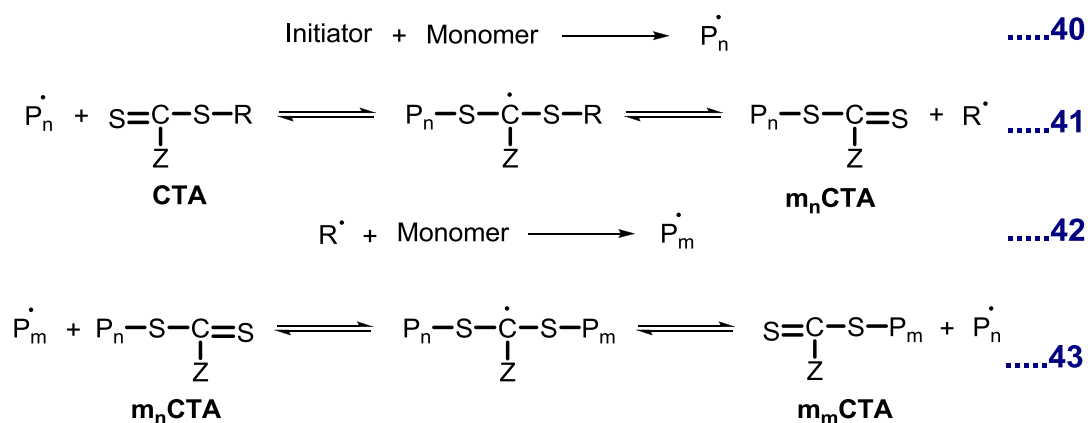


Figure 1.10. Stable free radical and alkoxyamine initiators

SFRP systems can be initiated in two different ways. One way is that along with stable free radicals, conventional radical initiators (AIBN or benzoyl peroxide) can be used. Alternatively, the dormant species (alkoxyamines) can be prepared in advance and used as unimolecular initiators like 2,2,6,6-tetramethyl-1-(1-phenylethoxy)piperidine (TEMPEP) [35, 43]. The free radicals from alkoxyamine are thermally generated by homolytic cleavage of the carbon oxygen bond of unimolecular initiators, leaving an initiated monomer and a nitroxide radical. The initiated monomer involved in the propagation by adding monomer to the growing chain end. The nitroxide radical subsequently recombines with the radical on the end of a growing chain to form a covalent bond, capping the chain and converting it to the dormant state. Thermal cleavage of the carbon oxygen bond again removes the nitroxide cap, allowing the chain to propagate once again. In this manner the chain is rapidly undergone conversion between active and dormant states (Scheme 1.6). NMP has been used to polymerize styrenes, acrylamides, acrylates, and acrylonitrile monomers. In general, reaction rates in NMP reactions are slow compared to classical free radical polymerizations and must be conducted at high temperatures.

(c) Reversible addition-fragmentation chain transfer (RAFT)

By this method, varieties of monomers including styrene, (meth)acrylamides, (meth)acrylates, acrylonitrile, vinyl acetates, vinyl formamide, vinyl chlorides as well as a range of other vinyl monomers can be polymerized. RAFT process is carried out in the same conditions as classic free radical polymerization except with the addition of a chain transfer agent (CTA) also referred to as RAFT agent [44].



Scheme 1.7. RAFT polymerization mechanism.

Polymerization begins when radicals are generated by a free radical initiator (Scheme 1.7). In the pre-equilibrium stage, the radicals on the ends of the propagating chains ($P_n^{\bullet}$) quickly attack the reactive C=S bonds of the CTA to produce a carbon centred intermediate radical. This species reversibly undergo fragmentation which can yield the $R^{\bullet}$ group as a radical fragment and leave the polymeric chain capped with the dithioester (m_nCTA). The $R^{\bullet}$ group released is free to initiate new chains ($P_m^{\bullet}$) by attacking monomer. At this point, the main equilibrium begins and is governed by the same mechanism of radical attack on the C=S bond of m_nCTA followed by fragmentation of the resulting intermediate radical ($P_n^{\bullet}$) and m_mCTA . In the main equilibrium stage, the rapid exchange of propagating chains and m_mCTA ensures each chain has the same probability of growth and minimizes the termination reactions. When polymerization is finished, the chains remain in the capped state and can be re-initiated to form more complex (block copolymer) molecules. A wide variety of RAFT agents bearing different Z and R groups have been synthesized. The Z group serves to activate or deactivate the reactivity of the C=S bond towards addition. The R group must form a stable free radical on fragmentation. Some of the RAFT agents are mentioned in Figure 1.11 [35, 44].

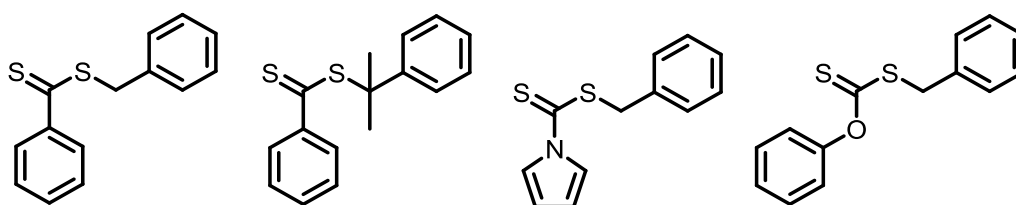


Figure 1.11. Structures of some of the RAFT agents

1.9. Ring opening polymerization (ROP)

The ring opening polymerization of heterocyclic monomers often undergoes through living polymerization. The polymer synthesized from ROP structurally resembles the condensation polymers whereas the ROP easily yields high molecular weight polymer at appreciably lower conversion and lesser time [36a]. The ROP of cyclic ethers (epoxides such as ethylene oxide (EO), propylene oxide (PO), 1,2-epoxybutane (1,2-EB), 1,2-epoxyhexane (EH), 2,3-epoxybutane (2,3-EB), 2-methyl-1,2-epoxypropane (MEP), cyclohexene oxide (CHO), styrene oxide (SO) and 3-phenoxy-1,2-epoxypropane (PEP)), cyclic esters (such as ϵ -caprolactone (CL), lactide (LA), glycolide (GA), δ -valerolactone (VL) and β -propiolactone (PL)) and cyclic carbonates have been the widely investigated class of heterocyclic monomers regarding both academic and industrial interest (Figure 1.12). The heterocyclic

monomers undergo heterolysis of functional group in the ring due to their highly polarized functional group and/or ring strain of the ring. Depending on the reactive intermediate, the ROP proceeds through cationic or anionic polymerization mechanism [45].

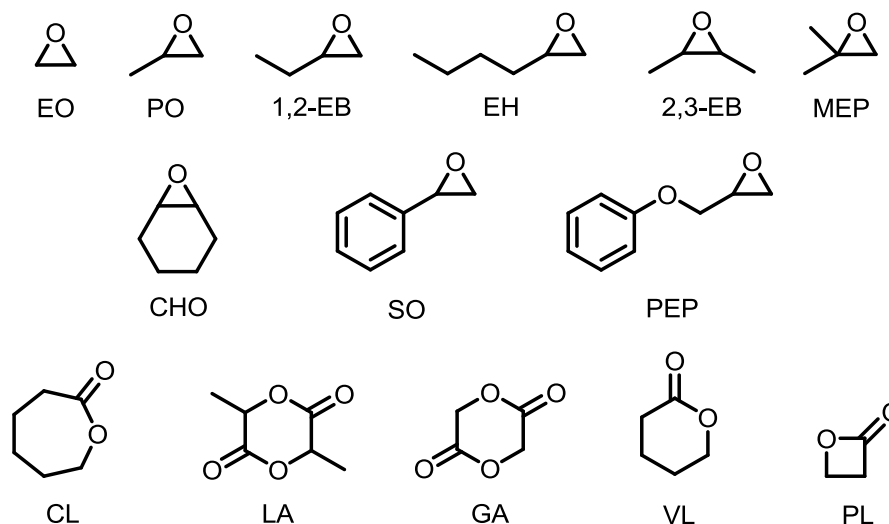
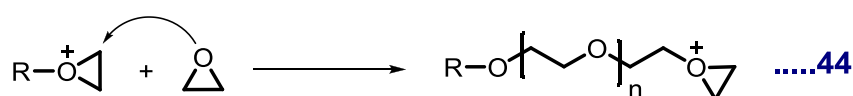


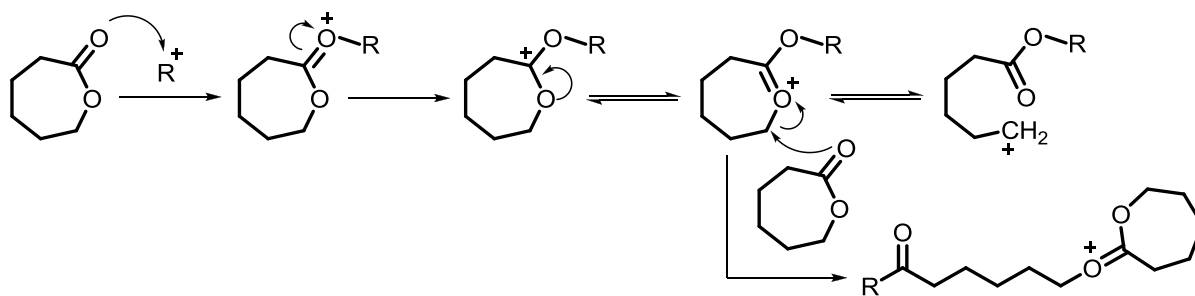
Figure 1.12. Structures of various cyclic ethers and cyclic lactones

1.9.1. Cationic ring opening polymerization

In cationic ROP, the electrophilic reagents are used as initiators and the heteroatom in monomer acts as a nucleophile. The strong Bronsted acids (such as trifluoroacetic, trifluorosulfonic, and trifluoromethanesulfonic), Lewis acid (like BF_3 , SbF_5 , SbCl_5 , AlBr_3 , SnCl_4 and FeCl_3) and alkyl esters of strong organic acids (such as sulfonic acid) are efficient initiators for cationic ROP [45, 46]. The monomers having polarized bonds and/or lone pair of electrons of heteroatom act as Lewis base that reacts with electrophile (R^+). The nucleophile (heteroatom in monomer) attacks the α -carbon atom of the initiating or propagating cationic species resulting in chain extension with ring opening. The mechanism involved in the cationic ROP of epoxides [47] and ϵ -caprolactone [48] are shown in scheme 1.8 and 1.9. The cationic ROP frequently suffers from backbiting side reaction. The rate of backbiting varies with the ring size and steric factors of the cyclic ether monomer. 1,4-dioxane is the major product in the cationic polymerization of ethylene oxide [45, 46].



Scheme 1.8. Cationic ROP of epoxide

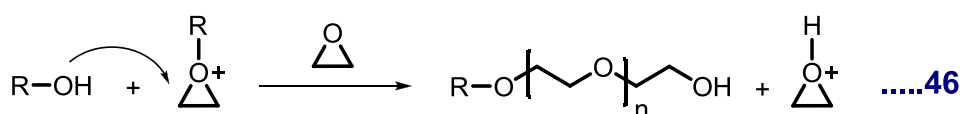


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Scheme 1.9. Cationic ROP of ϵ -caprolactone

1.9.2. Activated monomer ring opening polymerization (AM ROP)

Cyclic oligomer formation due to backbiting and intermolecular transfer reactions can be greatly suppressed and even eliminated by conducting the polymerizations in the presence of an alcohol using an acid initiator such as BF_3 or triflic acid. In these cases, the cationic species is not present in the chain end of the polymer, but rather in the activated monomer. It is called as activated monomer ROP. The monomer is activated by protonation and propagation involves nucleophilic attack of hydroxylic oxygen present in the chain end to α -carbon of activated monomer (Scheme 1.10) [45, 47]. In conventional ROP, the reaction of protonated monomer with unprotonated monomer occurs in the initiation step whereas in case of AM ROP, the initiation step involves the reaction of protonated monomer with alcohol. In this method, the end of the growing chain remains capped with hydroxyl group, which does not allow for the transfer reactions [47, 49].



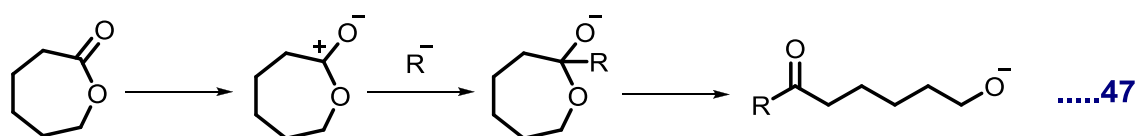
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Scheme 1.10. Activated monomer mechanism for ROP of epoxide

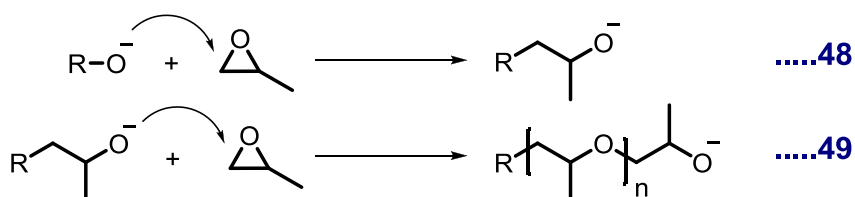
1.9.3. Anionic ROP

In anionic ROP, the nucleophilic anionic species acts as initiators. The nucleophilic reagents to initiate include organometals (alkyl lithium, alkyl magnesium bromide and alkyl aluminum), metal amides, alkoxides, phosphines, amines, alcohols and water [45, 50]. The monomers possess polarized bonds such as ester, carbonate and phosphate undergo anionic ROP and give corresponding polyester, polycarbonate, and polyphosphate respectively. Even

though the less electrophilic functions such as ether, amine and thioether present in the cyclic monomers, the three membered ring monomers undergo anionic ROP due to their ring strain. In case of the anionic ROP of ϵ -caprolactone and epoxide, initiation as well as propagation involves nucleophilic attack of the anionic species on carbon atom bonded with oxygen in monomer (Scheme 1.11 and 1.12) [45]. The side reactions observed in the anionic ROP of CL is that the backbiting of terminal alkoxide moiety to ester linkage present in the main chain of formed polyester, resulted in macrocyclic oligomers (intramolecular transesterification) [48b]. Most anionic ROP of epoxides proceed as living polymerizations with the ability to polymerize by the successive addition of monomer and form block copolymers. However, the anionic ROP of epoxide monomer often suffers from transfer to monomer side reactions led to the formation of low molecular weight oligomers [51].



Scheme 1.11. Anionic ROP of ϵ -caprolactone.



Scheme 1.12. Anionic ROP of epoxide.

Some initiators polymerize the cyclic monomers through anionic coordination mechanism. A wide variety of heterocyclic monomers have been polymerized successfully by ROP with coordination catalysts. It provides the control over the polymer molecular weight and affords the polymer with very narrow polydispersity and well defined end groups. The side reactions like transfer to monomer and backbiting is restricted in polymerizations initiated by the coordinated anionic initiator [45].

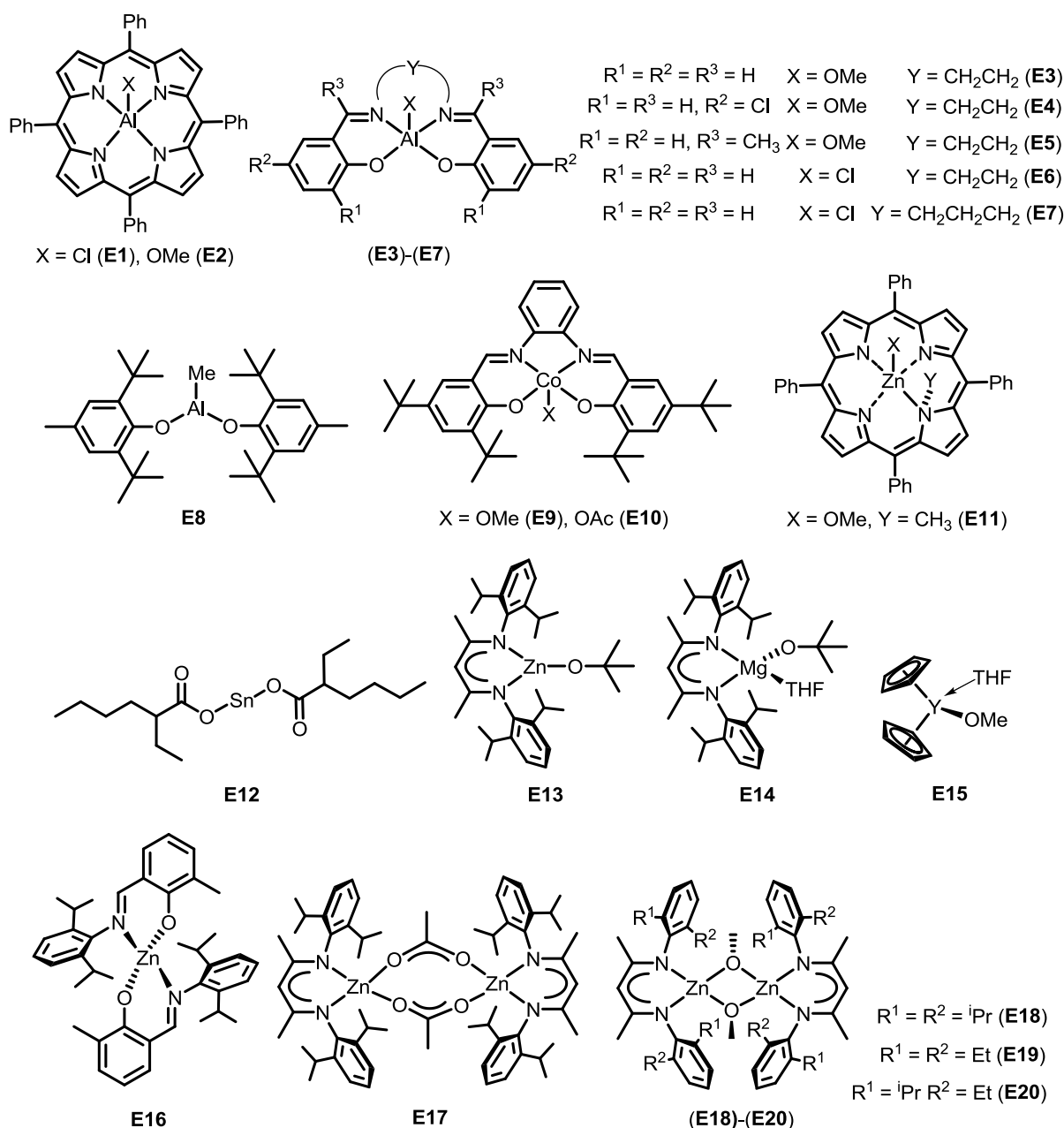
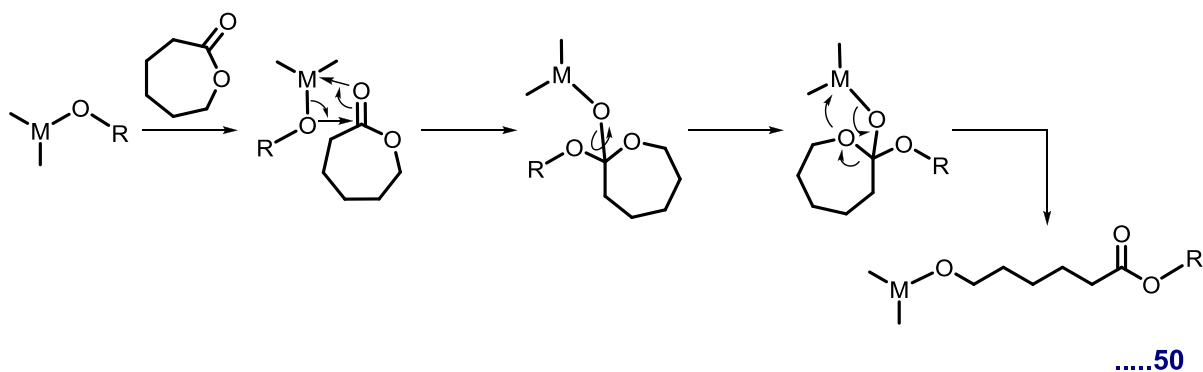


Figure 1.13. Structures of some of the metal complexes utilized for the ROP of cyclic monomers

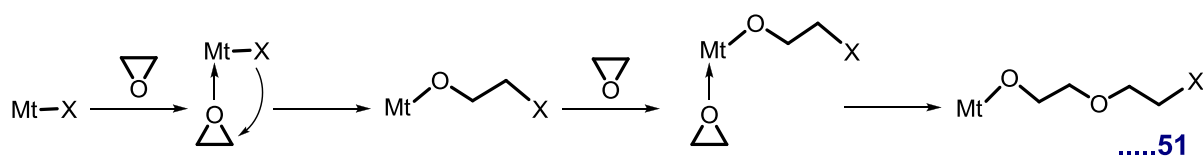
In case of ROP of cyclic monomers, the polymerization is initiated by the coordination of Lewis acid (metal catalyst) to oxygen (heteroatom) of monomer. This coordination weakens the C-O bond and facilitates the nucleophilic attack at the carbon atom directly attached to the oxygen. In propagation, the cyclic monomer is inserted into a metal-oxygen bond. The mechanism for coordination ROP of CL is depicted in scheme 1.13.

Examples of successful metal catalysts for the coordination ROP of CL are **E1-E5**, **E8** and **E12-E15** (Figure 1.13) [50a, 52].

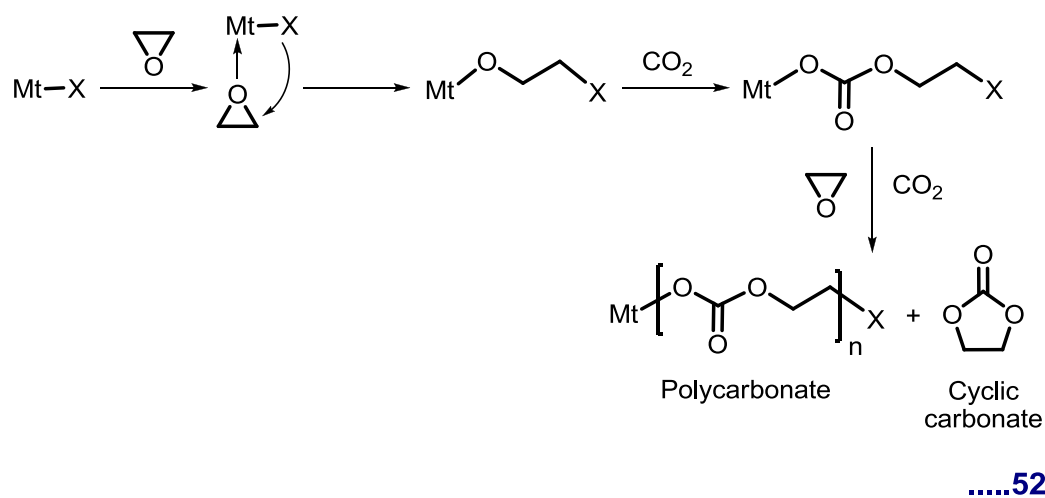


Scheme 1.13. Coordination ROP mechanism of ϵ -caprolactone.

The coordination ROP of epoxide is one of the best synthetic routes to prepare the polyether with definite properties. The ROP of epoxides was effectively catalysed by the metal catalysts like **E1**, **E2** and **E6-E11** (Figure 1.13) [53]. The mechanism involved in the coordination ROP of epoxides (Scheme 1.14) is as follows:



Scheme 1.14. Coordination ROP mechanism of epoxide.



Scheme 1.15. Mechanism for the synthesis of polycarbonate/cyclic carbonate by coordination ROP.

The copolymerization of propylene oxide and CO₂ was carried out for the first time in the presence of diethylzinc-water mixture catalyst by Inoue et al. Since this discovery, more effective metal based coordination catalysts have been found for the epoxide/CO₂ polymerization and their mechanism have been studied in detail (Scheme 1.15). The catalysts **E1**, **E2**, **E13** and **E16-E20** are some of the effective catalysts for the synthesis of polycarbonate from epoxide and CO₂ (Figure 1.13) [54].

1.10. Scope of the thesis

1.10.1. Enhancing battery performances

A battery for future demands should satisfy the requirements of light weight, high voltage, high energy density, low self-discharge, wide temperature range, long cycle life and no memory effect [55]. The current Li-ion batteries exhibit some of these merits but still lacks for long term transport purposes. To address these demands, intensive research efforts are being devoted to new generation of Li-ion batteries [6, 13, 55]. In order to improve the important parameters such as cycling efficiency and specific energy of lithium-ion cells, it is necessary to invent new anode, cathode and electrolyte materials with higher capacity and/or cell voltage. Achieving higher capacity and high cell voltage depends on the selection of electrode materials. In this respect, several approaches are being adopted to enhance the performance of state of the art lithium-ion batteries.

Commercially, LiCoO₂, LiNiO₂, and LiMn₂O₄ intercalation materials have been used as cathode materials for rechargeable Li-ion batteries [56]. These oxides generally possess layered or tunnelled structures for reversible intercalation/deintercalation of Li-ion [57]. More recently, LiFePO₄ (olivine structure; capacity, 170 mAh g⁻¹), nanocrystalline porous α -LiFeO₂-C composite, carbon composites of LiFePO₄ have attracted much attention due to its low toxicity, low cost, high rate capability, high thermal and chemical/electrochemical stability [58, 59]. LiMn_{1.5}Ni_{0.5}O₄ (spinel, 4.7 V) [60], LiMn_{0.67}Ni_{0.33}O₂ (layered, 3.2), xLi₂MnO₃·(1-x)LiMO₂ (M = Mn, Ni, Co; capacity, ~260 mAh g⁻¹) have potential to deliver all their theoretical electrode capacity [61]. A poly(3-decylthiophene)-coated LiCoO₂ cathode which undergo thermal shutdown action at elevated temperature is attractive as cathode because of safety concern [62]. LiFePO₄ (3.4 V), LiMnPO₄ (4.1 V), LiCoPO₄ (4.8 V), and LiNiPO₄ (5.2 V) are some of the promising high potential cathode materials [63].

There is also intensive investigation on nanostructured V_2O_5 (1D, 2D and 3D ordered macroporous) and MnO_2 as intercalation compounds for cathodes. Nano structured cathode materials possess short diffusion distance, reduced internal resistance, and high surface area that has improved the electrochemical kinetics and ionic/electronic diffusion. Nanostructures of α - MnO_2 (hollandite-type) and γ - MnO_2 demonstrate favourable electrochemical performance (capacity and cycling stability) than β - MnO_2 with the rutile structure [64].

Several efforts have been made to find higher capacity anode materials. Since 1991, graphite is a material of choice because it can accommodate one lithium atom per graphene unit having theoretical electrochemical capacity of 372 mAh g^{-1} . Similarly, Sn and Si can accommodate more than four lithium atoms per Sn or Si, providing theoretical capacities of 960 and 4009 mAh g^{-1} , when lithiated to the compositions $Li_{17}Sn_4(Li_{4.25}Sn)$ and $Li_{21}Si_5(Li_{4.20}Si)$, respectively. The theoretical capacity of a coupled $Li_{4.2}Si$ (anode) and lithium-metal-oxide (cathode) cell offers a theoretical energy density of 843 Wh/kg , i.e., 44% more than conventional LiC_6 /layered $Li_{1-x}MO_2$ cells (584 Wh/kg) [65].

1.10.2. Improvement on electrolyte

As discussed earlier, in order to achieve high energy density batteries, high capacity and/or high cell voltage should be attained. While constructing a battery with such a cathode materials, the electrolytes with wider electrochemical window ($> 5.5 \text{ V}$) are also needed. The commercialised non-aqueous electrolyte ($LiPF_6$ in mixture of ethylene carbonate and dimethyl carbonate) are only stable to approximately 4.2 V vs. lithium. Fluorinated electrolytes (5 V), ethyl methyl sulfone (5.9 V), ethyl methoxyethyl sulfone (5.6 V), methoxyethyl methyl sulfone (5.6 V) are the some of the most electrochemically stable electrolytes, where $LiTFSI$ is used as lithium salt [66, 67]. When lithium-ion cell was constructed using these solvents, the battery suffered by poor cycling performance, incomplete delithiation while charging and hence diminished capacity. Some of the gel polymer electrolytes were electrochemically stable up to 5.0 V . (Table 1.7) [68]. The SPEs mentioned in table possess anodic stability in the range of 4.4 - 5.2 V [69]. Introducing the fillers like Al_2O_3 , TiO_2 or various lithium salt to polymer increases the electrochemical stability and also the conductivity [70].

Table 1.7. Electrochemical properties of various SPEs [68, 69, 70].

Polymer/Composite	Lithium salt	Conductivity, σ (S cm ⁻¹) at RT	Anodic stability (V) vs. Li
Gel Polymer Electrolyte			
PMMA–PC/EC	LiClO ₄	0.7×10^{-3}	4.5-4.8 V
PEO:PEGDME:DEC (10 wt% LiAlO ₂)	LiTFSI	$0.09 \times 10^{-3} - 1.00 \times 10^{-3}$	~ 5.0 V
Solid Polymer Electrolyte			
Poly[oligo(ethylene glycol)oxalate]	LiTFSI	5.9×10^{-5}	4.4 V
PEO	LiClO ₄	5.7×10^{-7}	4.6 V
PEO	LiTFSI	1.7×10^{-5}	5.1 V
PEO/Al ₂ O ₃	LiClO ₄	1×10^{-7}	5.2 V
poly(lauryl methacrylate)-b-poly[oligo(oxyethylene) methacrylate]	LiCF ₃ SO ₃	10^{-5}	5.0 V
poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether)	LiClO ₄	10^{-7}	5.0 V
poly(epichlorohydrin-co-ethylene oxide-co-allyl glycidyl ether)	LiTFSI	10^{-6}	5.0 V

Albeit SPEs have more advantages over organic liquid electrolyte, the lithium-ion conductivity of SPEs is much lesser than the organic liquid electrolyte ($\sim 10^{-3}$ S cm⁻¹) by a factor of $1/10 - 1/10^3$. Since the room temperature ionic conductivity of poly(ethylene oxide) (PEO) is too low (10^{-7} S cm⁻¹) for practical applications, advanced SPEs are in demand to improve their performance and efficiency. Though various SPEs are under study, polysiloxanes presented in Table 1.6 showed good lithium-ion conductivity. The flame

retardant and high ionic conductivity of polyphosphazenes are very attractive especially in the potential application of larger batteries as SPEs. However, both of these polymers exist as liquid at room temperature. Thus, there is an urgent need to find alternative non-flammable electrolytes having good ionic conductivity that are stable over wider operating voltage and withstand higher voltage outputs.

1.10.3. Conduction mechanism

Some of its disadvantages such as high cost and more weight of the Li-ion batteries and also the imperatives to increase its energy density and operating temperature necessitate further evolution of new polymer electrolyte systems [6, 71]. This also further necessitates a thorough understanding of the conduction mechanism in order to focus on the enhancement of ionic conductivities of SPEs [6, 33]. According to the conventional theory, amorphous polymers exhibit ionic conductivity whereas crystalline polymers most likely behave as insulator. The ionic conductivity in amorphous polymer is due to the movement of lithium-ions, occurred by the local segmental motion of the polymer chains. This is more significant particularly above its glass transition temperature (T_g) since above T_g the superstructure of polymers has dynamic, disordered and flexible environment. Since the polymer chains are in constant motion above its T_g , a vacant space would continually generate and disappear, through which an ion can be transported by coordination [72].

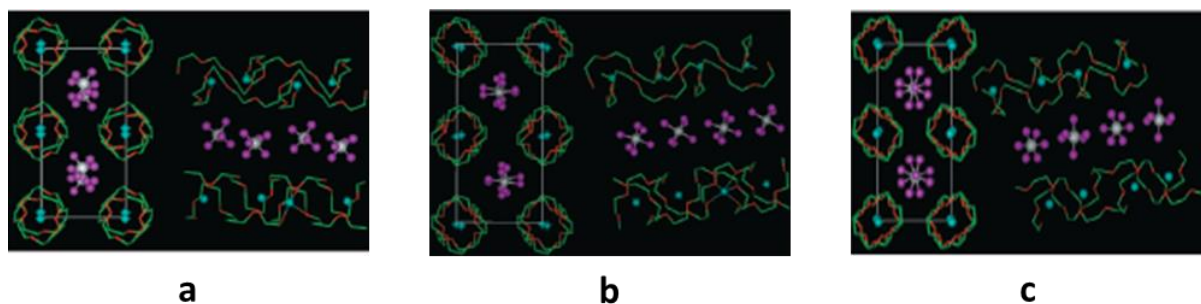


Figure 1.14. Structures of (a) $\text{PEO}_6\text{:LiPF}_6$, (b) $\text{PEO}_6\text{:LiAsF}_6$, and (c) $\text{PEO}_6\text{:LiSbF}_6$. View of the structure showing rows of Li^+ ions perpendicular to the page (Left side of a-c). View of the structure showing the relative position of the chains and their conformation (Right side of a-c). Hydrogen atoms are not shown. blue spheres, lithium; white spheres, arsenic; magenta spheres, fluorine; green spheres, carbon; red spheres, oxygen.

In contrast to this, Bruce and co-workers recently proved, compared with amorphous polymer electrolytes, crystalline polymer electrolytes have much efficient lithium-ion

conductivity. The crystalline polymer electrolytes, $\text{PEO}_6:\text{LiPF}_6$, $\text{PEO}_6:\text{LiAsF}_6$ and $\text{PEO}_6:\text{LiSbF}_6$ have a static, ordered environment and channel like network (Figure 1.14) [73]. The lithium-ions are residing in the cylindrical tunnels which were formed by the folding of pairs of PEO chains. The lithium-ions are coordinated to the ether oxygens of PEO. The anions are located outside to the tunnels and placed in the inter chain space that do not coordinate with the cations. The structure suggests that the lithium-ions can transport efficiently through this tunnels by appropriate coordination. In case of amorphous polymers, lithium-ion has to wait and find the next exact place for coordination to transport whereas in crystalline polymer electrolytes, lithium-ion might not to spend the time to find the exact place since it is already available [73]. From these findings, it is worth to note that,

- The ionic conductivity was not only associated with the amorphous region above T_g .
- It discloses the significance of structural arrangement of polymer framework for efficient ionic conductivity.

1.10.4. Ways to increase the conductivity of SPE

It was found that $-(\text{CH}_2\text{CH}_2\text{O})_n-$ (PEO) provides just the right space for maximum solvation than $-(\text{CH}_2\text{O})_n-$ and $-(\text{CH}_2\text{CH}_2\text{CH}_2\text{O})_n-$. Accordingly, PEO would be the most favourable basic unit for polymer electrolytes and studies on PEO-based matrices have been the mainstream for polymer electrolytes. However, as mentioned earlier, PEO possess very low lithium-ion conductivity at room temperature. One of the major factors causing the low ionic conductivity at ambient temperatures is the large crystalline area of PEO and less conformational flexibility (as reflected in terms of high T_g). Several modifications have been attempted to increase its ionic conductivity. These modifications are performed in the direction of decreasing the crystallinity and glass transition temperature (T_g) and also extending its amorphous phase because the amorphous region is responsible for the ion conduction [74].

Since the ionic transport is related to the freedom of chain movements and to their rearrangements, ionic conductivity depends on the local segmental motions of the polymer chains. Such a favourable situation is obtained only at temperatures above T_g since the ionic conductivity is dramatically increased on or after attaining the T_g . Hence, the polymer with low glass transition temperature is much preferable for the ionic conductivity. The possible ways to increase the amorphous region and low T_g in a polymer are preventing efficient packing of polymer chains and inducing conformational flexibility in a polymer chain. Both

of the possibilities might be achieved by introducing bulky rigid pendent groups in the polymer chains and/or by incorporating the heteroatoms into a polymer chain. For example, polysiloxanes and polyphosphazenes, due to their conformational flexibility showed inspiring lithium-ion conductivity of $4.5 \times 10^{-4} \text{ S cm}^{-1}$ and $5.0 \times 10^{-5} \text{ S cm}^{-1}$ respectively at room temperature [75]. The presence of atoms of varying sizes in a polymer chain attributable to the conformational flexibility of polymer chains that might offer the notable lithium-ion conductivity.

Designing and synthesizing advanced porous materials with required (interconnected voids) structural polymer framework for better lithium ion transport is more attractive way of improving Li-ion conductivity in SPEs. The porous polymer framework can be achieved in several methodologies [76]. In particular, intrinsic porous polymers are the desired one for lithium-ion conductivity since it can be prepared with the essential properties of lithium-ion conductivity. The intrinsic porous polymer framework can be generated by the inefficient packing of polymer chains while assemblage generates free volume (or empty space). These free volumes are thoroughly interconnected to afford interconnected perpetual pores and resembles like a porous 3D network. Our postulate is that lithium-ion can transport through these interconnected perpetual pores with possible coordination and may result good conductivity.

1.10.5. Focus of the Thesis

In order to qualify as electrolyte solvents, the polymers must be able to dissolve sufficient amounts of lithium salt. Therefore, polymers those with polar groups such as ether (-O-), carbonyl (C=O), ester (-OC=O), carbonate (-OC=OO-), phosphine oxide (P=O), phosphine sulfide (P=S), nitrile (-CN), sulfonyl (S=O) are the preferred polymer host for SPEs. Based on the requirement of heteroatom in a polymer chain and lithium-ion conductivity mechanism, primary focus is to synthesize the polyester (for example, polycaprolactone), polyethers and polycarbonate and to study their lithium-ion conductivities (Figure 1.15).

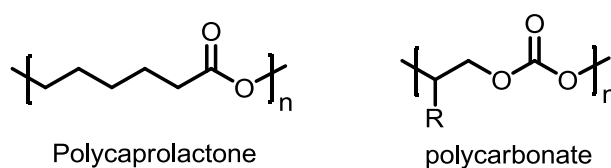


Figure 1.15. Structure of polycaprolactone and polycarbonate

In the case of organic liquid electrolyte batteries, cyclic carbonates (propylene carbonate, ethylene carbonate) and linear carbonates (diethyl carbonate, dimethyl carbonate and ethyl methyl carbonate) were utilized as the major solvents to prepare electrolyte. Generally, the solvents (cyclic and linear carbonates) were mixed together in different compositions to attain high ionic conductivity. In terms of dielectric constant and viscosity, the cyclic and linear carbonates behave like two different kinds of compounds. *i.e.*, the cyclic carbonates are polar ($\epsilon = 65-90$) and relatively viscous ($\eta = 1.9-2.5$ cP) whereas the linear carbonates are weakly polar ($\epsilon = \sim 3$) and fluid ($\eta = 0.6-0.7$ cP) in nature. The intramolecular strain of the cyclic structures favour the conformation of better alignment of molecular dipoles led to more polar. In the case of more flexible and open structure of linear carbonates, the mutual cancellation of dipoles led to weakly polar. The diversified properties of cyclic and linear carbonates pushed to synthesize the polymers containing carbonate functional group and to explore their ionic conductivity. The lithium-ion conductivity studies on polycarbonate were not much explored like polyethers. Further, polycaprolactone (PCL) has a glass transition temperature of about -60 °C and the melting temperature at around 60 °C. From this point of view, the property of PCL is attractive to investigate the ionic conductivity.

As discussed above, introduction of heteroatom–carbon bonds, in lieu of carbon–carbon bonds in a polymer chain, could provide additional conformational flexibility that favours the disordered arrangement and hence inefficient packing of polymer chains. So far, in order to impart the flame-retardant property for SPEs, phosphorus containing molecules might be either covalently attached to the polymer chains (as pendent group or polymer backbone) or blend with polymers. Phosphorus is an intumescent flame-retardant agent. It operates predominantly through a mechanism in which combustion of the outer layers of the polymeric material containing the flame retardant leads to an intumescent carbonaceous char. This acts as a physical and thermal barrier to further combustion by impeding heat transfer to the underlying layers of polymer and, therefore, preventing the release of further flammable volatiles. Therefore, there is enormous interest to have phosphorus atom in the electrolyte material [77].

In order to synthesize all these polymers, polycaprolactone, polycarbonate/cyclic carbonate and phosphorus containing polyethers, it might be handy if the common polymerization method was chosen (Figure 1.16). At the same time, the properties of all these polymers including molecular weight and polydispersity index (PDI) should be obtained well.

Thus, the metal catalyzed ring opening polymerization (ROP) of their respective monomers was preferred. The ROP can be performed in the presence of metal catalyst and initiator. The Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{N-(2,6-diisopropylphenyl)imino methyl}pyrrole were synthesized and utilized them as catalyst in the presence of various initiators for the ring opening polymerization of ϵ -caprolactone, epoxide and phosphorus containing epoxides.

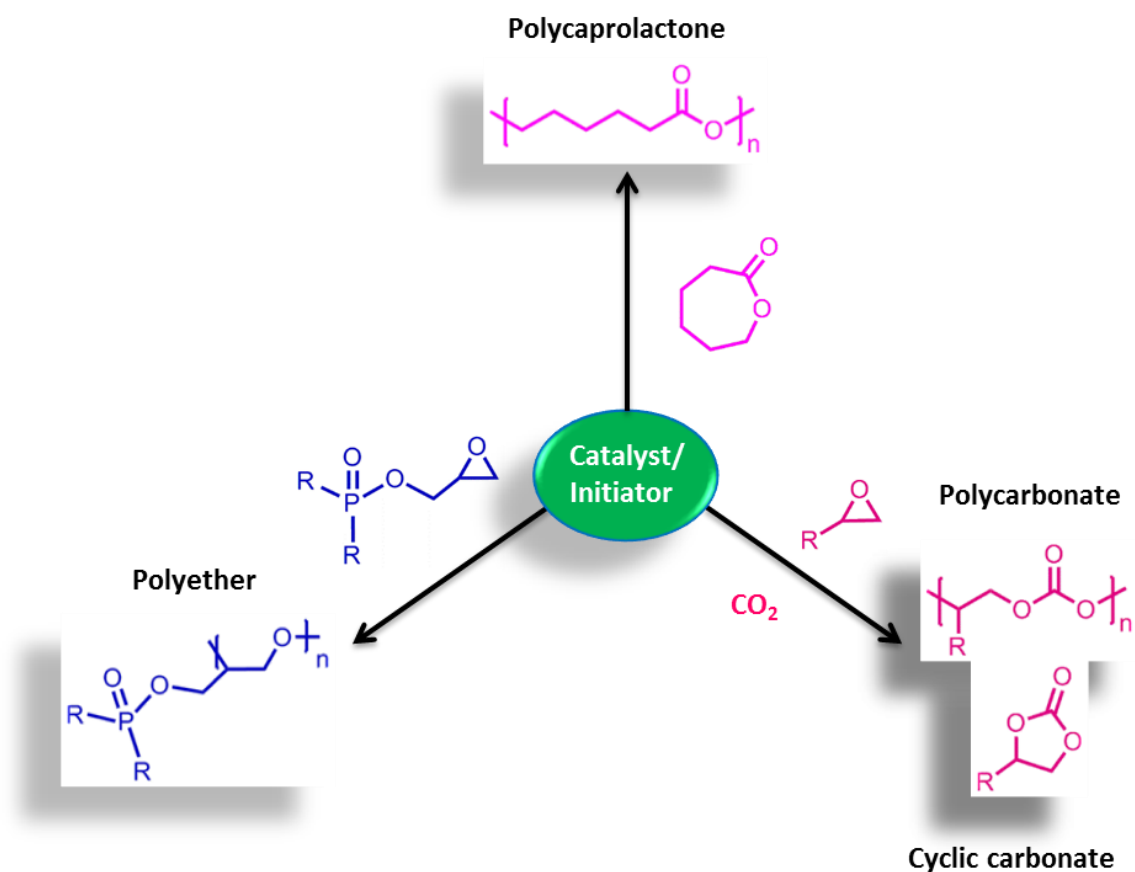


Figure 1.16. Synthetic approach for the syntheses of polymers

1.11. References

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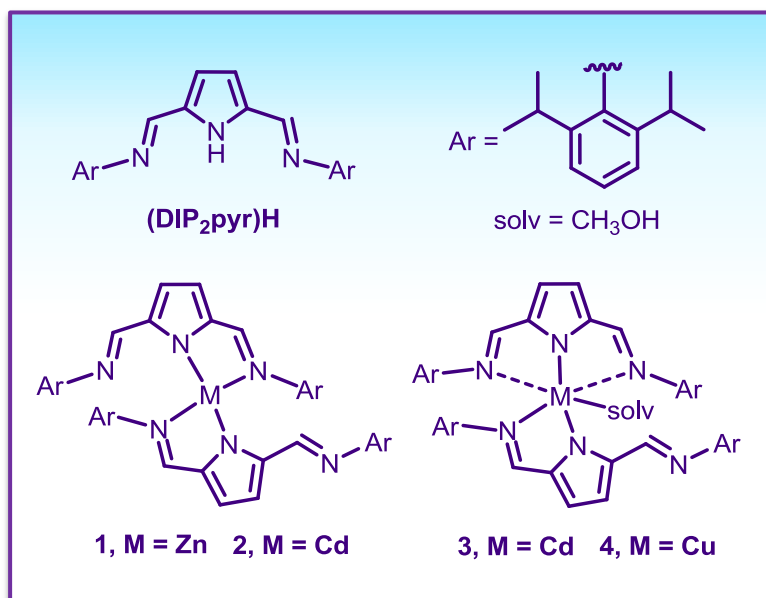
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CHAPTER 2

Zn(II), Cd(II) and Cu(II) Complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole: Syntheses and Structures

Abstract

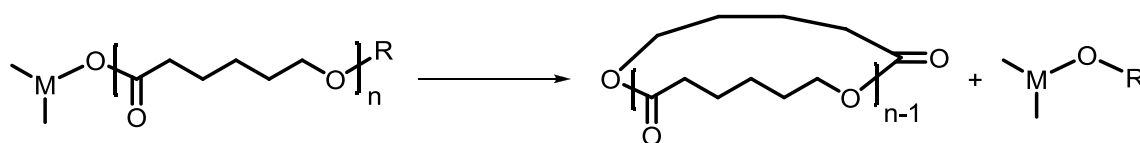
This chapter describes the syntheses of Zn(II) **1**, Cd(II) **2-3** and Cu(II) **4** complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H. The Zn(II) **1** and Cd(II) **2** complexes were synthesized from M[N(SiMe₃)₂]₂ (M = Zn or Cd) whereas Cd(II) **3** and Cu(II) **4** were synthesized from anhydrous MCl₂ (M = Cd or Cu) with ligand (DIP₂pyr)H in 1 : 2 ratio. The structures of these complexes were characterized by IR, UV, ¹H, ¹³C NMR and single crystal X-ray diffraction techniques.



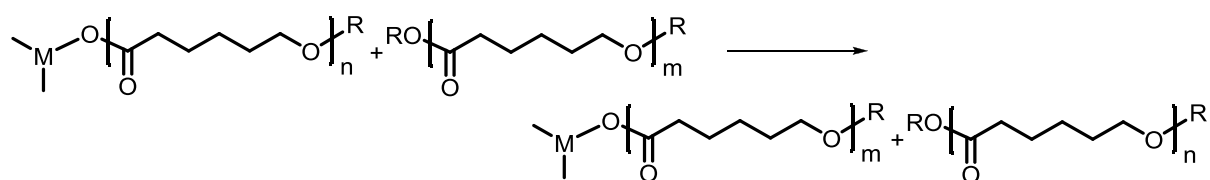
2.1. Introduction

Catalysis by metal complexes plays a prominent role in synthetic chemistry. As petroleum resources are depleting, there has been a significant interest for designing catalysts to produce useful basic chemicals and polymers from renewable feedstock [1]. Especially, an efficient catalyst to perform polymerization under mild temperature conditions and producing polymers with good properties is an active demand in frontier research area. Ever since the pioneering work of Ziegler-Natta, various catalysts including pure metals, metal salts and metal complexes have been studied for polymerization [2]. Specifically, catalytic activities of various metal complexes for the syntheses of polycaprolactone (PCL), polycarbonate and polyether are explored [3]. The present interest is to find a versatile metal complex for the synthesis of polycarbonates as well as for the ring opening polymerization of various cyclic monomers such as ϵ -caprolactone (CL) and epoxides preferentially from renewable carbon resources.

During cationic and anionic polymerization of CL, significant intramolecular transesterification and backbiting process (Scheme 2.1) lead to the formation of low molecular weight cyclic oligomers. Further, intermolecular transesterification also observed as side reactions particularly at high temperature (Scheme 2.2). These drawbacks collectively resulted in broadening of the polydispersity [4]. The polymer properties like molecular weight, polydispersity index (PDI), and microstructure are good when PCL is prepared by a ROP rather than through a condensation polymerization [5]. The ROP is performed in the presence of metal catalysts/initiators, organocatalysts or enzymes. Complexes of alkaline [6], alkaline-earth [7], Al [8], Ti [9], Zr [10], V [11], Cr [12], Fe [13], Co [14], Zn [15], Sn [16], Bi [17] and rare earth metals [18] with various ligands including ketimine, β -diketiminates, imine phenoxide, amine phenoxide, anilido-imine and cyclopentadienyl are used as catalysts for the ROP of CL. Among these catalysts, Mg, Al, Zn, Sn and rare earth metal complexes displayed moderate to excellent catalytic activities by yielding the polymers with narrow polydispersities and good thermal stabilities.



Scheme 2.1. Possible intramolecular transesterification (backbiting reaction) noticed in polycaprolactone synthesis.



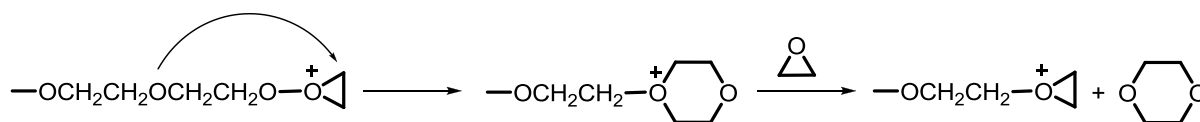
Scheme 2.2. Possible intermolecular transesterification reaction noticed in polycaprolactone synthesis.

Various zinc based heterogeneous catalysts has shown activity for the copolymerization of epoxides and CO_2 to produce polycarbonate. Majority of heterogeneous catalysts lacks in reproducibility and produce non-uniform polymers probably because of the presence of many different types of active sites [1d]. However, the homogeneous catalysts have advantage since they can be precisely modified and possible to study the mechanistic pathway in detail. The homogeneous catalysts such as tetraphenylporphyrinato aluminium complexes, aluminium calix[4]arene complex and aluminium alkoxides are active for the copolymerization of epoxides and CO_2 [19]. But aluminium catalysts often suffer with low activities and yield polycarbonates with high percentages of ether linkages. They produce copolymers in the presence of additives like N-methylimidazole (MeIm), 4-dimethylaminopyridine (DMAP), EtPh_3PBr and NEt_4Br [20].

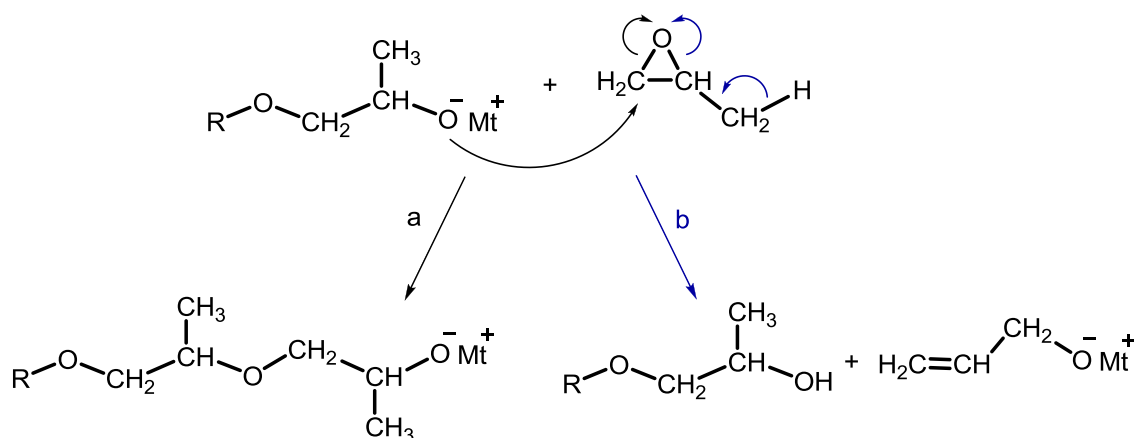
Tetraphenylporphyrinato and cyclohexyl/phenyl substituted salen chromium complexes in presence of DMAP or MeIm yields polycarbonate with high percentage of carbonate linkages [20c, 21]. Bis(phenoxide), alkyl, benzoate, bis(salicylaldiminato), (dialkylamino)ethylcyclopentadienyl, pyridine and β -diiminate based zinc catalysts are effective for the synthesise of polycarbonates [22]. However, these reactions require long reaction time, high temperatures and high pressures of CO_2 to induce the reaction with epoxides. The long-term obligation of the scientific community is to find an alternate efficient catalyst to perform this reaction under mild temperature conditions at atmospheric pressure. Our interest is to develop the active catalyst for the synthesis of polycarbonate at atmospheric pressure of CO_2 .

Cyclic carbonate is one of the major side product observed in the copolymerization of epoxides and CO_2 . Based on the catalyst, co-catalyst and reaction conditions, the following varieties of products can be obtained in the copolymerization of epoxides and CO_2 ; a) mixture of polycarbonate and cyclic carbonate; b) polycarbonate; c) cyclic carbonate.

Varieties of catalysts, such as salen complexes [23] of Zn, Co, Cr, Al, Cu, Mg and Sn, organocatalysts [24], ionic liquids [25], InBr_3 [26] and other ligand complexes [27] of Zn, Mo, Pd, Co, and Sn have been reported for the synthesis of cyclic carbonates alone from epoxides and CO_2 .



Scheme 2.3. Backbiting reaction in cationic polymerization



Scheme 2.4. a) Propagation steps involved in anionic ROP. b) Transfer to monomer reactions involved in anionic polymerization.

Polyethers are produced from epoxides by cationic, anionic or metal catalysed ring opening polymerization (ROP). The backbiting side reactions hinder the cationic polymerization leading to form low molecular weight oligomers (Scheme 2.3). Alkali metal derivatives are efficient initiators for the anionic polymerization of cyclic ethers. However, the high basicity of propagating species resulted in proton abstraction leading to form hydroxy ended oligomer chains and allyl alkoxide initiator (Scheme 2.4b). These drawbacks could be avoided if the polymerization is performed in the presence of metal complexes [28]. The ROP of epoxides are well studied in the presence of metal complexes such as tetraphenylporphyrin, salen and diphenolate complexes of Al, tetraphenylporphyrin complexes of Zn and salen complexes of Co [29].

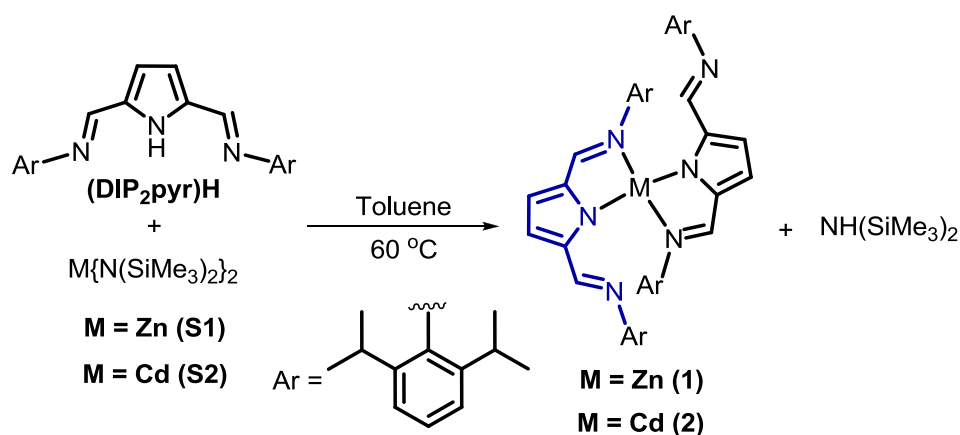
Critical insight into literature explains that the catalytic properties of metal complexes can be altered by changing ligands and the electronic and steric features on the ligands [8b, 30]. Therefore, finding a suitable ligand is important to achieve needed polymer properties.

Complexes of the 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H ligand with Cu, Zr, Fe, Co, Al, Cr, alkali-metals [31] and rare earth metals [32] have been reported. Some of these complexes showed catalytic activity for the polymerization of ethene, oligomerisation of ethene and propene and ROP of CL. These diversified nature of the ligand and its metal complexes encouraged us to explore new metal complexes based on this ligand. Metal complexes of (DIP₂pyr)H have never been attempted either for the ROP of epoxides or for the synthesis of polycarbonate from epoxide and CO₂. Moreover, the ROP of CL was not explored in the presence of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H. Therefore, Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H are synthesized and used as catalyst for the synthesis of PCL, polycarbonate and polyether from their corresponding monomers. Thus, this chapter describes the syntheses of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H.

2.2. Results and discussion

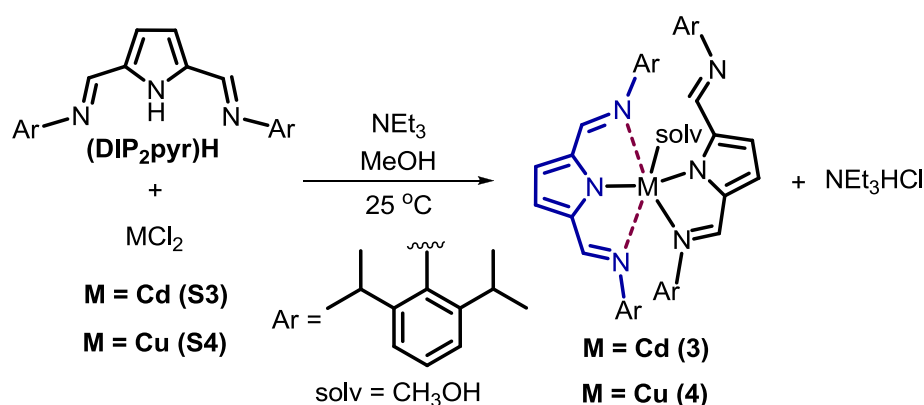
2.2.1. Synthesis and characterization

Studies have shown that large differences in catalytic efficacy result from the organic frameworks surrounding the metal. We have chosen bis(aryliminomethyl)pyrrole derivative as ligand. Recently, bis(aryliminomethyl)pyrrole derivatives have received considerable attention in organometallic catalysis due to their diverse bonding modes and easy coordination with metals. They also provide opportunities to tune the electronic environment and structural preference of metal complexes by changing the substituents on it [32, 33]. The ligand (DIP₂pyr)H was synthesized from pyrrole-2,5-dicarbaldehyde and 2,6-diisopropylaniline by condensation reaction according to literature procedure [32a].



Scheme 2.5. Synthesis of the Zn(II) **1** and Cd(II) **2** complexes.

Syntheses of metal complexes of (DIP₂pyr)H were carried out using two different methods. In the first approach, complexes **1** and **2** were conveniently prepared from the homoleptic diamido complex Zn[N(SiMe₃)₂]₂ **S1** or Cd[N(SiMe₃)₂]₂ **S2** by an amine elimination reaction. Treatment of **S1** or **S2** with two equivalents of (DIP₂pyr)H in toluene at 60 °C yielded the corresponding Zn(II) **1** or Cd(II) **2** complexes as yellow microcrystalline powders after filtration followed by evaporation of the solvent (Scheme 2.5). The complexes were purified from the reaction mixture by recrystallization from toluene-hexane through a diffusion method and the products were obtained in good yields.



Scheme 2.6. Synthesis of the Cd(II) **3** and Cu(II) **4** complexes.

Another approach involved the use of a base. The reaction of anhydrous CdCl₂ **S3** or CuCl₂ **S4** with two equivalents of (DIP₂pyr)H was carried out in methanol in presence of triethylamine at 25 °C as shown in Scheme 2.6. The reaction mixtures were filtered and the residues were purified by recrystallization from a CHCl₃-MeOH mixture to give the corresponding yellow colored Cd(II) **3** or brown colored Cu(II) **4** complexes in moderate yields. However, a similar method with ZnCl₂ yielded a product which degraded during purification.

2.2.2. Spectroscopic Study

Complexes **1-4** were characterized by IR and NMR (¹H, ¹³C) and their molecular structures were determined by single crystal X-ray diffraction techniques. The IR spectra of the complexes revealed stretching frequencies for the presence of coordinated (**1**, 1564; **2**, 1567; **3**, 1570; **4**, 1564 cm⁻¹) as well as uncoordinated (**1**, 1626; **2**, 1621; **3**, 1630; **4**, 1622 cm⁻¹) imino groups to metal center. The ¹H NMR spectra exhibited only one set of peaks for -HC=N- (**1**, 7.85; **2**, 7.91; **3**, 7.88 ppm) and the isopropyl groups (**1**, 0.90 and 3.08-2.86; **2**,

0.89 and 3.08-2.86; **3**, 0.90 and 2.98-2.85 ppm) instead of separate peaks for coordinated and uncoordinated imino groups. This observation disclosed the symmetrical coordination of the ligand to the metals and the free rotation of the 2,6-diisopropylaniline moieties of the ligand in solution. The ^{13}C NMR spectra also displayed one set of peaks for $-\text{HC}=\text{N}-$ (**1**, 158.8; **2**, 158.4; **3**, 158.6 ppm) and the isopropyl groups (**1**, **2** and **3**, 23.8 and 27.9 ppm). This disparity, when compared to the solid state, confirmed a fluxional behavior of the ligand in solution as observed in previous reports [31b, 32e].

2.2.3. Crystallographic characterization

Recently, the crystal structure of Zn(II) complex **1** has been reported by Lewinski *et al.*, which was found as a byproduct during oxygenation reactions [34]. The molecular structures of **1** and **2** are isostructural as shown in Figure 2.1 and 2.2. The metal center in complexes **1** and **2** adopts a four coordinate distorted tetrahedral geometry in which the $(\text{DIP}_2\text{pyr})^-$ ligand behaved as a bidentate rather than tridentate ligand, which coordinates through two nitrogen atoms (N, N') from each ligand. The smaller ionic radius of the metal center and steric bulkiness of the aryl substituents might influence the coordinated pattern of the ligand. One of the uncoordinated aryl imino moieties (**1**, **2**; C42–N6–C43) is rotated away from the metal center due to steric repulsion [31b, d].

The molecular structures of complexes **3** and **4** are isostructural (Figure 2.3 and 2.4) which revealed a six coordinate pseudo octahedral geometry about the metal center. The coordination sphere consist of three nitrogen atoms (N4, N5, N6) from one of the $(\text{DIP}_2\text{pyr})^-$ ligands, two nitrogen atoms (N1, N2) from another $(\text{DIP}_2\text{pyr})^-$ ligand and one oxygen (O1) from a solvent molecule methanol. It is interesting to note that in both **3** and **4**, one of the $(\text{DIP}_2\text{pyr})^-$ ligands was coordinated symmetrically to the metal center (Cd(II) **3**, Cu(II) **4**) through a N, N', N''-mode as a tridentate ligand. The apexes of pseudo octahedral structure were occupied by both arms of the $(\text{DIP}_2\text{pyr})^-$ ligand coordinated weakly to the metal center (**3**, N5–Cd1 = 2.716(3) and N6–Cd1 = 2.716(3) Å; **4**, N5–Cu1 = 2.738(3) and N6–Cu1 = 2.738(3) Å). Another $(\text{DIP}_2\text{pyr})^-$ ligand coordinated asymmetrically to the metal center *via* one arm through a N, N'-mode as a bidentate ligand whereas the uncoordinated arm (C10–N3–C11) bent away from the metal center.

In the pseudo octahedral structure, the square planar arrangement around the metal center (N1, N2, N4, O1) was confirmed by the sum of the four angles (360°). The angles between the apexes (N6–M1–N5) are not linear and are about 135.1° (**3**) and 141.2° (**4**).

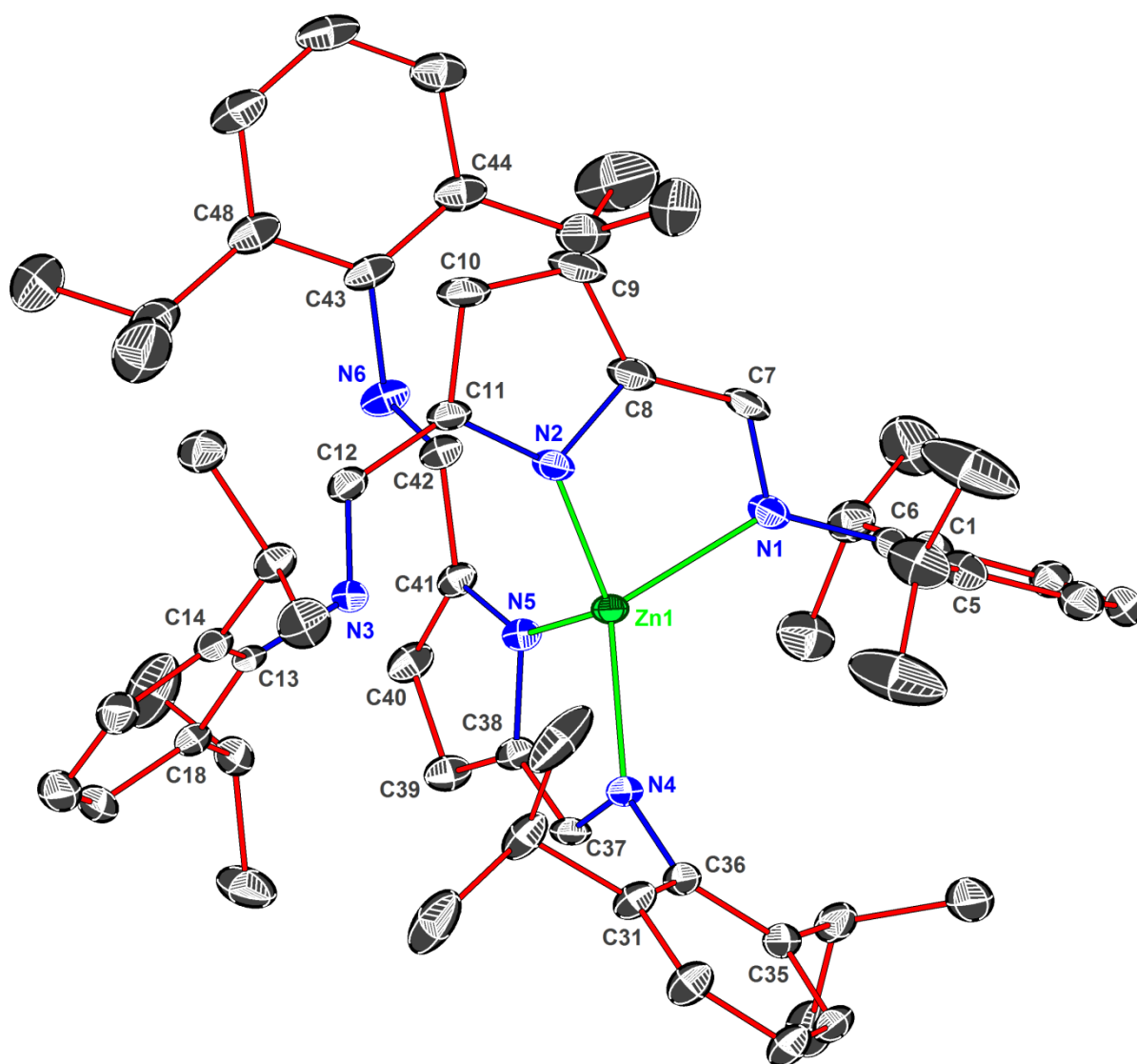


Figure 2.1. ORTEP of the molecular structure of **1**. Thermal ellipsoids are shown at 30% probability levels. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Zn1–N2 = 1.971(3), Zn1–N1 = 2.097(3), Zn1–N5 = 1.996(3), Zn1–N4 = 2.054(3), N2–Zn1–N1 = 82.55(12), N4–Zn1–N1 = 116.93(12), N5–Zn1–N4 = 84.00(11), N2–Zn1–N5 = 111.04(12), N5–Zn1–N1 = 117.46(12), N2–Zn1–N4 = 147.48(12), C9–C8–C7 = 133.2(4), C10–C11–C12 = 128.2(4), C7–N1–C6 = 117.7(3), C12–N3–C13 = 119.5(3), C42–N6–C43 = 118.1(3), C40–C41–C42 = 128.6(3), C39–C38–C37 = 132.5(3), C37–N4–C36 = 116.7(3).

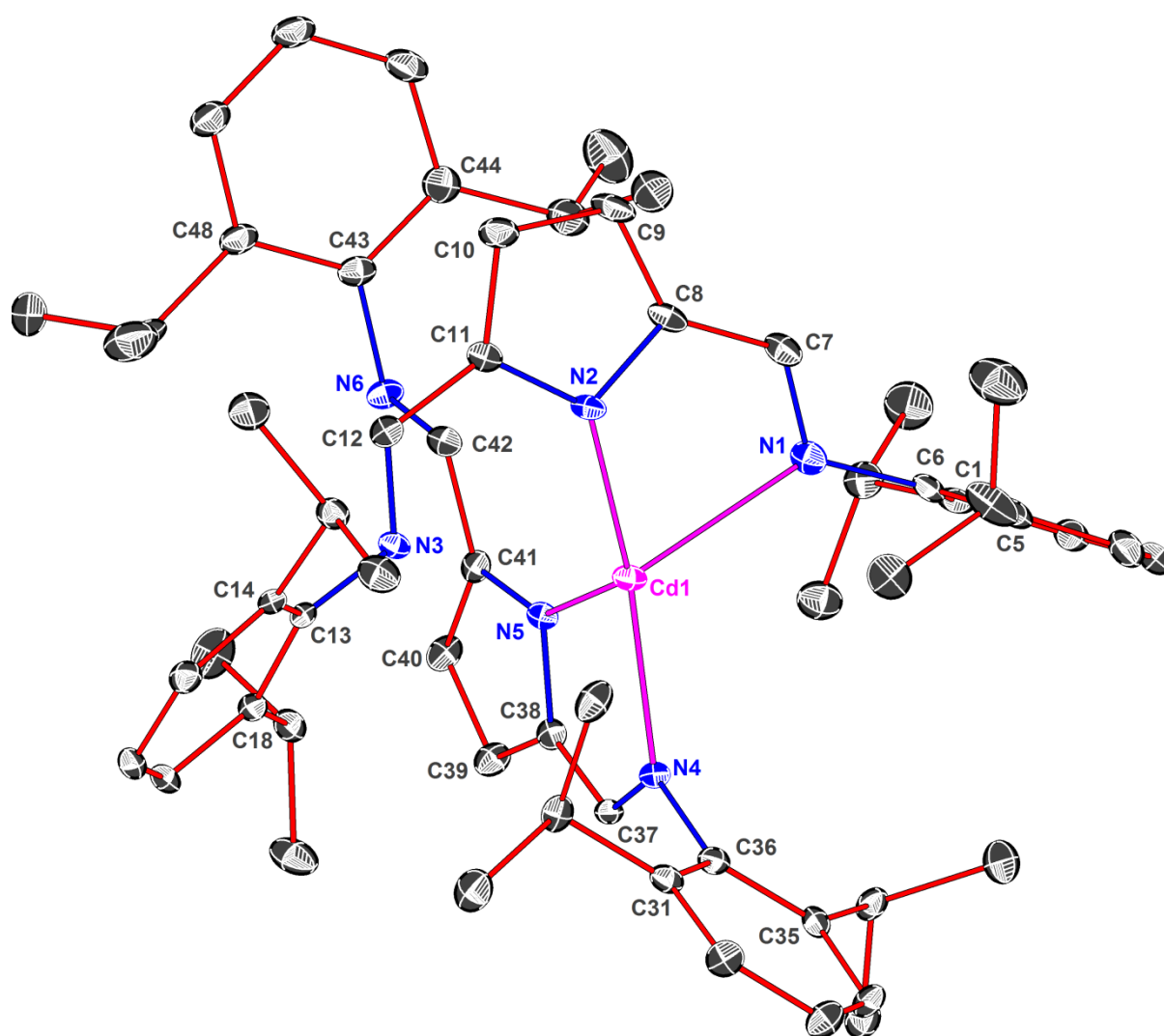


Figure 2.2. ORTEP of the molecular structure of **2**. Thermal ellipsoids are shown at 30% probability levels. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd1–N2 = 2.111(4), Cd1–N1 = 2.426(4), Cd1–N4 = 2.235(4), Cd1–N5 = 2.201(4), N2–Cd1–N1 = 73.23(14), N4–Cd1–N1 = 115.89(13), N5–Cd1–N4 = 77.89(14), N2–Cd1–N5 = 113.28(14), N2–Cd1–N4 = 162.53(15), N5–Cd1–N1 = 113.15(13), C10–C11–C12 = 131.4(5), C9–C8–C7 = 133.2(5), C7–N1–C6 = 119.5(4), C12–N3–C13 = 119.5(4), C39–C38–C37 = 130.1(4), C40–C41–C42 = 128.1(4), C42–N6–C43 = 118.9(4), C37–N4–C36 = 118.4(4).

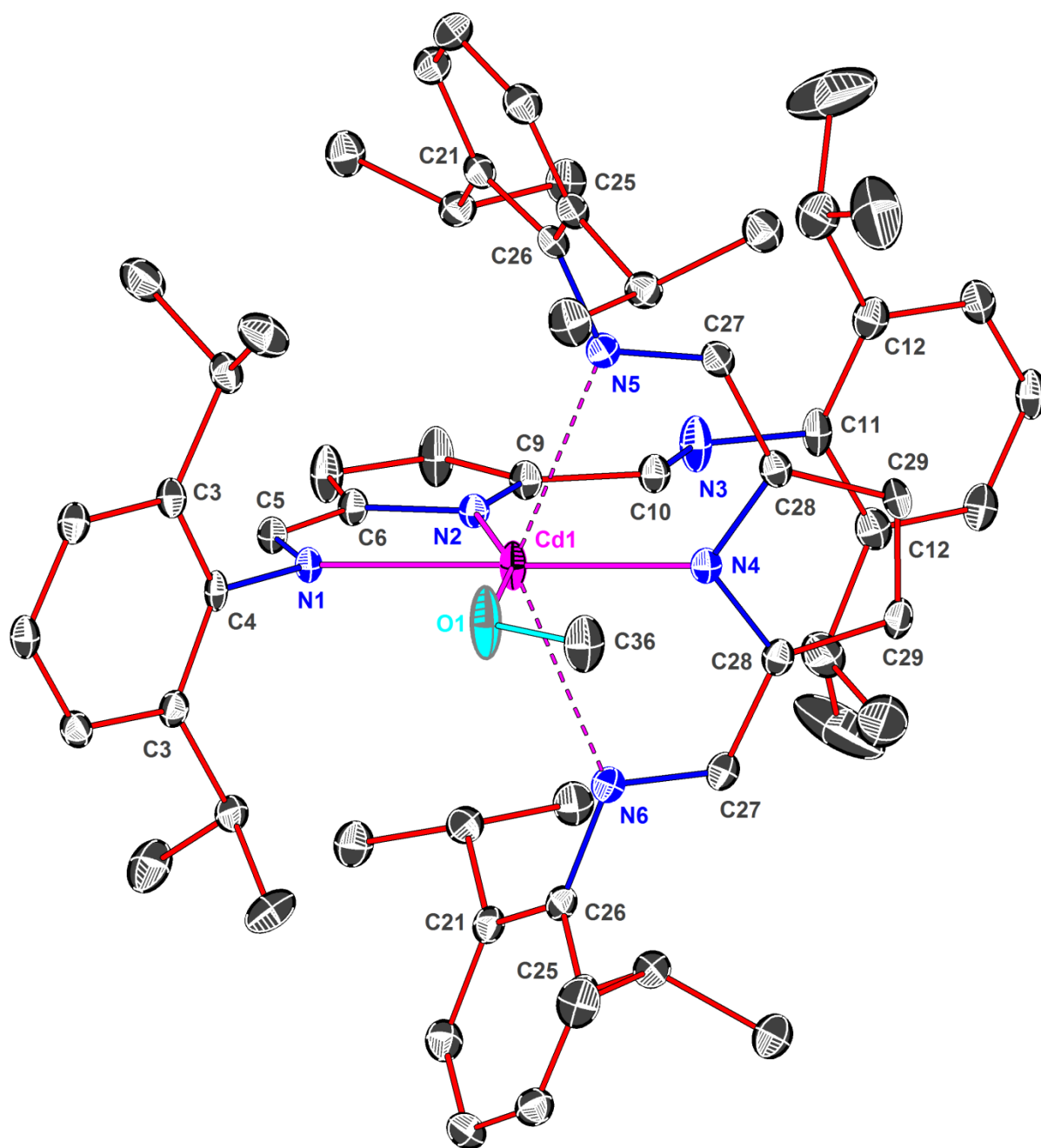


Figure 2.3. ORTEP of the molecular structure of **3**. Thermal ellipsoids are shown at 30% probability levels. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cd1–N2 = 2.271(3), N5–Cd1 = 2.716, Cd1–N4 = 2.149(3), N6–Cd1 = 2.716, Cd1–N1 = 2.275(3), Cd1–O1 = 2.336(3), N2–Cd1–N1 = 76.37(10), N1–Cd1–O1 = 85.08(11), N4–Cd1–O1 = 94.68(11), N4–Cd1–N2 = 103.87(10), N4–Cd1–N5 = 67.62, N4–Cd1–N6 = 67.62, N5–Cd1–N6 = 135.09, N6–Cd1–O1 = 90.12, N6–Cd1–N1 = 112.38, N6–Cd1–N2 = 96.86, C7–C6–C5 = 128.97, C8–C9–C10 = 127.1(3), C5–N1–C4 = 116.4(3), C10–N3–C11 = 128.5(3), C29–C28–C27 = 132.4(2), C27–N5–C26 = 118.0(2), N4–Cd1–N1 = 179.76(10), N2–Cd1–O1 = 161.45(11).

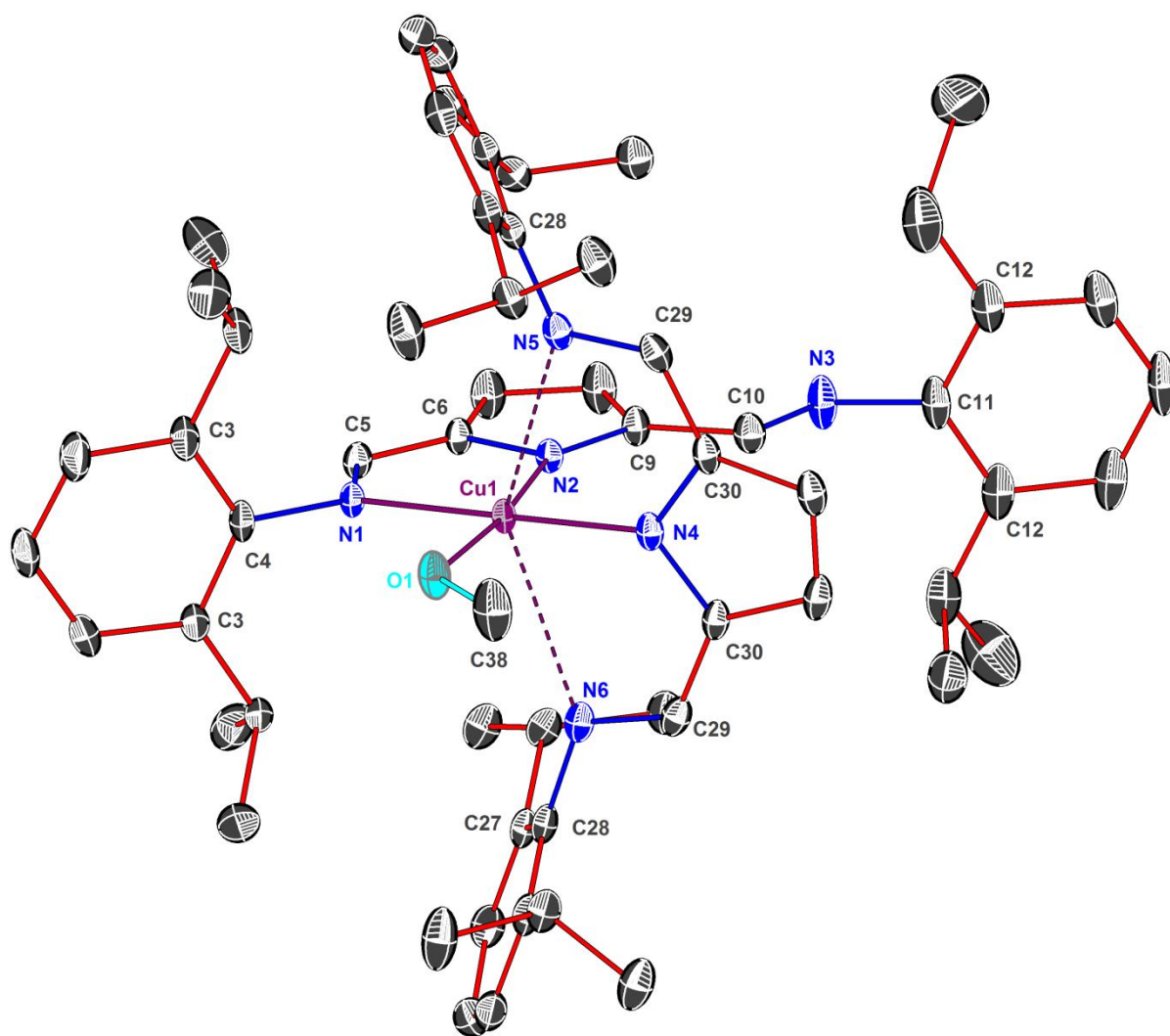


Figure 2.4. ORTEP of the molecular structure of **4**. Thermal ellipsoids are shown at 30% probability levels. The hydrogen atoms are omitted for clarity. Selected bond lengths [Å] and angles [°]: Cu1–N2 = 2.013(3), Cu1–N4 = 1.941(3), Cu1–O1 = 2.035(3), Cu1–N1 = 2.023(3), N5–Cu1 = 2.738(3), N6–Cu1 = 2.738(3), N1–Cu1–N2 = 83.10(13), N4–Cu1–O1 = 92.37(13), N2–Cu1–N4 = 96.30(12), N1–Cu1–O1 = 88.23(13), N4–Cu1–N5 = 70.76, N4–Cu1–N6 = 70.76, N6–Cu1–O1 = 88.47, N1–Cu1–N6 = 109.27, N2–Cu1–N6 = 94.38, N5–Cu1–N6 = 141.22, C5–C6–C7 = 132.4(4), C8–C9–C10 = 125.3(4), C10–N3–C11 = 126.6(4), C5–N1–C4 = 114.8(3), C31–C30–C29 = 130.6(3), C29–N5–C28 = 117.8(2), N1–Cu1–N4 = 179.40(13), N2–Cu1–O1 = 171.33(13).

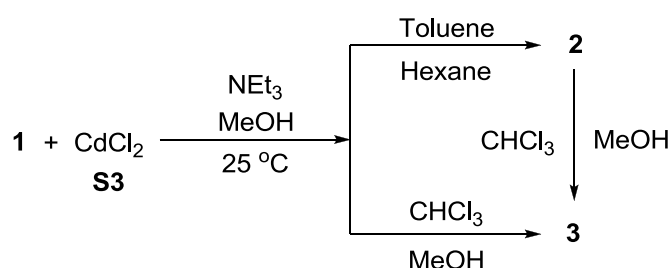
Table 2.1. Crystal data and structural refinement details for **1-4**

Parameters	1	2	3	4
Empirical formula	C ₆₀ H ₇₆ N ₆ Zn	C ₆₀ H ₇₆ CdN ₆	C ₆₁ H ₈₀ CdN ₆ O	C ₆₁ H ₈₀ CuN ₆ O
Formula weight	946.64	993.67	1025.71	976.85
Crystal System	Monoclinic	Monoclinic	Orthorhombic	Orthorhombic
Space group	P2(1)/n	P2(1)/n	Pnma	Pnma
a (Å)	10.559	10.739	19.145	18.870
b (Å)	21.306	20.900	21.378	21.946
c (Å)	24.365	23.604	14.170	13.737
α (deg)	90	90	90	90
β (deg)	97.43	97.12	90	90
γ (deg)	90	90	90	90
Volume (Å) ³	5435.2	5257.0	5799.7	5688.8
Temperature (K)	100(2)	100(2)	100(2)	100(2)
Z	4	4	4	4
μ mm ⁻¹	0.494	0.459	0.419	0.428
D (calcd.) (g/cm ³)	1.157	1.255	1.175	1.141
F(000)	2032	2104	2176	2100
Crystal size (mm)	0.16 × 0.12 × 0.10	0.18 × 0.12 × 0.10	0.22 × 0.18 × 0.14	0.20 × 0.16 × 0.12
θ range (deg)	1.27 to 25.05	1.31 to 24.98	1.72 to 25.07	1.75 to 25.40
Index ranges	-12 ≤ h ≤ 12 -21 ≤ k ≤ 25 -29 ≤ l ≤ 26	-12 ≤ h ≤ 12 -24 ≤ k ≤ 24 -27 ≤ l ≤ 28	-22 ≤ h ≤ 22 -25 ≤ k ≤ 25 -16 ≤ l ≤ 16	-22 ≤ h ≤ 22 -26 ≤ k ≤ 26 -16 ≤ l ≤ 16
Reflections collected / unique	24621 / 9522 R _{int} = 0.0807	49217 / 9219 R _{int} = 0.0788	54127 / 5296 R _{int} = 0.0534	54674 / 5392 R _{int} = 0.0668
Data completeness	98.9%	99.8%	99.9%	100.0%
Transmission (max/min)	0.9522 / 0.9251	0.9555 / 0.9219	0.9436 / 0.9134	0.9505 / 0.9194
Data / restraints / parameters	9522 / 0 / 652	9219 / 0 / 652	5296 / 0 / 366	5392 / 0 / 375
Goodness-of-fit on F ²	1.075	1.300	1.161	1.221
Final R indices [I > 2σ(I)]	R ₁ = 0.0720 wR ₂ = 0.1685	R ₁ = 0.0754 wR ₂ = 0.1345	R ₁ = 0.0440 wR ₂ = 0.0984	R ₁ = 0.0645 wR ₂ = 0.1377
R indices (all data)	R ₁ = 0.0946 wR ₂ = 0.1825	R ₁ = 0.0887 wR ₂ = 0.1392	R ₁ = 0.0472 wR ₂ = 0.1003	R ₁ = 0.0717 wR ₂ = 0.1418
Largest diff. peak / hole, e Å ⁻³	0.749 / -0.399	1.138 / -1.418	0.583 / -0.459	0.457 / -0.486

These deviations in the angle are probably due to the constrained angle of the coordinated arms. The C27–C28–C29 angle in the coordinating arm of the ligand in **3** is 132.4°. However, a similar C29–C30–C31 (130.6°) angle in **4** was contracted by 2° when compared to free ligand (132.6°). Similarly a subtle change in the Cu1–N5 and Cu1–N6 bond lengths and N6–Cu1–N5 bond angle was observed when compared to those in **3**. The crystallographic data for complexes **1–4** are listed in Table 2.1.

It is worth noting the formation of two different Cd–ligand complexes when the Cd precursor was varied. When Cd[N(SiMe₃)₂]₂ **S2** was used as the Cd source, it yielded a four coordinate complex with a tetrahedral structure (**2**) whereas when CdCl₂ was used as a source of Cd, it yielded a six coordinate complex with a pseudo octahedral structure (**3**). The complexes **2** and **3** were crystallized in monoclinic and orthorhombic crystal systems respectively.

According to Scheme 2.6, reaction mixture was purified by recrystallization from a CHCl₃–MeOH mixture to yield **3**. In order to confirm whether the product **3** was formed during the reaction or in the crystallization process, few controlled reactions were attempted as shown in Scheme 2.7. On completion of the reaction after 24 h, the reaction mixture was filtered and the residue was dried completely to ensure the absence of solvent molecules. The residue was kept in toluene-hexane for recrystallization. The X-ray quality crystals were obtained after a week and were found to be **2**. Furthermore, **2** was redissolved in a CHCl₃–MeOH mixture for recrystallization. The product was recrystallized to yield **3**.



Scheme 2.7. Transformation during the recrystallization process.

From this study, it was found that **3** was not formed during the reaction but was obtained through a transformation during the crystallization process. In the case of **2** and **3**, the formation of the product does not depend on the Cd source starting material but depends on the crystallization process. The same strategy was also attempted for copper but X-ray quality crystals were not formed in the non-coordinating solvents.

The UV-visible absorption spectrum of ligand (DIP₂pyr)H revealed absorptions at 325 and 317 nm, corresponding to $n\text{-}\pi^*$ and $\pi\text{-}\pi^*$ transitions (Figure 2.5). The complexes (**1-4**) showed absorbance similar to ligand (DIP₂pyr)H without any shift of absorption maxima. The complex **4** absorbed also at 378 nm because of d-d transition. Thermogravimetric analyses (Figure 2.6) revealed the complexes were highly stable and their decomposition temperatures ranged between 330-370 °C. Despite having same ligands, the Cd(II) complexes **2** and **3** showed a difference in their thermal stabilities because of the difference in structures.

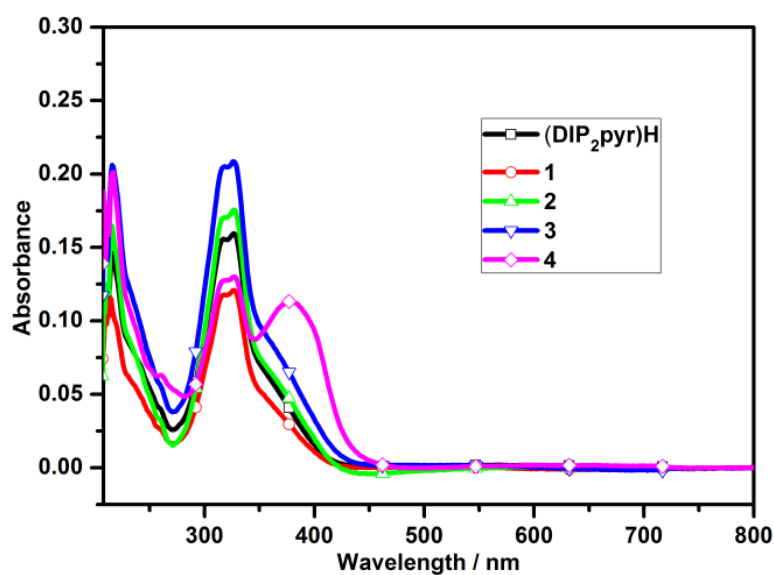


Figure 2.5. UV visible absorption spectra of (DIP₂pyr)H and its complexes **1-4** in hexane

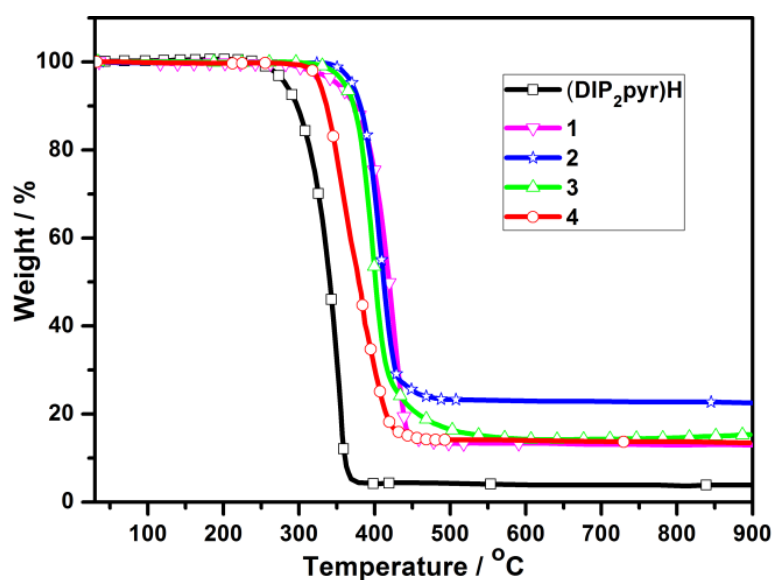


Figure 2.6. TGA plots of (DIP₂pyr)H and its complexes **1-4**

2.3. Conclusions

In conclusion, $\text{Zn}(\text{DIP}_2\text{pyr})_2$ **1**, $\text{Cd}(\text{DIP}_2\text{pyr})_2$ **2**, $\text{Cd}(\text{DIP}_2\text{pyr})_2 (\text{CH}_3\text{OH})$ **3** and $\text{Cu}(\text{DIP}_2\text{pyr})_2(\text{CH}_3\text{OH})$ **4** were successfully synthesized and were characterized by standard techniques. Two types of structures **2** and **3** were found for the same Cd(II) metal and $(\text{DIP}_2\text{pyr})\text{H}$ ligand and the transformation of **2** to **3** upon recrystallization was studied.

2.4. Experimental section

2.4.1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard schlenk techniques under dry nitrogen. All solvents which were used under an inert atmosphere were thoroughly deoxygenated using a freeze-pump-thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium benzophenone ketyl (diethyl ether, toluene), $\text{Mg}(\text{OMe})_2$ (methanol), P_2O_5 (triethylamine), CaCl_2 (chloroform). The compounds, 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole $(\text{DIP}_2\text{pyr})\text{H}$ [32a, 35], $\text{Zn}[\text{N}(\text{SiMe}_3)_2]_2$ (**S1**) [36] and $\text{Cd}[\text{N}(\text{SiMe}_3)_2]_2$ (**S2**) [36] were synthesized according to the literature procedures.

The structures of all the products were confirmed by IR, ^1H , ^{13}C NMR and HRMS spectra. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrometer using KBr pellets. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. The data were reported in parts per million (δ) using CDCl_3 as the solvent with a TMS internal standard or residual solvent peak as the reference for ^1H and ^{13}C (100 MHz) NMR. Elemental analysis was carried out using a Thermo Finnigan Flash EA 1112 analyzer. Single crystal X-ray data collection was carried out at 100(2) K on a Bruker Smart Apex CCD area detector system ($\lambda (\text{Mo K}\alpha) = 0.71073 \text{ \AA}$) with a graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97 [37] and refined using SHELXL-97 [38]. All hydrogen atoms were refined anisotropically.

2.4.2. Experimental procedure

General procedure for synthesis of metal complexes 1 and 2: A solution of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole $(\text{DIP}_2\text{pyr})\text{H}$ (2.4 mmol) in toluene (4 mL) was added

to a solution of $M[N(\text{SiMe}_3)_2]_2$ (1.2 mmol) in toluene (4 mL) at room temperature. The reaction mixture was stirred for 48 h at 60 °C. The reaction mixture was filtered off and the residue was washed with hexane (3×10 mL). The solvent was evaporated to give a yellow powder which was recrystallized from the mixture of toluene-hexane to yield pure crystals for X-ray analysis after a week.

Zn(DIP₂pyr)₂ (1): The compound was prepared from $\text{Zn}[N(\text{SiMe}_3)_2]_2$ (**S1**) (0.46 g, 1.2 mmol) using the general procedure to Yield **1** (0.74 g, 75%); M.p. 214 °C (toluene-hexane).

IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$) : 1626, 1564, 1325, 1167, 1099, 1049, 858, 688.

^1H NMR (400 MHz, CDCl_3) : δ 0.90 (d, $J = 6.4$ Hz, 48H, $\text{CH}(\text{CH}_3)$), 3.08–2.86 (m, 8H, $\text{CH}(\text{CH}_3)$), 6.97 (s, 4H, 3, 4-pyr), 7.05 (s, 12H, Ph), 7.85 (s, 4H, $\text{C}=\text{NH}$).

^{13}C NMR (100MHz, CDCl_3) : δ 23.8, 27.9, 118.9, 123.4, 125.1, 140.0, 141.8, 146.6, 158.8.

Anal. Calcd. for $\text{C}_{60}\text{H}_{76}\text{N}_6\text{Zn}$: C, 76.12; H, 8.09; N, 8.88.

Found : C, 76.32; H, 7.96; N, 8.75.

Cd(DIP₂pyr)₂ (2): The compound was prepared from $\text{Cd}[N(\text{SiMe}_3)_2]_2$ (**S2**) (0.55 g, 1.2 mmol) using the general procedure to Yield **2** (0.84 g, 71%). M.p. 236 °C (toluene-hexane).

IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$) : 1621, 1567, 1353, 1162, 1096, 1036, 855.

^1H NMR (400 MHz, CDCl_3) : δ 0.89 (d, $J = 6.8$ Hz, 48H, $\text{CH}(\text{CH}_3)$), 3.08–2.86 (m, 8H, $\text{CH}(\text{CH}_3)$), 6.90 (s, 4H, 3, 4-pyr), 7.05 (s, 12H, Ph), 7.91 (s, 4H, $\text{C}=\text{NH}$).

^{13}C NMR (100 MHz, CDCl_3) : δ 23.8, 27.9, 119.1, 123.3, 124.9, 139.8, 141.0, 147.2, 158.4.

Anal. Calcd. for $\text{C}_{60}\text{H}_{76}\text{N}_6\text{Cd}$: C, 72.52; H, 7.71; N, 8.46.

Found : C, 72.45; H, 7.78; N, 8.36.

General procedure for synthesis of metal complexes 3 and 4: Triethylamine (3.0 mmol) was added to a solution of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H

(0.88 g, 2.0 mmol) in methanol (20 mL), and heated to 50 °C with stirring. To this clear solution, a solution of MCl_2 (1.0 mmol) in methanol (5 mL) was added. The reaction mixture was cooled to room temperature and stirred for 24 h. The reaction mixture was filtered off and the residue was washed with methanol (30 mL). The residue was recrystallized from a mixture of CHCl_3 -MeOH to yield pure crystals for X-ray analysis after a week.

Cd(DIP₂pyr)₂(MeOH) (3): The compound was prepared from anhydrous CdCl_2 (0.18 g, 1.0 mmol) using the general procedure to Yield **3** (0.67 g, 65%). The residue was recrystallized from a mixture of CHCl_3 -MeOH-acetone to yield pure crystals for X-ray analysis after a week. M.p. 230 °C (CHCl_3 -MeOH-acetone).

IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$) : 1711, 1695, 1630, 1570, 1352, 1161, 1097, 1037, 842.

^1H NMR (400 MHz, CDCl_3) : δ 0.90 (d, $J = 6.8$ Hz, 48H, $\text{CH}(\text{CH}_3)$), 2.18 (s, 6H, CH_3COCH_3), 2.98–2.85 (m, 8H, $\text{CH}(\text{CH}_3)$), 3.14 (s, 3H, CH_3OH), 6.89 (s, 4H, 3, 4-pyr), 7.06 (s, 12H, Ph), 7.88 (s, 4H, C=NH).

^{13}C NMR (100 MHz, CDCl_3) : δ 23.8, 27.9, 30.95, 50.83, 119.1, 123.3, 124.9, 139.9, 141.0, 147.3, 158.6.

Anal. Calcd. for $\text{C}_{61}\text{H}_{80}\text{CdN}_6\text{O}$: C, 71.41; H, 7.87; N, 8.20.

Found : C, 71.55; H, 7.81; N, 8.15.

Cu(DIP₂pyr)₂(MeOH) (4): The compound was prepared from anhydrous CuCl_2 (0.13 g, 1.0 mmol) using the general procedure to Yield **4** (0.76 g, 78%). M.p. 202 °C (CHCl_3 -MeOH).

IR (KBr pellet, $\nu_{\text{max}}/\text{cm}^{-1}$) : 1622, 1564, 1342, 1170, 1099, 1043, 856.

Anal. Calcd. for $\text{C}_{61}\text{H}_{80}\text{CuN}_6\text{O}$: C, 75.08; H, 8.25; N, 8.61.

Found : C, 75.22; H, 8.09; N, 8.53.

Supporting information: ^1H and ^{13}C NMR spectra of Zn(II) **1** and Cd(II) **3** complexes are included at the end of this chapter (Figure 2.S1 - 2.S4).

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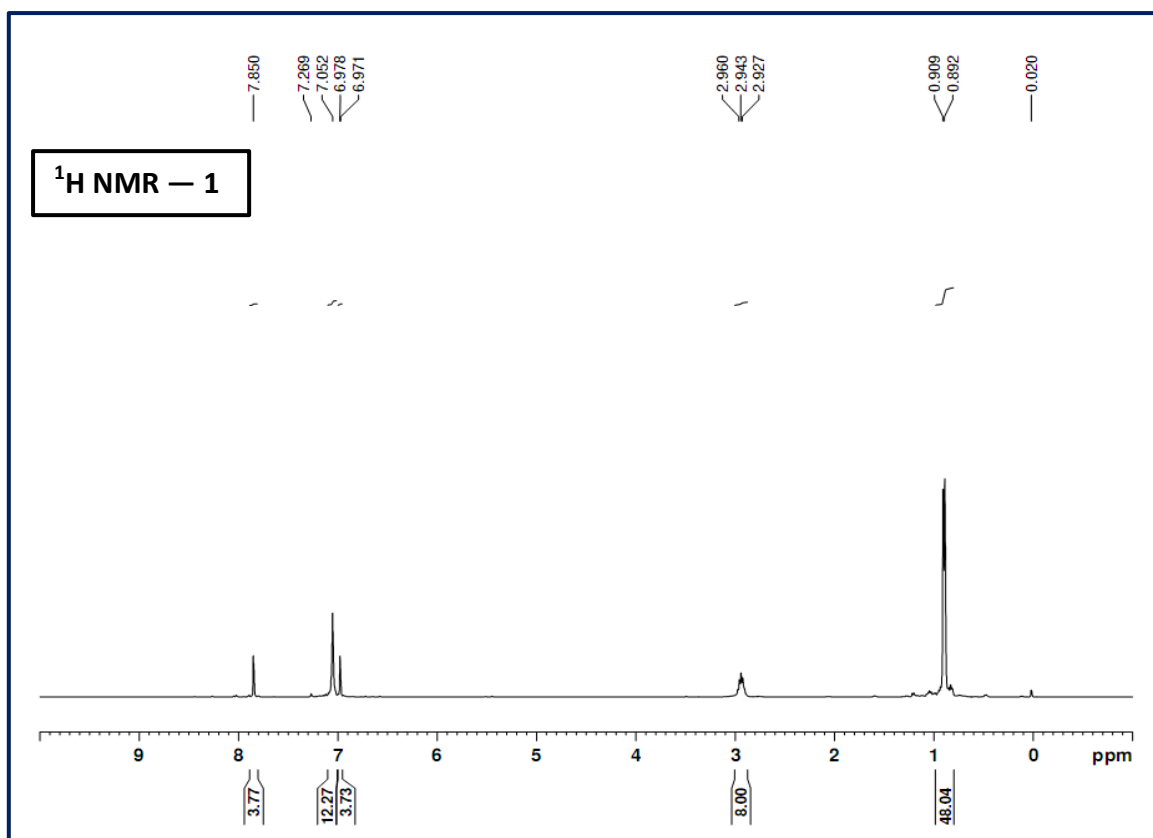


Figure 2.S1. ^1H NMR spectrum of Zn(II) **1** complex

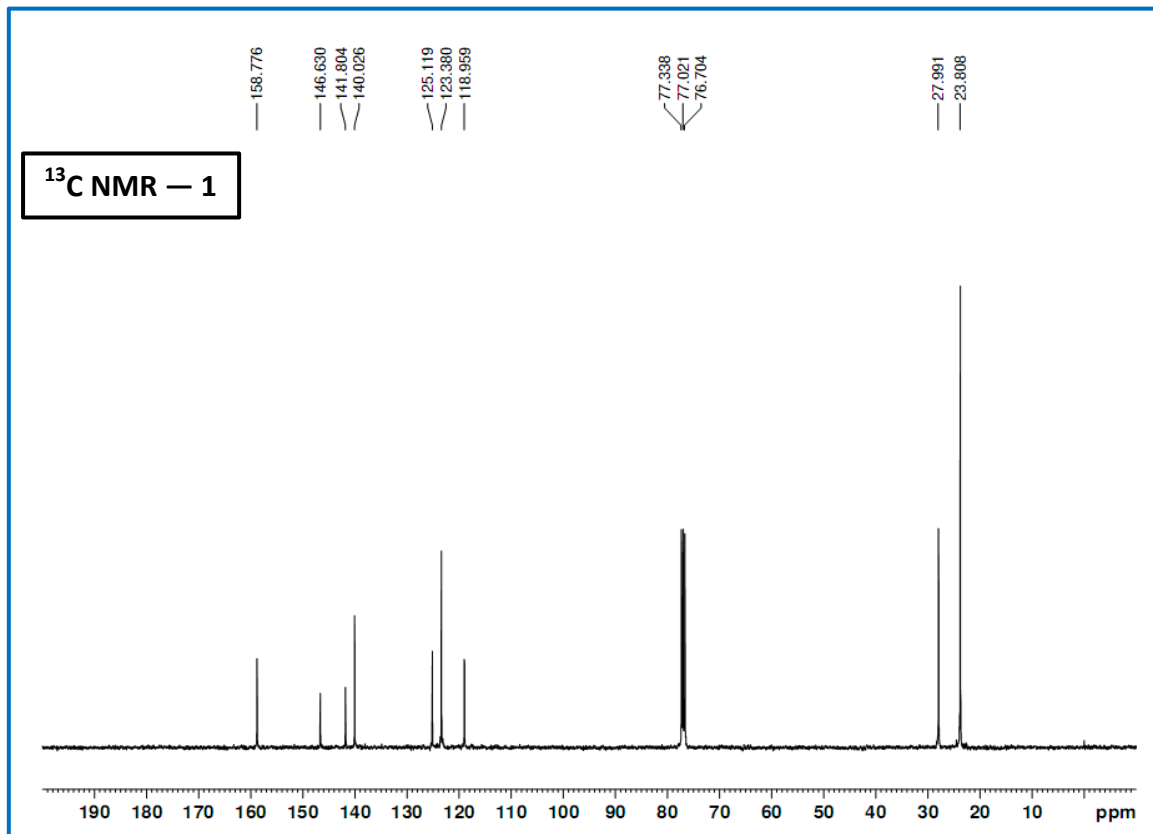


Figure 2.S2. ^{13}C NMR spectrum of Zn(II) **1** complex

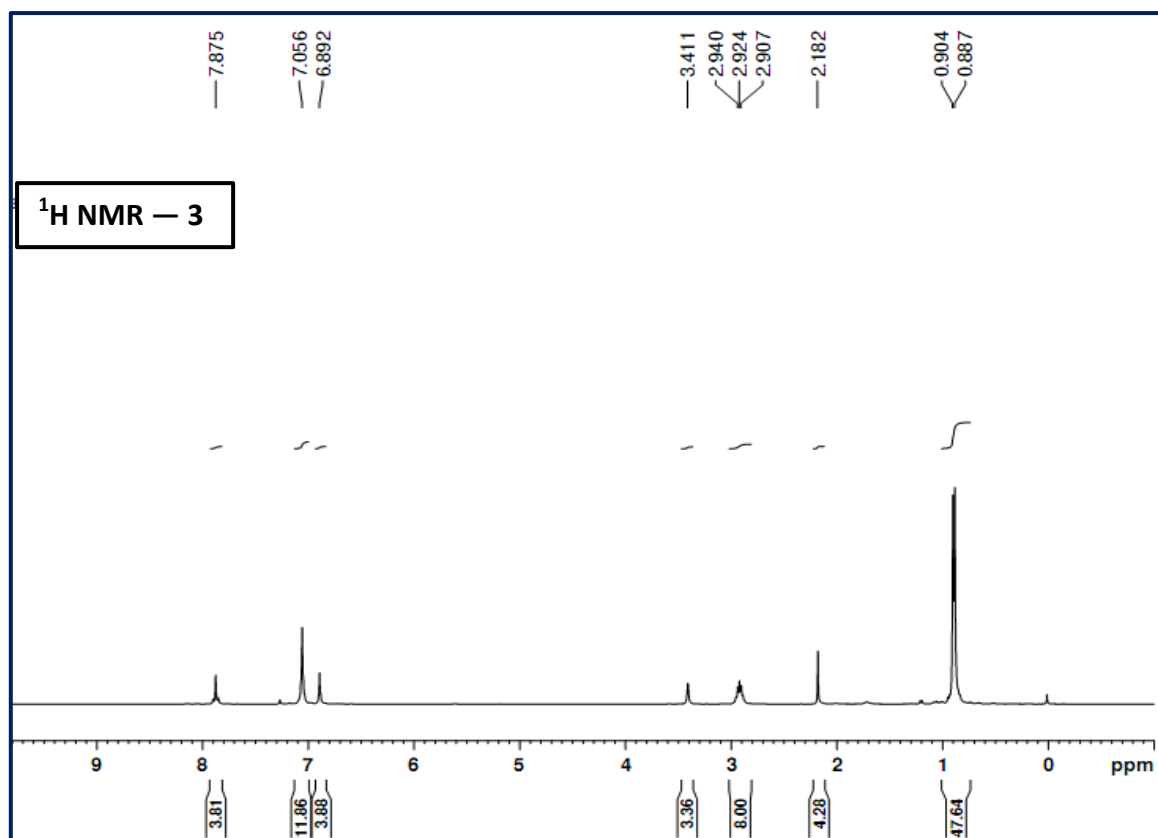


Figure 2.S3. ^1H NMR spectrum of Cd(II) **3** complex

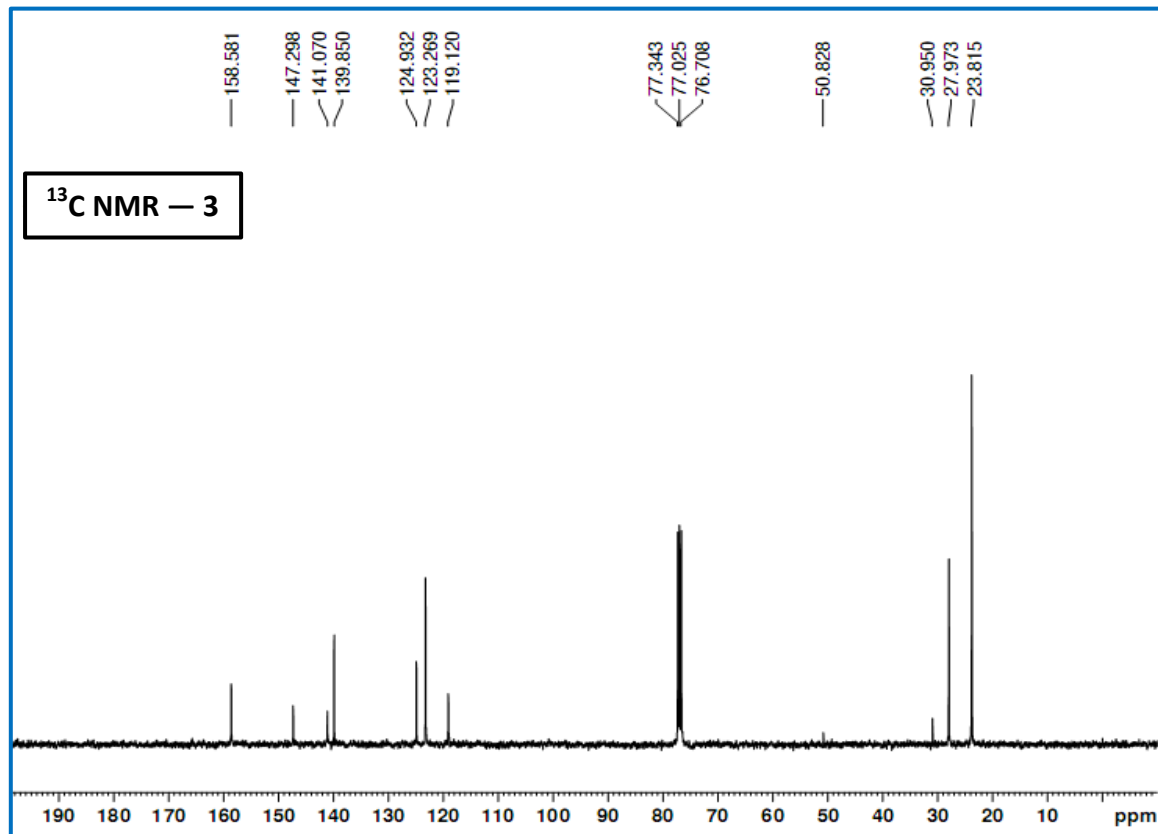


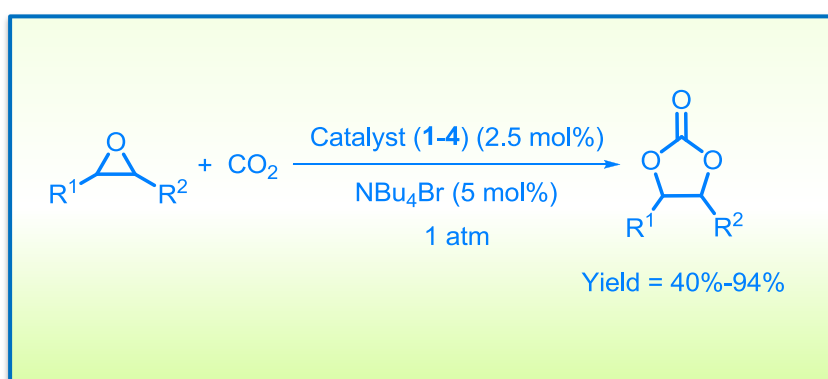
Figure 2.S4. ^{13}C NMR spectrum of Cd(II) **3** complex

CHAPTER 3

Efficient Cyclic Carbonate Synthesis from Epoxides and Carbon Dioxide at Atmospheric Pressure

Abstract

In this chapter, the catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) for the cycloaddition of CO₂ to an epoxide in the presence of tetrabutylammonium bromide (TBAB) under one atmosphere of pressure and mild temperature conditions to yield cyclic carbonate have been studied. Among these complexes **1-4**, Zn(II) **1** and Cu(II) **4** complexes were found to be versatile whereas the Cu(II) **4** complex was more selective in the conversion. They were highly effective for the conversion of monosubstituted terminal epoxides, disubstituted terminal, and internal epoxides to their corresponding cyclic carbonates with good to high yields.



3.1. Introduction

As petroleum resources are depleting, there has been a significant interest to attain an alternative feedstock for fuel and to search for new routes to basic valuable chemicals from renewable carbon resources such as CO₂ [1]. The Keeling curve demonstrated that ever since the industrial revolution, there has been a steady rise in CO₂ levels in the atmosphere. The rise was about 280 ppm in 1850 while 391 ppm in 2011 and continue to increase at an accelerating rate of 1.9 ppm per year [2]. The anthropogenic accumulation of CO₂ primarily originates from fossil fuel combustion for energy requirements. In an effort to mitigate global warming, carbon sequestration technologies were introduced to limit the amount of CO₂ entering atmosphere from industrial processes [3]. However, carbon sequestration is discouraged by industries due to the ambiguity in the process feasibility and high energy demand [4]. Therefore, utilization of CO₂ has the additional environmental benefit of maintaining climate change if the process is implemented at an industry level [5].

CO₂ is a cheap, nontoxic, non-flammable, naturally abundant carbon feedstock. However, CO₂ is a highly oxidized, thermodynamically stable molecule which hinders its utility as a starting material for the synthesis of various compounds. Highly reactive compounds have been explored for the reaction with CO₂. One such important commercial reaction is the insertion of CO₂ into an epoxide in the presence of a catalyst to generate polycarbonate or cyclic carbonate [6]. Polycarbonates have potential applications as exterior thermoplastic for engineering parts, safety glasses, eyewear lenses and packaging materials [7]. Cyclic carbonates have applications in a variety of fields such as electrolytes in secondary batteries, pharmaceutical intermediates, aprotic polar solvents in paint stripping, degreasing and cleaning applications [8].

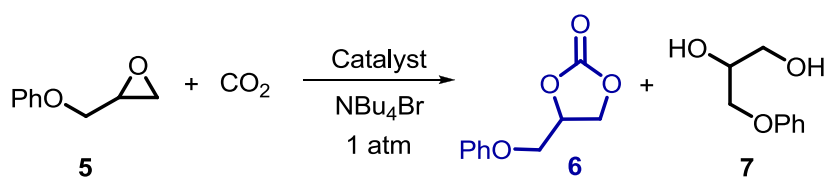
Currently, cyclic carbonates (propylene carbonate, ethylene carbonate) and linear carbonates (diethyl carbonate, dimethyl carbonate and ethyl methyl carbonate) are the major solvents for organic electrolytes. Surprisingly, polycarbonates are virtually unexplored as solid polymer electrolytes for Li-ion conductivity. Thus, this chapter describes the efficient catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) for the synthesis of cyclic carbonate from epoxide and CO₂ at atmospheric pressure under mild temperature conditions.

3.2. Results and discussion

Metal complexes with N, N', N''-tridentate coordination mode indicated remarkable activity in the ring opening polymerization of lactones [9, 10] and ethylene polymerization [11, 12]. However, epoxide-CO₂ copolymerization using N, N', N''-tridentate ligand complexes is not effectively explored. Initially, we tested the catalytic activity of complexes **1-4** for the copolymerization of **5** and CO₂ at 1 atm in the presence of tetrabutylammonium bromide (TBAB) as co-catalyst to produce polycarbonate. Interestingly, we obtained cyclic carbonate **6** in good yield instead of the corresponding polycarbonate. So in order to obtain polycarbonate, reactions were attempted in varying temperatures, in presence of various co-catalysts, different catalyst/co-catalyst loadings and with varieties of monomers (**8**, **11** and **13**). All the cases, we found only the formation of corresponding cyclic carbonates.

It is interesting to note that recent reports [13] on the electrosynthesis of cyclic carbonate; and utilization of alkylammonium salts, bimetallic aluminium-salen complexes, Zn clusters, ionic liquids and amidine derivatives as catalyst for cyclic carbonate synthesis are promising. However, these systems are highly efficient only to the synthesis of mono substituted terminal epoxides. The active catalyst for both mono and disubstituted epoxides at an atmospheric pressure of CO₂ is rarely reported [14]. We are interested to test our catalysts for the conversion of both mono and disubstituted terminal and internal epoxides to their corresponding cyclic carbonates.

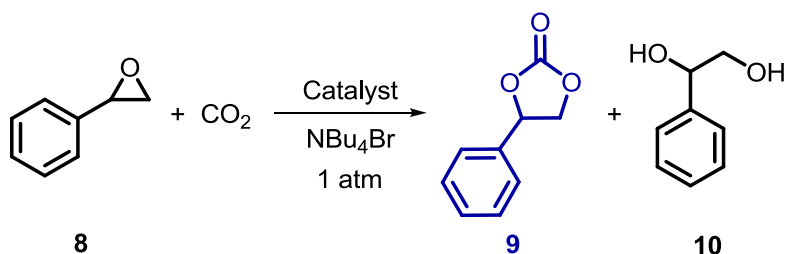
To check the catalytic activities of complexes **1-4** for the synthesis of cyclic carbonate from various mono and disubstituted epoxides (**5**, **8**, and **11**), reactions were attempted at 1 atm of CO₂ under mild temperature and solvent free conditions using TBAB as a co-catalyst. First, we examined the reaction of 2-(phenoxymethyl)oxirane **5** with CO₂ (1 atm) using **1** as a catalyst according to the scheme shown in Table 3.1 and the results are illustrated in Table 3.1. The reaction conditions were optimized by varying the molar ratio, temperature and time at 1 atm of CO₂ (Table 3.1). 2-(phenoxymethyl)oxirane **5** was efficiently converted to 4-(phenoxymethyl)-1,3-dioxolan-2-one **6** at 60 °C within 10 h using 2.5 mol% of **1** and 5 mol% of TBAB under solvent free conditions (Table 3.1, entry 10). From screening tests (Table 3.1), better results were achieved with a combination of 2.5 mol% of the catalyst **1** and 5.0 mol% of TBAB. This molar ratio was fixed for further investigations with other catalysts.

Table 3.1. Screening studies for the synthesis of **6**^a

Entry	Catalyst (mol%)	TBAB (mol%)	T (°C)	Time (h)	Conversion (%) by NMR		Yield (%) ^b of 6
					6	7	
1	1 (2.5)	–	30	24	–	–	–
2	–	5.0	30	24	4	–	–
3	–	5.0	60	10	21	–	–
4	–	5.0	105	4	45	–	–
5	1 (1.0)	1.0	30	24	31	–	24
6	1 (1.0)	1.0	60	10	51	5	43
7	1 (2.5)	1.0	60	10	63	6	56
8	1 (2.5)	2.5	60	10	72	8	65
9	1 (2.5)	5.0	30	24	49	–	40
10	1 (2.5)	5.0	60	10	84	8	76
11	1 (2.5)	5.0	60	20	60	35	53
12	1 (2.5)	5.0	105	2	59	34	52
13	1 (1.0)	2.5	60	10	73	11	66
14	1 (1.0)	5.0	60	10	78	12	70
15	2 (2.5)	5.0	30	24	18	–	10
16	2 (2.5)	5.0	60	10	51	14	44
17	2 (2.5)	5.0	105	2	55	39	48
18	3 (2.5)	5.0	30	24	14	–	–
19	3 (2.5)	5.0	60	10	48	10	38
20	3 (2.5)	5.0	105	2	49	36	42
21	4 (2.5)	5.0	30	24	30	–	22
22	4 (2.5)	5.0	60	10	73	–	67
23	4 (2.5)	5.0	60	20	96	–	91
24	4 (2.5)	5.0	105	2	78	–	70
25	4 (2.5)	5.0	105	4	94	–	90

^aReaction condition: CO₂ (1 atm, balloon) and solvent free conditions. ^bPurification by flash column chromatography.

Table 3.2. Optimization studies for the synthesis of **9**^a



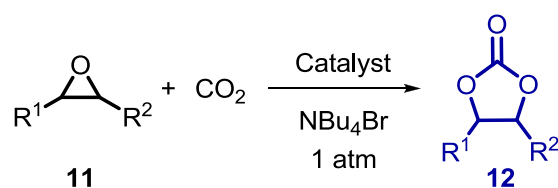
Entry	Catalyst	T (°C)	Time (h)	Epoxide 8 ^b (%) by NMR	Conversion (%) by NMR		Yield (%) ^c of 9
					9	10	
1 ^d	1	30	24	100	—	—	—
2 ^e	—	30	24	96	4	—	—
3 ^e	—	105	2	62	38	—	31
4 ^e	—	105	4	51	49	—	44
5	1	30	24	86	14	—	9
6	1	60	24	11	60	29	53
7	1	105	2	5	86	9	80
8	2	30	24	96	4	—	—
9	2	60	24	60	22	18	15
10	2	105	2	19	60	21	54
11	3	30	24	96	4	—	—
12	3	60	24	71	19	10	12
13	3	105	2	32	58	10	50
14	4	30	24	88	12	—	—
15	4	60	24	52	48	—	41
16	4	105	2	25	75	—	70
17	4	105	4	3	97	—	94

^aReaction condition: Epoxide **8** (1 mol), catalyst (2.5 mol%), TBAB (5 mol%) under CO₂ (1 atm, balloon). ^bUnreacted epoxide **8** (%) by NMR. ^cPurification by flash column chromatography. ^dWithout TBAB. ^eWithout catalyst.

When this reaction was examined with catalysts **2-4** (Table 3.1, entries 15-25), it was observed that conversion proceeded quickly in the presence of **1**. However, in case of **4** (2.5 mol%), the reaction was neat and cyclic carbonate **6** was obtained selectively (Table 3.1, entries 21-25) without any diol formation (*vide-infra*). The maximum yield was attained with an extended reaction time and/or with an increased reaction temperature. The reaction was further established for 2-phenyloxirane **8** according to the scheme shown in Table 3.2. The reaction conditions were investigated with **1-4** and the results are displayed in Table 3.2 (entries 5-17). As observed in the previous case, **1** showed a better catalytic activity and yielded (80%) the corresponding cyclic carbonate 4-phenyl-1,3-dioxolan-2-one **9** at 105 °C within 2 h at 1 atm of CO₂ (Table 3.2, entry 7). When **4** was used as the catalyst, the maximum yield (94%) of cyclic carbonate **9** was selectively obtained at 105 °C within 4 h (Table 3.2, entry 17).

In order to confirm the catalytic activities of our catalysts, eight controlled reactions (Table 3.1 and 3.2, entries 1-4) at 30 °C, 60 °C and 105 °C were carried out. Cycloaddition reactions did not proceed when only catalyst **1** was present (Table 3.1 and 3.2, entry 1). On the other hand, in the absence of **1**, TBAB (5 mol%) alone showed low catalytic activity (Table 3.1 and 3.2, entries 2-4). However, the combination of a catalyst **1** and TBAB exhibited high catalytic activity which highlights the necessity for the coexistence of both to effectively catalyze these reactions.

Since **1** and **4** displayed better catalytic activities, the scope of these catalysts was further explored for the cycloaddition of CO₂ with different monosubstituted aliphatic terminal epoxides **11a-c** at 1 atm of CO₂. The results are shown in Table 3.3 (entries A1-C2). The displayed reaction conditions were optimized conditions for the synthesis of the corresponding cyclic carbonate **12**. All these epoxides selectively yielded cyclic carbonate **12** in the presence of **1** or **4** and TBAB in good yields. The reaction of 2-methyloxirane **11a** with CO₂ in the presence of **1** or **4** and TBAB yielded 4-methyl-1,3-dioxolan-2-one **12a** at 10 °C in a moderate yield (Table 3.3, entries A1 and A2).

Table 3.3. Scope of catalysts **1** and **4**^a

Entry	Catalyst	Epoxide	T (°C)	Time (h)	Cyclic Carbonate	Yield ^b	TON ^c	TOF ^d
A1	1	 11a	10	10	 12a	67	26.8	2.68
A2	4		10	10		64	25.6	2.56
A3	1		25	6		45	18	3
A4	4		25	6		40	16	2.66
B1	1	 11b	25	20	 12b	84	33.6	1.68
B2	4		25	20		82	32.8	1.64
C1	1	 11c	25	18	 12c	79	31.6	1.76
C2	4		25	18		76	30.4	1.69
D1	1	 11d	25	10	 12d	86	34.4	3.44
D2	4		25	10		81	32.4	3.24
E1	1	 11e	25	24	 12e	42 ^e	16.8	0.7
E2	4		25	24		36 ^e	14.4	0.6
F1	1	 11f	105	20	 12f	73 ^f	29.2	1.46
F2	4		105	20		68 ^f	27.2	1.36

^aReaction condition: Epoxide (1 mol), catalyst (2.5 mol%), TBAB (5.0 mol%) under CO₂ (1 atm, balloon). ^bPurification by flash column chromatography. ^cMoles of epoxide consumed

per mole of catalyst. ^dMoles of epoxide consumed per mole of catalyst per hour. ^e,
^fDiastereomers were separated. ^ecis : trans ratio (95:5). ^fcis : trans ratio (96:4).

The catalytic activities of **1** and **4** were investigated with disubstituted epoxides **11d-f**. Disubstituted terminal and internal epoxides were successfully converted to the corresponding cyclic carbonates **12d-f** at 1 atm of CO₂. The reaction conditions are detailed in Table 3.3 (entries D1–F2). It was observed that *cis*-2,3-dimethyloxirane **11e** was efficiently converted to *cis*-4,5-dimethyl-1,3-dioxolan-2-one **12e** with good selectivity (ratio of cis : trans; 95 : 5) (Table 3.3, entries E1 and E2).

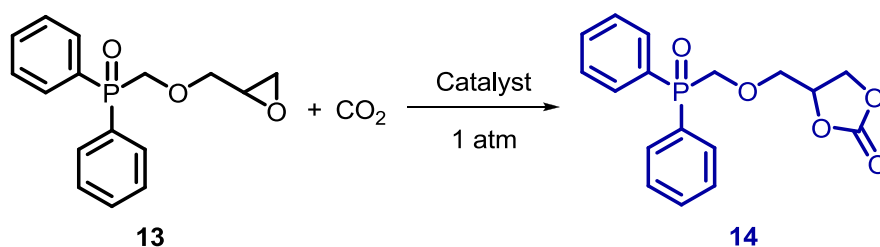
It was also interesting to note that *cis*-cyclohexene oxide (CHO) **11f** yielded *cis*-cyclohexene carbonate (CHC) **12f** (ratio of cis : trans; 96 : 4) (Table 3.3, entry F1 and F2). In the course of fixation of CO₂ to the epoxide, the formation of *cis*-CHC from *cis*-CHO has rarely been reported [14, 15]. In the presence of **1** or **4**, even at a moderate temperature, *cis*-CHO yielded the corresponding *cis*-CHC with good selectivity. One atmospheric pressure of CO₂, a moderate reaction temperature and co-catalyst loading (5.0 mol%) could have not favored *trans*-cyclohexene carbonate formation (4%) [14, 15]. Catalysts **1** and **4** proved to be highly active and also selective for the conversion of disubstituted epoxides under mild conditions at 1 atm of CO₂.

Further, the scope of the complexes was tested for phosphorus containing epoxide to synthesize cyclic carbonate having phosphorus atom. The cycloaddition of monosubstituted phosphorus containing epoxide 2-[[[(diphenylphosphoryl)methoxy]methyl]oxirane (**13**) with CO₂ was investigated in the presence of **1-4** as catalysts and TBAB as co-catalyst. The results from these reactions are summarized in the Table 3.4. The compound **13** was efficiently converted to 4-[[[(diphenylphosphoryl)methoxy]methyl]-1,3-dioxolan-2-one **14** (yield 84%) at 105 °C within 3 h in the presence of **1** and TBAB under the pressure of 1 atm CO₂ (Table 3.4, entry 4). Similarly, the complex **4** catalyzed the reaction effectively with a maximum yield of 93% within 5 h (Table 3.4, entry 11).

We have described that the combination of a catalyst and a co-catalyst exhibited high catalytic activities. Therefore, in view of finding better combination, this reaction was further tested with other co-catalysts 4-dimethyl aminopyridine (DMAP) and bis(triphenyl phosphine)iminium chloride (PPNCl). The results of these reactions are displayed in the Table 3.4 (entries 5–8). However, it was observed that the combination **1**/TBAB delivered the best result among all. The other combinations such as **4**/DMAP and **4**/PPNCl were also tested

whereas **4**/TBAB combination gave the maximum yield (Table 3.4, entries 11-13). It is worth stating here is that since the compound **14** is a cyclic carbonate possessing phosphorus atom within the molecule, it is expected to impart flame retardant property to the system when it is employed as an electrolyte in secondary batteries.

Table 3.4. Screening studies for the synthesis of **14**^a



Entry	Catalyst	Co-catalyst	T (°C)	Time (h)	Yield (%) ^b
1	1	-	105	3	-
2	-	TBAB	105	3	31
3	1	TBAB	60	20	42
4	1	TBAB	105	3	84
5	1	DMAP	60	20	41
6	1	DMAP	105	3	76
7	1	PPNCl	60	20	38
8	1	PPNCl	105	3	74
9	2	TBAB	105	3	59
10	3	TBAB	105	3	54
11	4	TBAB	105	5	93
12	4	DMAP	105	5	82
13	4	PPNCl	105	5	78

^aReaction condition: Epoxide **13** (1 mol), catalyst (2.5 mol%), co-catalyst (5 mol%), CO₂ (1 atm, balloon). ^bPurification by flash column chromatography.

In our work, only a few reactions (12 entries out of 48 entries from Table 3.1, 3.2 and 3.3; except the control reactions) required high temperature while the majority of the reactions proceeded within a temperature range of 30-60 °C. Though a little excess of catalyst/co-catalyst loadings (2.5 and 5.0 mol%, respectively) was required, most of the reactions were selective and proceeded at a lower temperature at one atmosphere of CO₂. It should be mentioned that there are some literature reports wherein one equivalent of ammonium salts and/or a high pressure of CO₂ was required [16-20]. The bimetallic Fe(III) complex [14] was reported to be active for both mono and disubstituted epoxides at an atmospheric pressure of CO₂, while a bimetallic Al(III) salen complex [13b] was active only for monosubstituted epoxides. However, the monometallic complexes described here were highly active for both substituted terminal and internal epoxides under mild conditions. It is interesting that all these cycloaddition reactions were carried out in a normal schlenk tube and did not require an autoclave. These facts confirm the usefulness of our catalyst in these conversion reactions. Hence, the present work adds significant improvement to the CO₂ fixation reactions.

During these reactions, glycol formation was also observed in some cases (18 out of 48 entries from Table 3.1, 3.2 and 3.3) along with cyclic carbonate in the presence of catalysts **1-3** especially at higher temperatures even at strictly anhydrous conditions. The reaction mixtures were extracted with CHCl₃ from a water workup and were purified by column chromatography to separate the cyclic carbonates and diols. However, a similar diol formation was not observed in the presence of catalyst **4** (Table 3.1, entries 21-25; Table 3.2, entries 14-17; Table 3.3, entries A1-F2).

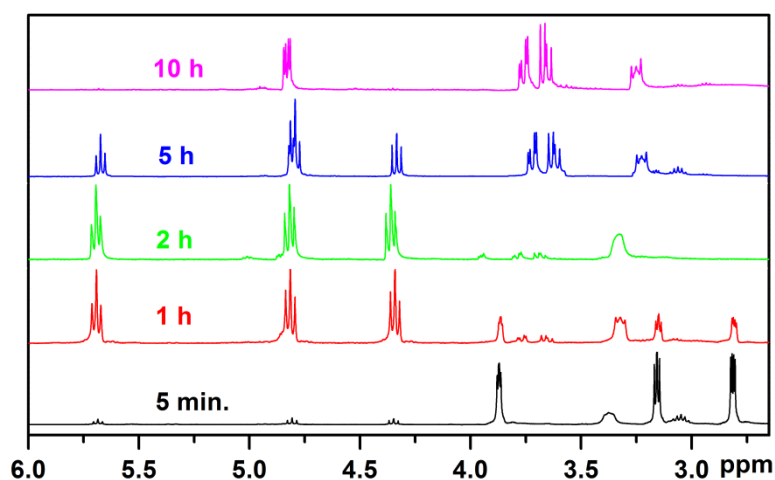


Figure 3.1. Progress of diol **10** formation monitored by ¹H NMR.

Table 3.5. Progress of diol **10** formation^a

Entry	Time	Unreacted epoxide 8 (%) by NMR	Conversion (%) by NMR		Yield (%) ^b of 10
			9	10	
1	5 min.	94	6	–	–
2	1 h	26	67	5	–
3	2 h	5	86	9	5
4	5 h	–	37	63	56
5	10 h	–	–	99	95

^aReaction condition: Epoxide **8** (1 mol), catalyst **1** (2.5 mol%), TBAB (5 mol%) under CO₂ (1 atm, balloon) at 105 °C. ^bPurification by flash column chromatography.

To further probe the formation of the diol, a set of reactions were carried out with 2-phenyloxirane **8** in the presence of catalyst **1** and TBAB under 1 atm of CO₂ at 105 °C for 5 min., 1 h, 2 h, 5 h and 10 h as independent experiments. The reaction progress was monitored using ¹H NMR spectra. The spectra are shown in Figure 3.1 and results are illustrated in Table 3.5. When the reaction was stopped at 5 min., cyclic carbonate formation was just commencing and no diol formation was observed. When the reaction was stopped at 1 h, 67% of cyclic carbonate **9** was formed from 2-phenyloxirane **8**. In the 2 h reaction, 2-phenyl oxirane **8** was almost consumed to yield cyclic carbonate **9** and 5% of diol **10** was isolated. When the reaction was performed for 5h at 105 °C, cyclic carbonate **9** gradually underwent degradation to yield diol **10** (56% isolated yield). When the reaction was prolonged to 10 h, cyclic carbonate **9** was completely converted to diol **10**. These observations showed that the diol formation was enhanced with an increase in temperature and time under these conditions. From this monitoring, it was found that diol formation was not due to epoxide cleavage but was a degradation product of cyclic carbonate. The majority of our reactions (30 out of 48 entries from Table 3.1, 3.2 and 3.3) were selective in their activity for cyclic carbonate formation. Specifically, in presence of catalyst **4**, all the reactions were selective.

The mechanism for the conversion of epoxide to cyclic carbonate in the presence of bimetallic Al(III) salen complex/TBAB was previously thoroughly examined [13d]. The decomposition of the tetraalkylammonium salts and the formation of amine carbamate salts are also well known in the literature [1c, 7g, 13d]. Though we could not isolate any intermediate species, based on earlier reports we propose a mechanism for cyclic carbonate formation in the presence of our catalyst system as follows. First, the epoxide could have

coordinated to the lewis acid **1** to form **a** which underwent epoxide ring opening by bromide ions to generate **b**. Then, the activated form of CO₂ **c** was inserted into the Zn–O bond generating species **d** followed by ring closure by backbiting to give cyclic carbonate and regenerating **1** and TBAB as shown in Figure 3.2. However, to confirm the actual mechanism, further investigations are required.

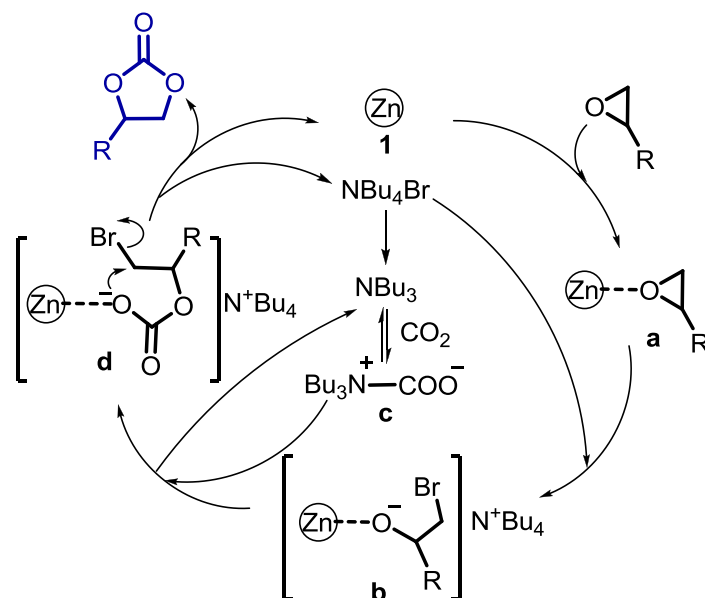


Figure 3.2. Possible cyclic carbonate formation mechanism

To check the catalyst reusability, 2-methyloxirane **11a** system was chosen. After the reaction (Table 3.3, entry A1), 4-methyl-1,3-dioxolan-2-one **12a** was distilled from the reaction mixture. 2-methyloxirane **11a** was again added to the residue and the process was repeated for 6 more times whereupon the yield started decrease from 67% to 30%. On adding TBAB (5 mol%) to the system, the yield was restored and the process was repeated 4 more times.

3.3. Conclusions

In conclusion, all the mono metallic complexes were found to be efficient for cyclic carbonate formation rather than polycarbonate under one atmosphere of pressure at a mild temperature conditions. Our catalyst systems were highly effective for the conversion of monosubstituted terminal epoxides, disubstituted terminal and internal epoxides. The corresponding cyclic carbonates were obtained with good to high yields. Among these complexes, catalysts **1** and **4** were found to be versatile.

The epoxide to cyclic carbonate conversion proceeded quickly in the presence of **1**, whereas in case of **4**, the reaction was neat and the cyclic carbonate was obtained selectively without any diol formation. Moreover, the catalysts were also selective for the conversion of *cis*-CHO to *cis*-CHC. From time dependant ^1H NMR spectral studies, the diol formation was concluded to be a degradation product of the cyclic carbonate. Catalyst usability studies showed that the catalyst was highly stable and can be recycled 10 times.

3.4. Experimental section

3.4.1. Materials and instrumentation

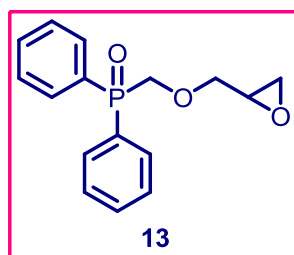
All manipulations involving air and moisture sensitive compounds were carried out using standard schlenk techniques under dry nitrogen. All solvents which were used under an inert atmosphere were thoroughly deoxygenated using a freeze-pump-thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The following drying agents were used: sodium benzophenone ketyl (diethyl ether, toluene), $\text{Mg}(\text{OMe})_2$ (methanol), P_2O_5 (triethylamine), CaCl_2 (chloroform). Epoxides **5**, **8** and **11a-f** (Aldrich) were dried prior to use by refluxing with CaH_2 for 12 h followed by distillation. The compound (diphenylphosphoryl)methanol [21] was synthesized according to the literature procedure. Tetrabutylammonium bromide (Merck) was dried at 50 °C for 4 h under vacuum.

The Structures of all the products were confirmed by IR, ^1H , ^{31}P , ^{13}C NMR and HRMS spectra. Infrared spectra were recorded on a JASCO FT/IR-5300 spectrometer using KBr pellets. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. The chemical shifts are reported in parts per million (δ) relative to tetramethylsilane as reference for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz). The $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectra referenced to 85% H_3PO_4 . Mass spectra were obtained from a Shimadzu-LCMS-2010 at an ionizing voltage of 70 eV using EI technique. HRMS spectra were recorded on a Bruker maXis instrument using ESI technique. Elemental analysis was carried out using Thermo Finnigan Flash EA 1112 analyzer.

3.4.2. Experimental procedure

Synthesis of 2-(((diphenylphosphoryl)methoxy)methyl)oxirane (13): Sodium hydride (0.10 g, 1.1 mmol) was added to a solution of (diphenylphosphoryl)methanol (0.50 g, 1 mmol) in DMAc (6.0 mL) at 0 °C under nitrogen. The mixture was stirred for 30 min. at 0

°C. To this, epichlorohydrin (0.3 mL, 2 mmol) was added drop wise. The reaction mixture was then allowed to warm to 25 °C within 1 h. After 5 h stirring, methanol (1 mL) was added and the reaction mixture was poured in to water (25 mL). The reaction mixture was neutralized with dilute HCl and extracted with ethyl acetate (30 mL × 3). The organic layer was washed with water (20 mL × 2). Solvent was evaporated to give the crude product which was purified by column chromatography on silica gel eluting with ethyl acetate/methanol (9 : 1) to give colorless liquid product **13** (Yield 82%).



^1H NMR (400 MHz, CDCl_3) : δ 2.53-2.48 (m, 1H, $-\text{OCHCH}_2$), 2.77-2.72 (m, 1H, $-\text{OCHCH}_2$), 3.12-3.07 (m, 1H, $-\text{CH}_2\text{CHCH}_2$), 3.48 (dd, $J = 11.8$ Hz and $J = 6$ Hz, 1H, $-\text{OCH}_2\text{CH}$), 3.92 (dd, $J = 11.8$ Hz and $J = 2.6$ Hz, 1H, $-\text{OCH}_2\text{CH}$), 4.33 (dd, $J = 13.3$ Hz and $J = 6.3$ Hz, 1H, $-\text{PCH}_2\text{O}$), 4.44-4.38 (m, 1H, $-\text{PCH}_2\text{O}$), 7.53-7.47 (m, 4H, $-\text{C}_6\text{H}_5$), 7.60-7.54 (m, 2H, $-\text{C}_6\text{H}_5$), 7.86-7.78 (m, 4H, $-\text{C}_6\text{H}_5$).

^{13}C NMR (100 MHz, CDCl_3) : δ 43.8 ($-\text{OCH}_2\text{CH}$), 50.5 ($-\text{CH}_2\text{CHCH}_2$), 69.6 (d, $J = 86.9$ Hz, $-\text{PCH}_2\text{O}$), 74.0 (d, $J = 9.9$ Hz, $-\text{OCH}_2\text{CH}$), 128.6 (d, $J = 11.8$ Hz, $-\text{C}_6\text{H}_5$), 130.2 ($-\text{C}_6\text{H}_5$), 131.5 (dd, $J = 9.3$ Hz and $J = 3.5$ Hz, $-\text{C}_6\text{H}_5$), 132.3 ($-\text{C}_6\text{H}_5$).

^{31}P NMR (162 MHz, CDCl_3) : δ 27.93.

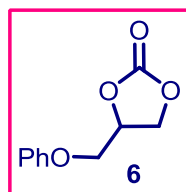
HRMS calcd. for $\text{C}_{16}\text{H}_{17}\text{O}_3\text{P}$: 311.0813 $[\text{M} + \text{Na}]^+$

Found : 311.0813.

General procedure for the synthesis of cyclic carbonate: A dry, pre-evacuated schlenk tube was filled with CO_2 . The epoxide (1 mol), catalyst (2.5 mol%) and tetrabutyl ammonium bromide (5.0 mol%) was then added and a CO_2 balloon was connected. The reaction mixture was stirred at the required temperature under CO_2 (balloon). After the reaction time, water

was poured into the reaction mixture and extracted with chloroform. The organic layer was separated and evaporated to give the crude product which was purified by flash column chromatography to yield the cyclic carbonate.

4-(Phenoxymethyl)-1,3-dioxolan-2-one (6):

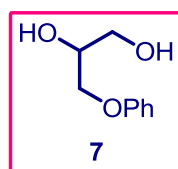


^1H NMR (400 MHz, CDCl_3) : δ 4.14 (dd, $J = 10.6$ and 3.2 Hz, 1H, PhOCH_2), 4.24 (dd, $J = 10.6$ and 3.9 Hz, 1H, PhOCH_2), 4.57–4.50 (m, 1H, OCH_2), 4.66–4.58 (m, 1H, OCH_2), 5.00–4.98 (m, 1H, CH_2), 6.91 (d, $J = 7.84$ Hz, 2H, C_6H_5), 7.02 (t, $J = 7.36$ Hz, 1H, C_6H_5), 7.31 (t, $J = 8.36$ Hz, 2H, C_6H_5).

^{13}C NMR (100 MHz, CDCl_3) : δ 66.3, 66.9, 74.1, 114.6, 122.0, 129.7, 154.7, 157.8.

m/z (EI) : 194 (M^+ , 100).

3-Phenoxypropane-1,2-diol (7):



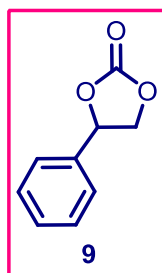
^1H NMR (400 MHz, CDCl_3) : δ 2.54 (br s, 2H, OH), 3.80–3.67 (m, 2H, OCH_2), 4.09–3.99 (m, 2H, $\text{C}_6\text{H}_5\text{OCH}_2$), 4.26–4.16 (m, 1H, CHO), 6.94–6.86 (m, 2H, C_6H_5), 6.97 (t, $J = 7.32$ Hz, 1H, C_6H_5), 7.33–7.27 (m, 2H, C_6H_5).

^{13}C NMR (100 MHz, CDCl_3) : δ 68.8, 69.2, 72.6, 114.6, 121.2, 129.5, 158.5.

m/z (EI) : 168 (M^+ , 100), 125 (20).

HRMS calcd. for $\text{C}_9\text{H}_{12}\text{O}_3$: 191.0684 [$\text{M} + \text{Na}$] $^+$

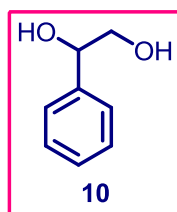
Found : 191.0684.

4-Phenyl-1,3-dioxolan-2-one (9):

^1H NMR (400 MHz, CDCl_3) : δ 4.35 (t, J = 8.0 Hz, 1H, OCH_2), 4.81 (t, J = 8.0 Hz, 1H, OCH_2), 5.68 (t, J = 8.0 Hz, 1H, PhCHO), 7.48–7.39 (m, 3H, C_6H_5), 7.39–7.32 (m, 2H, C_6H_5).

^{13}C NMR (100 MHz, CDCl_3) : δ 71.2, 78.0, 125.9, 129.3, 129.8, 135.8, 154.9.

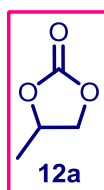
m/z (EI) : 164 (M^+ , 100), 139 (10).

1-Phenylethane-1,2-diol (10):

^1H NMR (400 MHz, CDCl_3) : δ 2.31 (br s, 2H, OH), 3.66–3.54 (m, 1H, OCH_2), 3.79–3.64 (m, 1H, OCH_2), 5.00–4.92 (m, 1H, CHO), 7.34–7.29 (m, 1H, C_6H_5), 7.43–7.34 (m, 4H, C_6H_5).

^{13}C NMR (100 MHz, CDCl_3) : δ 68.1, 74.7, 126.0, 128.0, 128.5, 140.5.

m/z (EI) : 138 (M^+ , 100), 125 (20).

4-Methyl-1,3-dioxolan-2-one (12a):

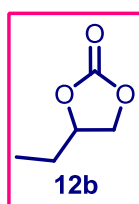
^1H NMR (400 MHz, CDCl_3) : δ 1.45 (d, $J = 6.3$ Hz, 3H, CH_3), 3.99 (dd, $J = 8.4$ and 7.2 Hz, 1H, OCH_2), 4.52 (dd, $J = 8.3$ and 7.2 Hz, 1H, OCH_2), 4.88–4.78 (m, 1H, CHO).

^{13}C NMR (100 MHz, CDCl_3) : δ 19.4, 70.7, 73.6, 155.1.

HRMS calcd. for $\text{C}_4\text{H}_6\text{O}_3$: 125.0215 $[\text{M} + \text{Na}]^+$

Found : 125.0215.

4-Ethyl-1,3-dioxolan-2-one (12b):



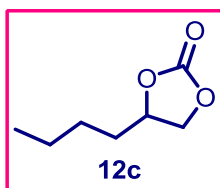
^1H NMR (400 MHz, CDCl_3) : δ 1.04 (t, $J = 7.5$ Hz, 3H, CH_3), 1.91–1.72 (m, 2H, CH_2), 4.09 (dd, $J = 8.3$ and 7.1 Hz, 1H, OCH_2), 4.53 (t, $J = 8.2$ Hz, 1H, OCH_2), 4.70–4.63 (m, 1H, CHO).

^{13}C NMR (100 MHz, CDCl_3) : δ 8.5, 27.0, 69.0, 78.0, 155.1.

HRMS calcd. for $\text{C}_5\text{H}_8\text{O}_3$: 139.0371 $[\text{M} + \text{Na}]^+$

Found : 139.0395.

4-Butyl-1,3-dioxolan-2-one (12c):



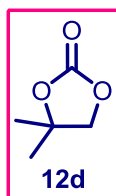
^1H NMR (400 MHz, CDCl_3) : δ 0.92 (t, $J = 6.6$ Hz, 3H, CH_3), 1.53–1.29 (m, 4H, CH_2), 1.74–1.63 (m, 1H, CH_2), 1.89–1.75 (m, 1H, CH_2), 4.07 (t, $J = 7.6$ Hz, 1H, OCH_2), 4.52 (t, $J = 8.0$ Hz, 1H, OCH_2), 4.76–4.66 (m, 1H, CHO).

^{13}C NMR (100 MHz, CDCl_3) : δ 13.8, 22.2, 26.4, 33.5, 69.4, 77.1, 155.1.

HRMS calcd. for $C_7H_{12}O_3$: 167.0684 $[M + Na]^+$

Found : 167.0696.

4,4-Dimethyl-1,3-dioxolan-2-one (12d):



^1H NMR (400 MHz, $CDCl_3$) : δ 1.52 (s, 6H, CH_3), 4.15 (s, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$) : δ 26.3, 74.0, 75.8, 155.1.

HRMS calcd. for $C_5H_8O_3$: 139.0371 $[M + Na]^+$

Found : 139.0395.

cis-4,5-Dimethyl-1,3-dioxolan-2-one (12e):



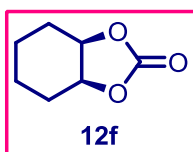
^1H NMR (400 MHz, $CDCl_3$) : δ 1.36 (d, J = 6.4 Hz, 6H, CH_3), 4.90–4.70 (m, 2H, CHO).

^{13}C NMR (100 MHz, $CDCl_3$) : δ 14.1, 76.4, 155.1.

HRMS calcd. for $C_5H_8O_3$: 139.0371 $[M + Na]^+$

Found : 139.0395.

cis-1,2-Cyclohexylene carbonate (12f):



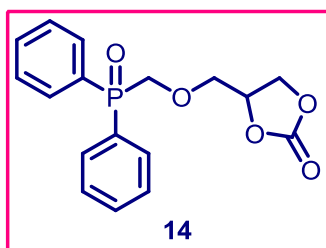
^1H NMR (400 MHz, CDCl_3) : δ 1.47–1.36 (m, 1H, CH_2), 1.68–1.56 (m, 1H, CH_2), 1.94–1.84 (m, 2H, CH_2), 4.71–4.64 (m, 1H, CHO).

^{13}C NMR (100 MHz, CDCl_3) : δ 19.2, 26.8, 75.7, 155.4.

HRMS calcd. for $\text{C}_7\text{H}_{10}\text{O}_3$: 165.0528 $[\text{M} + \text{Na}]^+$

Found : 165.0551.

4-(((diphenylphosphoryl)methoxy)methyl)-1,3-dioxolan-2-one (14):



^1H NMR (400 MHz, CDCl_3) : δ 3.78 (dd, $J = 11.1$ Hz and $J = 3.3$ Hz, 1H, - OCH_2CH), 3.89 (dd, $J = 11.1$ Hz and $J = 3$ Hz, 1H, - OCH_2CH), 4.13 (dd, $J = 8.4$ Hz and $J = 5.8$ Hz, 1H, - OCH_2CH), 4.27 (dd, $J = 13.4$ Hz and $J = 6.5$ Hz, 1H, - PCH_2O), 4.34 (d, $J = 8.4$ Hz, 1H, - OCH_2CH), 4.39 (dd, $J = 13.4$ Hz and $J = 3.9$ Hz, 1H, - PCH_2O), 4.78-4.71 (m, 1H, - CH_2CHCH_2), 7.52-7.45 (m, 4H, - C_6H_5), 7.59-7.53 (m, 2H, - C_6H_5), 7.80-7.71 (m, 4H, - C_6H_5).

^{13}C NMR (100 MHz, CDCl_3) : δ 65.8 (- OCH_2CH), 69.8 (d, $J = 84.9$ Hz, - PCH_2O), 72.3 (d, $J = 8.7$ Hz, - OCH_2CH), 74.7 (- CH_2CHCH_2), 129-128.6 (m, - C_6H_5), 130.1 (dd, $J = 99.8$ Hz and $J = 14$ Hz, - C_6H_5), 131.5-131 (m, - C_6H_5), 132.6 (d, $J = 5.1$ Hz, - C_6H_5), 154.7 (- OCO).

^{31}P NMR (162 MHz, CDCl_3) : δ 28.29.

HRMS calcd. for $\text{C}_{17}\text{H}_{17}\text{O}_5\text{P}$: 355.0711 $[\text{M} + \text{Na}]^+$

Found : 355.0712.

Supporting information: ^1H and ^{13}C NMR spectra of **6**, **7** and **14**; ^{31}P NMR spectrum of **14** are included at the end of this chapter (Figure 3.S1 - 3.S7).

3.5. References

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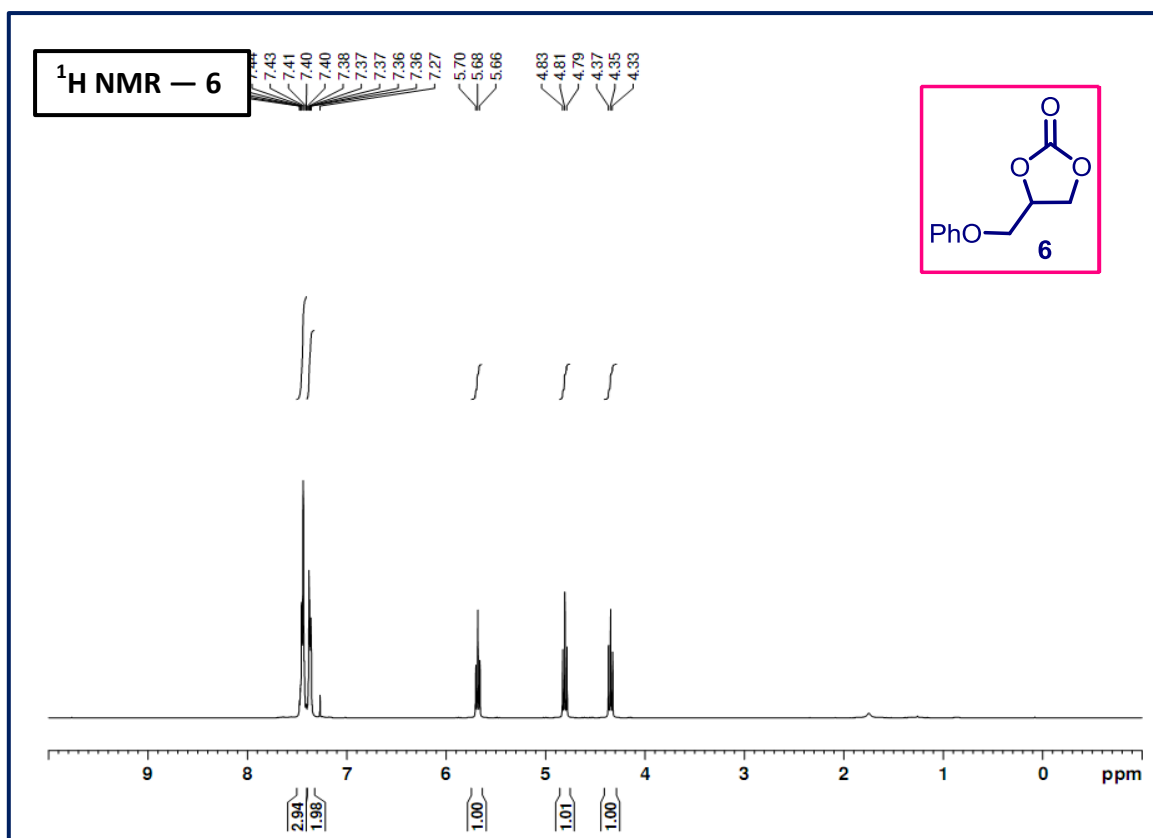


Figure 3.S1. ^1H NMR spectrum of compound **6**

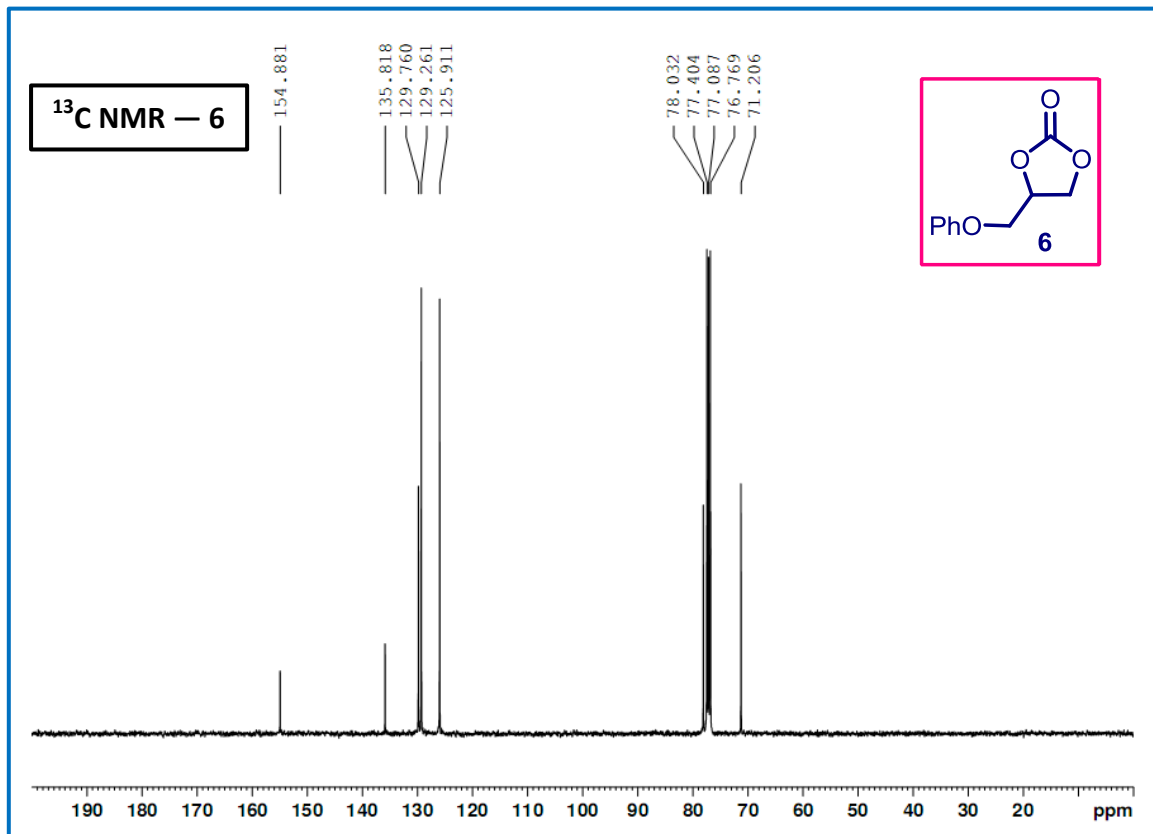
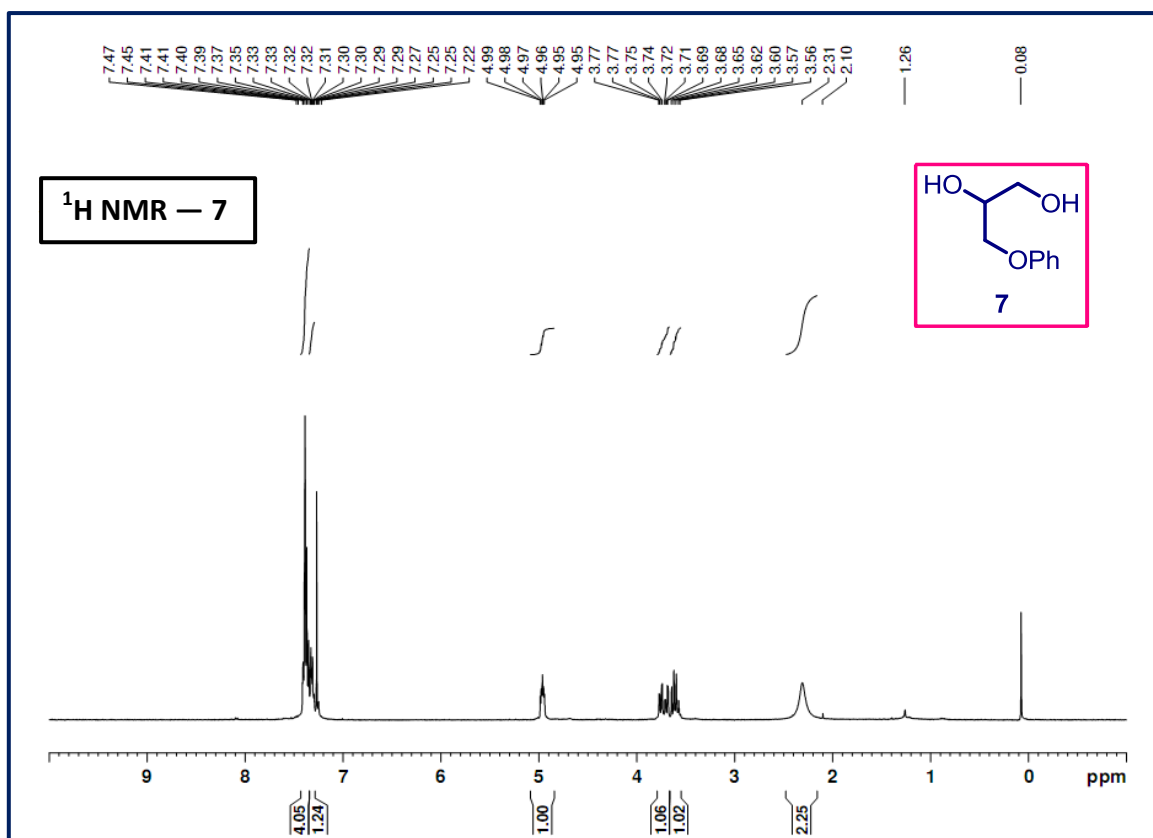
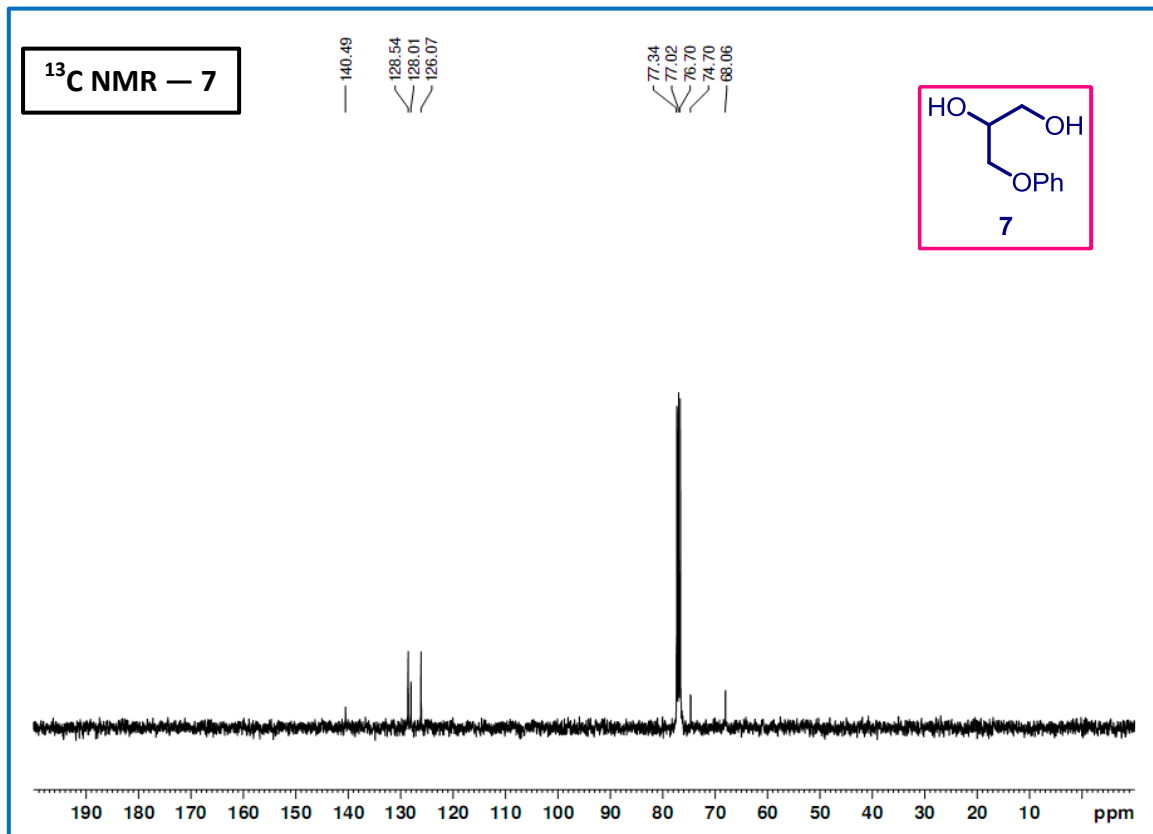


Figure 3.S2. ^{13}C NMR spectrum of compound **6**

Figure 3.S3. ^1H NMR spectrum of compound 7Figure 3.S4. ^{13}C NMR spectrum of compound 7

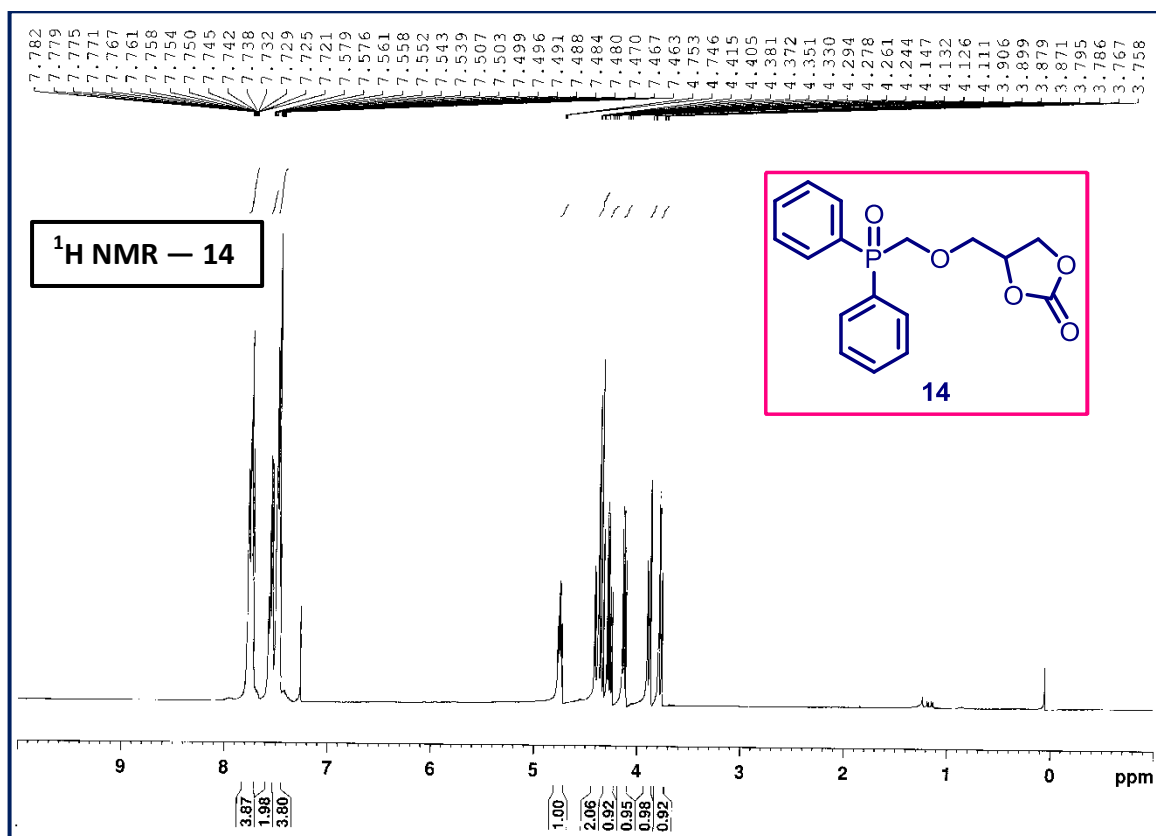


Figure 3.S5. ¹H NMR spectrum of compound 14

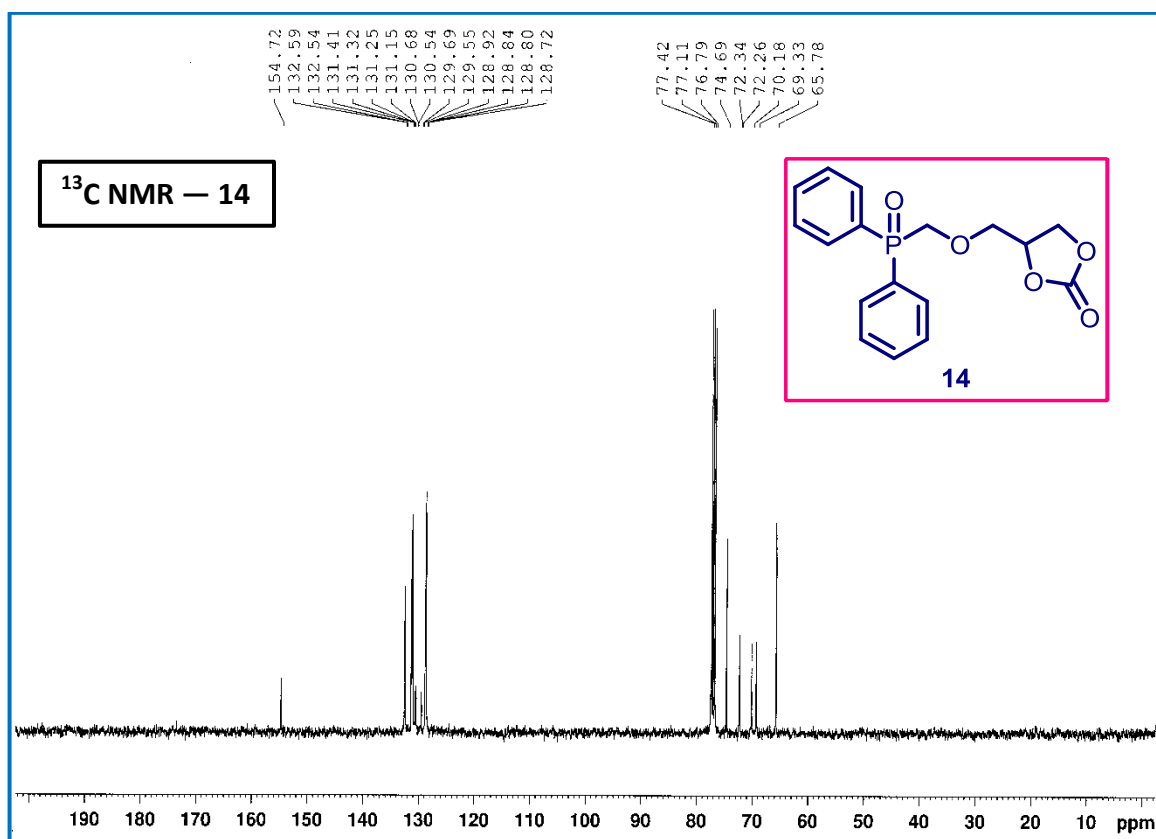


Figure 3.S6. ¹³C NMR spectrum of compound 14

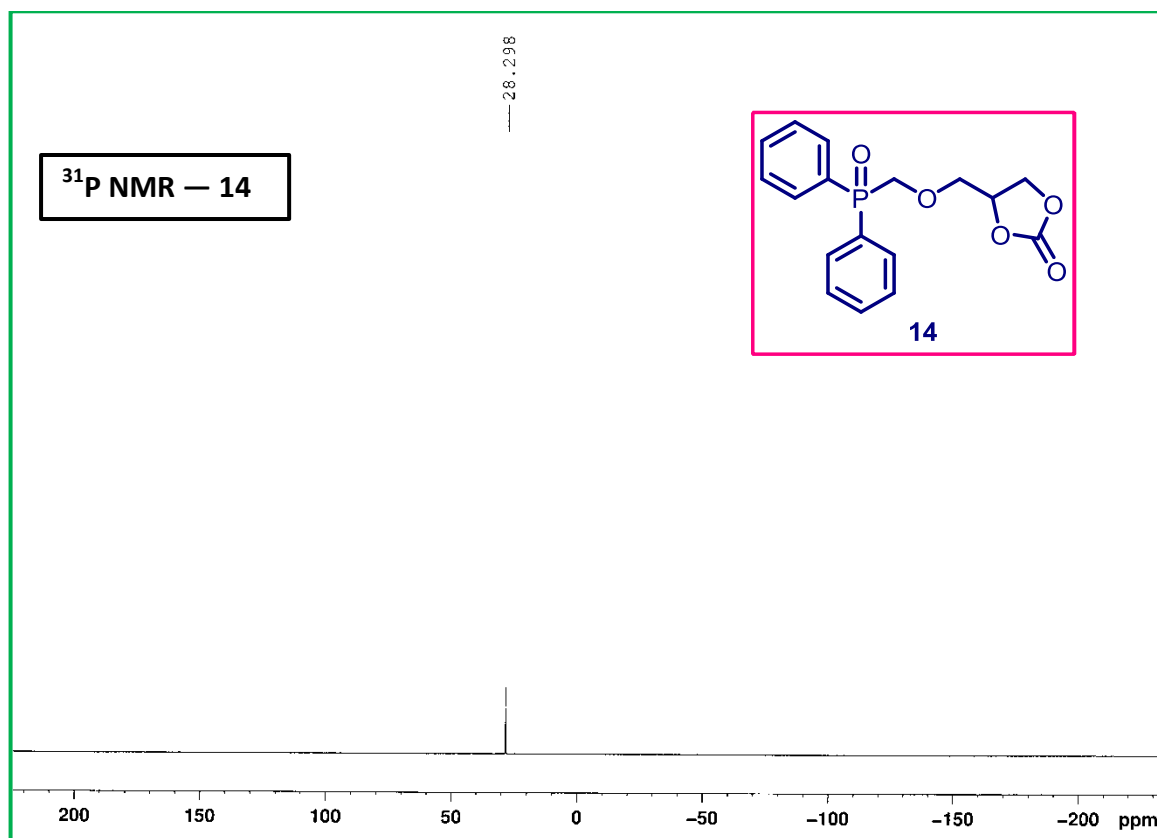


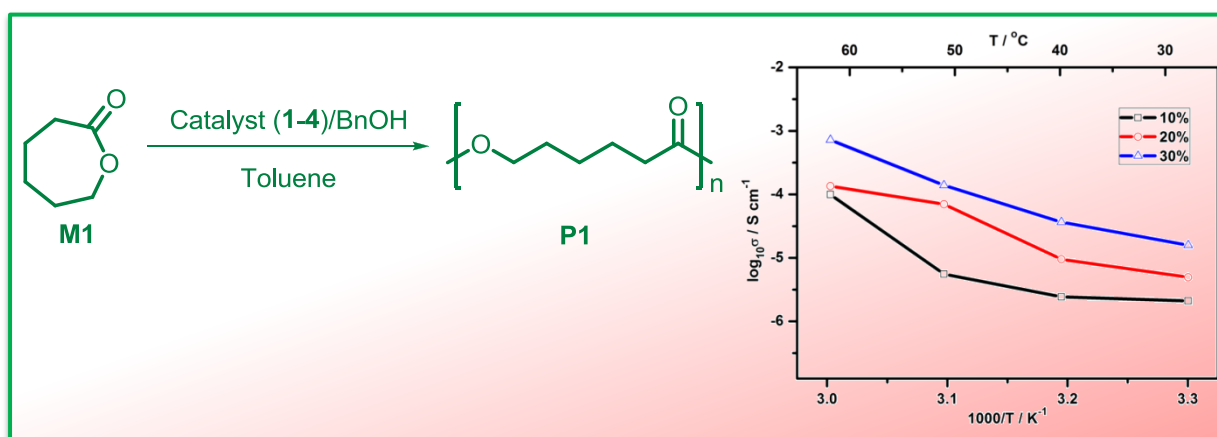
Figure 3.S7. ³¹P NMR spectrum of compound **14**

CHAPTER 4

Versatile Metal Complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole for Ring Opening Polymerization of ϵ -caprolactone

Abstract

This chapter describes the catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) for ring opening polymerization (ROP) of ϵ -caprolactone (**M1**). The ROP of **M1** was investigated in the presence and absence of benzyl alcohol (BnOH). All these complexes were active for ROP of **M1** under mild temperature. In particular, the complexes **1** and **4** exhibited remarkable catalytic activity for ROP of **M1** at 25 °C in toluene in the presence of BnOH. The ROP of **M1** catalysed by **1** and **4** complexes, not only proceeded through living polymerization but also immortal. Further, the synthesized polycaprolactone (**P1**) was examined for lithium-ion conductivity by preparing solid polymer electrolyte (SPE1) using lithium bis(trifluoromethanesulfonyl)imide (LiTFSI). The conductivity of **SPE1** with 30 wt% of LiTFSI was $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $7.2 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C.



4.1. Introduction

The increasing environmental issues compel to replace existing materials and use eco-friendly materials [1]. There is a growing interest in finding a highly ionic conductive solid polymer electrolyte (SPE) with biodegradable properties to replace organic solvents in high-energy density lithium-ion batteries [2]. Many strategies have been deployed to increase Li-ion conductivity of polymers. Few examples are; addition of a plasticizer to polymer matrix forming a gel polymer electrolyte; addition of fillers to polymer matrix forming a nanocomposite; designing new polymeric matrices by synthetic processes or modifying existing polymer-salt complexes [3]. Several biodegradable polymers such as cellulose, starch, chitosan and poly(vinyl alcohol) have been studied as polymer electrolytes [4].

Over past two decades, huge interests are in producing biodegradable and biocompatible materials using renewable resources such as CO₂ and carbohydrates [5]. For example, cyclic and polycarbonates are synthesized by epoxide-CO₂ coupling reactions [6]. Likewise, poly(ϵ -caprolactone) (**P1**) and polylactide (PLA) are prepared by ROP of ϵ -caprolactone (**M1**) and lactide (LA) respectively. The **M1** and LA can be produced from carbohydrates - D-fructose and starch respectively [7]. Cyclic and polycarbonates are used as electrolytes, aprotic polar solvents, packaging materials and exterior thermoplastics for engineering parts [8]. Because of the biocompatibility, **P1** is used in pharmaceutical and biomedical fields, especially as scaffolds in tissue engineering and drug delivery and used as packaging material [9]. Therefore, it is necessary to control the properties of **P1** for a wide utility.

The unique properties of **P1** like aliphatic thermoplastic, biocompatible, permeable, hydrophobic, non-toxic for living organisms, natural degradation, mechanically stable and flexible, makes an ideal host material for solid polymer electrolyte. **P1** can act as host polymer for lithium-ion conduction because it contains a Lewis base (ester oxygen) that can coordinate lithium-ions [10]. Since the glass transition temperature (T_g , -60 °C) of **P1** is as like polyethylene oxide (PEO), the polymer chain would exhibit segmental motion, enabling the ions to easily hop from one complexation site to another [11]. A few attempts have been made to use **P1** as polymer host for polymer-salt electrolyte systems [12]. We are interested to study the conductivity behaviour of **P1**-LiTFSI blend systems.

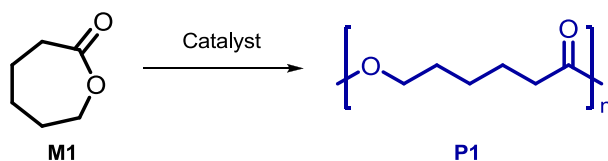
It has been proved that the synthesis of **P1** by a ROP provide good polymer properties like molecular weight, polydispersity index (PDI), and microstructure rather than through a

condensation polymerization [13]. In recent years, the ROP of ϵ -caprolactone (**M1**) is performed in the presence of metal catalysts/initiators, organocatalysts or enzymes. In this chapter, the catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP2pyr)H (**1-4**) for ROP of **M1** is described. We have also studied the conductivity behavior of **P1** produced from these reactions.

4.2. Results and discussion

4.2.1. Ring opening polymerization

The ligands having only nitrogen donors exhibited better catalytic activity for ROP than the ligands with both nitrogen and oxygen donors [5a]. The metal complexes **1-4** comprising pyrrolyl ligands produced in our lab have only nitrogen as donating atoms. Therefore, we explored the catalytic activities of complexes **1-4** for ROP of **M1** under various conditions for a detailed study. We have carried out the ROP in two different methods, viz., bulk polymerization (BP-ROP) and solution polymerization (SP-ROP).



Scheme 4.1. ROP of ϵ -caprolactone (**M1**)

4.2.2. Bulk and solution phase ring opening polymerization (BP-ROP and SP-ROP)

First, we examined the ROP of **M1** using **1** as a catalyst without alcohol as initiator and solvent (BP-ROP) (Scheme 4.1). The Table 4.1 illustrates results of these reactions. By varying catalyst loading, temperature and time, the reaction conditions were optimized to achieve good yield and higher molecular weight with narrow PDI (Table 4.1, entries 1-7). Among different catalyst loadings tried (Table 4.1, entries 1-5), the ratio 100:1 ($[\mathbf{M1}]_0:[\mathbf{C}]_0$) yielded a polymer with moderate properties (Table 4.1, entry 3). The BP-ROP of **M1** was also examined using catalysts **2**, **3** and **4** at different temperatures in neat conditions (Table 4.1, entries 8-16). The reaction proceeded faster in the presence of **1** than other catalysts (**2-4**) as noted. The SP-ROP of **M1** was also carried out in toluene in the presence of **1-4** (but without alcohol) at different temperatures (Table 4.2). Few reactions performed by varying catalyst loadings (Table 4.2, entries 1-5) of **1**, and also changing the catalysts to **2-4** (Table 4.2, entries 7-12). Conversion in SP-ROP was roughly equal to that in BP-ROP (Table 4.1).

But, the PDI became narrower while performing the reaction in a solvent (Table 4.2). Based on the data listed in Table 4.1 and 4.2, the catalytic activity of complexes for BP-ROP and SP-ROP followed the order **1>4>3>2**.

Table 4.1. Optimization studies for BP-ROP of **M1**^a

Entry	Catalyst (C)	[M1] ₀ : [C] ₀	T (°C)	Time (h)	Conversion (%) ^b	M _n (kg mol ⁻¹) (exp) ^c	M _n (kg mol ⁻¹) (theo) ^d	PDI ^e
1	1	100:0.1	25	8	8	10.0	9.1	1.32
2	1	100:0.5	25	8	24	6.4	5.5	1.27
3	1	100:1	25	8	71	10.4	8.1	1.30
4	1	100:1.5	25	8	73	6.1	5.6	1.28
5	1	100:2	25	8	78	5.2	4.5	1.26
6	1	100:1	60	5	82	10.9	9.4	1.32
7	1	100:1	100	2	89	11.6	10.2	1.38
8	2	100:1	25	8	57	7.8	6.5	1.43
9	2	100:1	60	5	66	9.0	7.5	1.51
10	2	100:1	100	2	69	8.9	7.9	1.56
11	3	100:1	25	8	60	7.9	6.8	1.39
12	3	100:1	60	5	71	9.7	8.1	1.45
13	3	100:1	100	2	75	9.8	8.6	1.48
14	4	100:1	25	8	62	7.8	7.1	1.35
15	4	100:1	60	5	74	9.8	8.4	1.42
16	4	100:1	100	2	77	9.8	8.7	1.46

^aReaction condition: reactions were carried out in neat condition (without solvent).

^bObtained from ¹H NMR. ^cMolecular weight measured by GPC and calibrated against polystyrene standard. ^dCalculated from $([M1]_0/[C]_0) \times 114.14 \times \text{conversion}$. ^eObtained from GPC analysis.

Table 4.2. Optimization studies for SP-ROP of **M1**^a

Entry	Catalyst (C)	[M1] ₀ : [C] ₀	T (°C)	Time (h)	Conversion (%) ^b	M _n (kg mol ⁻¹) (exp) ^c	M _n (kg mol ⁻¹) (theo) ^d	PDI ^e
1	1	100:0.1	25	8	7	8.7	7.9	1.29
2	1	100:0.5	25	8	22	5.8	5.0	1.18
3	1	100:1	25	8	69	8.6	7.8	1.15
4	1	100:1.5	25	8	72	5.9	5.4	1.14
5	1	100:2	25	8	78	5.0	4.4	1.14
6	1	100:1	60	5	84	9.8	9.5	1.18
7	2	100:1	25	8	54	6.9	6.1	1.24
8	2	100:1	60	5	71	9.0	8.1	1.28
9	3	100:1	25	8	59	7.5	6.7	1.21
10	3	100:1	60	5	76	9.8	8.6	1.26
11	4	100:1	25	8	60	7.1	6.8	1.18
12	4	100:1	60	5	79	9.8	9.0	1.24

^aReaction condition: reactions were carried out in toluene, [M1]₀ = 0.5 M. ^bObtained from

¹H NMR. ^cMolecular weight measured by GPC and calibrated against polystyrene standard.

^dCalculated from ([M1]₀/[C]₀) × 114.14 × conversion. ^eObtained from GPC analysis

4.2.3. Significance of alcohols as initiator

It is also important to probe the role of alcohol in ROP because a closer look in literature showed an alcohol is used as initiator in various occasions. To understand the significance of alcohol as initiator, we conducted ROPs in the presence of various alcohols using **1** or **4** at 25 °C (Table 4.3). The rate of SP-ROP in toluene initiated by benzyl alcohol (BnOH) and catalysed by **1** was remarkably high even at 25 °C (Table 4.3, entry 5). The reaction proceeded in a controlled manner and achieved good control in PDI (1.12) with improved molecular weight of produced polymers. In the presence of EtOH, good conversion achieved whereas lesser control in molecular weight distribution noted. However, *i*-PrOH yielded polymers with similar conversion rate but with narrow PDI. Because of steric hindrance and lesser nucleophilicity of *t*-BuOH, lesser conversion rate for **M1** to polymer witnessed. The trend implied that the ROP was accelerated by an alcohol having more nucleophilic character

and moderate steric feature. These results encouraged us to perform BP-ROP and SP-ROP in the presence of BnOH for a detailed study.

Table 4.3. SP-ROP of **M1** in presence of various initiators^a

Entry	Catalyst (C)	Initiator (I)	Conversion (%) ^b	M_n (kg mol ⁻¹) (exp) ^c	M_n (kg mol ⁻¹) (theo) ^d	PDI ^e
1	1	MeOH	74	9.0	8.4	1.23
2	1	EtOH	89	10.9	10.1	1.30
3	1	<i>i</i> -PrOH	87	10.3	9.9	1.15
4	1	<i>t</i> -BuOH	68	8.7	7.7	1.29
5	1	BnOH	98	11.9	11.1	1.12
6	4	MeOH	54	6.8	6.1	1.21
7	4	EtOH	71	9.7	8.1	1.28
8	4	<i>i</i> -PrOH	70	8.4	7.9	1.20
9	4	<i>t</i> -BuOH	52	6.9	5.9	1.27
10	4	BnOH	80	9.9	9.3	1.19

^aReaction condition: $[M1]_0:[C]_0:[ROH]_0 = 100:1:1$ in toluene at 25 °C for 6 h. $[M1]_0 = 0.5$ M. ^bObtained from ¹H NMR. ^cMolecular weight measured by GPC and calibrated against polystyrene standard. ^dCalculated from $([M1]_0/[C]_0) \times 114.14 \times \text{conversion}$. ^eObtained from GPC analysis.

4.2.4. Effect of BnOH in BP-ROP and SP-ROP

First, the BP-ROP of **M1** was tested using BnOH as initiator at different temperatures using **1-4** (Table 4.4). The molar ratio of $[M1]_0:[C]_0:[BnOH]_0$ used for reactions was varied and optimized as 100:1:1 (Table 4.4, entries 1-5). When BP-ROP was performed without BnOH, the PDI of resulting polymers were broad (Table 4.1). But, the reactions initiated by BnOH progressed much faster and yielded polymers with fairly narrow PDI (Table 4.4). The catalysts **1-4** are soluble in **M1** that promoted for increased rate of reactions and good conversions even in neat condition. Despite higher reaction temperatures (60 and 100 °C), PDI of resulting polymers was within narrow range probably because of minimum intermolecular and intramolecular transesterification reactions. This represented the steric hindrance around the metal center plays an important role in ROP by preventing chain

aggregation/transfer. So the reactions maintained selectivity at higher temperatures also. Thus, bulky groups were not only helpful to protect metal center but also in controlling PDI.

Table 4.4. Optimization studies for BP-ROP of **M1** in the presence of BnOH^a

Entry	Catalyst (C)	[M1] ₀ : [C] ₀ : [BnOH] ₀	T (°C)	Time (h)	Conversion (%) ^b	M _n (kg mol ⁻¹) (exp) ^c	M _n (kg mol ⁻¹) (theo) ^d	PDI ^e
1	1	100:0.1:0.1	25	6	8	10.0	9.1	1.24
2	1	100:0.5:0.5	25	6	31	7.9	7.0	1.21
3	1	100:1:1	25	6	94	10.9	10.7	1.19
4	1	100:1.5:1.5	25	6	95	8.0	7.2	1.18
5	1	100:2:2	25	6	95	5.8	5.4	1.16
6	1	100:1:1	60	3	90	10.8	10.2	1.23
7	1	100:1:1	100	2	92	11.2	10.5	1.29
8	2	100:1:1	25	6	78	9.3	8.9	1.20
9	2	100:1:1	60	3	80	10.0	9.1	1.25
10	2	100:1:1	100	2	75	9.9	8.5	1.31
11	3	100:1:1	25	6	71	9.0	8.1	1.22
12	3	100:1:1	60	3	76	9.1	8.6	1.26
13	3	100:1:1	100	2	73	9.0	8.3	1.33
14	4	100:1:1	25	6	83	10.5	9.4	1.20
15	4	100:1:1	60	3	81	9.7	9.2	1.24
16	4	100:1:1	100	2	78	9.4	8.9	1.29

^aReaction condition: reactions were carried out in neat condition (without solvent).

^bObtained from ¹H NMR. ^cMolecular weight measured by GPC and calibrated against polystyrene standard. ^dCalculated from ([**M1**]₀/[C]₀) × 114.14 × conversion. ^eObtained from GPC analysis.

The SP-ROP of **M1** in toluene in the presence of BnOH and **1-4** was examined at different temperatures. The results (Table 4.5) revealed the polymerization initiated by BnOH progressed rapidly in toluene and achieved maximum conversion with excellent control in PDI. In the presence of BnOH, efficiency of complexes in catalysing BP-ROP and SP-ROP of **M1** is in the order **1**>**4**>**2**>**3** which is different from reactions conducted without BnOH. Without initiator, the complex **3** displayed better conversion than the complex **2**. This is

because the complex **3** have a solvent molecule methanol within structure which probably acted as an initiator speeding up reaction rate. With initiator, the complex **2** achieved more conversion than the complex **3**. In BP-ROP and SP-ROP conducted in the presence of BnOH and **3**, it seems a competition between methanol and BnOH to initiate the reaction impeded the reaction rate.

Table 4.5. Optimization studies for SP-ROP of **M1** in the presence of BnOH^a

Entry	Catalyst (C)	[M1] ₀ : [C] ₀ : [BnOH] ₀	T (°C)	Time (h)	Conversion (%) ^b	M _n (kg mol ⁻¹) (exp) ^c	M _n (kg mol ⁻¹) (theo) ^d	PDI ^e
1	1	100:0.1:0.1	25	6	9	11.0	10.2	1.19
2	1	100:0.5:0.5	25	6	41	10.0	9.3	1.14
3	1	100:1:1	25	6	98	11.9	11.1	1.12
4	1	100:1.5:1.5	25	6	98	7.8	7.4	1.12
5	1	100:2:2	25	6	98	5.9	5.5	1.10
6	1	100:1:1	60	3	98	12.1	11.1	1.14
7	2	100:1:1	25	6	64	7.9	7.3	1.19
8	2	100:1:1	60	5	76	9.2	8.6	1.20
9	3	100:1:1	25	6	57	7.9	6.5	1.21
10	3	100:1:1	60	5	65	8.5	7.4	1.24
11	4	100:1:1	25	6	80	9.9	9.3	1.19
12	4	100:1:1	25	9	95	11.4	10.8	1.19
13	4	100:1:1	60	5	85	9.6	9.7	1.16

^aReaction condition: reactions were carried out in toluene, [**M1**]₀ = 0.5 M. ^bObtained from

¹H NMR. ^cMolecular weight measured by GPC and calibrated against polystyrene standard.

^dCalculated from ($[\mathbf{M1}]_0/[\mathbf{C}]_0 \times 114.14 \times \text{conversion}$). ^eObtained from GPC analysis.

Table 4.6. Results of living and immortal SP-ROP of **M1**^a

Entry	Catalyst (C)	[M1] ₀ : [C] ₀ : [BnOH] ₀	Conversion (%) ^b	M _n (kg mol ⁻¹) (exp) ^c	M _n (kg mol ⁻¹) (theo) ^d	PDI ^e
1	1	200:1:1	86	20.1	19.6	1.15
2	1	300:1:1	81	29.6	27.7	1.18
3	1	400:1:1	74	34.0	33.7	1.20
4	4	200:1:1	82	19.8	18.7	1.22
5	4	300:1:1	73	26.2	24.9	1.25
6	4	400:1:1	68	32.8	31.0	1.29
7	1	100:1:2	97	6.0	5.5	1.12
8	1	100:1:4	98	2.9	2.7	1.08
9	1	100:1:6	98	2.1	1.8	1.06
10	4	100:1:2	93	5.7	5.3	1.16
11	4	100:1:4	94	2.8	2.6	1.12
12	4	100:1:6	95	1.9	1.8	1.10

^aReaction condition: reactions were carried out in toluene at 25 °C either for 6 h (**1**) or 9 h (**4**), [M1]₀ = 0.5 M. ^bObtained from ¹H NMR. ^cMolecular weight measured by GPC and calibrated against polystyrene standard. ^dCalculated from ([M1]₀/[C]₀) × 114.14 × conversion or ([M1]₀/[BnOH]₀) × 114.14 × conversion. ^eObtained from GPC analysis.

4.2.5. Mechanism of SP-ROP

For all polymers, the molecular weight [M_n(exp)] measured by GPC matched well with the molecular weight [M_n(theo)] calculated from initial monomer/catalyst ratio. Also, their PDIs were in narrow range. These observations exposed the control in ROP and the nature of catalysis is single site catalysis. Complexes **1** and **4** were utilized for studying the mechanism of polymerization since they showed good catalysis yielding polymers with narrow PDI. To understand the order of ROP, reactions were monitored with time in the presence of either **1** or **4** and BnOH at 25 °C. Semi logarithmic plot of ln[M1]₀/[M1]_t versus time revealed linearity proving the first order dependence of polymerization on monomer concentration (Figure 4.1).

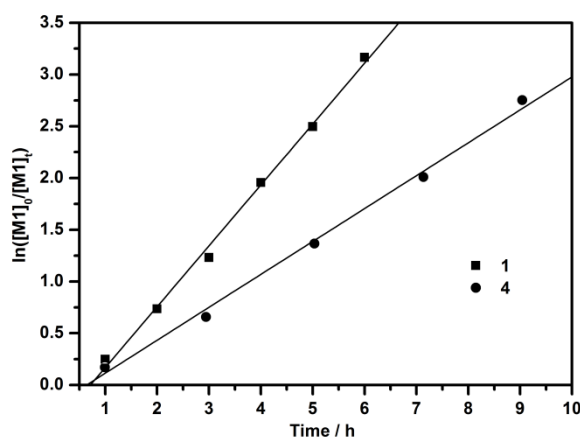


Figure 4.1. Plot of $\ln([M1]_0/[M1]_t)$ versus time for the polymerization of **M1** catalysed by **1** and **4** in presence of BnOH. Reaction condition: $[M1]_0:[C]_0:[BnOH]_0 = 100:1:1$ in toluene at 25 °C, $[M1]_0 = 0.5$ M.

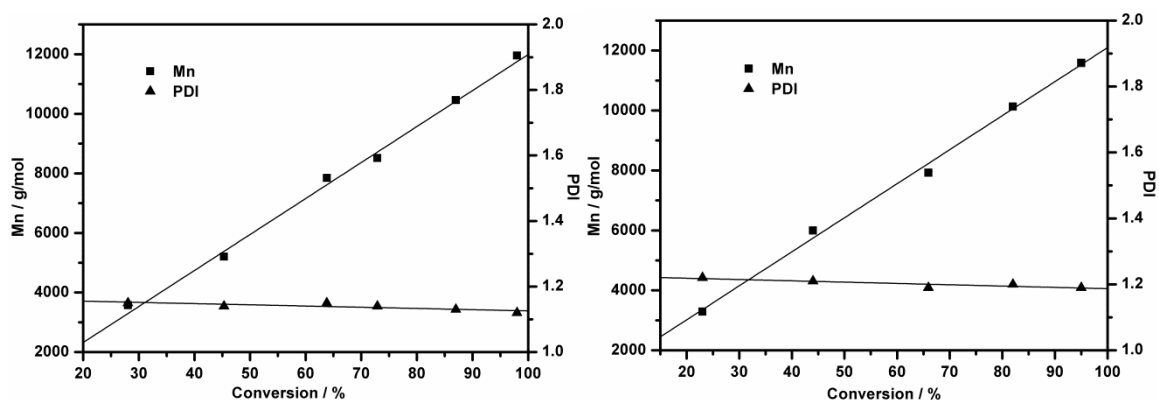


Figure 4.2. Plot of molecular weight (M_n) and polydispersity (PDI) versus monomer conversion for the ROP of **M1** catalysed by **1** (left) and **4** (right) in presence of BnOH. Reaction condition: $[M1]_0:[C]_0:[BnOH]_0 = 100:1:1$ in toluene at 25 °C, $[M1]_0 = 0.5$ M.

Few reactions were conducted to check the living character of polymerization by changing **M1**/C molar ratios (Table 4.5, entries 3 and 12; Table 4.6, entries 1-6). Increasing **M1**/C molar ratio increased the molecular weights of resultant polymers but the polymers were obtained with narrower PDI (in the presence of **1**, PDI = 1.12-1.20; in the presence of **4**, PDI = 1.19-1.29). Further, the molecular weights of resultant polymers were increased linearly with increasing monomer conversion which inferred that the polymerization proceeded through a living polymerization manner (Figure 4.2). The living polymerization behaviour was further confirmed from the linear relationship of molecular weight with the initial monomer/catalyst ratio $[M1]_0/[C]_0$ (Figure 4.3).

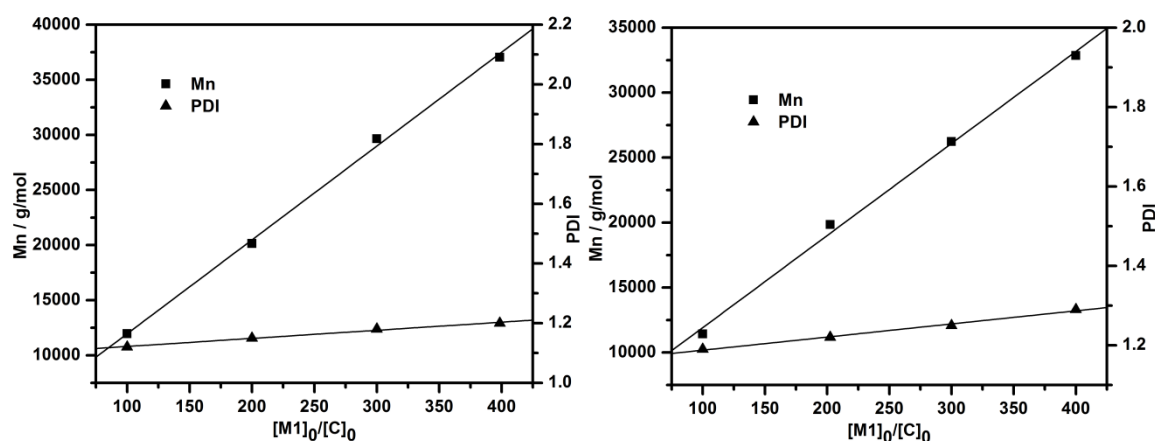


Figure 4.3. Plot of molecular weight (M_n) and polydispersity (PDI) versus $[M1]_0/[C]_0$ for the ROP of **M1** catalysed by **1** (left) and **4** (right) in presence of BnOH. Reaction condition: $[M1]_0:[C]_0:[BnOH]_0 = 100:1:1$ in toluene at 25 °C, $[M1]_0 = 0.5$ M.

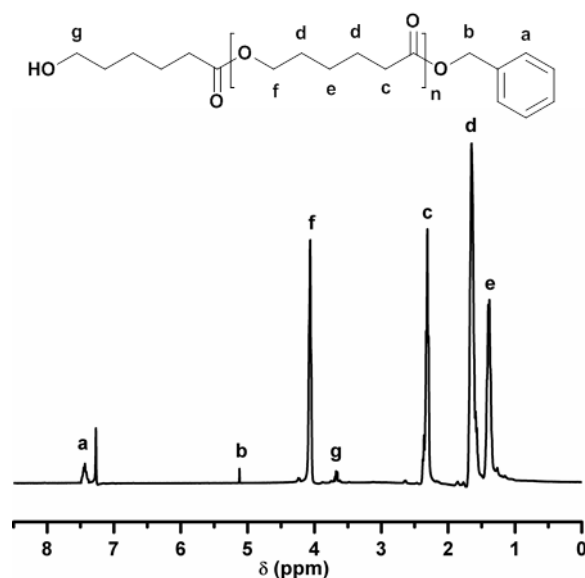


Figure 4.4. ^1H NMR spectrum of **P1**. Reaction condition: $[M1]_0:[C]_0:[BnOH]_0 = 100:1:1$ in toluene at 25 °C, 6 h, $[M1]_0 = 0.5$ M.

The ROP was examined by varying **M1**/BnOH molar ratios ($[M1]_0/[BnOH]_0$) in the presence of **1** or **4** (Table 4.5, entries 3 and 12; Table 4.6, entries 7-12). The decreasing $[M1]_0/[BnOH]_0$ ratio decreased the molecular weights of polymers and there were obtained with narrow PDI. These studies revealed the immortal character of ROP of **M1**. The ROP in the presence of **1** using BnOH and toluene was progressing by coordination-insertion mechanism. The ^1H NMR spectrum of **P1** is shown in Figure 4.4. The presence of phenyl ring protons (**a**, 7.37 ppm) and CH_2 (**b**, 5.12 ppm) signal of BnO group suggested that the polymerization was initiated by the insertion of BnO group to **M1**.

4.2.6. Solid polymer electrolyte

Solid polymer electrolytes (**SPE1**) were prepared by dissolving **P1** and varying amounts (10 wt%, 20 wt%, 30 wt% and 40 wt%) of lithium bis(trifluoromethanesulfonyl)imide (LiTFSI) in THF. After evaporating and drying the reaction mixture, the residues were made into pellets for conductivity measurements. To understand the thermal properties, TG and DSC analyses on the solid electrolytes were performed.

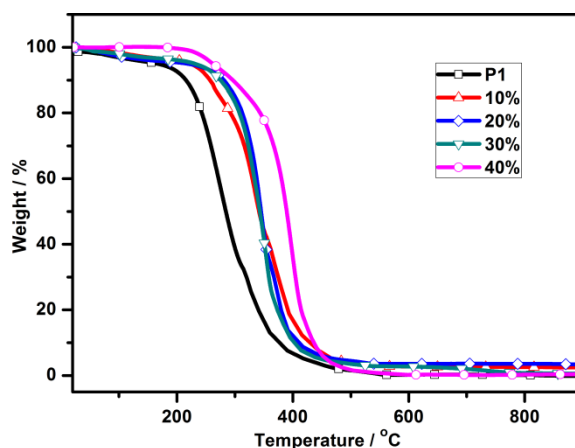


Figure 4.5. TGA plots of **P1** and **SPE1** (10%-40%)

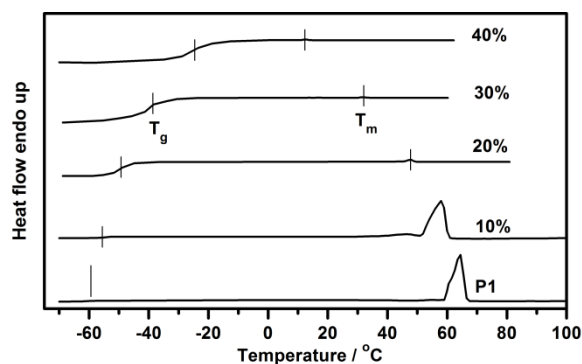


Figure 4.6. DSC plots of **P1** and **SPE1** (10%-40%)

Table 4.7. Properties of **P1** and **SPE1** (10%-40%)

SPE1 (wt% of LiTFSI)	O : Li	conductivity , σ (S cm ⁻¹)		T _d (°C)	T _g (°C)	T _m (°C)	ΔH_m (J g ⁻¹)	χ_c (%)
		30 °C	60 °C					
P1	-	1.5×10^{-11}	-	215.2	-60.0	64.1	83.8	60.1
10%	22.7:1	2.1×10^{-6}	9.9×10^{-5}	238.2	-55.3	57.9	40.3	28.7
20%	10.0:1	4.9×10^{-6}	3.6×10^{-5}	250.1	-49.2	47.9	17.8	12.8
30%	5.9:1	1.6×10^{-5}	7.2×10^{-4}	263.4	-38.1	31.8	11.9	8.5
40%	3.8:1	-	-	277.8	-24.5	12.7	2.1	1.5

4.2.7. Thermal studies

The DSC analysis of **P1** exhibits two transitions (Figure 4.6): (1) a glass transition temperature (T_g) at $-60\text{ }^{\circ}\text{C}$ corresponding to amorphous parts of **P1** (T_g is not visible in Figure 4.6 but can be able to see in magnified thermogram); (2) a melting temperature (T_m) for the crystalline parts of **P1** at $64.1\text{ }^{\circ}\text{C}$. The TGA analyses on **SPE1** with 10 wt% - 40 wt% of LiTFSI [**SPE1** (10%-40%)] revealed increase in the thermal stabilities compared with **P1** (Figure 4.5 and Table 4.7). The glass transition temperatures (T_g) and melting temperatures (T_m) of **SPE1** (10%-40%) determined through DSC analyses are shown in Table 4.7. As seen in DSC plots, there were increase in T_g of **SPE1** (10%-40%) compared with their respective polymer. The increased T_d and T_g is attributed to the coordination of heteroatoms present in the polymer with lithium-ions. Because of the coordination of polymer chains with lithium ions, segmental motion of the polymer chain was restricted. Obviously, increasing the salt concentration would increase more coordination with polymer chains and more control on the segmental motion of the chains leading increased T_g . Similarly, the increased T_d of **SPE1** (10%-40%) compared to **P1** is owing to polymer-lithium ion interactions. So, it needs more energy to break the coordination bonds at first followed by to break the polymer chains.

The T_g of **SPE1** (10%-40%) increases continuously from $-55\text{ }^{\circ}\text{C}$ to $-24\text{ }^{\circ}\text{C}$ while increasing the lithium salt content from 10 wt% of LiTFSI (10%) to 40% respectively (Table 4.7). Based on the following observations from DSC analyses, we concluded LiTFSI is completely miscible in **P1** and affords a homogeneous amorphous phase: (a) absence of peaks matching the melting temperature (T_m) of lithium salt; (b) a single T_g ; (c) increase in T_g with the addition of lithium salt. The absence of melting point of salts might because of solvation of lithium-ions by polymers. The possibility of polymer chain coordination with lithium ion would facilitate the solvation. It is worth to mention here that the T_g of **P1**/LiClO₄ [12a] reached the maximum at 25 wt% of LiClO₄ and started to decrease with further addition of LiClO₄. This is due to the repulsion between free anions and/or ion aggregation. In contrast, even when the salt content is as high as 40%, T_g of **SPE1** reported here continues to increase.

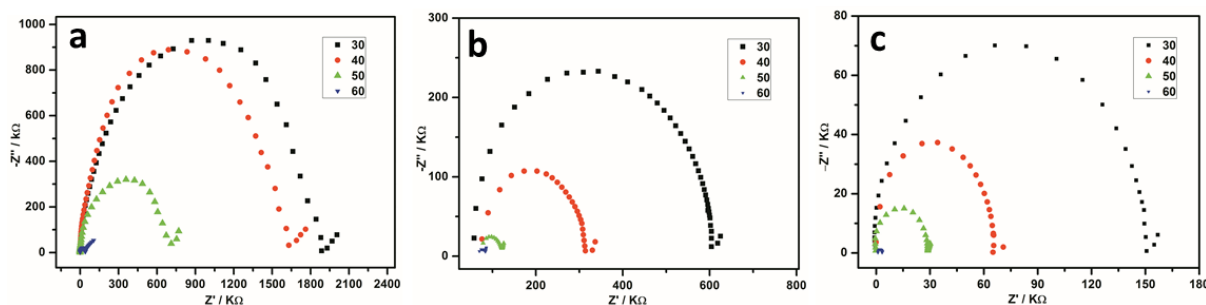


Figure 4.7. Temperature dependent nyquist plots of **SPE1** with a) **10%** b) **20%** c) **30%**

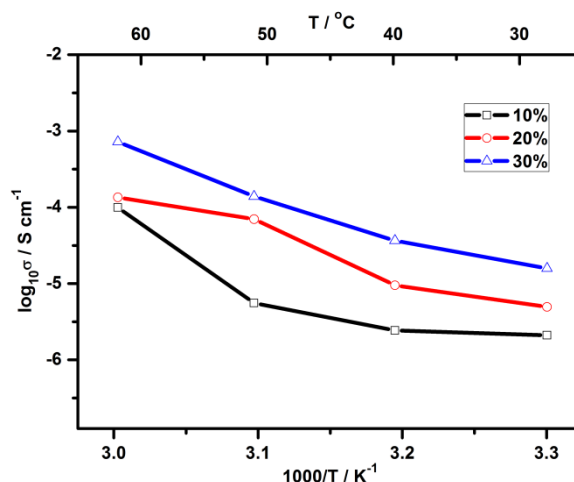


Figure 4.8. Arrhenius plot of temperature dependent conductivities of **SPE1** (**10%-30%**)

DSC plots of **SPE1** (**10%-40%**) (Figure 4.6) show the decrease in melting temperature with increase of lithium salt content from **10%** to **40%**. The difference in decrease of melting temperature with increasing lithium salt content is much higher than **P1**/LiClO₄ [12a]. The T_m of **P1** was decreased to 12.7 °C at **40%** (Table 4.7). When increasing the LiTFSI content in **SPE1**, the endothermic peak decreased progressively and reduces the degree of crystallization. The melting peak disappears when the LiTFSI content is increased to 30 wt% in **SPE1**. Lithium-ions were involved in crosslinking of the polymer chains by coordination. Further, the incorporation of the LiTFSI disrupts the **P1** chain arrangement and lowers its crystallinity. The area under the endothermic melting peak corresponds to the crystallinity of the sample. The degree of crystallinity (χ_c) of **P1** can be calculated by comparing its melting enthalpy (ΔH_m) with that of pure polycaprolactone. The enthalpy of melting (ΔH_m^0) of 100% crystalline polycaprolactone is 139.5 J g⁻¹ [14]. The melting enthalpy (ΔH_m) obtained from DSC analysis showed the decrease in crystallinity with the increase of salt concentration and eventually it became negligible after **20%** (Table

4.7). The variation in T_d , T_g , T_m and crystallinity showed the major role of counter anion of lithium salt in finding an optimum polymer electrolyte.

4.2.8. Lithium-ion conductivity

The Li-ion conductivities of **SPE1 (10%-30%)** were determined from the bulk resistances which were obtained from complex impedance spectra [15]. The measured conductivities of **SPE1 (10%-30%)** at room temperature as well as at 60 °C are presented in Table 4.7. Figure 4.7 and 4.8 displays the temperature dependent (30-60 °C with increment of 10 °C) nyquist plots of **SPE1 (10%-30%)** as well as Arrhenius plots of conductivities for **SPE1 (10%-30%)**. The room temperature lithium-ion conductivity of **P1** is $1.5 \times 10^{-11} \text{ S cm}^{-1}$. However, the addition of **10%** to **P1** attains the lithium-ion conductivity of $2.1 \times 10^{-6} \text{ S cm}^{-1}$ at room temperature. The increase in LiTFSI content in **SPE1** promotes the lithium-ion conductivity and reached the maximum of $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at **30%** at room temperature. As expected, the lithium-ion conductivities were also increasing with temperature. The **SPE1 30%** attained maximum conductivity of $7.2 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C.

4.3. Conclusions

The Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (**1-4**) were examined as catalyst to produce cyclic carbonates from renewable resources and ROP of **M1**. Further, all these complexes were active for ROP of **M1**, among them **1** and **4** complexes were highly efficient. The BP-ROP of **M1** yielded polymers with broad PDI compared with SP-ROP route. In the presence of BnOH, temperature and time of BP-ROP and SP-ROP of **M1** was lesser than the polymerization performed without BnOH. Complete study on the polymerization behavior revealed, the ROP of **M1** progressed in a controlled, living fashion and with immortal character. The applications on epoxide/ CO_2 coupling and ROP of **M1** proved the versatility of ligand (DIP₂pyr)H and its complexes (**1-4**).

Unlike LiClO_4 , the less tendency of ion aggregation of LiTFSI enabled to utilize more amounts of lithium salt in the preparation of **SPE1**. The admittance to use more lithium salt content helps to achieve higher conductivity. The conductivity of **SPE1** with 30 wt% of LiTFSI was $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $7.2 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C.

4.4. Experimental section

4.4.1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard schlenk techniques under dry nitrogen. The solvents, toluene, THF, methanol and chloroform were dried and purified using suitable drying agents, sodium benzophenone ketyl, $\text{Mg}(\text{OMe})_2$ and CaCl_2 respectively followed by distillation under nitrogen. The compounds, 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP_2pyr)H [16] and **1-4** [17] were synthesized by following procedures reported in literature. ϵ -caprolactone (**M1**), BnOH (Aldrich) and LiTFSI (Acros) were used without any further purification.

All products were confirmed by ^1H , ^{13}C , ^{31}P NMR and HRMS data. The NMR spectra were recorded using a Bruker Avance 400 MHz FT NMR spectrometer at room temperature in CDCl_3 . The data are reported in parts per million (δ) with reference to TMS or 85% H_3PO_4 as appropriate. HRMS spectra were recorded on a Bruker maXis instrument using ESI technique. The GPC measurements were performed on a JAI NEXT series recycling preparative HPLC equipped with UV and RI detector. The separation was achieved using a JAIGEL 3H column (600×20 mm) operated at 25°C with a flow rate of 3.5 mL/min. using chloroform as the eluent. The molecular weight and molecular weight distributions were calculated using polystyrene as a standard.

The impedance measurements of polymer electrolytes were performed in Zahner zennium electrochemical work station with built in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz to 4 MHz. The specimens in the form of pellets were sandwiched between two gold plated electrodes housed in a homemade cell. For variable temperature measurements, cell was equilibrated at each temperature for 30 min. before measuring. The conductivity was calculated according to the equation $\sigma = d/(\text{AR}_b)$, where d is the thickness of the polymer electrolyte disc, A is the surface area of the pellet and R_b is the bulk resistance value which can be obtained from the Nyquist plot [18].

4.4.2. Experimental procedure

General procedure for the ring opening polymerization of ϵ -caprolactone (M1**):** Typical polymerization reactions were carried out in nitrogen filled schlenk tube equipped with a stir bar.

For polymerization in neat condition (BP-ROP): To a stirred mixture of catalyst (0.02 mmol) and BnOH (0.02 mmol), **M1** (2 mmol) was added. As time progresses, an increase in the viscosity of solution was observed. After the reaction time, the polymerization was terminated by addition of glacial acetic acid and the resulting viscous solution was poured in to cold methanol. The polymer precipitated methanol was collected, washed and dried under vacuum.

For solution polymerization (SP-ROP): To a stirred solution of toluene (4 mL) and catalyst (0.02 mmol), BnOH (0.02 mmol) was added. The **M1** (2 mmol) was then added to the solution. The reaction mixture was stirred at the needed temperature for the prescribed time. Samples were taken from the reaction mixture at a regular time interval to determine the monomer conversion by ^1H NMR spectroscopy. After the reaction time, the polymerization was quenched by addition of glacial acetic acid into the solution and the resulting solution was poured in to cold methanol with stirring. The white precipitate was collected by filtration, washed with cold methanol and dried under vacuum.

General preparation of solid polymer electrolytes SPE1 (10%-30%): The polymer **P1** were dried at 50 °C under vacuum for 8 h. $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ was dried at 150 °C under vacuum for 10 h before use. All manipulations were carried out in an MBraun glove box filled with ultrapure nitrogen gas. Electrolytes with different ratio were prepared as follows: the polymer was dissolved in THF with lithium salt and stir for 12 h at 25 °C. After this, THF was evaporated under vacuum and dried the residue at 50 °C for 12 h. The residue was loaded in to a die and then pressed to make a pellet. Specimens of 0.09-0.12 cm thickness and 0.9 cm diameter were obtained for conductivity studies. These pellets were sandwiched between two gold plated electrodes housed in a homemade cell for conductivity studies. The consistency of results was checked by repeating three times.

4.5. References

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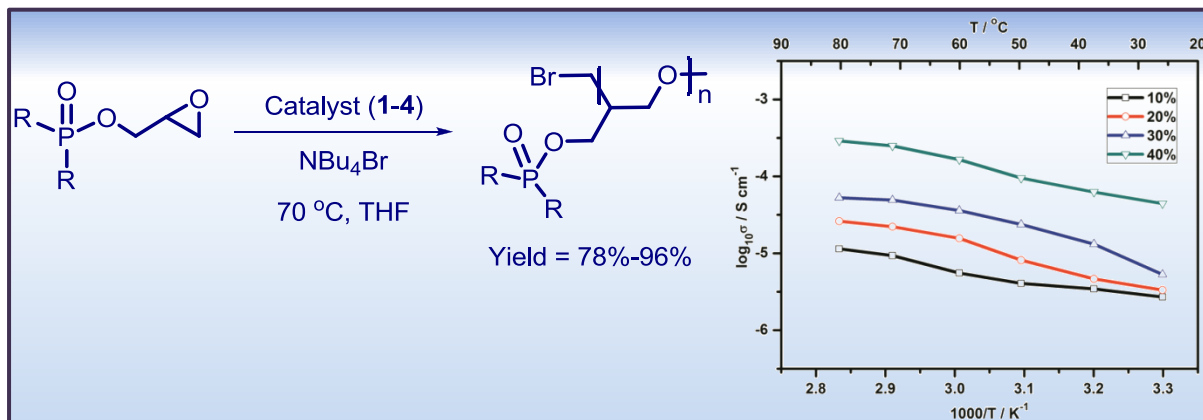
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CHAPTER 5

Polyethers with Phosphate Pendant Groups by Monomer Activated Anionic Ring Opening Polymerization: Syntheses, Characterization and their Lithium-ion Conductivities

Abstract

In this chapter, the preparations and lithium-ion conductivities of various solid polymer electrolytes for potential use in high-energy density lithium-ion batteries have been described. The ring opening polymerization of epoxides (**M2-M7**), catalyzed by Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) in the presence of tetrabutylammonium bromide (TBAB), yielded polyethers (**P2-P7**) in which phosphates are attached as pendant groups. A reaction condition where Zn(II) catalyst used slightly excess to TBAB increased the polymerization rate remarkably and yielded the polyethers with higher molar masses in short time. These polymerizations proceeded following a “monomer activated anionic ring opening polymerization” mechanism. These living like polymerizations also progressed according to “formation of polymer chain per initiator” model. The solid-state lithium-ion conductivities of these polymers were examined using LiTFSI. The conductivity of one of the solid polymer electrolyte **SPE3** with 40 wt% of LiTFSI was $5.2 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $2.9 \times 10^{-4} \text{ S cm}^{-1}$ at 80 °C.



5.1. Introduction

Several variations have been tried to increase the ionic conductivity of poly(ethylene oxide) (PEO) since its room temperature ionic conductivity is low (10^{-7} S cm $^{-1}$) for practicable applications [1]. Some effective variations are; the PEO based composites produced by mixing with polymer blends [2], inorganic fillers [3], plasticisers [4] and ionic liquids [5]; PEO based network polymers [6], cross-linked by siloxane polymers [7]; and block copolymers [8]. One of the major reasons causing the low ionic conductivity at ambient temperatures is the large crystalline area of PEO and less conformational flexibility. Therefore, there are interests towards decreasing crystallinity and increasing conformational flexibility. Since the amorphous region is responsible for the ion-conductivity, extending the amorphous phase can also improve the conductivity of polymers [9]. The ionic conductivity in amorphous polymers caused by mobility of ions promoted by local segmental motion of the polymer chains above T_g . Beyond T_g , the polymer's superstructures have disordered and flexible environment. Therefore, when the chains are in constant motion, vacant spaces would continually create and disappear through which ions transported. Because of the conformational flexibility induced by the presence of atoms of varying sizes in the polymer chains, the polyphosphazenes [10] and polysiloxanes [11] showed lithium ion conductivities of 5.0×10^{-5} S cm $^{-1}$ and 4.5×10^{-4} S cm $^{-1}$ respectively. Our interest is impelling conformational flexibilities and expanding the amorphous region; and examine the properties like crystallinity, T_g and ionic conductivity of the polymer.

Lithium-ion batteries are the major power sources for portable electronics. In the lithium-ion batteries, the electrodes are separated by an inert, porous polymer separator which is usually poly(propylene) soaked with low molecular weight organic liquids containing a dissolved salt. However, these organic liquids have potential fire hazard especially with large batteries that are useful for electric vehicles [12]. Thus, the research on finding solid polymer electrolyte (SPE) with flame-retardant properties to replace organic solvents in high-energy density lithium-ion batteries is always been in demand. The flame-retardant property for polymer electrolytes so far achieved by blending phosphorus containing molecules or covalently attaching them direct to the polymer chains [13]. Varieties of polymers in which phosphorus is a part of polymer chains are well-known. However, the present interest is producing polyethers with bulky rigid pendant groups such as substituted phosphates. These rigid groups would be influencing the assembly of chains in the polymer matrices and create perpetual free volume for the mobility of lithium-ion.

Poly(propylene oxide)s and PEO are important classes of polymers, they gained importance in biological and industrial applications especially in lithium-ion batteries [14]. These polymers are produced from propylene oxides or EO respectively by cationic, anionic or metal catalysed ring opening polymerization (ROP). The backbiting side reactions hinder the cationic polymerization leading to form low molecular weight oligomers. Alkali metal derivatives are efficient initiators for the anionic polymerization of cyclic ethers. However, the high basicity of propagating species resulted in proton abstraction leading to form hydroxy ended oligomer chains and allyl alkoxide initiator [15]. More recently, the polyethers with high molecular weights were produced by monomer activated anionic polymerization with restricted transfer to monomer side reactions. This was realised in the presence of combination of alkali metal salts or ammonium salts and a trialkylaluminium [16]. Similarly, a bimetallic cobalt catalyst/PPNX was reported to be active in catalysing enantioselective ROP of propylene oxide [17].

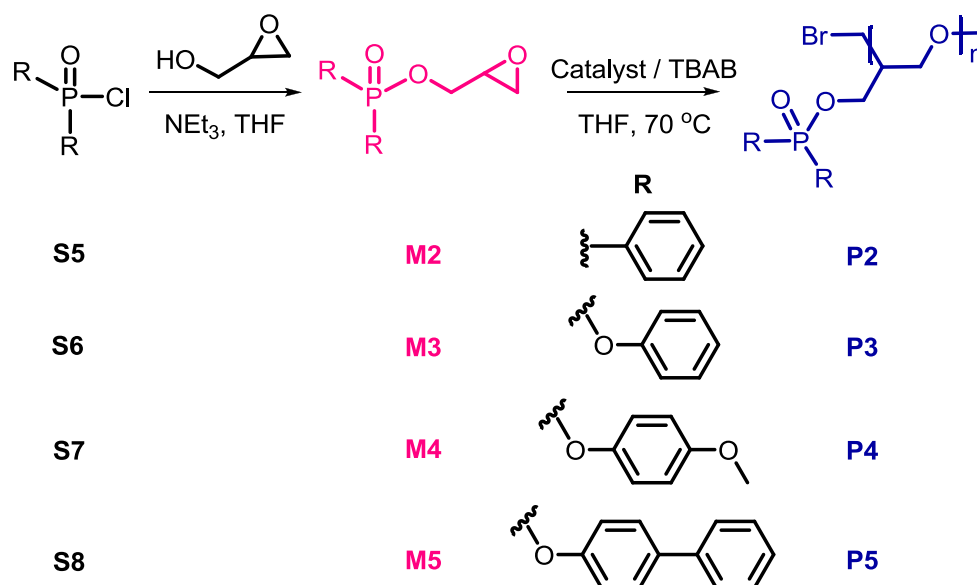
The threefold interest in this chapter is as follows. (i) Designing and synthesis of polymers having conformational flexibility, (ii) Production of poly(ethylene oxide)s with phosphates as pendant group and by it creating suitable superstructure for lithium-ion mobility, (iii) Exploring the catalytic activities of Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**) for ring opening polymerization of cyclic ethers.

5.2. Results and discussion

Polymers containing phosphorus can be classified as; (i) polymers with phosphorus in the main-chain (ii) polymers with organic groups having phosphorus as pendant groups. The first-class of polymers comprises the polymers with P-N, P-C, P-O and P-B bonds in main chain. The second-class covers typical carbon polymers where the phosphonates or phosphinates are hanging [18-20]. Integrating phosphorus into polymer chains would increase the conformational flexibility, thus leading to interesting chemical and physical properties including amorphous nature, high temperature stability and flame-retardancy [21]. Although phosphorus containing polymers are attractive mainly because of their flame-retardant property [22], in recent years, their biodegradability is also much sought. The biodegradable polymers - polyphosphoesters (PPE) [23] are promising for clinical and pharmaceutical applications, whereas the solid polymer electrolyte based on PPE is unexplored [9c, 24]. Our interest is producing polyethers with phosphate pendant groups as solid polymer electrolyte for lithium-ion transport.

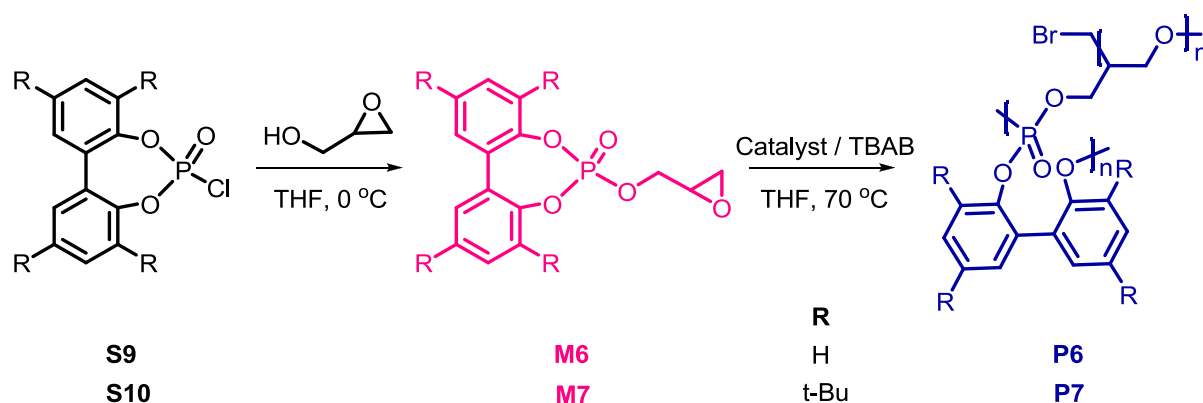
5.2.1. Synthesis of monomers (M2-M7)

Chosen monomers **M2-M7** having bulky groups was to get preferably linear polymers in which the bulky groups would be side group. Because of the uneven shapes and sizes of these bulky groups, they would influence the orientation of polymer chains and thus enlarge the amorphous region. Schemes 5.1 and 5.2 show the syntheses of monomers (**M2-M7**). The starting materials **S5** and **S6** (chlorodiarylphosphine oxides) used in the syntheses of monomers **M2** and **M3** respectively were purchased from commercial sources. But, the starting materials **S7-S10** were prepared by reacting POCl_3 with suitable equivalents of respective compounds 4-methoxyphenol, 4-phenylphenol, biphenyl-2,2'-diol and 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-diol in the presence of NEt_3 in THF at 0 °C.



Scheme 5.1. Syntheses of phosphorus containing linear polyethers by ROP of epoxide.

For the compounds **S7** and **S8**, filtering the reaction mixtures and evaporating the solvent yielded crude products. However, purification of **S7** and **S8** was unsuccessful because these compounds were not stable at room temperature as suggested by $^{31}\text{P}\{^1\text{H}\}$ NMR spectra. So, further steps to syntheses of monomers (**M4** and **M5**) were carried out without purification. However, the compounds **S9** and **S10** were isolated in pure by removing NEt_3HCl through filtrations and evaporation of the filtrates. The starting materials, **S9** and **S10** were stable solids and characterised by ^1H , $^{13}\text{C}\{^1\text{H}\}$ and $^{31}\text{P}\{^1\text{H}\}$ NMR spectral data. The molecular structure of **S9** (Figure 5.1) determined using X-ray crystallography clearly showed the presence of a seven-membered ring in it.



Scheme 5.2. Syntheses of phosphorus containing branched polyethers by ROP of epoxide.

The reactions of starting materials **S5-S9** with glycidol in THF in the presence of NEt₃ yielded the monomers **M2-M6** respectively. Similarly, a reaction of **S10** with glycidol in THF but in the presence of NaH yielded the monomer **M7** in good yield. The monomers **M2**, **M3** and **M6** were isolated in pure by filtering the reaction mixtures followed by evaporating the filtrates. The other monomers **M4**, **M5** and **M7** were purified by column chromatography. The monomers (**M2-M7**) were characterized using ¹H, ¹³C{¹H} and ³¹P{¹H} NMR spectral data which showed the data were consistent with expected molecular structures. The crystal structure of **M5** (Figure 5.1) determined using X-ray crystallography clearly showed the spatial orientations of the bulky groups around tetrahedral phosphorus. The monomers **M2-M4** were liquids whereas **M5-M7** were solids.

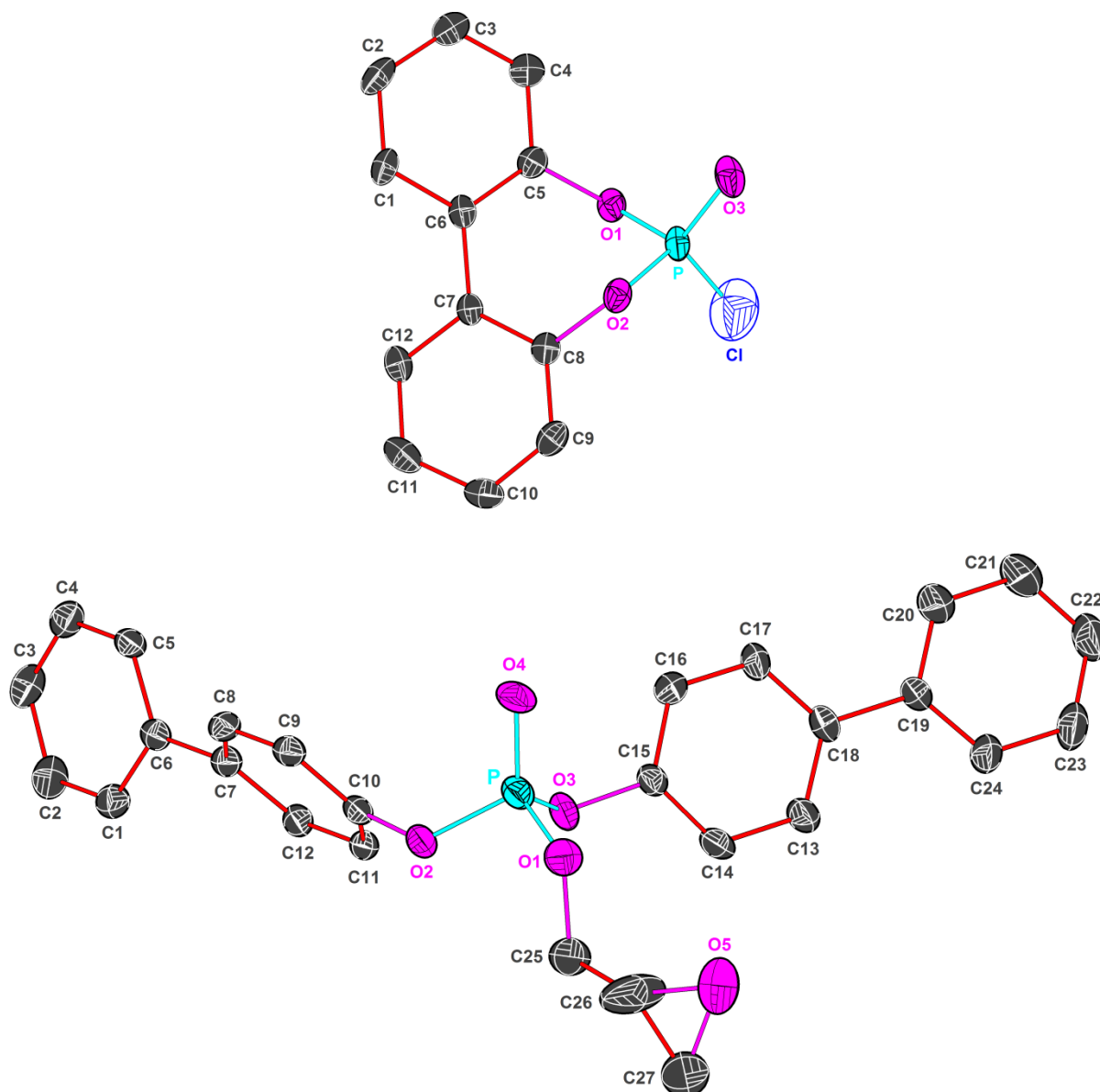


Figure 5.1. ORTEP of the molecular structure **S9** (top) and **M5** (down). Thermal ellipsoids are shown at 30% probability levels. Hydrogen atoms are omitted for clarity.

Table 5.1. Crystal data and structural refinement details for **S9** and **M5**

Parameters	S9	M5
Empirical formula	C ₁₂ H ₈ ClO ₃ P	C ₂₇ H ₂₃ O ₅ P
Formula weight	266.60	458.42
Crystal System	Orthorhombic	Monoclinic
Space group	Pca2(1)	P21/C
a (Å)	16.914(3)	21.297(2)
b (Å)	4.7950(7)	5.7997(4)
c (Å)	13.573(2)	18.6774(16)
α (deg)	90	90
β (deg)	90	103.403(9)
γ (deg)	90	90
Volume (Å) ³	1100.8(3)	2244.1(3)
Temperature (K)	300(2)	300(2)
Z	4	4
μ mm ⁻¹	0.483	0.160
D (calcd.) (g/cm ³)	1.609	1.357
F(000)	544	960
Crystal size (mm)	0.16 × 0.14 × 0.12	0.16 × 0.14 × 0.10
θ range (deg)	2.41 to 25.05	2.62 to 28.92
Index ranges	-20 ≤ h ≤ 20 -5 ≤ k ≤ 5 -16 ≤ l ≤ 16	-21 ≤ h ≤ 26 -7 ≤ k ≤ 5 -20 ≤ l ≤ 23
Reflections collected / unique	9531 / 1942 R _{int} = 0.0499	9500 / 5069 R _{int} = 0.0780
Data completeness	99.8 %	85.7 %
Transmission (max/min)	0.944 / 0.926	0.861 / 1.000
Data / restraints / parameters	1942 / 1 / 155	5069 / 0 / 302
Goodness-of-fit on F ²	1.122	0.900
Final R indices [I > 2σ(I)]	R ₁ = 0.0750 wR ₂ = 0.2413	R ₁ = 0.0704 wR ₂ = 0.1202
R indices (all data)	R ₁ = 0.0845 wR ₂ = 0.2530	R ₁ = 0.2342 wR ₂ = 0.1790
Largest diff. peak / hole, e Å ⁻³	0.373 / -0.992	0.567 / -0.461

5.2.2. Ring opening polymerization

In our continuous interest on Zn(II), Cd(II) and Cu(II) complexes of (DIP₂pyr)H (**1-4**), we have further explored their catalytic activities for the ring opening polymerization of epoxides. The metal complexes **1-4** were prepared according to Scheme 2.5 and 2.6. At first, the catalytic activity of Zn(II) complex **1** for the ROP of oxiran-2-ylmethyl diphenylphosphate (**M3**) in the presence of tetrabutylammonium bromide (TBAB) as initiator at 70 °C in THF was tested. It was found to be good catalyst by yielding the polyether (**P3**) with narrow polydispersity.

A set of controlled experiments performed in THF at 70 °C to understand the role of both catalyst and initiator (C and I). Either catalyst or initiator alone did not catalyse the reactions (Table 5.2, entries 1 and 2). However, when both of them are present in different molar ratios, we observed the following; (i) When the C/I molar ratio was less than 1, only subtle polymerization occurred. (ii) When the C/I molar ratio equalled 1, the reaction yielded little more polyether (Table 5.2, entries 3 and 4) but did not complete within 24 h as checked by ¹H NMR. (iii) When the C/I molar ratio exceeded slightly 1, say 1.1 (Table 5.2, entry 5), the ROP proceeded much faster and reached completion within seven hours. So the reaction-condition was optimized by varying the C/I (**1**/TBAB) molar ratio, temperature and time to achieve good conversion and higher molecular weight with narrow PDI (Table 5.2, entries 3-10). Among the different catalyst/initiator loadings tried, the C/I molar ratio of 1.5 yielded the polymer within 4 h at 70 °C with moderate properties (Table 5.2, entry 8). From here, this molar ratio (C/I) was fixed for further investigations. Under this reaction-condition, the catalysts **2-4** were examined for the ROP of **M3** in the presence of TBAB in THF at 70 °C (Table 5.2, entries 11-13). The ROP proceeded faster in the presence of **1** than other catalysts **2-4**. The molecular weight [Mn(exp)] measured by GPC matched well with theoretical molecular weight [Mn(theo)] calculated (based on a formation of one polymer chain per initiator) from the initial monomer/initiator ratio, and their PDIs were also in a narrow range.

The ROP of **M3** was examined with a different initiator, bis(triphenylphosphine)iminium chloride (PPNCl) in the presence of **1** at 70 °C in THF (Table 5.2, entry 16). Even after 24 h, the ROP did not complete probably because of the poor solubility of PPNCl in THF. So, the reaction was carried out in dichloromethane (DCM) at 40 °C (Table 5.2, entry 17). But since the high molecular mass polyether (**P3**) was insoluble in DCM, once the reaction progressed, the polymer precipitated out from the reaction mixture. Instead of

Table 5.2. Results of optimization studies for ROP^a of **M3** to form **P3**

Entry	Catalyst (C)	[C] ₀ /[I] ₀	[M3] ₀	Reaction time (h)	Properties of the P3		
					M _n (kg mol ⁻¹) (exp) ^b	M _n (kg mol ⁻¹) (theo) ^c	PDI ^d
1 ^e	-	-	100	120	-	-	-
2 ^f	1	-	100	120	-	-	-
3	1	0.5	100	24	-	30.6	-
4	1	1.0	100	24	-	30.6	-
5	1	1.1	100	7	31.4	33.6	1.21
6	1	1.3	100	6	40.2	39.8	1.18
7 ^g	1	1.5	100	24	43.1	45.9	1.08
8	1	1.5	100	4	46.9	45.9	1.15
9	1	1.8	100	3	57.8	55.1	1.23
10	1	2.0	100	3	64.2	61.2	1.28
11	2	1.5	100	14	42.3	45.9	1.27
12	3	1.5	100	16	43.2	45.9	1.34
13	4	1.5	100	10	46.0	45.9	1.19
14	1	1.5	200	15	90.6	91.8	1.18
15	1	1.5	300	48	136.7	137.8	1.20
16	1	1.5 ^h	100	24	-	45.9	-
17 ⁱ	1	1.5 ^h	100	10	16.3	45.9	1.25
18 ^j	-	<i>t</i> -BuOK	100	168	16.5	-	1.64
19 ^j	-	<i>t</i> -BuOK	100	72	20.8	-	1.85

^aReactions were conducted in THF at 70 °C in presence of catalyst (C) and TBAB (I) as initiator. The reactions were carried out up to 100% conversion based on ¹H NMR.

^bMolecular weight measured by GPC and calibrated against polystyrene standard.

^cMolecular weight calculated from ([M3]₀/[I]₀) × molecular weight of monomer × conversion. ^dObtained from GPC analysis. ^eIn the presence of TBAB alone. ^fIn the presence of catalyst alone. ^gReaction at 25 °C. ^hIn presence of PPNCI as initiator instead of TBAB.

ⁱConducted in DCM at 40 °C. ^jWithout catalyst.

1/TBAB, a well-known anionic initiator potassium *tert*-butoxide (*t*-BuOK) was examined for the ROP of **M3** (Table 5.2, entries 18 and 19). In this case, the significant contribution of side reactions probably resulted in low molecular weight polymer with broader PDI and this also was consuming extensive time for polymerization. These facts confirmed the usefulness of our catalyst in these ROP reactions.

Scope of the catalyst was further explored for the ROP of various substituted epoxides having phosphorus as monomers (**M2**, **M4** and **M5**). These reactions yielded the polymers **P2**, **P4** and **P5** respectively. Table 5.3 display the properties of polymers obtained from these reactions. The ROP of **M2**, **M4** and **M5** were also progressing according to the mechanism of polymer chain per initiator. This was reflected by good agreement of measured molecular weight [$M_n(\text{exp})$] with calculated molecular weight [$M_n(\text{theo})$]. Even though the active nucleophilic site (epoxide oxygen) was away from substituents, electron releasing groups attached to phosphorus indicated a trend in the rate of ROP. According to the results displayed in Table 5.3 (entries 1-4), in the presence of catalyst **1**, the rate of conversion of monomers to polymers was in the order **M4**>**M5**>**M3**>**M2**.

Table 5.3. Results of syntheses of various phosphorus containing polyethers (**P2-P7**)^a and their properties

Entry	Epoxides (M)	Time (h)	Polymers (P)	Properties of polymers				
				M_n (kg mol ⁻¹) (exp) ^b	M_n (kg mol ⁻¹) (theo) ^c	PDI ^d	T _d (°C)	T _g (°C)
1	M2	10	P2	40.6	41.1	1.21	350.1	227.7
2	M3	4	P3	46.9	45.9	1.15	159.5	80.8
3	M4	3	P4	56.0	55.0	1.19	144.7	-10.6
4	M5	4	P5	67.9	68.8	1.16	159.3	82.5
5	M6	8	P6	32.2	45.6	1.20	167.9	98.4
6	M7	6	P7	50.3	79.3	1.18	203.4	74.7

^aReaction condition: $[M]_0:[C]_0:[I]_0 = 100:1:0.67$ in THF at 70 °C. ^bMolecular weight measured by GPC and calibrated against polystyrene standard. ^cMolecular weight calculated from $([M]_0/[I]_0) \times \text{molecular weight of monomer} \times \text{conversion}$. ^dObtained from GPC analysis.

5.2.3. Branched polymers

The epoxide ring opening polymerization (in THF at 70 °C) of monomers **M6** and **M7** were interesting since they differed from the other four monomers. These monomers yielded respective polyethers (**P6** and **P7**; Table 5.3, entries 5 and 6) whose measured molecular weights [$M_n(\text{exp})$] were much lower than theoretical molecular weights [$M_n(\text{theo})$]. This suggested the ROP did not follow the polymer chain per initiator mechanism while other monomers following. The monomer **M7** underwent faster polymerization than **M6** showing the bulky groups in it did not disturb the growth of PEO chain since the electronic effects dominated; also the bulky group is much away from the growing chain. To deduce the structure of polymers **P6** and **P7**, we analysed the following observations. (i) Both these polymers are soluble in polar solvents. (ii) At the start of reaction, number of initiator molecules is much less than monomer molecules. (iii) No monomers remained unreacted in these reactions. (iv) The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of **P6** displayed two kinds of peaks at 1.77 and -0.72 ppm. Comparing with the chemical shift of the monomer, the minor peak at 1.77 ppm might represent the phosphorus at terminal repeating unit of a chain, while the broad peak at -0.72 ppm representing the phosphorus atoms in the chain [25]. In the ^1H NMR of **P6**, the peaks of all aromatic protons merged (Figure 5.3) while the aliphatic protons merged among themselves. The polymer **P7** also presented a similar $^{31}\text{P}\{^1\text{H}\}$ and ^1H NMR.

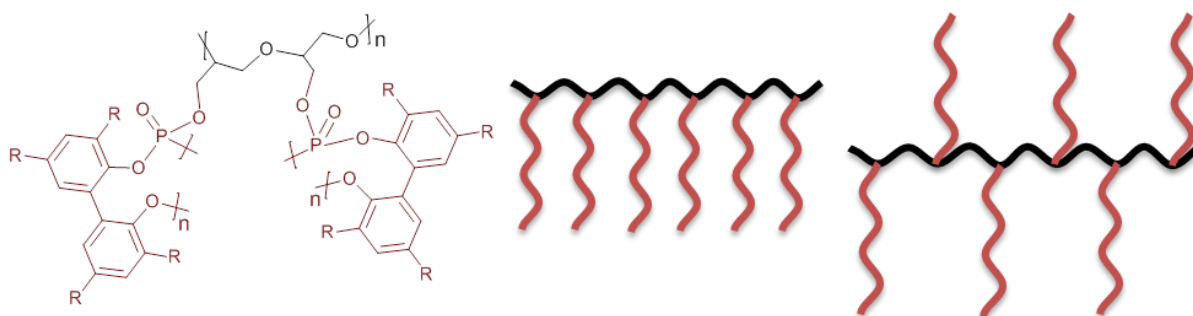


Figure 5.2. Possible branching structures of **P6** and **P7**

From these observations we inferred as follows. At first, it appeared the pendant rings opened by reaction with initiators are taking part in side reactions with proximal pendant groups along the same chain. This parallel chain could be formed because of breaking of P-O bonds in the seven membered rings in the monomers. This side reaction would consume few initiator molecules. Also, no monomers remained unconsumed. Breaking C-O bond in the same ring was ruled out because such a case should yield a positive-charge on the biphenyl

group of tricyclic ring. In these circumstances, according to the polymer chain per initiator mechanism, the measured molecular weights should be higher than the theoretical molecular weights. Thus the parallel chain model would not explain the much lower measured molecular weight than the theoretical value. Solubility of the polymers in polar solvents ruled out the possibility of inter-chain side reaction leading to traditional cross-linked polymers. Finally, we inferred the polymers **P6** and **P7** as comb-like branched polymers (Figure 5.2). This is possible because of breaking of P-O bonds in the seven membered rings in the pendant ring and reacting with a new monomer instead the proximal monomer leading the growth of branched chain. This perceptive would explain the lower molecular weight since the polymer chain branching would consume few monomers. The comb-like polymer model would also explain two peaks in the ^{31}P NMR because there are two different kinds of repeating units (in chain and terminal) in the pendant chain.

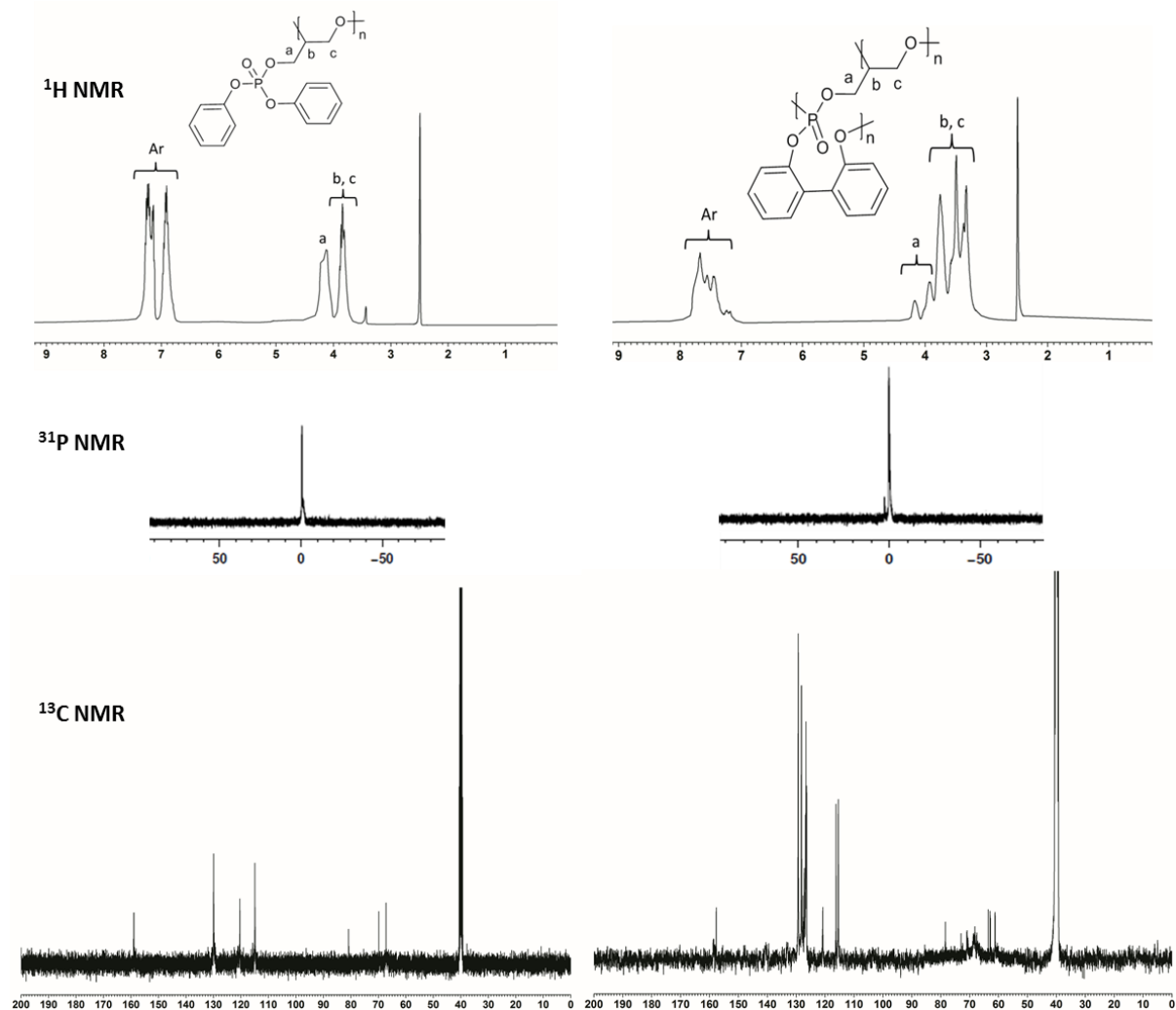


Figure 5.3. ^1H , ^{31}P and ^{13}C NMR spectra of **P3** (left) and **P6** (right)

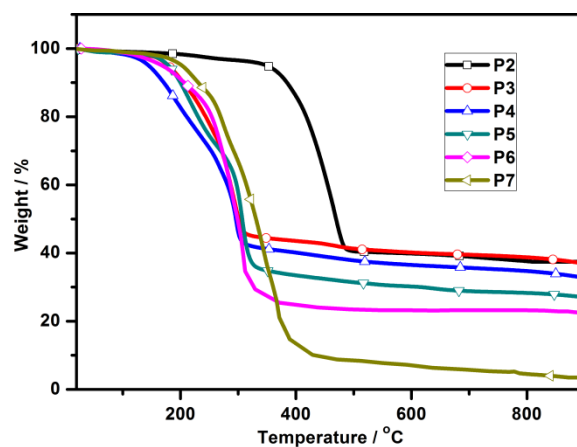


Figure 5.4. TGA plots of polyethers **P2-P7**

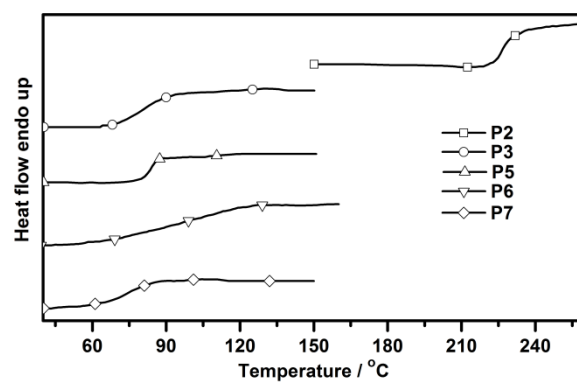


Figure 5.5. DSC plots of polyethers **P2-P7**

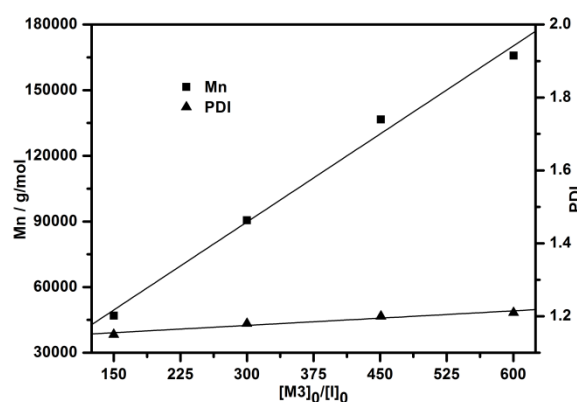


Figure 5.6. Plot of molecular weight (M_n) and polydispersity (PDI) versus $[M3]_0/[I]_0$ for the ROP of **M3** catalysed by **1** in presence of TBAB. Reaction condition: $[M3]_0:[C]_0:[I]_0 = 100:1:0.67$ in THF at 70 °C, $[M3]_0 = 0.94$ M.

5.2.4. Properties of the polymers

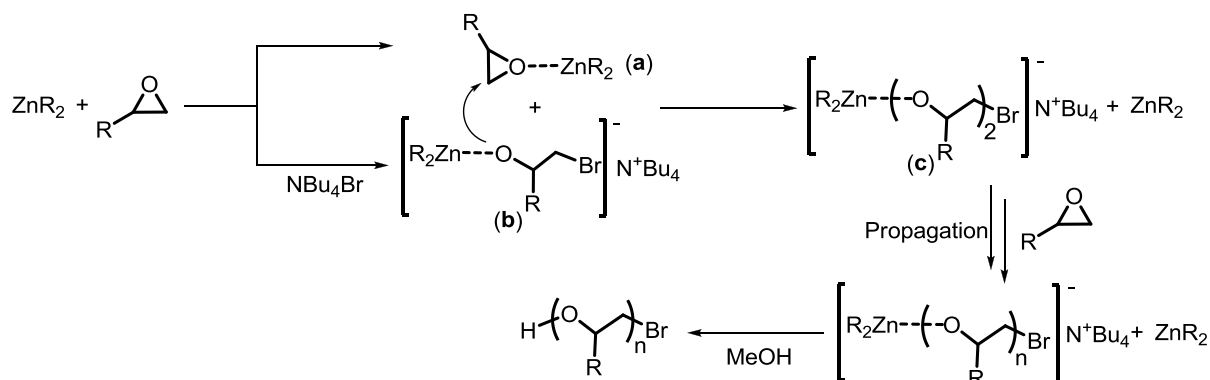
The polymers **P2**, **P3** and **P5-P7** are solids, while **P4** is a liquid. All these polymers **P2-P7** are soluble in polar solvents like THF, dimethyl sulphoxide, and dimethyl acetamide. Table 5.3 lists the glass-transition temperature (T_g), decomposition temperature (T_d), molecular weight (M_n) and PDI of all these polymers. The molecular weights (M_n) of polymers **P2-P7** is in the range of 40-80 kg mol⁻¹. Thermogravimetric analyses (Figure 5.4) disclosed the polymers **P3-P7** are thermally stable until heating up to 160 °C while **P2** is stable up to 350 °C. The T_g of the polymers **P3** and **P5 – P7** lies in the temperature range of 75 °C - 100 °C while the polymers **P2** and **P4** have T_g at 227 °C and -10 °C respectively (Figure 5.5). All are amorphous polymers since the DSC graphs did not show crystalline melting temperature peak for any polymers. Compared with **P3-P7**, the **P2** have higher thermal stability (T_d) and high T_g . This could be explained by the columnar stacking of phenyl rings because of strong non-covalent interactions that would ensure a space efficient packing. Thus the phosphate group attached to PEOs provided significant changes in their properties especially the crystallinity and T_g .

5.2.5. Mechanism of polymerization

The reaction optimization study showed that while increasing the monomer/initiator molar ratio (M/I), the molecular weight of the resultant polymers was increasing but with narrow PDI (Table 5.2, entries 8, 14 and 15). In these reactions, existed linear-relationship (Figure 5.6) of molecular weight with the ratio of initial monomer to initiator concentrations that is $[M]_0/[I]_0$ also confirmed the dependent of the molecular weight on monomer concentration. All these observations revealed the ROP underwent in a controlled living like polymerization and clearly suggested the negligible contribution of “transfer to monomer process” to the molecular weight as reflected by PDI.

Though we could not isolate any intermediate species, based on our observations and earlier reports [16, 26], we postulate a mechanism for ROP as shown in Scheme 5.3. The first step involved activating epoxide monomer by coordinating with a zinc catalyst. In the presence of TBAB, the activated monomer underwent epoxide ring opening by the nucleophilic attack of bromide ions to form initiating complex (**b**). Further, the excess zinc catalyst activated the monomer (**a**) for the nucleophilic attack of initiating complex to yield the growing species (**c**). Thus the propagation step proceeded and polymerization happened rapidly. When the C/I molar ratio was less than or equal to 1, the zinc catalyst involved in

forming of initiating complex only. Therefore, little excess of catalyst required to trigger the polymerization. This was matching well with the living like polymerization mechanism.



Scheme 5.3. Proposed mechanism for the monomer activated anionic ROP of epoxide

5.2.6. Lithium-ion conductivity

Solid polymer electrolytes (**SPE2**, **SPE3** and **SPE5-SPE7**) were prepared by dissolving respective polymers (**P2**, **P3** and **P5-P7**) and varying amounts of lithium salt (LiTFSI) in THF. Since the polymer **P4** was liquid we did not make electrolyte from it. After evaporating and drying the solvent, the residues were made into pellets for conductivity measurements. To understand the thermal properties, TG and DSC analyses on the solid electrolytes **SPE2**, **SPE3** and **SPE5-SPE7** were performed (Figure 5.7-5.11; a and b). Absence of peaks matching the melting temperature (T_m) of lithium salt in DSC curves for **SPE2**, **SPE3** and **SPE5-SPE7** revealed the salt did not exist as aggregates. The absence of melting point of salts might because of solvation of lithium ions by polymers. The possibility of polymer chain coordination with lithium ion would facilitate the solvation. The **SPE2**, **SPE3** and **SPE5-SPE7** with 40 wt% of LiTFSI [**SPE2**, **SPE3** and **SPE5-SPE7** (40%)] also did not show the peak for T_m which inferred the effective solvation by polymers even for higher wt% of lithium salt.

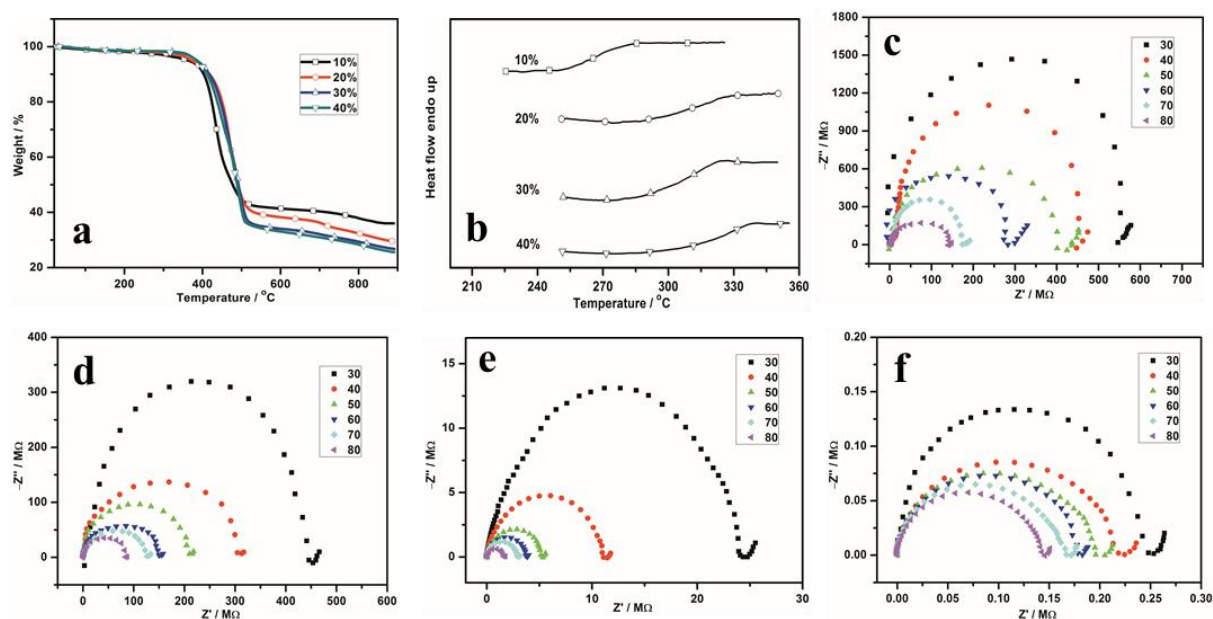


Figure 5.7. (a) TGA and (b) DSC plots of SPE2 (10%-40%). Temperature dependent nyquist plots of SPE2 c) 10% d) 20% e) 30% f) 40%.

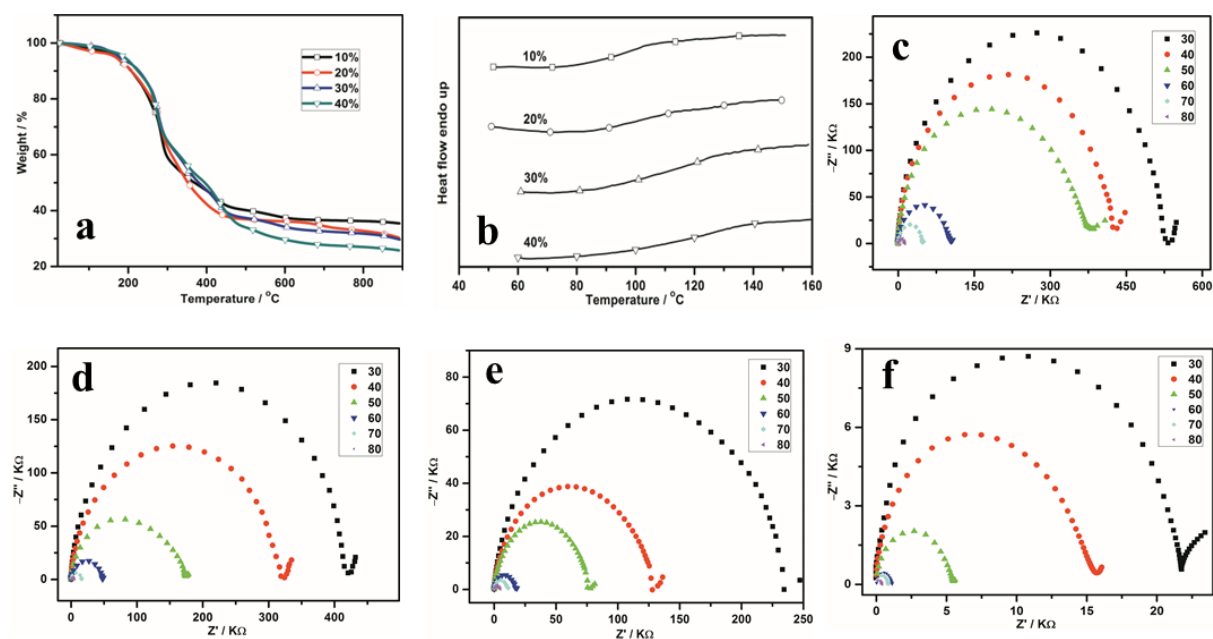


Figure 5.8. (a) TGA and (b) DSC plots of SPE3 (10%-40%). Temperature dependent nyquist plots of SPE3 c) 10% d) 20% e) 30% f) 40%.

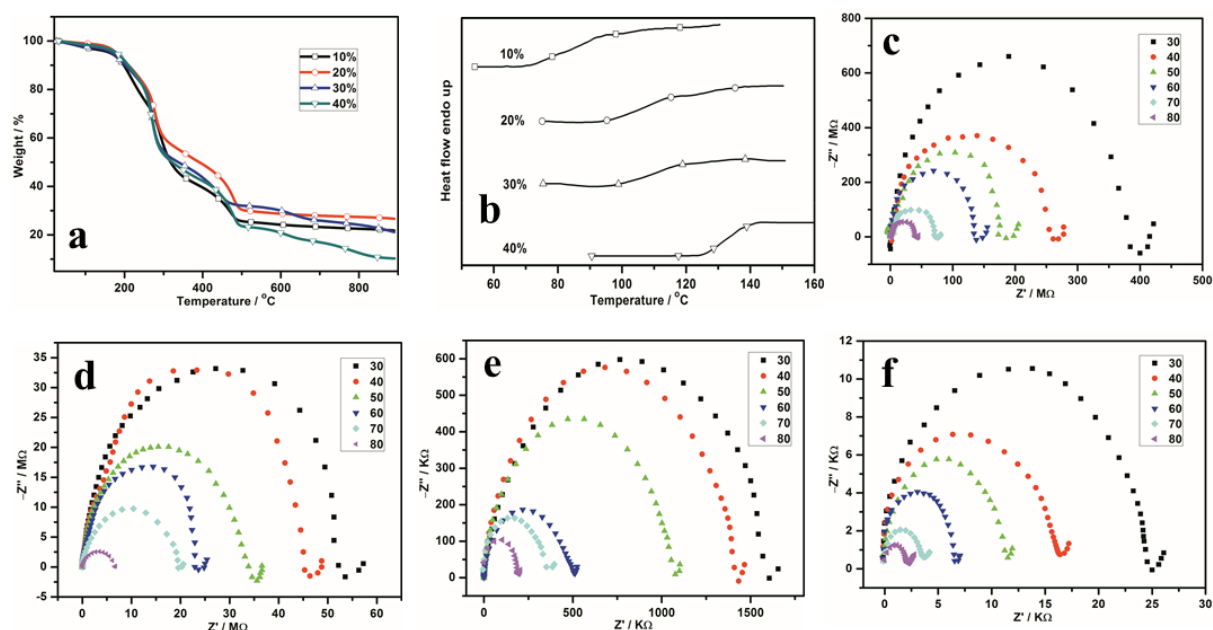


Figure 5.9. (a) TGA and (b) DSC plots of SPE5 (10%-40%). Temperature dependent nyquist plots of SPE5 c) 10% d) 20% e) 30% f) 40%.

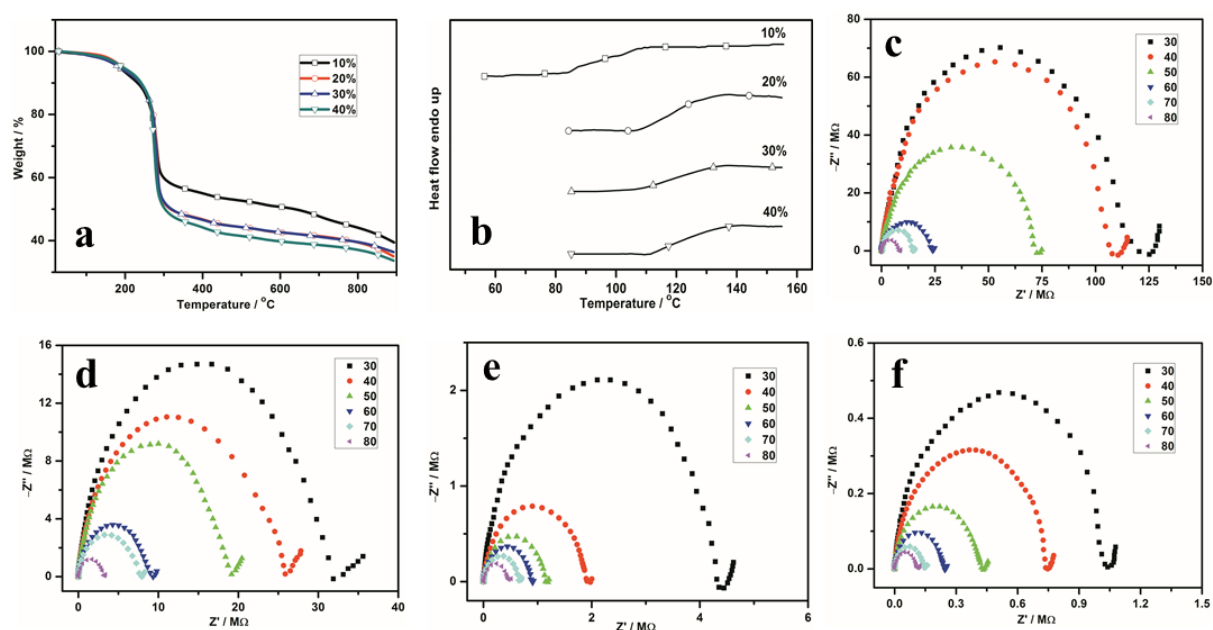


Figure 5.10. (a) TGA and (b) DSC plots of SPE6 (10%-40%). Temperature dependent nyquist plots of SPE6 c) 10% d) 20% e) 30% f) 40%.

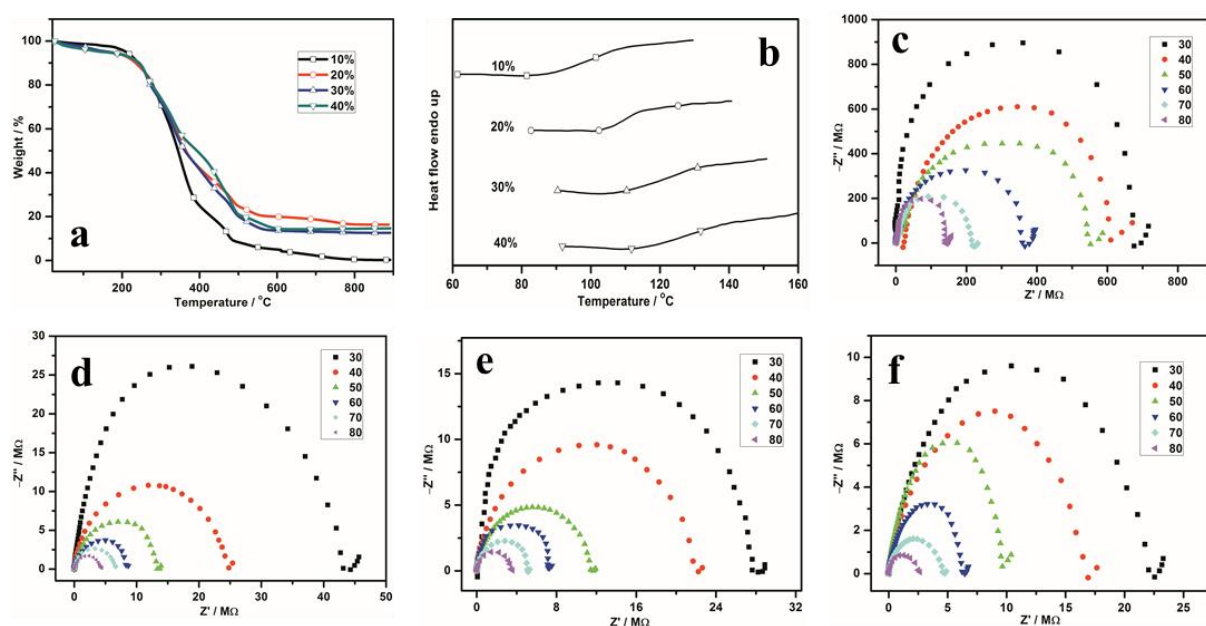


Figure 5.11. (a) TGA and (b) DSC plots of SPE7 (10%-40%). Temperature dependent nyquist plots of SPE7 c) 10% d) 20% e) 30% f) 40%.

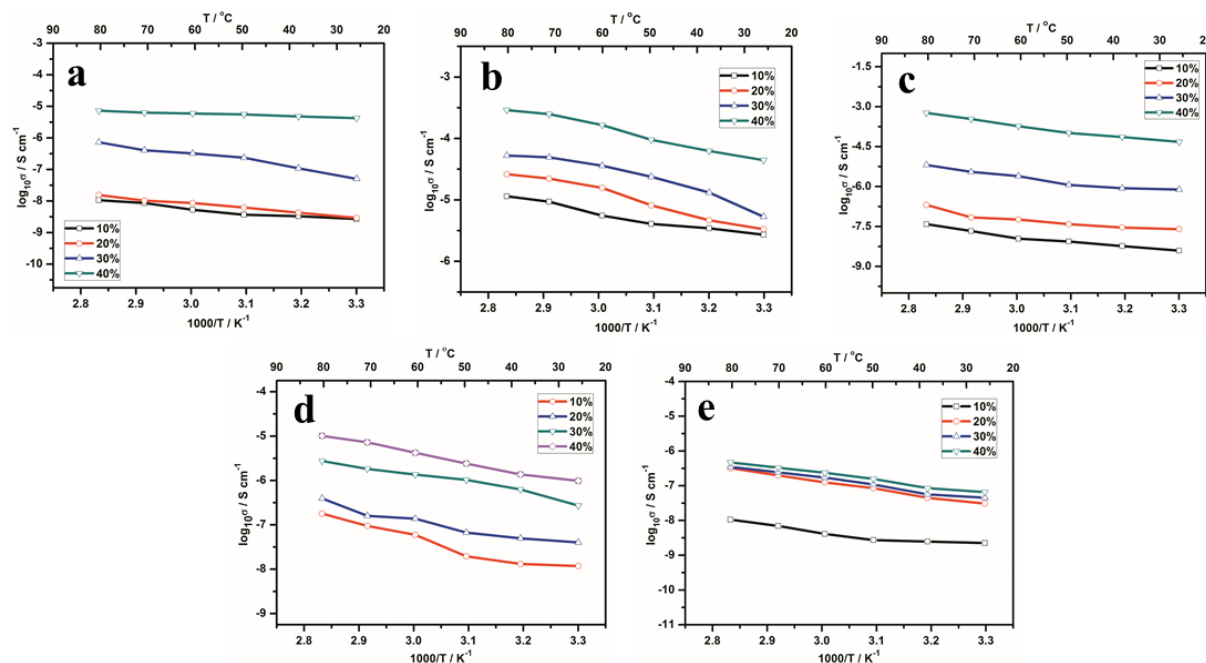


Figure 5.12. Arrhenius plot of temperature dependent conductivity of a) SPE2 b) SPE3 c) SPE5 d) SPE6 e) SPE7

Table 5.4. Properties of **SPE2 (10%-40%)**

SPE2 (wt% of LiTFSI)	O:Li	Conductivity σ (S cm ⁻¹)		T _d (°C)	T _g (°C)
		30 °C	80 °C		
SPE2 (10%)	28.2:1	2.7×10^{-9}	1.1×10^{-8}	362.6	267.2
SPE2 (20%)	12.6:1	2.9×10^{-9}	1.6×10^{-8}	372.0	308.7
SPE2 (30%)	7.3:1	5.0×10^{-8}	7.2×10^{-7}	385.3	310.6
SPE2 (40%)	4.5:1	4.2×10^{-6}	7.2×10^{-6}	390.2	326.4

Table 5.5. Properties of **SPE3 (10%-40%)** and **SPE5 (10%-40%)**

SPEs (wt% of LiTFSI)	SPE3					SPE5				
	O : Li	conductivity σ (S cm ⁻¹)		T _d (°C)	T _g (°C)	O : Li	conductivity σ (S cm ⁻¹)		T _d (°C)	T _g (°C)
		30 °C	80 °C				30 °C	80 °C		
SPE (10%)	42.2:1	2.7×10^{-6}	1.1×10^{-5}	167.5	89.7	28.2:1	3.9×10^{-9}	3.8×10^{-8}	166.7	99.2
SPE (20%)	18.8:1	3.3×10^{-6}	2.6×10^{-5}	168.9	108.3	12.5:1	2.5×10^{-8}	2.0×10^{-7}	168.4	107.0
SPE (30%)	10.9:1	5.3×10^{-6}	3.2×10^{-5}	177.4	124.1	7.3:1	7.7×10^{-7}	6.5×10^{-6}	180.0	110.1
SPE (40%)	7.0:1	5.2×10^{-5}	2.9×10^{-4}	188.8	133.5	4.7:1	4.8×10^{-5}	1.8×10^{-4}	182.1	130.3

The TGA analyses on **SPEs** revealed increase in the thermal stabilities of **SPE2**, **SPE3** and **SPE5-SPE7** compared with their respective polymers **P2**, **P3** and **P5-P7** (Table 5.4-5.6). The glass transition temperatures (T_g) of **SPE2**, **SPE3** and **SPE5-SPE7** having 10-40 wt% of LiTFSI respectively [**SPE2**, **SPE3** and **SPE5-SPE7 (10%-40%)**] determined through DSC analyses are shown in Table 5.4-5.6. As seen in DSC plots, there were increase in T_g of **SPE2**, **SPE3** and **SPE5-SPE7** compared with their respective polymers. The increase was more with increasing salt contents. The increased T_d and T_g can be explained through coordination of polymer chains with lithium ions by as follows. Coordination of polymer with lithium ions would affect the stretching of polymer chains thus restricting their segmental motion. Obviously, more salt molecules would encourage more coordination by polymer chains and increased control on the segmental motion of the chains leading

increased T_g . Similarly, because of the coordination of polymer chains with lithium ions, it needs more energy to break the coordination bonds at first followed by to break the polymer chains.

Table 5.6. Properties of **SPE6 (10%-40%)** and **SPE7 (10%-40%)**

SPEs (wt% of LiTFSI)	SPE6					SPE7				
	O : Li	conductivity σ (S cm ⁻¹)		T_d (°C)	T_g (°C)	O : Li	conductivity σ (S cm ⁻¹)		T_d (°C)	T_g (°C)
		30 °C	80 °C				30 °C	80 °C		
SPE (10%)	42.5:1	1.2×10^{-8}	1.8×10^{-7}	183.7	110.0	24.5:1	2.2×10^{-9}	1.1×10^{-8}	210.4	102.0
SPE (20%)	18.9:1	4.0×10^{-8}	3.9×10^{-7}	190.0	119.4	10.9:1	3.1×10^{-8}	3.2×10^{-7}	215.8	111.2
SPE (30%)	11.0:1	2.7×10^{-7}	2.7×10^{-6}	193.9	122.1	6.3:1	4.5×10^{-8}	3.5×10^{-7}	220.6	123.5
SPE (40%)	7.1:1	9.8×10^{-7}	1.0×10^{-5}	198.7	130.3	4.1:1	5.0×10^{-8}	4.7×10^{-7}	228.5	130.7

The bulk resistances determined from complex impedance spectra revealed the Li-ion conductivities of **SPE2**, **SPE3** and **SPE5-SPE7** [27]. The measured conductivities of **SPE2**, **SPE3** and **SPE5-SPE7** at room temperature as well as at 80 °C are presented in Table 5.4-5.6. Figure 5.7-5.11 (c-f) displays the temperature dependent (30-80 °C with increment of 10 °C) nyquist plots of **SPE2 (10%-40%)**, **SPE3 (10%-40%)** and **SPE5-SPE7 (10%-40%)** respectively. Arrhenius plots of conductivities for **SPE2 (10%-40%)**, **SPE3 (10%-40%)** and **SPE5-SPE7 (10%-40%)** are shown in Figure 5.12. The electrolyte **SPE2** showed lowest conductivity among all in room temperature as well as at elevated temperatures. The conductivities of **SPE2**, **SPE3** and **SPE5-SPE7** at room temperature lies in the range of 2.7×10^{-9} - 5.2×10^{-5} S cm⁻¹. Among **SPE2 (10%-40%)**, **SPE3 (10%-40%)** and **SPE5-SPE7 (10%-40%)**, the **SPE3 (40%)** has demonstrated highest conductivity of 5.2×10^{-5} S cm⁻¹ at room temperature. Further, the conductivities of **SPE2 (10%-40%)**, **SPE3 (10%-40%)** and **SPE5-SPE7 (10%-40%)** were increasing with the amounts of lithium salt. As expected, they were also increasing with temperature. Thus the **SPE3 (40%)** attained maximum conductivity of 2.9×10^{-4} S cm⁻¹ at 80 °C. Comparing with **SPEs** made up of linear polymer

(SPE2, SPE3 and SPE5), the ionic conductivity of SPEs prepared from branched polymers (SPE6 and SPE7) was lesser probably because of its higher T_g .

5.3. Conclusions

In conclusion, we have synthesized polyethers with phosphate side-groups that could find use as solid polymer electrolytes in lithium-ion batteries. Compared with the conventional anionic initiators, our system (Zn(II)/TBAB) catalysed the polymerization without any side reactions and yielded the polymers with fairly high molecular weights. So far, other than poly(ethylene oxide), only few polymers like polysiloxane, polyphosphazene have shown potential as lithium ion conducting polymer electrolytes; but, both are liquids at room temperature. However, the polyethers (**P2-P7**) produced by us are stable, solids (except **P4**) at room temperature and completely amorphous in nature. Therefore, the polymers **P3** and **P5** demonstrated promising solid-state ionic conductivity. The solid polymer electrolyte **SPE3** (40%), prepared from **P3**, showed the highest conductivity of $2.9 \times 10^{-4} \text{ S cm}^{-1}$ at 80 °C. Apart from these, the presence of phosphorus in these polymers would impart flame-retardant property to SPEs.

5.4. Experimental section

5.4.1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard Schlenk techniques under the atmosphere of dry nitrogen. All solvents to be used under inert atmosphere were thoroughly deoxygenated using freeze-pump-thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen atmosphere. The compound, 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-diol was synthesized according to the literature procedure [28]. The compounds, chlorodiphenylphosphine oxide (**S5**), diphenyl phosphoryl chloride (**S6**), 4-methoxyphenol, 4-phenylphenol, biphenyl-2,2'-diol, glycidol and lithium bis(trifluoromethanesulfonyl)imide $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ (LiTFSI) were purchased from Aldrich and were used as received without purification. Tetrabutylammonium bromide (TBAB) (Merck) was dried at 50 °C for 4 h under vacuum prior to use.

The structures of all the products were confirmed by ^1H , ^{31}P , ^{13}C NMR spectra and HRMS data. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature using either CDCl_3 or DMSO-d_6 as solvent. The chemical

shifts are reported in parts per million (δ) relative to tetramethylsilane as reference for ^1H and $^{13}\text{C}\{^1\text{H}\}$ NMR (100 MHz). The $^{31}\text{P}\{^1\text{H}\}$ NMR (162 MHz) spectra referenced to 85% H_3PO_4 . HRMS spectra were recorded on a Bruker maXis instrument using ESI technique. Single crystal X-ray data collection was carried out at 298(2) K on a Bruker Smart Apex CCD area detector system (λ (Mo $\text{K}\alpha$) = 0.71073 Å) with a graphite monochromator. The data were reduced using SAINTPLUS and the structures were solved using SHELXS-97 and refined using SHELXL-97 [29]. All hydrogen atoms were refined anisotropically. The Netzsch STA 409 PC model was used for thermogravimetric and differential thermal analysis (TG-DTA) to examine the thermal stability. The decomposition behaviour of polymers was studied from 30 to 900 °C under the nitrogen flow with a heating rate of 10 °C/min. The temperature of 5% weight loss was chosen as onset point of decomposition (T_d). The glass transition temperatures (T_g) of polyethers were measured on a Differential Scanning Calorimeter (DSC) from PerkinElmer (Pyris Diamond DSC 8000). The measurements were performed at a heating rate of 10 °C/min under the nitrogen. T_g was assigned as the inflection point in the thermogram. The molecular weights of the polymers were determined by the Gel Permeation Chromatography (GPC) of Shimadzu 10AVP model equipped with refractive index (RI) detector. The separation was achieved using a Phenogel mixed bed column (300 × 7.80 mm) operated at 30 °C with a flow rate of 0.5 mL/min. using tetrahydrofuran (THF) as the eluent. The molecular weight and molecular weight distributions were calculated using polystyrene as a standard.

The impedance measurements of polymer electrolytes were performed in Zahner zennium electrochemical work station with built in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz to 4 MHz. Initially films were made by dissolving polymer and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in THF at room temperature, but the films of **SPE2**, **SPE3** and **SPE5-SPE7** were brittle. Therefore, instead of making films, pellets were made for measurements. The consistency of result was checked by repeating measurements three times. The specimens in the form of pellets were sandwiched between two gold plated electrodes housed in a homemade cell. For variable temperature measurements, cell was equilibrated at each temperature for 30 min. before measuring. The conductivity was calculated according to the equation $\sigma = d/(AR_b)$, where d is the thickness of the polymer electrolyte disc, A is the surface area of the pellet and R_b is the bulk resistance value which can be obtained from the Nyquist plot [30].

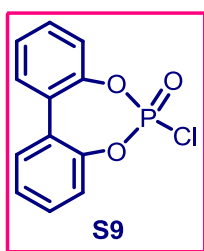
5.4.2. Experimental procedure

General procedure for the synthesis of chlorodiaryl phosphine oxide (S7-S10): A solution of appropriate phenol (50 mmol) or diol (25 mmol) in THF (10 mL) was added to a solution of POCl_3 (2.3 mL, 25 mmol) in THF (15 mL) at 0 °C. To this, NEt_3 (7.0 mL, 50 mmol) was slowly added for 10 min at 0 °C. While adding NEt_3 , immediate formation of white precipitate (NEt_3HCl) was observed. This reaction mixture was stirred for 2 h at 0 °C. After this, the reaction mixture was filtered to remove NEt_3HCl and the filtrate was evaporated under vacuum to obtain pure products.

Synthesis of chlorodi(4-methoxyphenoxy)phosphine oxide (S7): Prepared according to the general procedure by using 4-methoxyphenol (6.21 g, 50 mmol). The product was obtained as a colourless viscous oil. Since the isolated chloro product was not stable at room temperature, it was used for the next step without purification.

Synthesis of chlorodi(4-phenylphenoxy)phosphine oxide (S8): Prepared according to the general procedure by using 4-phenylphenol (8.51 g, 50 mmol). The product was obtained as a white powder. Since the isolated chloro product was not stable at room temperature, it was used for the next step without purification.

Synthesis of (1,1'-biphenyl-2,2'-dioxy)chlorophosphine oxide (S9): Prepared according to the general procedure by using biphenyl-2,2'-diol (4.66 g, 25 mmol). The product was obtained as white powder (Yield 95%).



^1H NMR (400 MHz, CDCl_3) : δ 7.60-7.56 (m, 2H, $-\text{C}_6\text{H}_4$), 7.53-7.47 (m, 2H, $-\text{C}_6\text{H}_4$), 7.46-7.40 (m, 2H, $-\text{C}_6\text{H}_4$), 7.38-7.33 (m, 2H, $-\text{C}_6\text{H}_4$).

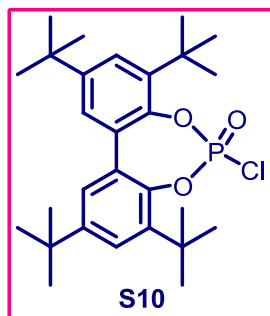
^{13}C NMR (100 MHz, CDCl_3) : δ 147.5 (d, $J = 11.4$ Hz), 130.5, 130.2, 128.1, 127.4, 121.5 (d, $J = 4.5$ Hz).

^{31}P NMR (162 MHz, CDCl_3) : δ 9.92.

HRMS calcd. for $C_{12}H_8ClO_3P$: 288.9797 $[M + Na]^+$

Found : 288.9797.

Synthesis of (3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-dioxy)chlorophosphine oxide (S10): Prepared according to the general procedure by using 3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-diol (10.27 g, 25 mmol). The product was obtained as white powder (Yield 98%).



^1H NMR (400 MHz, $CDCl_3$) : δ 7.56-7.52 (m, 2H, $-C_6H_2$), 7.22 (d, $J = 2.4$ Hz, 2H, $-C_6H_2$), 1.52 (s, 18H, $-CH_3$), 1.36 (s, 18H, $-CH_3$).

^{13}C NMR (100 MHz, $CDCl_3$) : δ 148.7, 144.3 (d, $J = 11.7$ Hz), 140.2 (d, $J = 4.9$ Hz), 129.8, 126.9, 125.8, 35.6, 34.8, 31.4.

^{31}P NMR (162 MHz, $CDCl_3$) : δ 4.32.

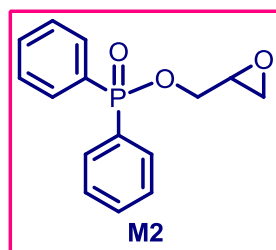
HRMS calcd. for $C_{28}H_{40}ClO_3P$: 491.2482 $[M + H]^+$

Found : 491.2486.

General procedure for the syntheses of monomers M2-M7: A solution of glycidol (1.6 mL, 24 mmol) in THF (10 mL) was added to a solution of appropriate chloro compound (S5-S10) (20 mmol) in THF (15 mL) at 0 °C. NEt_3 (5.6 mL, 40 mmol) was slowly added to the reaction mixture at 0 °C for 10 min. The immediate formation of white precipitate (NEt_3HCl) was observed. The reaction mixture was stirred for 2 h at 0 °C. The reaction mixture was filtered to remove NEt_3HCl and the filtrate was evaporated under vacuum to obtain the products.

Synthesis of oxiran-2-ylmethyl diphenylphosphinate (M2): Prepared according to the general procedure by using chlorodiphenylphosphine oxide (S5) (4.73 g, 20mmol). After the

addition of NEt_3 , the reaction mixture was stirred for 12 h at 25 °C. The product was obtained as colourless viscous oil (Yield 96%).



^1H NMR (400 MHz, CDCl_3) : δ 7.88-7.79 (m, 4H, $-\text{C}_6\text{H}_5$), 7.57-7.50 (m, 2H, $-\text{C}_6\text{H}_5$), 7.50-7.42 (m, 4H, $-\text{C}_6\text{H}_5$), 4.35-4.27 (m, 1H, $-\text{POCH}_2\text{CH}$), 3.98-3.89 (m, 1H, $-\text{POCH}_2\text{CH}$), 3.31-3.25 (m, 1H, $-\text{CH}_2\text{CHCH}_2$), 2.85-2.80 (m, 1H, $-\text{OCH}_2\text{CH}$), 2.68-2.63 (m, 1H, $-\text{OCH}_2\text{CH}$).

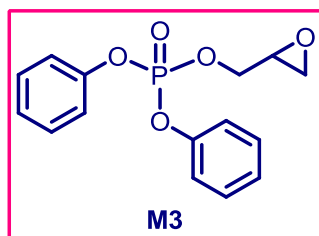
^{13}C NMR (100 MHz, CDCl_3) : δ 132.4, 131.8-131.5 (m), 130.3 (d, $J = 16.3$ Hz), 128.6 (d, $J = 12.8$ Hz), 65.3 (d, $J = 5.3$ Hz), 50.4 (d, $J = 7.7$ Hz), 44.7.

^{31}P NMR (162 MHz, CDCl_3) : δ 32.95.

HRMS calcd. for $\text{C}_{15}\text{H}_{15}\text{O}_3\text{P}$: 297.0657 $[\text{M} + \text{Na}]^+$

Found : 297.0655.

Synthesis of oxiran-2-ylmethyl diphenylphosphate (M3): Prepared according to the general procedure by using diphenyl phosphoryl chloride (**S6**) (5.37 g, 20 mmol). After the addition of NEt_3 , the reaction mixture was stirred for 12 h at 25 °C. The product was obtained as colourless viscous oil (Yield 98%).



^1H NMR (400 MHz, CDCl_3) : δ 7.38-7.31 (m, 4H, $-\text{C}_6\text{H}_5$), 7.26-7.17 (m, 6H, $-\text{C}_6\text{H}_5$), 4.35-4.28 (m, 1H, $-\text{POCH}_2\text{CH}$), 4.19-4.10 (m, 1H, -

POCH₂CH), 3.27-3.21 (m, 1H, -CH₂CHCH₂), 2.85-2.80 (m, 1H, -OCH₂CH), 2.65 (dd, *J* = 4.8 Hz and *J* = 2.6 Hz, 1H, -OCH₂CH).

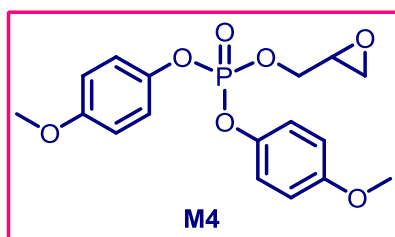
¹³C NMR (100 MHz, CDCl₃) : δ 150.4 (d, *J* = 6.0 Hz), 129.9, 125.5, 120.1, 69.4 (d, *J* = 5.7 Hz), 49.8 (d, *J* = 7.7 Hz), 44.5.

³¹P NMR (162 MHz, CDCl₃) : δ -11.81.

HRMS calcd. for C₁₅H₁₅O₅P : 329.0555 [M + Na]⁺

Found : 329.0555.

Synthesis of bis(4-methoxyphenyl)oxiran-2-ylmethyl phosphate (M4): Prepared according to the general procedure by using chlorodi(4-methoxyphenoxy)phosphine oxide (**S7**) (6.57 g, 20 mmol). The crude product was purified by column chromatography on silica gel eluting with hexane/ethylacetate (1 : 1) to give pure light brown colour viscous oil (Yield 88%).



¹H NMR (400 MHz, CDCl₃) : δ 7.16-7.11 (m, 4H, -C₆H₅), 6.86-6.81 (m, 4H, -C₆H₅), 4.47-4.40 (m, 1H, -POCH₂CH), 4.15-4.06 (m, 1H, -POCH₂CH), 3.77 (s, 6H, -OCH₃), 3.26-3.20 (m, 1H, -CH₂CHCH₂), 2.84-2.80 (m, 1H, -OCH₂CH), 2.64 (dd, *J* = 4.8 Hz and *J* = 2.6 Hz, 1H, -OCH₂CH).

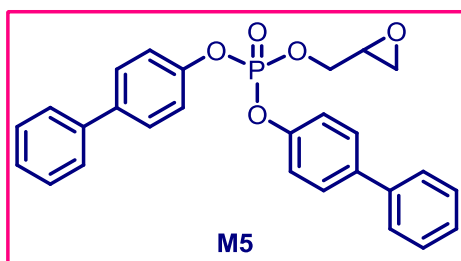
¹³C NMR (100 MHz, CDCl₃) : δ 157.0, 144.0 (d, *J* = 6.6 Hz), 121.0, 114.7, 69.3 (d, *J* = 5.8 Hz), 55.6, 49.8 (d, *J* = 7.8 Hz), 44.5.

³¹P NMR (162 MHz, CDCl₃) : δ -10.72.

HRMS calcd. for C₁₇H₁₉O₇P : 367.0947 [M + H]⁺

Found : 367.0948.

Synthesis of dibiphenyl-4yl-oxiran-2-ylmethyl phosphate (M5): Prepared according to the general procedure by using chlorodi(4-phenylphenoxy)phosphine oxide (**S8**) (8.42 g, 20 mmol). The crude product was purified by column chromatography on silica gel eluting with hexane/ethylacetate (3 : 1) to give pure white colour powder (Yield 81%).



^1H NMR (400 MHz, CDCl_3) : δ 7.60 (t, J = 8.6 Hz, 8H, $-\text{C}_6\text{H}_5$), 7.47 (t, J = 7.2 Hz, 4H, $-\text{C}_6\text{H}_5$), 7.42-7.34 (m, 6H, $-\text{C}_6\text{H}_5$), 4.62-4.52 (m, 1H, $-\text{POCH}_2\text{CH}$), 4.29-4.18 (m, 1H, $-\text{POCH}_2\text{CH}$), 3.37-3.30 (m, 1H, $-\text{CH}_2\text{CHCH}_2$), 2.93-2.85 (m, 1H, $-\text{OCH}_2\text{CH}$), 2.77-2.70 (m, 1H, $-\text{OCH}_2\text{CH}$).

^{13}C NMR (100 MHz, CDCl_3) : δ 149.9 (d, J = 7.2 Hz), 140.1, 138.8, 128.9, 128.6, 127.5, 127.1, 120.5-120.3 (m), 69.6 (d, J = 5.8 Hz), 49.8 (d, J = 7.6 Hz), 44.6.

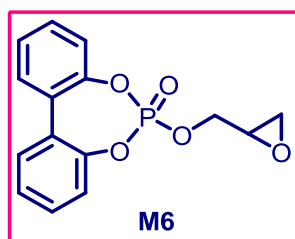
^{31}P NMR (162 MHz, CDCl_3) : δ -11.53.

HRMS calcd. for $\text{C}_{27}\text{H}_{23}\text{O}_5\text{P}$: 459.1361 $[\text{M} + \text{H}]^+$

Found : 459.1360.

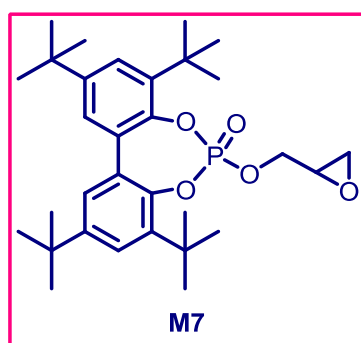
Synthesis of 2-(((1,1'-biphenyl-2,2'-dioxy)phosphine oxide)methyl)oxirane (M6):

Prepared according to the general procedure by using (1,1'-biphenyl-2,2'-dioxy)chlorophosphine oxide (**S9**) (5.33 g, 20 mmol). The product was obtained as pale yellow colour powder (Yield 90%).



^1H NMR (400 MHz, CDCl_3)	: δ 7.55 (d, $J = 7.6$ Hz, 2H, $-\text{C}_6\text{H}_4$), 7.49-7.43 (m, 2H, $-\text{C}_6\text{H}_4$), 7.39 (d, $J = 7.5$ Hz, 2H, $-\text{C}_6\text{H}_4$), 7.37-7.31 (m, 2H, $-\text{C}_6\text{H}_4$), 4.62-4.54 (m, 1H, $-\text{POCH}_2\text{CH}$), 4.26-4.17 (m, 1H, $-\text{POCH}_2\text{CH}$), 3.36-3.30 (m, 1H, $-\text{CH}_2\text{CHCH}_2$), 2.92-2.87 (m, 1H, $-\text{OCH}_2\text{CH}$), 2.74-2.69 (m, 1H, $-\text{OCH}_2\text{CH}$).
^{13}C NMR (100 MHz, CDCl_3)	: δ 147.7 (d, $J = 14.9$ Hz), 130.2, 129.9, 128.2, 126.6, 121.4, 69.8 (d, $J = 4.3$ Hz), 49.8 (d, $J = 7.4$ Hz), 44.6.
^{31}P NMR (162 MHz, CDCl_3)	: δ 1.76.
HRMS calcd. for $\text{C}_{15}\text{H}_{13}\text{O}_5\text{P}$	: 305.0579 $[\text{M} + \text{H}]^+$
Found	: 305.0579.

Synthesis of 2-(((3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-dioxy)phosphine oxide)methyl)oxirane (M7): Prepared according to the general procedure by using (3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-dioxy)chlorophosphine oxide (**S10**) (9.82 g, 20 mmol) and NaH (40 mmol) as base instead of NEt_3 . The crude product was purified by column chromatography on silica gel eluting with hexane/ethylacetate (3:1) to give pure white colour powder (Yield 84%).



^1H NMR (400 MHz, CDCl_3)	: δ 7.50 (s, 2H, $-\text{C}_6\text{H}_2$), 7.22-7.19 (m, 2H, $-\text{C}_6\text{H}_2$), 4.48-4.40 (m, 1H, $-\text{POCH}_2\text{CH}$), 4.19-4.10 (m, 1H, $-\text{POCH}_2\text{CH}$), 3.28-3.22 (m, 1H, $-\text{CH}_2\text{CHCH}_2$), 2.85-2.80 (m, 1H, $-\text{OCH}_2\text{CH}$), 2.65 (dd, $J = 4.8$ Hz and $J = 2.5$ Hz, 1H, $-\text{OCH}_2\text{CH}$), 1.52 (d, $J = 3.4$ Hz 18H, $-\text{CH}_3$), 1.36 (s, 18H, $-\text{CH}_3$).
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^{13}C NMR (100 MHz, CDCl_3) : δ 148.0, 144.4 (d, $J = 9.5$ Hz), 140.1 (d, $J = 4.5$ Hz), 130.0, 126.7, 125.3, 69.8 (d, $J = 6.0$ Hz), 49.8 (d, $J = 7.0$ Hz), 44.7, 35.5, 34.7, 31.4, 31.1.

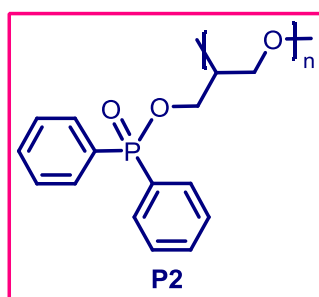
^{31}P NMR (162 MHz, CDCl_3) : δ -3.01.

HRMS calcd. for $\text{C}_{31}\text{H}_{45}\text{O}_5\text{P}$: 551.2902 $[\text{M} + \text{Na}]^+$

Found : 551.2903.

General procedure for the ROP of epoxides: All the polymerization reactions were performed in the pressure tube. To the solution of monomer (**M2-M7**) (10 mmol) in THF (2.5 mL), catalyst (0.1 mmol) and TBAB (0.067 mmol) was added under stirring. The pressure tube was heated to 70 °C and stirred for the required time. After the reaction time, methanol was added to the reaction mixture to quench the polymerization and the solvent was evaporated under vacuum. The product was purified by dissolving in THF and reprecipitated in hexane and this process was repeated for three more times.

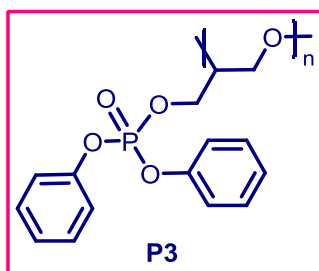
Synthesis of polymer P2: The ROP was carried out according to the general procedure by using oxiran-2-ylmethyl diphenylphosphinate (**M2**) (Yield 92%).



^1H NMR (400 MHz, CDCl_3) : δ 7.69-7.57 (m, $-\text{C}_6\text{H}_5$), 7.26-7.13 (m, $-\text{C}_6\text{H}_5$), 4.29-4.07 (m, $-\text{POCH}_2\text{CH}$), 3.92-3.64 (m, $-\text{OCH}_2\text{CH}$ and $-\text{CH}_2\text{CHCH}_2$).

^{31}P NMR (162 MHz, CDCl_3) : δ 28.65.

Synthesis of polymer P3: The ROP was carried out according to the general procedure by using oxiran-2-ylmethyl diphenylphosphate (**M3**) (Yield 98%).

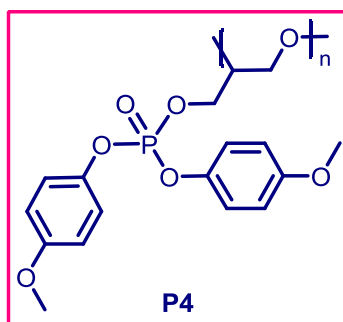


^1H NMR (400 MHz, CDCl_3) : δ 7.43-7.09 (m, $-\text{C}_6\text{H}_5$), 7.03-6.75 (m, $-\text{C}_6\text{H}_5$), 4.33-3.99 (m, $-\text{POCH}_2\text{CH}$), 3.93-3.72 (m, $-\text{OCH}_2\text{CH}$ and $-\text{CH}_2\text{CHCH}_2$).

^{13}C NMR (100 MHz, CDCl_3) : δ 158.9, 129.8, 120.2, 115.1, 80.8, 70.1, 67.3.

^{31}P NMR (162 MHz, CDCl_3) : δ -0.75.

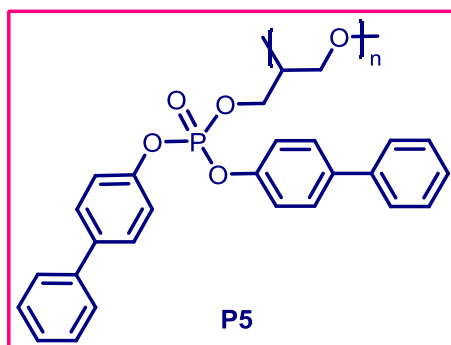
Synthesis of polymer P4: The ROP was carried out according to the general procedure by using bis(4-methoxyphenyl)oxiran-2-ylmethyl phosphate (**M4**) (Yield 95%).



^1H NMR (400 MHz, CDCl_3) : δ 6.99-6.78 (m, $-\text{C}_6\text{H}_5$), 6.75-6.62 (m, $-\text{C}_6\text{H}_5$), 4.43-4.15 (m, $-\text{POCH}_2\text{CH}$), 4.09-3.80 (m, $-\text{OCH}_2\text{CH}$ and $-\text{CH}_2\text{CHCH}_2$), 3.70-3.60 (m, $-\text{OCH}_3$).

^{31}P NMR (162 MHz, CDCl_3) : δ -5.82.

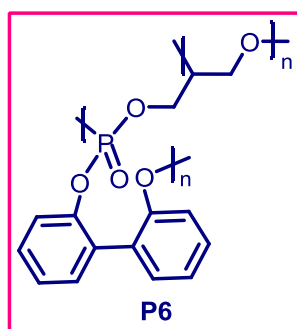
Synthesis of polymer P5: The ROP was carried out according to the general procedure by using dibiphenyl-4-yl-oxiran-2-ylmethyl phosphate (**M5**) (Yield 90%).



^1H NMR (400 MHz, CDCl_3) : δ 7.66-7.50 (m, $-\text{C}_6\text{H}_5$), 7.44-7.35 (m, $-\text{C}_6\text{H}_5$), 7.32-7.19 (m, $-\text{C}_6\text{H}_5$), 4.32-4.16 (m, $-\text{POCH}_2\text{CH}$), 3.95-3.73 (m, $-\text{OCH}_2\text{CH}$ and $-\text{CH}_2\text{CHCH}_2$).

^{31}P NMR (162 MHz, CDCl_3) : δ -4.69.

Synthesis of polymer P6: The ROP was carried out according to the general procedure by using 2-(((1,1'-biphenyl-2,2'-dioxy)phosphine oxide)methyl)oxirane (**M6**) (Yield 78%).

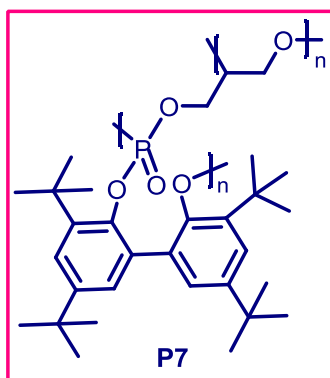


^1H NMR (400 MHz, CDCl_3) : δ 7.83-7.30 (m, $-\text{C}_6\text{H}_5$), 4.27-3.83 (m), 3.81-3.65 (m), 3.59-3.44 (m), 3.41-3.19 (m).

^{13}C NMR (100 MHz, CDCl_3) : δ 158.6, 157.6, 129.3, 128.2, 127.7, 127.5, 127.2, 126.7, 126.4, 120.8, 116.2, 115.4, 78.2, 73.2, 68.7, 63.6, 60.8.

^{31}P NMR (162 MHz, CDCl_3) : δ 1.77, -0.72.

Synthesis of polymer P7: The ROP was carried out according to the general procedure by using 2-(((3,3',5,5'-tetra-*tert*-butyl-1,1'-biphenyl-2,2'-dioxy)phosphine oxide)methyl)oxirane (**M7**) (Yield 81%).



^1H NMR (400 MHz, CDCl_3) : δ 7.53-7.49 (m, $-\text{C}_6\text{H}_2$), 7.33-7.30 (m, $-\text{C}_6\text{H}_2$), 7.26-7.22 (m, $-\text{C}_6\text{H}_2$), 7.05-7.01 (m, $-\text{C}_6\text{H}_2$), 4.38-4.21 (m), 4.20-4.07 (m), 4.04-3.84 (m), 1.48-1.42 (m, $-\text{CH}_3$), 1.33-1.27 (m, $-\text{CH}_3$).

^{31}P NMR (162 MHz, CDCl_3) : δ -2.80, -5.61.

General preparation of solid polymer electrolytes SPE2, SPE3 and SPE5-SPE7: The polymers (**P2**, **P3** and **P5-P7**) were dried at 60 °C under vacuum for 8 h. $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ was dried at 150 °C under vacuum for 10 h before use. All manipulations were carried out in an MBraun glove box filled with ultrapure nitrogen gas. Electrolytes with different ratio were prepared as follows: the polymer was dissolved in THF with lithium salt and stir for 12 h at 25 °C. After this, THF was evaporated under vacuum and dried the residue at 60 °C for 12 h. The residue was loaded in to a die and then pressed to make a pellet. Specimens of 0.07–0.08 cm thickness and 0.9 cm diameter were obtained for conductivity studies. These pellets were sandwiched between two gold plated electrodes housed in a homemade cell for conductivity studies. The consistency of results was checked by repeating three times.

Supporting information: ^1H , ^{13}C and ^{31}P NMR spectra of **M3** and **M6** are included at the end of this chapter (Figure 5.S1 - 5.S6).

5.5. References

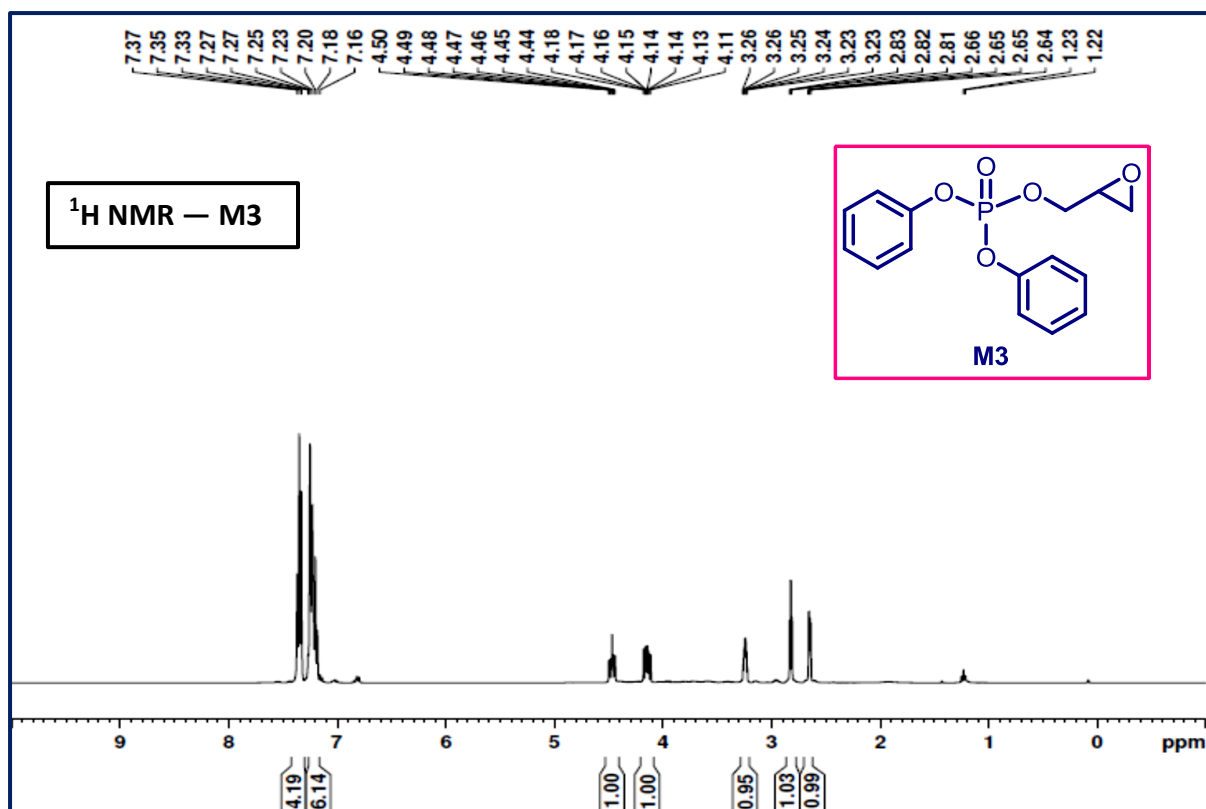
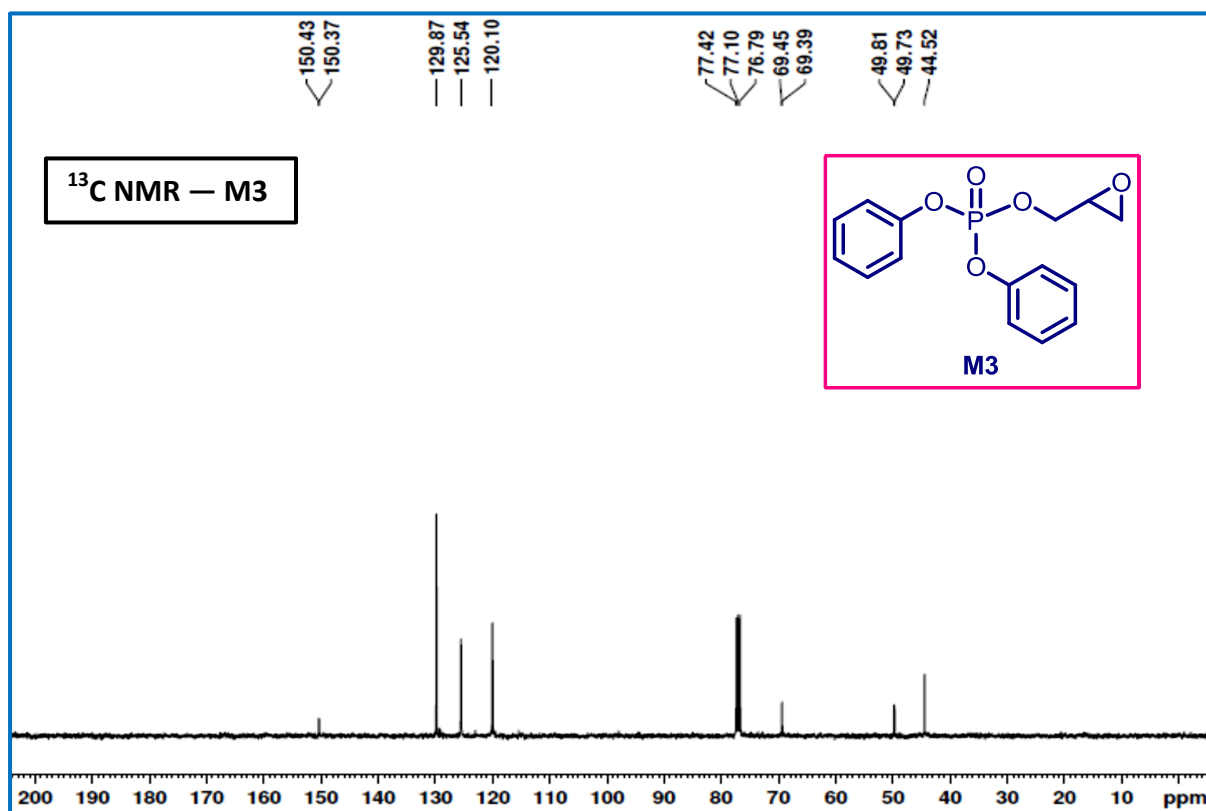
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Figure 5.S1. ^1H NMR spectrum of compound M3Figure 5.S2. ^{13}C NMR spectrum of compound M3

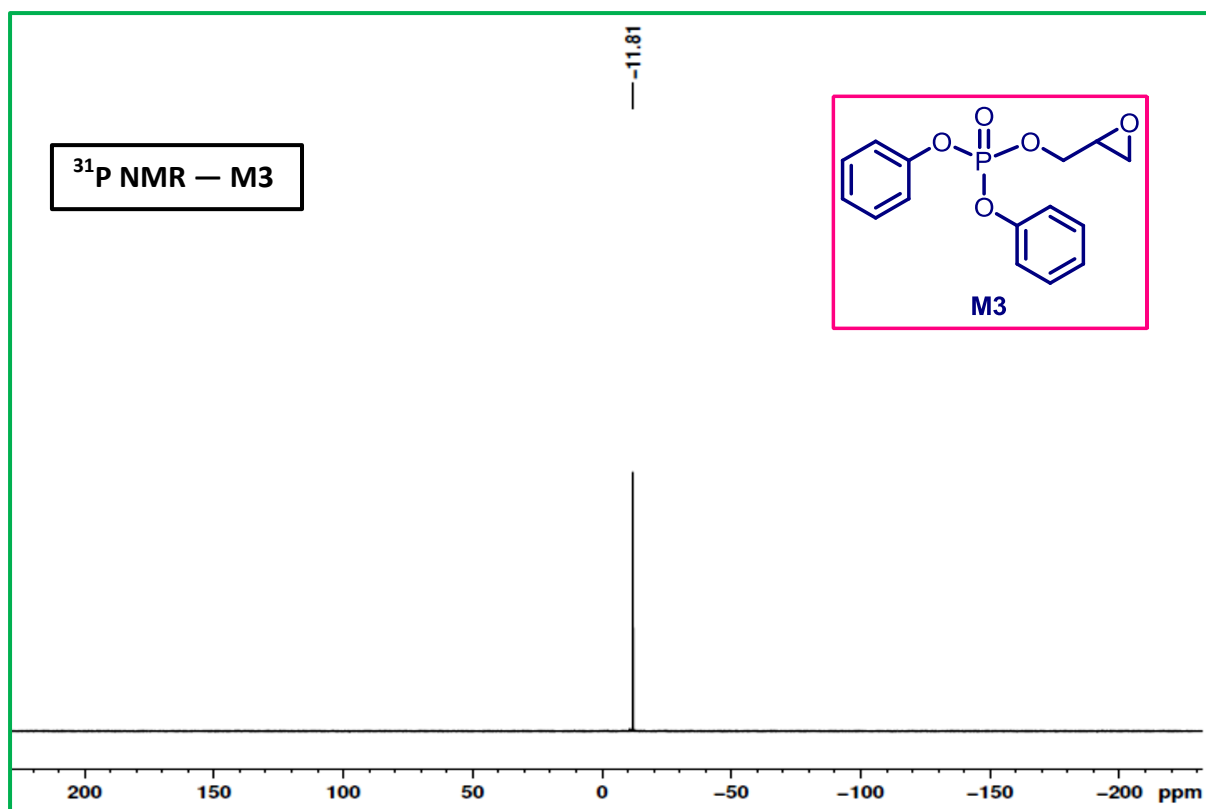


Figure 5.S3. ³¹P NMR spectrum of compound M3

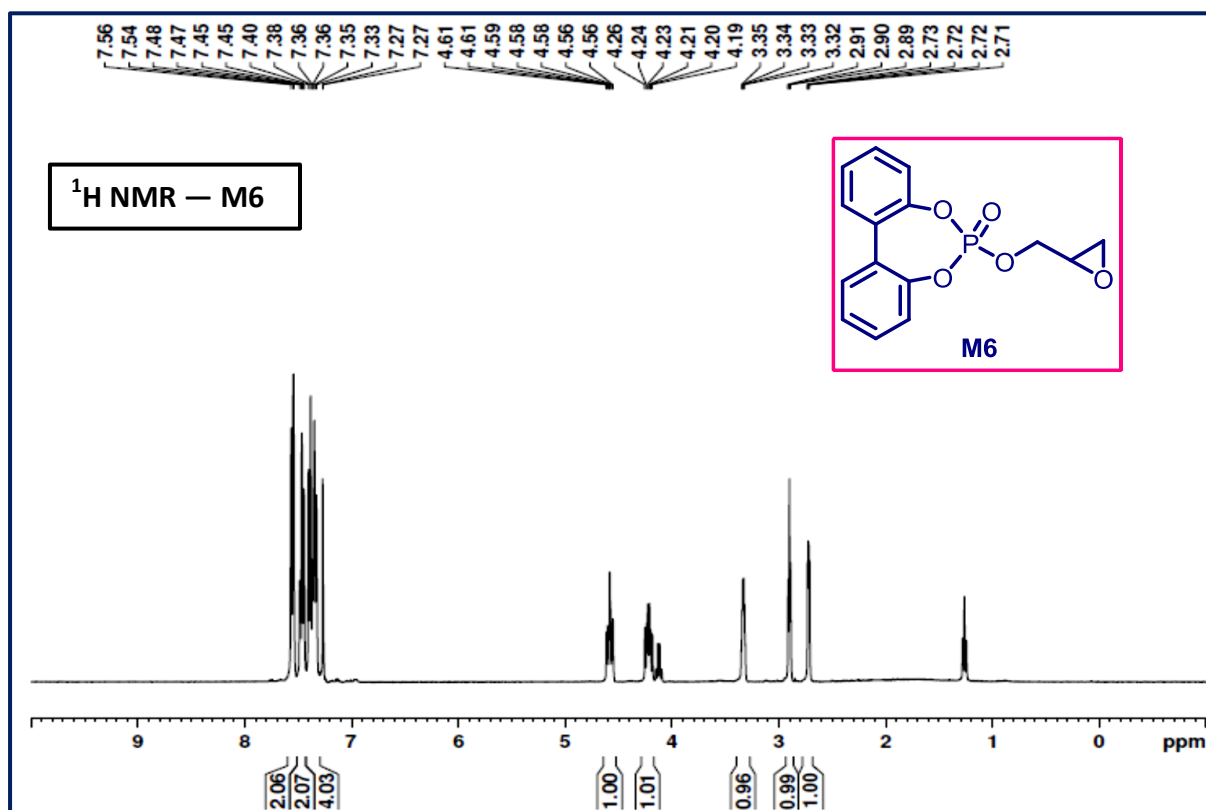
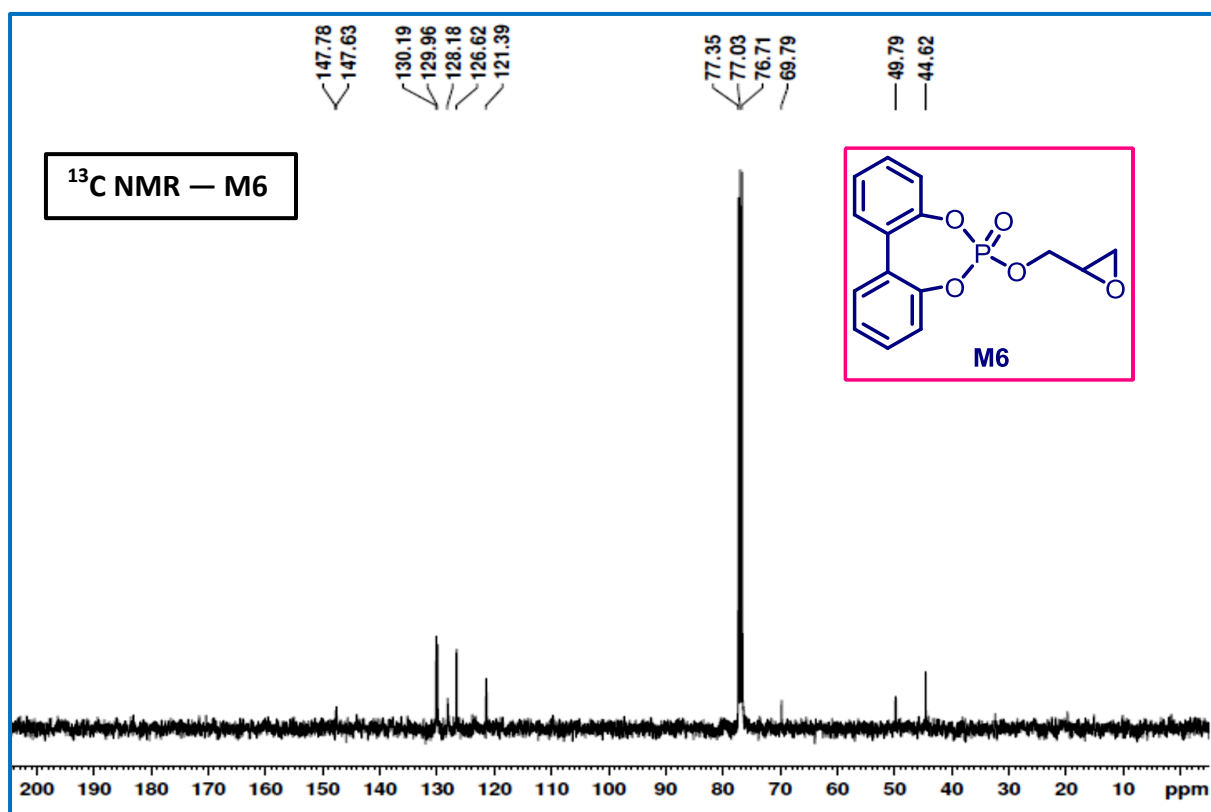
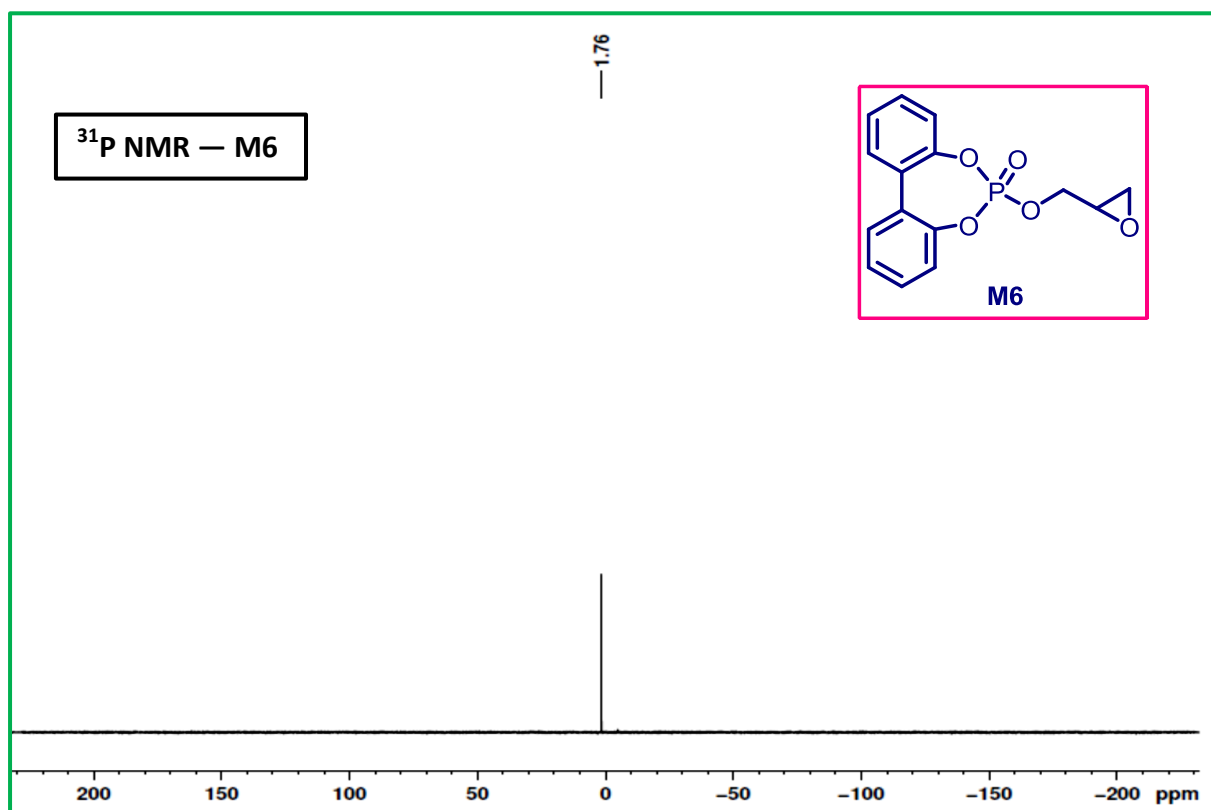


Figure 5.S4. ¹H NMR spectrum of compound M6

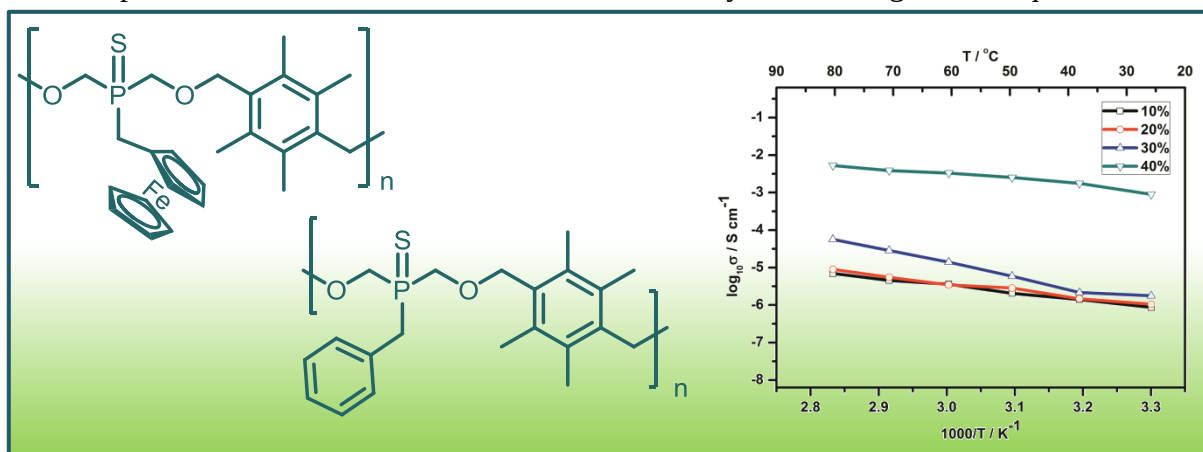
Figure 5.S9. ^{13}C NMR spectrum of compound M6Figure 5.S6. ^{31}P NMR spectrum of compound M6

CHAPTER 6

Intrinsic Porous Polymer Framework: A New Generation of Solid Polymer Electrolyte

Abstract

Rechargeable lithium-ion batteries are the major power sources for portable electronics. However, the current technology cannot be promoted to automobile batteries due to the potential fire hazard of organic liquid present in batteries. A better solid polymer electrolyte (SPE) with flame retardance property for high-energy density lithium ion batteries is always been in demand to replace the organic liquid. In this chapter, syntheses of intrinsic porous polymers for lithium-ion conductivity are described. The copolymerization of substituted bis(hydroxymethyl)phosphine sulfide [RP(S)(CH₂OH)₂ R = ferrocenylmethyl (**M8**), benzyl (**M9**)] with dibromo monomer (**M10**) are successfully carried out to produce novel intrinsic porous polyethers containing phosphorus. These polymers are obtained by nucleophilic substitution reactions and characterized using ¹H, ³¹P NMR, gel permeation chromatography and BET adsorption and desorption isotherm. The mesoporosity in these polymers is confirmed by nitrogen adsorption and desorption analyses. The porosity is explained by inefficient packing of polymer chains producing interconnected voids throughout the bulk material. This intrinsic porous polymer is examined for lithium-ion conductivity by preparing SPE using LiTFSI. The conductivity of **SPE9** with 40 wt% of LiTFSI is 8.9×10^{-4} S cm⁻¹ at room temperature and 5.3×10^{-3} S cm⁻¹ at 80 °C. These all solid-state polymer electrolytes have potential to achieve the conductivity of organic liquid/Li salt.



6.1. Introduction

Advanced materials and molecules for energy harvesting and storage devices are in demand to improve their performance and efficiency. Case in point, the Li-ion batteries are fast developing as replacement to lead-acid batteries to run automobiles [1]. However, some of its disadvantages - such as high cost and more weight of the Li-ion batteries - and the imperatives to increase its energy density and working temperature necessitate further evolution of new electrode materials and polymer electrolyte systems [2]. Further, there is a need for a thorough understanding of the conduction mechanism to focus on improving ionic conductivities of solid polymer electrolytes [3].

According to the conventional theory, amorphous polymers exhibit ionic conductivity whereas crystalline polymers most likely behave as insulator. The ionic conductivity in amorphous polymer is due to the movement of ions, ensued by the local segmental motion of the polymer chain particularly above its glass transition temperature (T_g). Above T_g , the superstructure of polymers has disordered and flexible environment. Since the polymer chains are in constant motion above its T_g , a vacant space would continually create and disappear, through which an ion move by coordination. It means, an ion has to wait to find a new coordination site and a free volume for hopping. This clearly describes the rate of ion transport depends on local chain dynamics of polymer [4]. Our interest is creating a fixed perpetual free volume through which the ion would move without delay. It would improve the mobility of ion leading to higher ionic conductivity. For that, we have chosen to synthesize porous materials with a needed structural framework (interconnected voids) for better lithium ion transport.

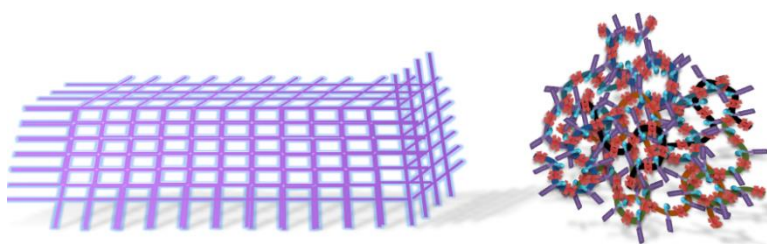


Figure 6.1. Schematic representation of a) crystalline porous polymer framework (left) b) amorphous covalent organic framework (right)

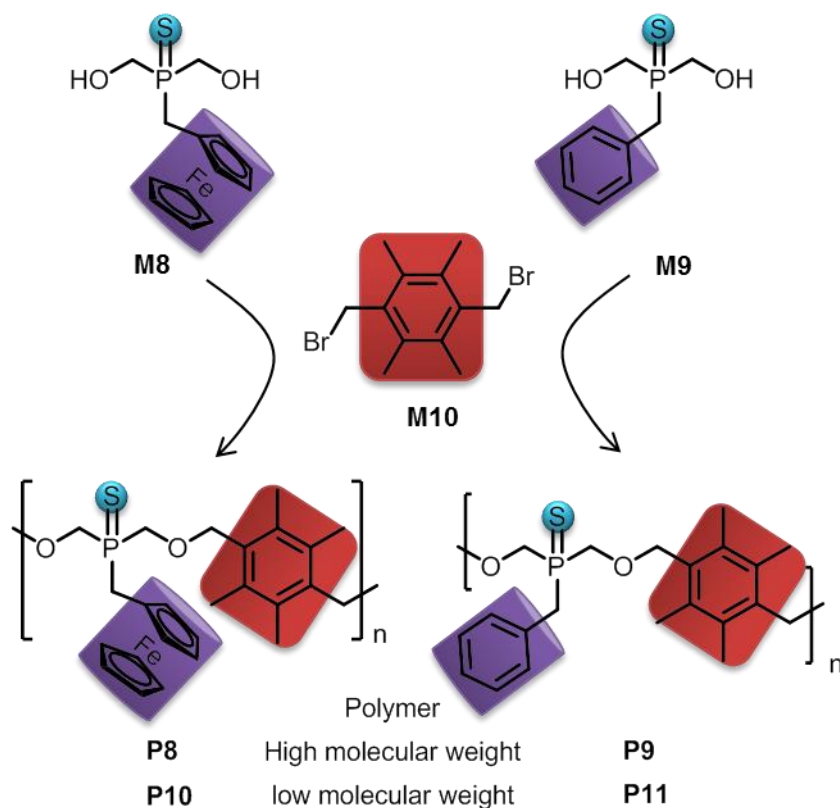
Unlike in densely packed material, in porous material the moving ions have chance to interact throughout the material [5]. This would lead to more interaction of lithium ions with

high surface area of porous material that may contribute in promoting the conductivity. Many efforts are directed toward synthesizing new porous polymers for lithium ion transport without sacrificing their properties. One such approach is constructing perfect porous polymer framework (Figure 6.1a) through a crystalline arrangement of polymer chains either by metal organic framework (MOFs) or covalent organic framework (COFs). MOFs and COFs are well-known for applications in gas storage, catalysis and molecular separation [6]; but synthesizing the porous material by MOF and COF approach for lithium ion transport without sacrificing their desired properties is challenging. Alternatively, an amorphous covalent organic framework can be achieved in hyper-cross linked polymers or intrinsic porous polymers (Figure 6.1b). Herein, we describe the synthesis of intrinsic porous soluble polymers and their influence on ionic conductivity.

6.2. Results and discussion

Introduction of phosphorus-carbon bonds [7], in lieu of carbon-carbon bonds in a polymer chain, could provide additional conformational flexibility favouring disordered arrangement and inefficient packing of polymer chains. This may lead to interesting physical and chemical properties such as amorphous nature, flame retardant and stability at high temperatures to the polymers [8]. Polyphosphazenes [9] and polysiloxanes [10], due to their conformational flexibility, can be good hosts for lithium ion conductivity, accordingly they were reported to have maximum conductivity of $5 \times 10^{-5} \text{ S cm}^{-1}$ and $4.5 \times 10^{-4} \text{ S cm}^{-1}$, respectively.

Over the decades, many phosphorus-containing polymers are reported. Closer look into the literature showed that the most of these phosphorus containing polymers can be grouped as polymers with phosphorus atoms in main chain or a phosphorus containing group is attached as a pendant group to main chain. The first group of polymers includes polymers with P-N, P-C, P-O and P-B bonds in main chain. The second group comprises mostly phosphonates or phosphinates attached to typical carbon polymers [7, 11-16]. In order to synthesize phosphorus containing polymers; various phosphorus containing monomers are employed. Perhaps, use of substituted bis(hydroxymethyl) phosphine sulphides [17] (Scheme 6.1) could be one strategy to introduce phosphorus-carbon bonds in the main chain of a polymer.



Scheme 6.1. Synthesis of polymers **P8-P11**. Reaction condition: NaH, DMAc, 60 °C (**P8** and **P9**), 25 °C (**P10** and **P11**).

It is known that the reactivity of alkyl/aryl bis(hydroxymethyl) phosphines differed from their oxides and sulfides. The hydroxymethyl groups of these phosphines behaved like masked -PH_2 groups. But their reactivity became similar to a normal diol when the phosphines were converted to phosphine sulfides or oxides [18]. However, use of substituted bis(hydroxymethyl) phosphine sulfides as monomers have been virtually unexplored [19]. This also urged us to study the chemistry of substituted bis(hydroxymethyl)phosphine sulfides as monomers in a polymer synthesis. The monomers ferrocenylmethyl bis(hydroxymethyl)phosphine sulfide [17] (**M8**) and benzyl bis(hydroxymethyl)phosphine sulfide [18] (**M9**) were prepared from $\text{P}(\text{CH}_2\text{OH})_4\text{Cl}$. 1,4-bis(bromomethyl)-2,3,5,6-tetramethylbenzene (**M10**) was synthesized from durene according to the literature procedures [20].

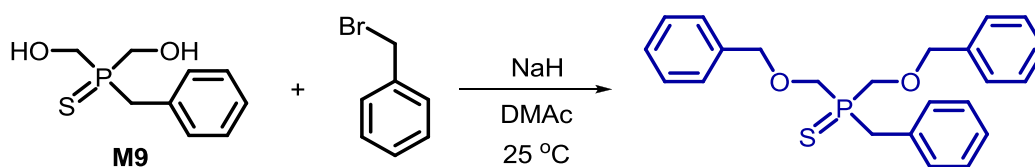
Based on the functional groups present in the monomers (**M8-9** and **M10**), condensation polymerization method was preferred to synthesize the copolymers. Further, in view of understanding the influence of molecular weight on the ionic conductivities of polymers, we desired to synthesize same polymers of varying molecular weights. The

monomers **M8** or **M9** was copolymerized with **M10** (1 : 1 ratio) in the presence of NaH as a base in dimethylacetamide (DMAc) to yield polyethers **P8-P11** (Table 6.1). The condensation polymers **P8** and **P9** were prepared successfully via nucleophilic substitution reaction at 60 °C whereas the low molecular weight polymers **P10** and **P11** were synthesized at 25 °C. Further increase in reaction temperature led to the formation of insoluble polymers. The crude polymers were purified by washing with methanol in a Soxhlet extractor for 24 h. These reactions yielded novel polyethers wherein the phosphorus atoms are in main chain of the polymers. To confirm the possibility of such nucleophilic substitution reactions, we have carried out a model reaction wherein the monomer **M9** was reacted with benzyl bromide and corresponding product was isolated and characterized (Scheme 6.2).

Table 6.1. Properties of polymers **P8-P11**

Monomer	T (°C) ^a	Polymer	T _d (°C)	T _g (°C)	M _n (g mol ⁻¹)	M _w (g mol ⁻¹)	PDI
M8	60	P8	288.1	137.0	6834	11892	1.74
M9	60	P9	354.4	143.4	9581	14564	1.52
M8	25	P10	276.2	130.1	1791	2806	1.56
M9	25	P11	250.3	112.3	2099	4260	2.03

^aTemperature at which the polymerization was carried out.



Scheme 6.2. Model reaction

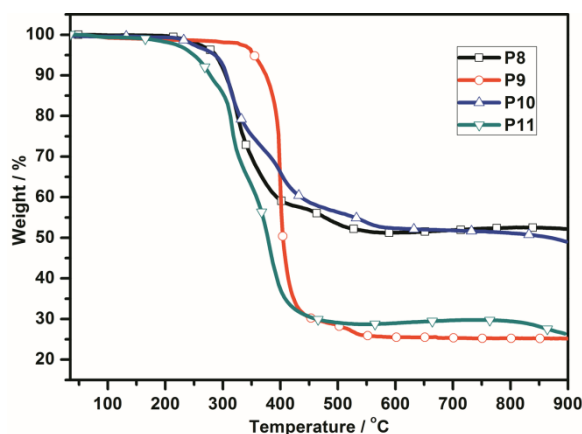


Figure 6.2. TGA plots of polyether **P8-P11**

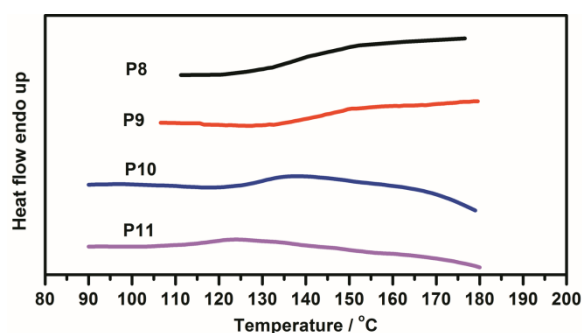


Figure 6.3. DSC plots of **P8-P11**

All these polyethers were solids and readily soluble in chloroform and dimethyl sulfoxide. The polyethers **P8-P11** were characterized by ^1H and ^{31}P NMR spectral data which showed that the data were consistent with the expected molecular structure. The $^{31}\text{P}\{^1\text{H}\}$ NMR spectra of polymers (**P8**: 45.4 and **P9**: 47.9 ppm) showed a single peak whereas polymers **P10** and **P11** showed two sets of peaks appearing around 41–42.8 and 45–46.1 ppm. The difference in ^{31}P NMR spectra of high and low molecular weight polymers was due to the chain length. When the length of the polymer chain was small, then the terminal groups were distinguishable from inner groups. Comparing with the chemical shifts of monomers (**M8**: 47.2 ppm and **M9**: 49.2 ppm), the first set of peaks were assigned to the core internal phosphorus atoms of the polymers while the second set of peaks for the terminal group phosphorus atoms of the polymers [21]. The copolymers **P8** and **P9** possess relatively higher molecular weight (M_w) than **P10** and **P11** (Table 6.1).

Thermogravimetric analyses on polyethers were carried out and the data are displayed in Table 1. The polymers were thermally stable at least up to 250 °C (Figure 6.2). In these polyethers, both T_d and T_g increased with increase in chain length (Table 6.1). The absence of

melting temperature (T_m) in DSC curves confirmed that the polymers (**P8-P11**) were completely amorphous even with low molecular weight polymers **P10** and **P11** (Figure 6.3). The amorphous nature of these polymers further revealed the presence of highly disordered and thereby inefficient packing of polymer chains.

Table 6.2. Conductivity of **P10** with various lithium salts at room temperature

Polymer	Lithium Salt	% of Lithium Salt (wt%)	O : Li	Conductivity, σ (S cm ⁻¹)
P10	LiN(SO ₂ CF ₃) ₂	10	5.4 : 1.0	2.0×10^{-5}
		20	2.4 : 1.0	2.9×10^{-5}
		30	1.4 : 1.0	7.4×10^{-5}
		40	0.9 : 1.0	1.4×10^{-4}
	LiSO ₃ CF ₃	10	2.9 : 1.0	1.6×10^{-6}
		20	1.3 : 1.0	5.9×10^{-6}
		30	0.8 : 1.0	0.6×10^{-5}
		40	0.5 : 1.0	4.2×10^{-5}
	LiClO ₄	10	2.0 : 1.0	1.4×10^{-6}
		20	0.9 : 1.0	6.8×10^{-6}
		30	0.5 : 1.0	4.0×10^{-5}
		40	0.3 : 1.0	7.9×10^{-5}

Solid polymer electrolytes (**SPE8-SPE11**) were prepared by blending the polymers (**P8-P11**) with the lithium salt in suitable ratios and lithium ion conductivities were determined. At first, the conductivity of **P10** was tested with three different lithium salts such as lithium bis(trifluoromethanesulfonyl)imide [LiN(SO₂CF₃)₂] (LiTFSI), LiSO₃CF₃, LiClO₄ at room temperature to find the better combination (Table 6.2). Among these, LiTFSI was found to be a good candidature and hence utilized for further studies.

SPE8-SPE11 were characterized by using IR, TGA and DSC. The stacked IR spectra of **P8** and **SPE8** with 10-40 wt% of LiTFSI [**SPE8** (10%-40%)] is shown in Figure 6.4. IR absorption peak for C-O-C group of **P8** appeared at 1088 cm⁻¹, but the absorption peak for C-O-C group of **SPE8** was shifted to lower frequency (1053 cm⁻¹). The intensity of peak at 1053 cm⁻¹ increased with the increasing wt% of lithium salt. The shift in frequency supports the interaction of C-O-C group with lithium ion [22].

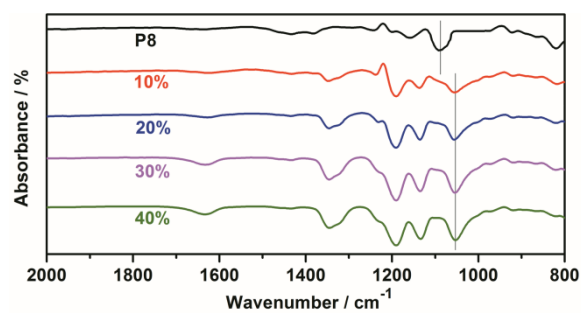


Figure 6.4. Stacked IR spectra of **P8** and **SPE8** (10%-40%)

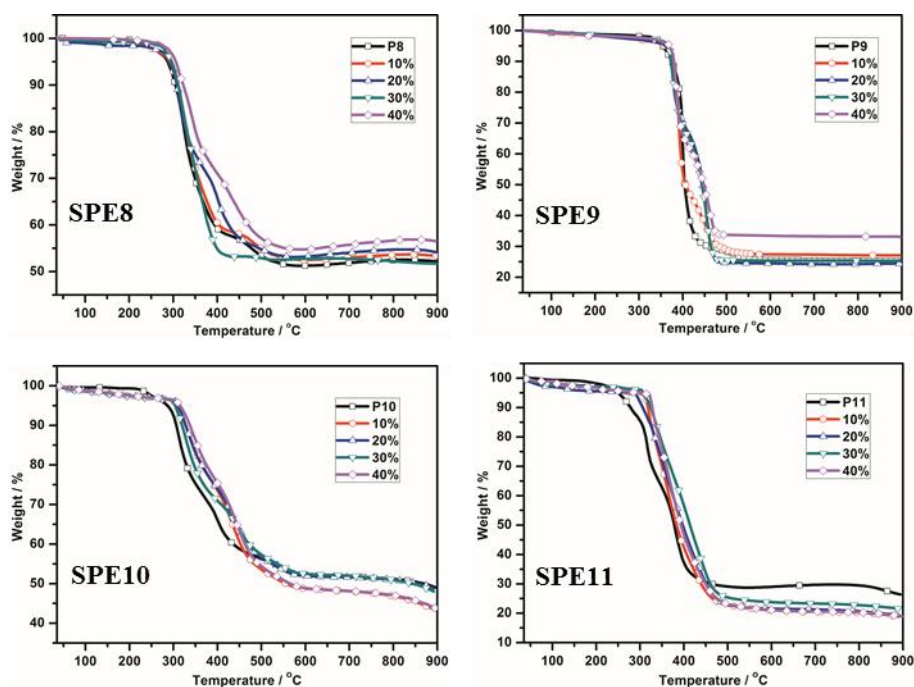


Figure 6.5. TGA plots of **SPE8** (10%-40%)-**SPE11** (10%-40%)

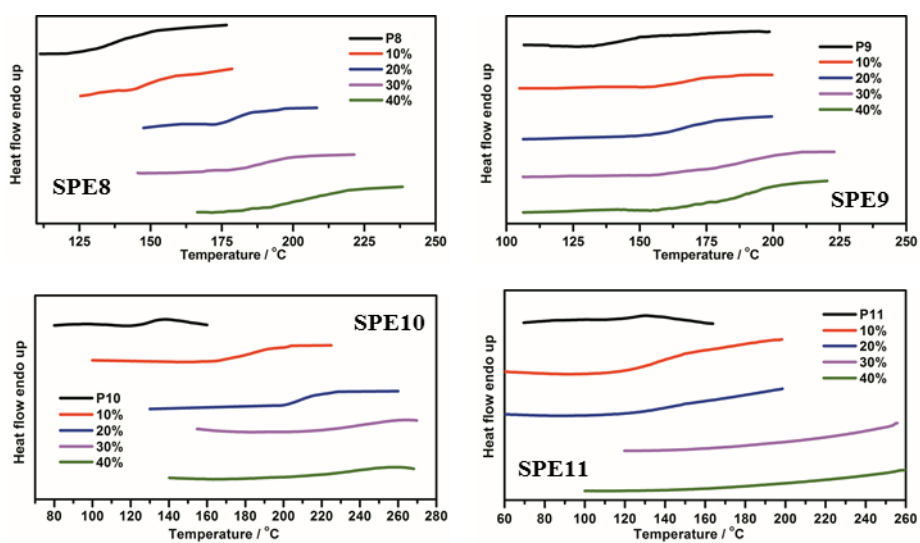


Figure 6.6. DSC plots of **SPE8** (10%-40%)-**SPE11** (10%-40%)

The TGA analyses (Figure 6.5) revealed that thermal stability of **SPE8-SPE10** and **SPE11** were increased to 300 °C and 370 °C respectively compared to their corresponding polymers **P8-P11** (Table 6.1). The glass transition temperatures (T_g) of **SPE8-SPE11** (10%-40%) obtained from DSC are shown in Table 6.3 and 6.4. The absence of melting temperature (T_m) peak of **SPE8-SPE11** in DSC clearly indicated, after blending with polymers, the LiTFSI did not exist in the form of aggregates (ion-pair). **SPE8-SPE11** with 40 wt% of LiTFSI [(**SPE8-SPE11** (40%))] also did not show the peak for T_m which implied the effective solvation by polymers even with higher wt% of lithium salt. For higher concentration of lithium salts, T_g of **SPE8-SPE11** was not obvious from DSC graphs even after varying the scanning rates and with more amounts of samples (Figure 6.6). The increase in T_g of **SPE8-SPE11** comparing with respective polymers and difficulty in measuring T_g of **SPE8-SPE11** with higher salt concentration can be attributed to the effective coordination of oxygen atoms in the polymer chains with lithium ions. With higher salt contents, coordination of polymer with lithium ions could have restricted the stretching and segmental motion of polymer chains.

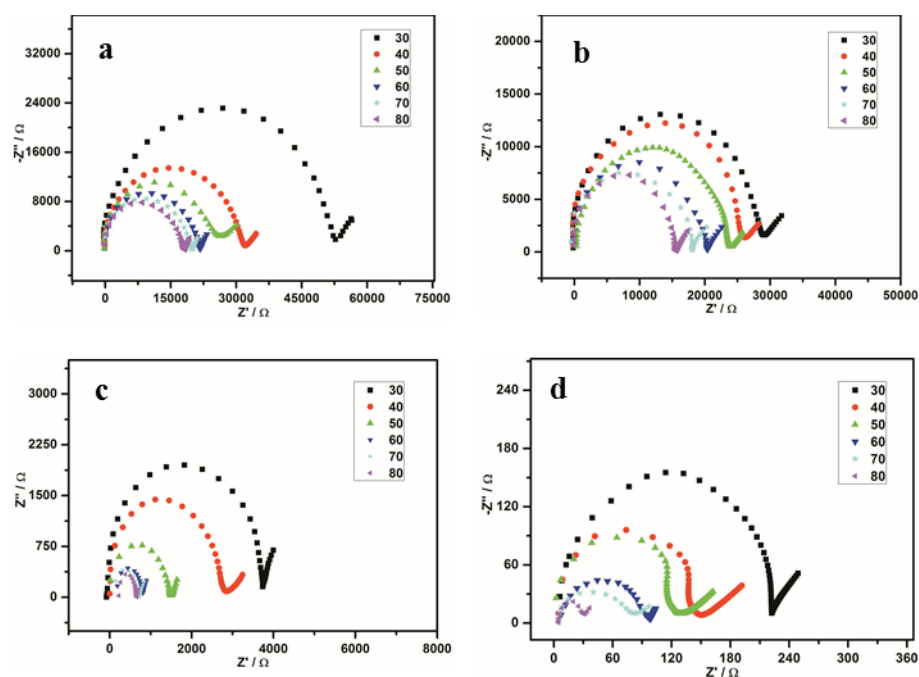


Figure 6.7. Temperature dependent nyquist plots of **SPE8** a) 10% b) 20% c) 30% d) 40%

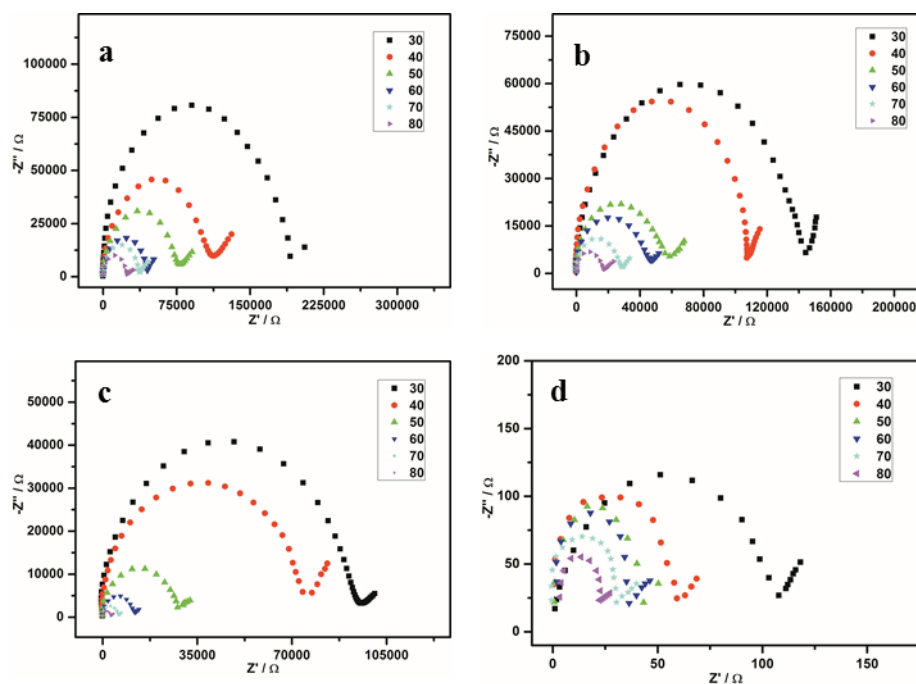


Figure 6.8. Temperature dependent nyquist plots of SPE9 a) 10% b) 20% c) 30% d) 40%

Table 6.3. Properties of SPE8 (10%-40%)-SPE9 (10%-40%)

SPEs (wt% of LiTFSI)	SPE8			SPE9		
	O:Li	Conductivity σ (S cm ⁻¹) ^a	T _g (°C)	O:Li	Conductivity σ (S cm ⁻¹) ^a	T _g (°C)
SPE (10%)	5.4:1	2.1×10^{-6}	148.7	6.9:1	8.7×10^{-7}	156.4
SPE (20%)	2.4:1	4.2×10^{-6}	179.3	3.1:1	1.1×10^{-6}	166.5
SPE (30%)	1.4:1	1.6×10^{-5}	189.1	1.8:1	1.8×10^{-6}	171.0
SPE (40%)	1.0:1	4.5×10^{-4}	204.8	1.2:1	8.9×10^{-4}	192.8

^aRoom temperature conductivity.

Table 6.4. Properties of SPE10 (10%-40%)-SPE11 (10%-40%)

SPEs (wt% of LiTFSI)	SPE10			SPE11		
	O:Li	Conductivity σ (S cm ⁻¹) ^a	T _g (°C)	O:Li	Conductivity σ (S cm ⁻¹) ^a	T _g (°C)
SPE (10%)	5.4:1	2.0×10^{-5}	184.3	6.9:1	7.7×10^{-7}	148.9
SPE (20%)	2.4:1	2.9×10^{-5}	207.8	3.1:1	1.1×10^{-6}	154.5
SPE (30%)	1.4:1	7.4×10^{-5}	226.4	1.8:1	2.8×10^{-5}	206.6
SPE (40%)	1.0:1	1.4×10^{-4}	236.1	1.2:1	7.7×10^{-5}	209.6

^aRoom temperature conductivity.

The conductivities of these electrolytes were calculated from the bulk resistance determined from complex impedance spectra [23]. The room temperature conductivities of **SPE8-SPE11 (10%-40%)** are shown in Table 6.3 and 6.4. Among all combinations studied, at room temperature, the **SPE9 (40%)** exhibited the highest conductivity of $8.9 \times 10^{-4} \text{ S cm}^{-1}$. The nyquist and Arrhenius plots of temperature dependent conductivities of **SPE8-SPE11 (10%-40%)** are shown in Figure 6.7, 6.8 and 6.9. And the conductivities of **SPE8 (40%)** and **SPE9 (40%)** at increasing temperature is listed in Table 6.5. It is evidenced from Arrhenius plots that when the temperature was increased the conductivities of **SPE8 (10%-40%)** and **SPE9 (10%-40%)** also increased. The maximum conductivity of $5.3 \times 10^{-3} \text{ S cm}^{-1}$ was attained for **SPE9 (40%)** at 80°C . The conductivity of **SPE9 (40%)** reached the value of $10^{-3} \text{ S cm}^{-1}$ within 40°C . To the best of our knowledge, this is the highest conductivity achieved so far in all solid state polymer electrolytes. It is worth mentioning here is that the highest conductivity was achieved in its pure form without any extra additives added to it. Hence, these **SPE8-SPE11** have potential to utilize for automobile lithium ion batteries.

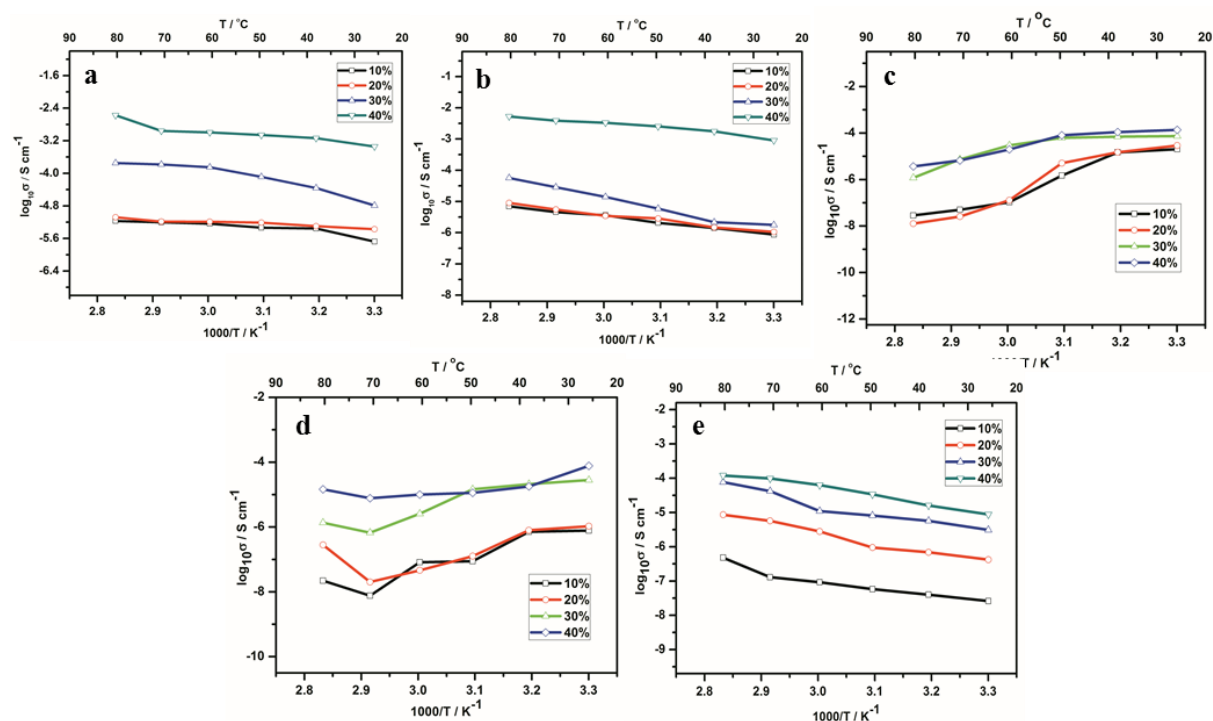


Figure 6.9. Arrhenius plots of temperature dependent conductivities of a) **SPE8** b) **SPE9** c) **SPE10** d) **SPE11** e) **SPE11 2nd heating**

Table 6.5. Conductivities of **SPE8 (40%)-SPE11 (40%)** at increasing temperature

T (°C)	Conductivity σ (S cm ⁻¹) with 40 wt% of LiTFSI			
	SPE8	SPE9	SPE10	SPE11
30	4.5×10^{-4}	8.9×10^{-4}	1.4×10^{-4}	7.7×10^{-5}
40	7.3×10^{-4}	1.8×10^{-3}	1.1×10^{-4}	1.8×10^{-5}
50	8.7×10^{-4}	2.5×10^{-3}	7.9×10^{-5}	1.1×10^{-5}
60	1.0×10^{-3}	3.3×10^{-3}	2.0×10^{-5}	1.0×10^{-5}
70	1.1×10^{-3}	3.9×10^{-3}	6.6×10^{-6}	7.7×10^{-6}
80	2.7×10^{-3}	5.3×10^{-3}	3.7×10^{-6}	1.5×10^{-5}

Generally in amorphous polymers, conductivities would be high after T_g . But, our polymers showed good conductivities even at temperature less than T_g . This observation demands an alternative explanation to the one based on T_g alone. The highest conductivity noted in this study can be explained using intrinsic porosity of polymers. In cross-linked polymers, the porosity is produced by the molecular structure of polymer chains. Recently, McKeown et al. described the polymers of intrinsic microporosity as the polymers having interconnected voids that resulted by space inefficient packing. This was due to rigid, bulky, non-planar and contorted molecular structures of polymer chains. Here, the porosity was obtained due to the shape and arrangement of polymer chains [24].

The polyethers **P8–P11** are produced using flexible monomers (**M8** and **M9**) having bulky rigid pendant groups and a steric rigid co-monomer (**M10**). Repetitive combination of flexible monomers and steric rigid co-monomers could yield unsymmetrical shape to polymer chains (Figure 6.10a). Further, the steric control of bulky rigid pendant groups *i.e.* ferrocenylmethyl (**P8** and **P10**) or benzyl (**P9** and **P11**), as well as a rigid tetramethylbenzene unit (**M10**) could restrict the polymer chains coming closer and prevent tight folding of polymer chains within or between them. Additionally, the rigid bulky groups could also restrict the rotational freedom of polymer backbone. All these circumstances collectively resulting disordered arrangement and inefficient packing of polymer chains. The space filling molecular model of a fragment of one of the conformation of **P9** clearly showed the inefficient packing of polymer chain (Figure 6.11).

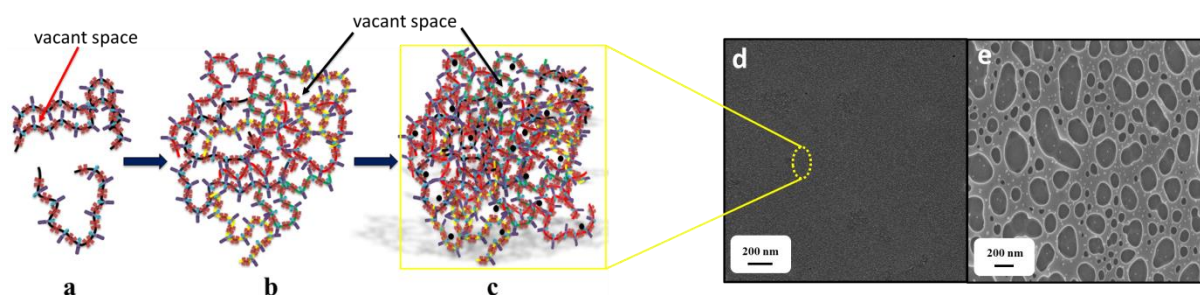


Figure 6.10. Schematic representation of a) a fragment of building block polymer chain **P8** or **P9** b) If the building block grows in 2D c) If the building block grows in 3D (**SPE**) (Black dots represent lithium-ion). d) FE-SEM image of **SPE10** coated on a glass plate from a concentrated solution. e) FE-SEM image of **SPE10** coated on a glass plate from a dilute solution (White dots represent lithium-ion). This representation is to explain how the free volume would be created while packing due to the inefficient shape of building block (not drawn according to scale).

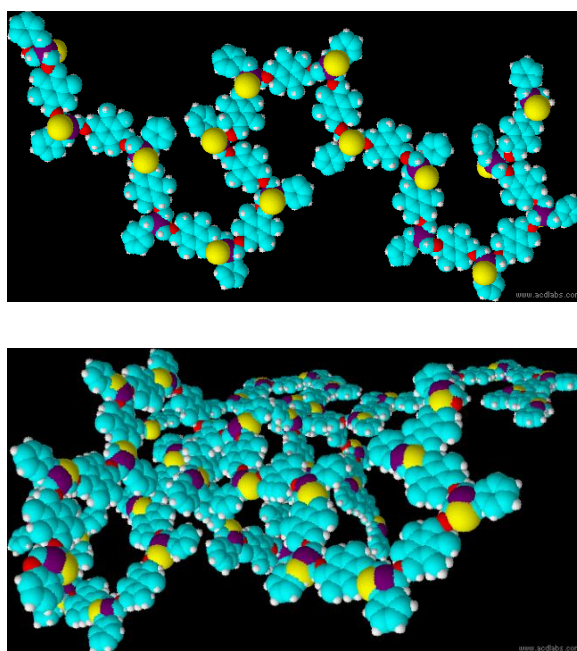


Figure 6.11. Space filling molecular model of a fragment of one of the conformation of **P9** (2D) (top), **P9** (3D) (down) showing the unsymmetrical shape and inefficient packing of polymer chain.

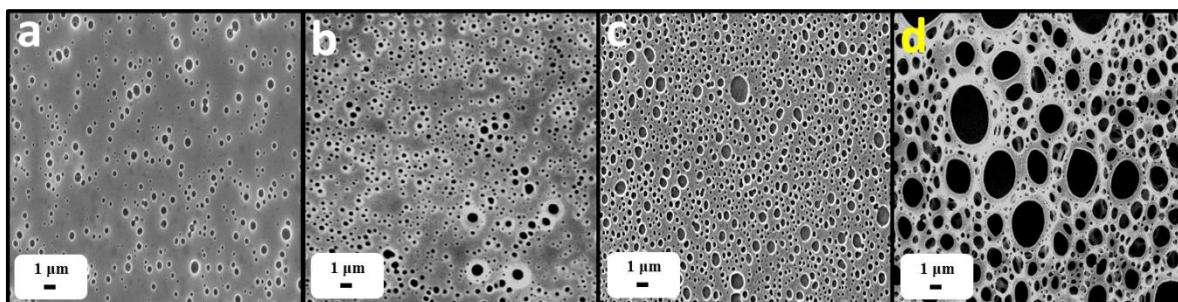


Figure 6.12. FE-SEM images of a) **P8** b) **P9** c) **P10** d) **P11**. Polymer samples dissolved in chloroform (dilute concentration) and coated on glass plate by drop casting.

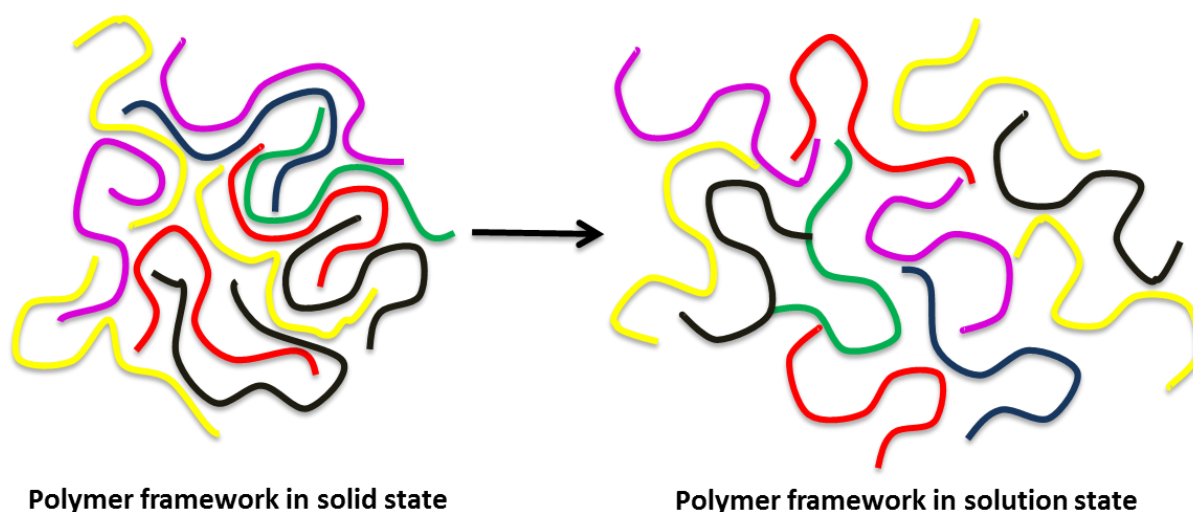


Figure 6.13. Schematic representation of an intrinsic porous polymer framework (2D) produced by a linear polymer (non-network): a) in solid state (left); b) in solution (right). This figure represents the possible formation of bigger pores while drop casting on glass plate.

Figure 6.10 schematically explain the formation of porous framework by polymer chains. When polymer chains with restricted segmental motion are packing, a space would create (Figure 6.10a). As several polymer chains are arranged, it can form perpetual interconnected free volume (vacant space) (Figure 6.10b and 6.10c). The interconnected free volume would introduce intrinsic porous nature to the polymer matrix (Figure 6.10c). This framework structure resembles the network structure of cross-linked polymers and would structurally mimic the porous crystalline polymer framework. Now, the lithium ions can mobile through the intrinsic pores with possibility of coordination in all three directions. These facile transports resulted in the impressive conductivity. Bruce and co-workers showed for the first time that crystalline polymer electrolyte $\text{PEO}_6\text{:LiAsF}_6$, which has a static, ordered environment, channel like network, can lead to efficient transport of ions than its amorphous

polymer [25]. It clearly suggested the ionic conductivity is not only associated to amorphous region above its T_g . The ionic conduction in $\text{PEO}_6\text{:LiAsF}_6$ is facilitated by ordered-network irrespective of the amorphous state above T_g . The higher conductivity reported here are obtained due to the movement of ions through the perpetual free volume (fixed path). Like $\text{PEO}_6\text{:LiAsF}_6$, our finding supports the fixed path mechanism for the movement of ions rather than T_g .

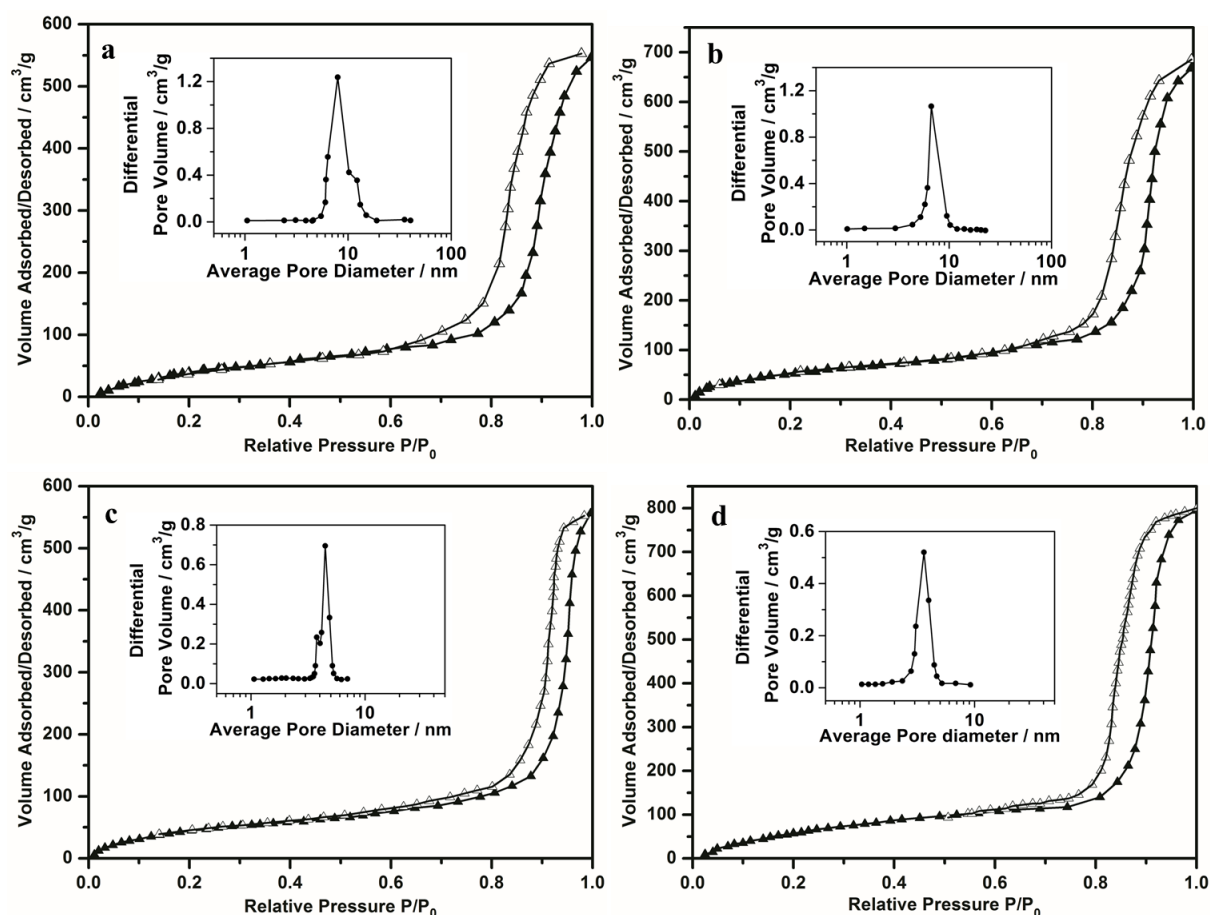


Figure 6.14. Nitrogen adsorption (filled triangles)-desorption (empty triangles) isotherm of powdered sample a) **P8** b) **P9** c) **P10** d) **P11**. Inset: pore size distribution calculated from adsorption data by BJH method.

The nitrogen adsorption and desorption analyses on powdered samples confirmed the presence of mesoporosity in polymers **P8-P11** (Figure 6.14). The adsorption and desorption analyses by BET method presented type IV isotherm and the specific surface areas of powdered samples of **P8-P11** were 135, 180, 220 and 230 $\text{m}^2 \text{g}^{-1}$ respectively. The BJH method was applied to find out the pore size distribution using adsorption isotherm data. The maximum sizes of pore diameters of **P8-P11** were 10, 6, 5 and 4 nm respectively [26]. The

FE-SEM picture (Figure 6.10e) of **SPE10** coated on a glass surface showed lithium ions as white dots as embedded in the polymer matrix. However, the mesopores described in Figure 6.10c were invisible in microscope pictures (Figure 6.10d) due to the constraint of molecular level resolution. The FE-SEM pictures of **P8-P11** coated on glass plate by drop casting are shown in Figure 6.12 and the possible formation of bigger pores is schematically represented in Figure 6.13.

Normally, local segmental motion of polymer chains increases with increasing temperature leading to increase in conductivity. As expected, conductivities of **SPE8 (10%-40%)** and **SPE9 (10%-40%)** increased with increasing temperature. In contrast, the conductivity of **SPE10 (10%-40%)** and **SPE11 (10%-40%)** decreased with increase in temperature (Table 6.5 and Figure 6.9c and 6.9d). These observations also suggested influence of porous framework structure as well as T_g based mechanism on conductivity. Since the polymer chain lengths of **P10** and **P11** were smaller, perhaps the polymer chains stretch and unfold easily with increasing temperature and begin to rearrange in such a way destroying the framework. Since the interconnected pores were disconnected, a sudden decrease in conductivity above 50 °C was observed. But, the polymers **P8** and **P9** presumably retain their framework because of longer chain lengths. Further, FE-SEM picture (Figure 6.15) showed disrupted framework of chains after heating **SPE10 (10%)**. TEM images (Figure 6.15) showed collapse of framework followed by agglomeration of polymer chains encompassing lithium salt to form granules. This was probably resulting chaotic conductivities at higher temperatures.

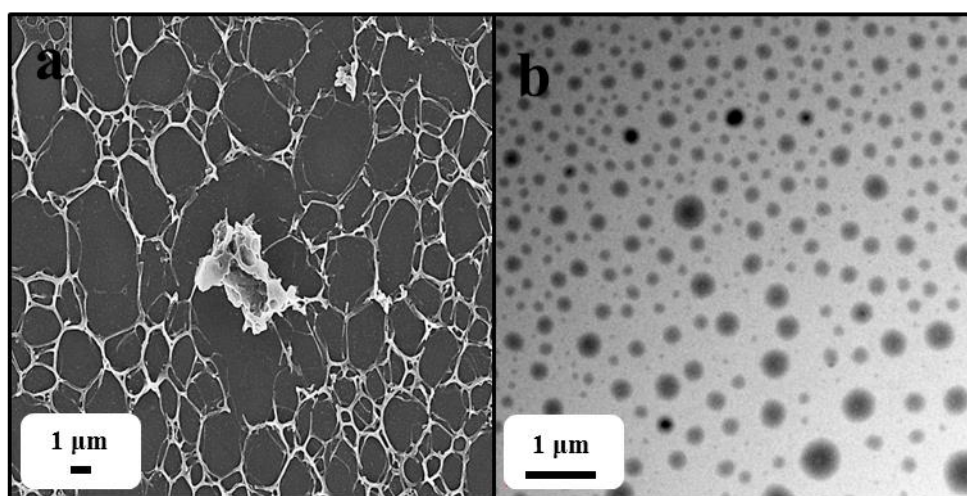


Figure 6.15. a) FE-SEM image of coated **SPE10 (10%)** after heating. b) TEM image of dispersed **SPE10 (10%)** after heating.

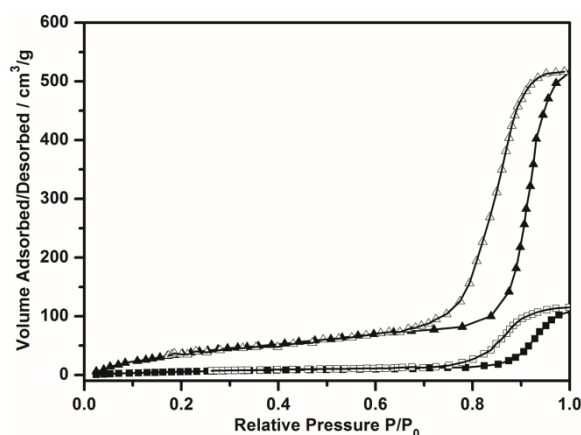


Figure 6.16. Nitrogen adsorption (filled triangles and squares) – desorption (empty triangles and squares) isotherms of powdered sample **SPE10 (10%)** (triangles) and pre-heated sample **SPE10 (10%)** (squares).

The BET isotherm experiment for **SPE10 (10%)** (Figure 6.16) revealed the specific surface area as $160 \text{ m}^2 \text{ g}^{-1}$ which was lesser than that of polymer **P10** ($220 \text{ m}^2 \text{ g}^{-1}$). **SPE10** was degassed at 60°C for 15 h during BET analysis, which was enough to collapse mesoporosity of polymer. The nitrogen adsorption and desorption analysis of preheated (80°C) **SPE10 (10%)**, showed the loss its mesoporosity and became nonporous with the specific surface area of $30 \text{ m}^2 \text{ g}^{-1}$. All these observations augment the support of intrinsic porous framework formed because of the inefficient packing of polymer chains.

With **SPE11 (40%)**, the conductivity started increasing after 70°C and attained the value of $1.5 \times 10^{-5} \text{ S cm}^{-1}$ at 80°C (Figure 6.9d). After the measurements at 80°C , all the samples **SPE11 (10%-40%)** were allowed to cool to room temperature and the measurements were repeated from 30 to 80°C . It was found that the conductivities of **SPE11 (10%-40%)** increased with increasing temperature (Figure 6.9e) probably because of simple hopping mechanism described elsewhere.

6.3. Conclusions

In conclusion, we have described the synthesis of intrinsic porous polymer framework as a new generation of solid polymer electrolyte for lithium ion mobility. Other than poly(ethylene oxide), only few polymers like polysiloxane, polyphosphazene have been shown as a potential candidate for lithium-ion polymer electrolytes; however, both were liquids at room temperature. The synthesized phosphorous containing polyethers **P8-P11** were highly stable polymers, solids at room temperature and completely amorphous in nature.

We have explained that the intrinsic porous polymer framework can be generated by the inefficient packing of polymer chains while assemblage generates free volume (or empty space). These free volumes are thoroughly interconnected to afford interconnected perpetual pores and resembles like a porous 3D network. This study demonstrated that cross linked polymer or polymer with crystalline network structure is not a prerequisite for the generation of porosity within an organic material [27].

The conductivity of **SPE9 (40%)** has shown the highest value of $8.9 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature, which demonstrates the significance of structural arrangement of polymer framework. Apart from these, presence of phosphorus in these polymers will bring flame-retardant property to **SPEs** [28]. The conductivity of low molecular weight intrinsic porous polymers decay at higher temperatures due to the disruption of porous polymer framework. The **SPE8** and **SPE9** can be utilized as solid polymer electrolyte in automobile lithium-ion batteries.

6.4. Experimental section

6.4.1. Materials and instrumentation

All manipulations involving air and moisture sensitive compounds were carried out using standard Schlenk techniques under dry nitrogen. All solvents to be used under inert atmosphere were thoroughly deoxygenated using freeze–pump–thaw method before use. They were dried and purified by refluxing over a suitable drying agent followed by distillation under nitrogen. The compounds, ferrocenylmethyl bis(hydroxymethyl)phosphine sulfide [17] (**M8**), benzyl bis(hydroxymethyl)phosphine sulfide [18] (**M9**) and 1,4–bis(bromomethyl)–2,3,5,6–tetramethylbenzene [20] (**M10**) were synthesized according to the literature procedures. The compound lithium bis(trifluoromethanesulfonyl)imide, $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ purchased from Acros was used as received without purification.

Structures of all monomers and polymers were confirmed by ^1H and ^{31}P NMR spectroscopy. All the NMR spectra were recorded on a Bruker Avance 400 MHz FT NMR spectrometer at room temperature. Chemical shifts were reported in parts per million (δ) relative to tetramethylsilane as reference for ^1H and ^{13}C NMR. The ^{31}P (162 MHz) spectra were referred to 85% H_3PO_4 . The Netzsch STA 409 PC model was used for thermogravimetric and differential thermal analysis (TG–DTA) to examine the thermal stability. The decomposition behavior of polymers was studied from 30 °C to 900 °C under

the nitrogen flow with a heating rate of 10 °C/min. A Differential Scanning Calorimeter (DSC) from PerkinElmer (Pyris Diamond DSC 8000) was used to find the glass transition temperature (T_g). Measurements were performed at a heating rate of 10 °C/min from 25 °C to 240 °C in case of polyethers and 25 °C to 280 °C in case of solid polymer electrolytes. Mass spectra was obtained using Shimadzu–LCMS–2010 instrument operating at an ionizing voltage of 70 eV using EI technique. Molecular weights of the polymers were determined by using Gel Permeation Chromotography (GPC) of Shimadzu 10AVP model equipped with refractive index (RI) detector. The separation was achieved using a Phenogel mixed bed column (300 × 7.80 mm) operated at 30 °C with a flow rate of 0.5 mL/min. using tetrahydrofuran (THF) as the eluent and polystyrene as the standard.

Field emission scanning electron microscope (FESEM) images were obtained from model Ultra55 of Carl Zeiss with an operating voltage of 20 KV. Sample was dissolved in chloroform and coated on glass plate by drop casting. Transmission electron microscope (TEM) images were recorded in FEI Tecnai G² S–TWIN with an operating voltage of 200 KV. Samples were dispersed in acetone and drop casted on 200 mesh carbon coated copper grid. The nitrogen adsorption/desorption measurements were carried out at 77 K using Micromeritics ASAP 2020 porosimeter. The Brunauer-Emmett-Teller (BET) method was applied to calculate the surface areas of powdered samples. The pore size distributions were determined by Barrett-Joyner-Halenda (BJH) method using adsorption isotherm data. The polymer samples (**P8-P11**) were degassed at 90 °C for 15 h under high vacuum (10^{-5} bar) before analysis. The samples were then transferred to the analysis system under nitrogen and again degassed under high vacuum at 90 °C for 5 h. Likewise, the **SPE10** was degassed at 60 °C for 15 h before analysis and again degassed at 60 °C for 5 h in analysis system.

6.4.2. Conductivity studies

The impedance measurements of polymer electrolytes were performed in Zahner zennium electrochemical work station with built-in Thales software for data acquisition. The measurements were done in the frequency range of 1 Hz to 4 MHz. The polymers (**P8-P11**) were dried at 90 °C under vacuum for 8 h. $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ was dried at 150 °C under vacuum for 10 h before use.

All manipulations were carried out in MBraun glove box filled with ultrapure nitrogen gas. Electrolytes with different ratio were prepared by the efficient grinding of polymer with lithium salt followed by mechanical blending for 72 h. They were loaded in to a die and then

pressed to make a pellet for the measurements. The consistency in results was checked by repeating three times. The homogeneities of the blended **SPE8-SPE11** were confirmed as follows: After blending the polymer with lithium salt, samples were taken from the four different regions and their glass transition temperature (T_g) was examined. The T_g of all the samples were matching well with each other.

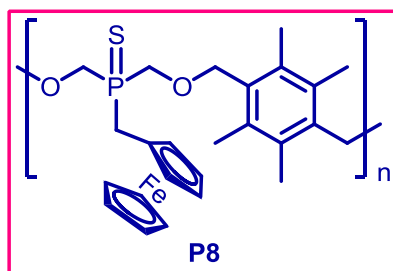
Moreover, films were made by dissolving the polymer and $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ in mixture of solvents THF/ CHCl_3 at room temperature. However, films of **SPE8-SPE11** were brittle. So it was difficult to cut into a proper shape for conductivity studies. Hence the alternative way of making pellets were chosen. After evaporating the solvent from the reaction mixture, pellets were made from the completely dried residue for the measurement. The conductivity measured from blended **SPEs** and **SPEs** derived from evaporation method was in good agreement.

The specimens in the form of pellets were sandwiched between two gold plated electrodes housed in a homemade cell. For variable temperature measurements, cell was equilibrated at each temperature for 30 min. before the measurements. The conductivity was calculated [23, 29] according to the equation $\sigma = d/(\text{AR}_b)$, where d is the thickness of the polymer electrolyte disc, 'A' is the surface area of the pellet and R_b is the bulk resistance value which can be obtained from the Nyquist plot.

6.4.3. Experimental section

General procedure for the synthesis of polymers P8-P11: To a solution of $\text{RP}(\text{S})(\text{CH}_2\text{OH})_2$ (7.7 mmol) and 1,4-bis (bromomethyl)-2,3,5,6-tetramethylbenzene (7.7 mmol) in N, N-dimethylacetamide (DMAc) (30 mL), sodium hydride (19.3 mmol) was added at 0 °C under nitrogen. The mixture was then allowed to warm to 25 °C within 1 h. After 40 h stirring at required temperature, the reaction mixture was poured into 3% hydrochloric acid (500 mL) to precipitate the polymer as powder. The product was purified by washing with methanol for 24 h using soxhlet apparatus to yield pure polymer.

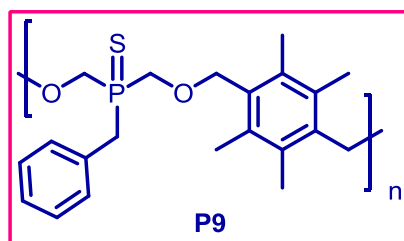
Polymer 8 (P8): Yield 81%.



^1H NMR (400 MHz, CDCl_3) : δ 4.82–4.61 (m, 4H, OCH_2Ph), 4.30–4.03 (m, 9H, Fc), 3.96–3.77 (m, 4H, PCH_2O), 3.28–2.94 (m, 2H, FcCH_2), 2.47–2.07 (bs, 12H, CH_3).

^{31}P NMR (162 MHz, CDCl_3) : δ 45.44.

Polymer 9 (P9): Yield 72%.



^1H NMR (400 MHz, CDCl_3) : δ 7.67–7.27 (m, 5H, C_6H_5), 4.67–4.36 (m, 4H, OCH_2Ph), 4.18–3.68 (m, 4H, PCH_2O), 3.56–3.32 (m, 2H, PhCH_2), 2.47–1.96 (bs, 12H, CH_3).

^{31}P NMR (162 MHz, CDCl_3) : δ 47.94.

Polymer 10 (P10): Yield 78%.

^1H NMR (400 MHz, CDCl_3) : δ 4.83–4.56 (m, 4H, OCH_2Ph), 4.34–4.00 (m, 9H, Fc), 3.97–3.69 (m, 4H, PCH_2O), 3.23–2.86 (m, 2H, FcCH_2), 2.46–2.05 (bs, 12H, CH_3).

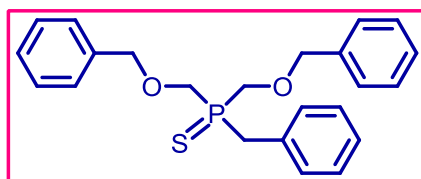
^{31}P NMR (162 MHz, CDCl_3) : δ 44.98 (m), 41.03 (m).

Polymer 11 (P11): Yield 75%.

^1H NMR (400 MHz, CDCl_3) : δ 7.76–7.35 (m, 5H, C_6H_5), 4.92–4.49 (m, 4H, OCH_2Ph), 4.03–3.53 (m, 4H, PCH_2O), 3.41–3.00 (m, 2H, PhCH_2), 2.42–1.99 (bs, 12H, CH_3).

^{31}P NMR (162 MHz, CDCl_3) : δ 46.19 (m), 42.84 (m).

Model reaction: To a solution of **M9** (0.20 g, 1 mmol) and benzyl bromide (0.34 g, 2 mmol) in DMAc (2.4 mL) was added sodium hydride (0.05 g, 2 mmol) at 0 °C under nitrogen. The mixture was then allowed to warm to 25 °C within 1 h. After 3 h stirring, methanol (1 mL) was added and the reaction mixture was poured in to water (25 mL). The reaction mixture was extracted with chloroform (20 mL $\times$ 3). The organic layer was washed with water (20 mL $\times$ 2). Solvent was evaporated to give the crude product which was purified by column chromatography on silica gel eluting with hexane/ethyl acetate (9 : 1) (Yield 79%).



^1H NMR (400 MHz, CDCl_3) : δ 7.42–7.32 (m, 10H, C_6H_5), 7.30–7.26 (m, 5H, C_6H_5), 4.65 (dd, $J = 21.4$ Hz, $J = 11.8$ Hz, 4H, OCH_2Ph), 3.95–3.84 (m, 4H, OCH_2P), 3.38 (d, $J = 13.8$ Hz, 2H, PCH_2Ph).

^{13}C NMR (100 MHz, CDCl_3) : δ 136.7, 130.2, 130.1, 128.9, 128.5, 128.4, 128.3, 128.2, 128.1, 127.3, 75.5 (d, $J = 10.3$ Hz), 67.3 (d, $J = 63.9$ Hz), 33.5 (d, $J = 44.2$ Hz).

^{31}P NMR (162 MHz, CDCl_3) : δ 43.50.

m/z (EI) : 397 ($\text{M}^+ + 1$).

General preparation of solid polymer electrolytes SPE8-SPE11: The polymers (**P8-P11**) were dried at 90 °C under vacuum for 8 h. $\text{LiN}(\text{SO}_2\text{CF}_3)_2$ was dried at 150 °C under vacuum for 10 h before use. All manipulations were carried out in an MBraun glove box filled with ultrapure nitrogen gas. Electrolytes with different ratio were prepared by the efficient grinding of polymer with lithium salt followed by blending for 72 h. They were loaded into a die and then pressed to make a pellet. Specimens of 0.07–0.08 cm thickness and 0.9 cm diameter were obtained for conductivity studies. These pellets were sandwiched between two gold plated electrodes housed in a homemade cell for conductivity studies. The consistency of results was checked by repeating three times.

Supporting information: ^1H and ^{31}P NMR spectra of **P8** and **P10** are included at the end of this chapter (Figure 6.S1 - 6.S4).

6.5. References

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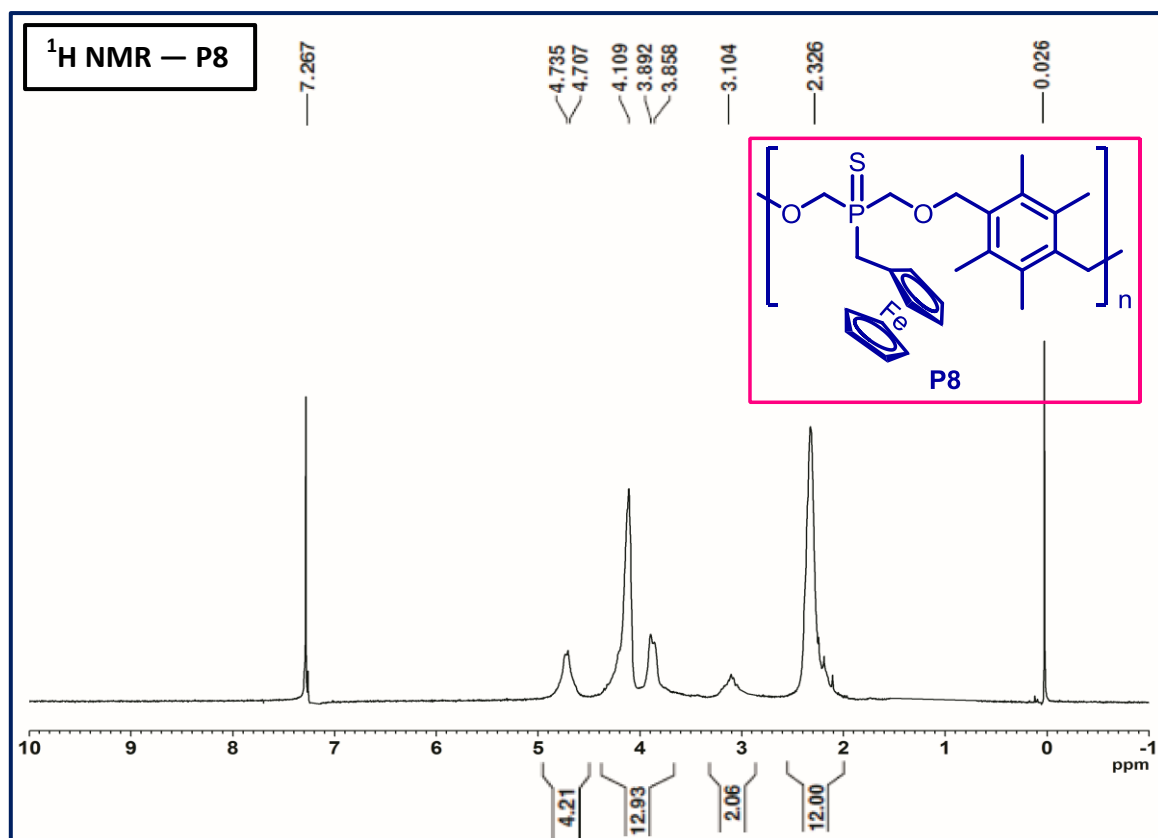


Figure 6.S1. ^1H NMR spectrum of polymer **P8**

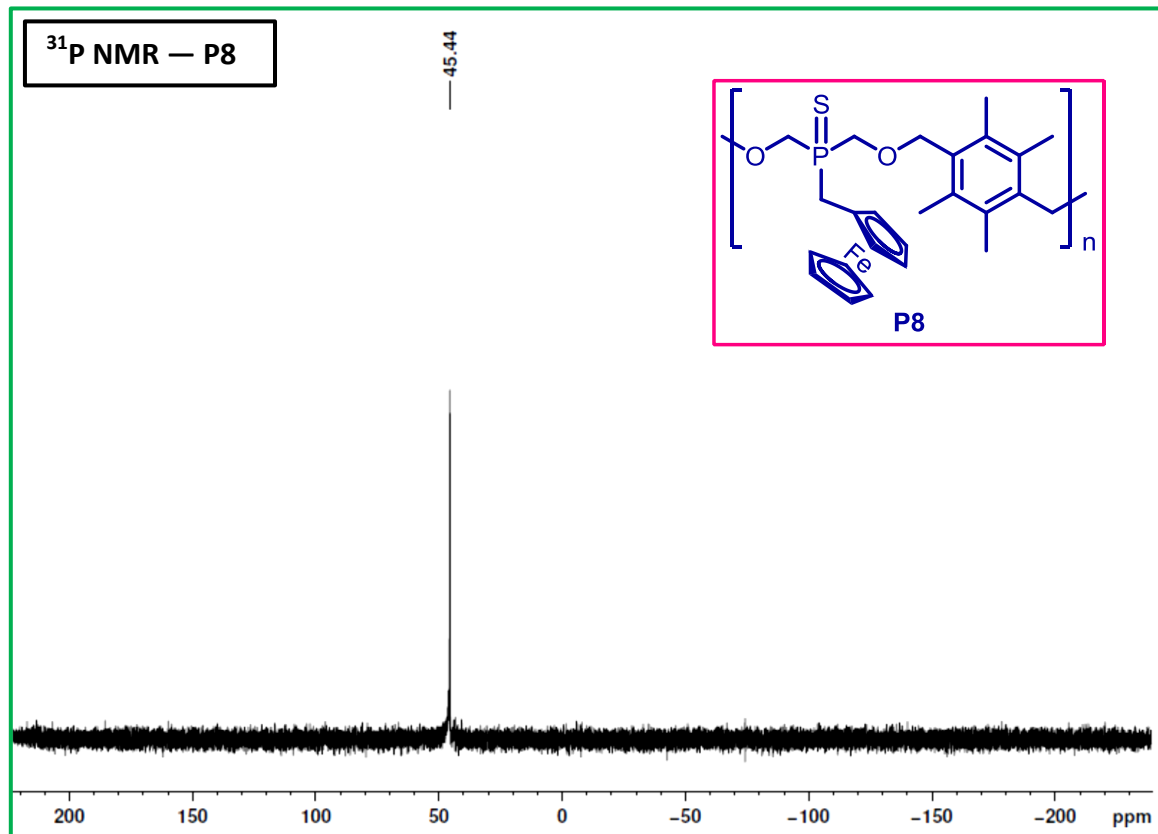


Figure 6.S2. ^{31}P NMR spectrum of polymer **P8**

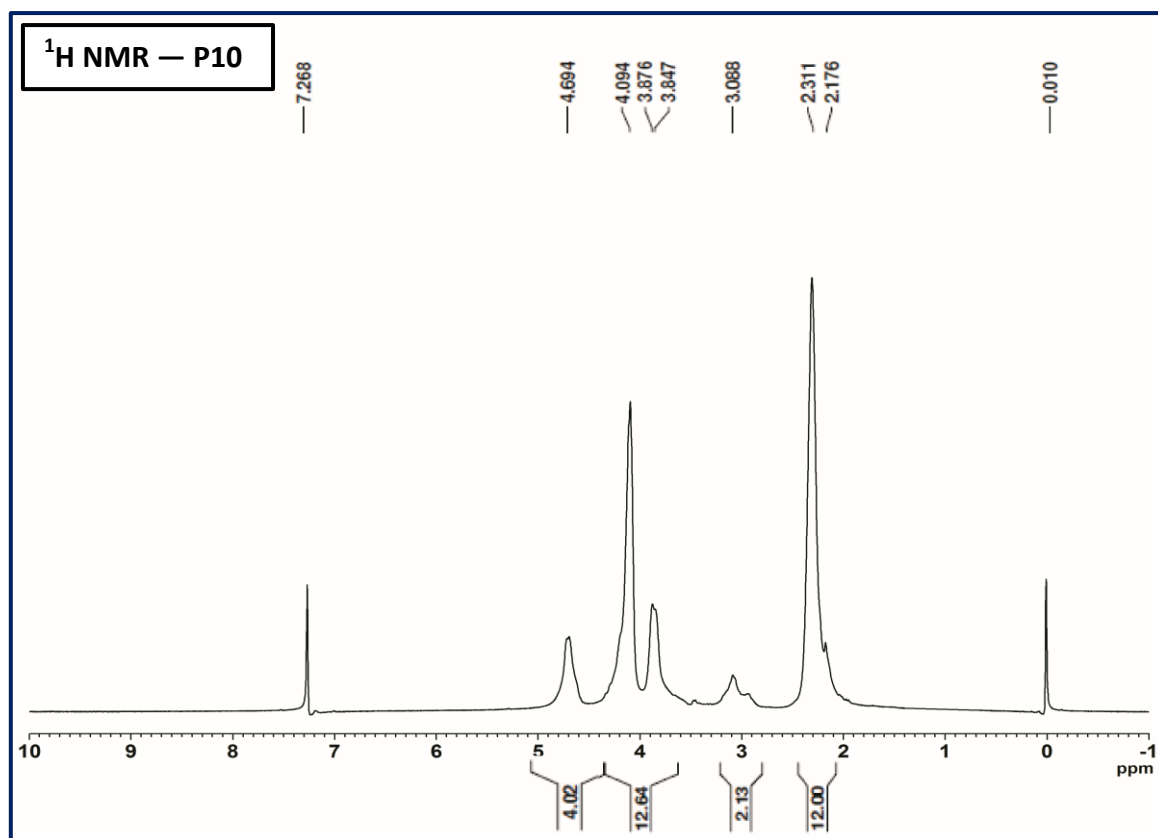


Figure 6.S3. ^1H NMR spectrum of polymer **P10**

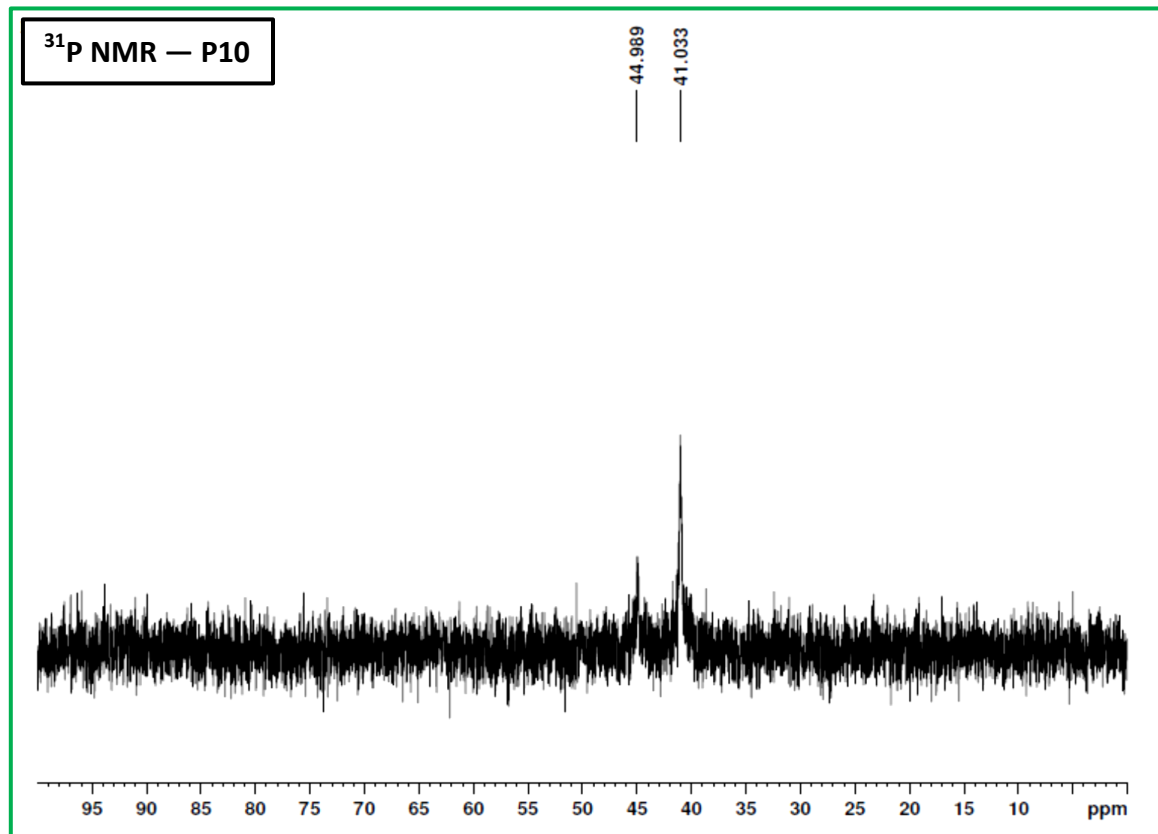


Figure 6.S4. ^{31}P NMR spectrum of polymer **P10**

Summary and Conclusion

7. Summary and Conclusion

The requirements of energy storage and portability increase the demand for efficient energy storage devices. Especially, the lithium-ion batteries having high specific capacity and high energy density is attracted much attention because of its potential application for the long range transport purposes. Replacement of organic liquids by SPE in lithium-ion battery not only confirms the safety consideration but also useful to attain the following merits: varieties of shape, size, wide operating temperature range, high electrochemical stability and light weight fabrication. Therefore, it is necessary to prepare novel SPE having good lithium-ion conductivity as well as with flame retardant property.

As discussed in the chapter 1, amorphous polymers exhibit ionic conductivity because the ionic conductivity of these polymers depends on local segmental motions of polymer chains and such a favourable situation was obtained only at temperatures above T_g . Hence, the polymer with low glass transition temperature was preferred for ionic conductivity. In contrast, an interesting finding by Bruce et al showed that the ionic conductivity was not only associated with the amorphous region above T_g but also the structural arrangement of polymer framework for efficient ionic conductivity. Based on these findings, it was expected that the polymers having conformational flexibility and with suitable superstructure (polymer framework) would be good for lithium-ion mobility. It was further foreseen that the conformational flexibility in a polymer chain could be induced if efficient packing of polymer chains is hindered by some way. Therefore, in order to achieve these properties two kinds of polymers were designed for synthesis. They are a) polyethers with bulky phosphate pendant groups; b) polyethers with phosphorus present in the main chain along with bulky co-monomers. These polymers were used to produce SPE for Li-ion conductivity studies. The systematic approach followed in producing SPEs is depicted schematically in Figure 7.1.

Though various methods are known to synthesize polymers, the polymers obtained by ROP would provide good properties like molecular weight, PDI and microstructure. So it was preferred to synthesize the polymers by ROP. Further, concerning the depletion of petroleum resources, there was also interest to utilize easily available and cheapest starting materials from renewable resources such as CO_2 and carbohydrates. Al and Cr based tetraphenyl porphyrinato complexes; Al, Cr and Co based salen complexes were known for their multiple catalytic activities for the synthesis of a range of small molecules and/or polymers. Even though many catalysts were independently known for their activity, there is always an

increasing interest to find an efficient, multiple catalytically active catalysts with improved efficiency.

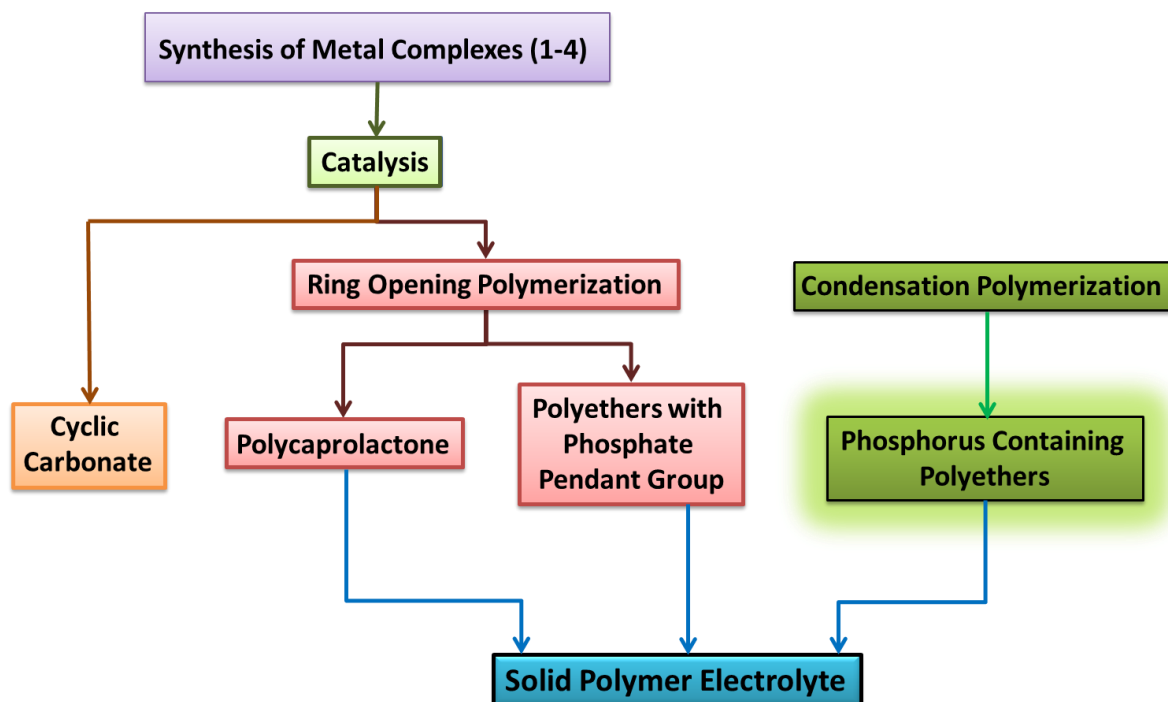


Figure 7.1. The systematic approach followed in the thesis for producing SPEs.

With an aim of producing multipurpose catalyst, Zn(II) **1**, Cd(II) **2-3** and Cu(II) **4** complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole (DIP₂pyr)H were synthesized and used for the synthesis of small molecules and polymers. The attempted synthesis of polycarbonate from copolymerization of epoxide-CO₂ using **1-4** as catalyst, instead of polycarbonate, yielded cyclic carbonates. However, the catalysts were highly efficient for the conversion of mono and disubstituted epoxides to their corresponding cyclic carbonates with good to high yields. Further, the epoxides having phosphorus in the pendant groups were successfully converted to its corresponding cyclic carbonates. The much needed cyclic carbonates with possible flame retardant property has been achieved which would have potential application as electrolytes.

Since the primary intention was to prepare polymer electrolytes, the catalytic activities of complexes were further explored to various polymerizations with the aim of producing polymers for lithium-ion transport. The recent developments in synthesis of ϵ -caprolactone (**M1**) from D-fructose (renewable resource), cheaply available starting material, biodegradable and biocompatibility of polycaprolactone (PCL or **P1**), mechanical stability of

PCL membrane and more importantly the glass transition temperature of PCL and their ability to dissolve the lithium salts are attractive to synthesize PCL and study its lithium-ion conductivity behavior. Even though the synthesis of PCL by ROP is well known, the synthesis of PCL by using the catalysts **1** - **4** was helpful to deduce the catalytic behavior of the complexes reported in the chapter 2.

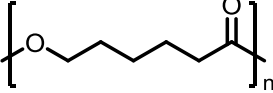
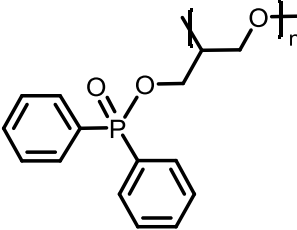
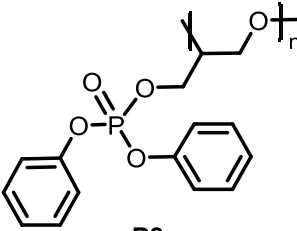
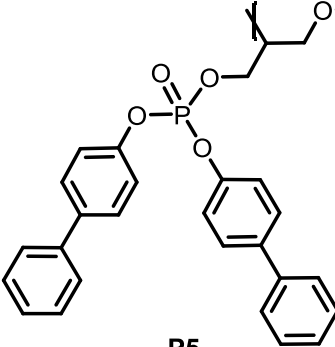
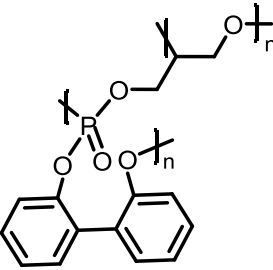
The complexes particularly **1** and **4** exhibited remarkable catalytic activity for ROP of **M1** even at 25 °C in toluene in the presence of BnOH. The ROP catalyzed by our complexes proceeded through living polymerization but also immortal. The synthesized PCL (**P1**) was examined for lithium-ion conductivity by preparing **SPE1**. The conductivity of **SPE1** with 30 wt% of LiTFSI was $1.6 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $7.2 \times 10^{-4} \text{ S cm}^{-1}$ at 60 °C. Unlike LiClO₄, the admittance to use more lithium salt content (even up to 40 wt% of LiTFSI) helped to achieve higher conductivity. Even though the higher conductivity was achieved using PCL as host polymer, the melting temperature of PCL (60 °C) hinders its utility to operate in a wider temperature range. Therefore, the focus was shifted to synthesize polymers with good ionic conductivity which can operate in a wider temperature range.

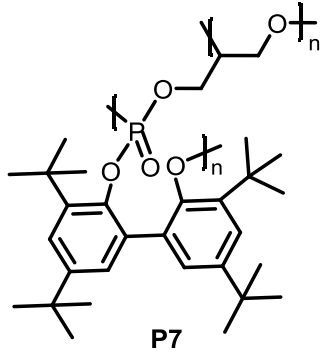
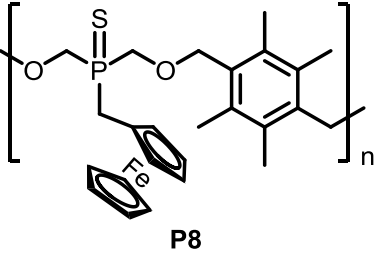
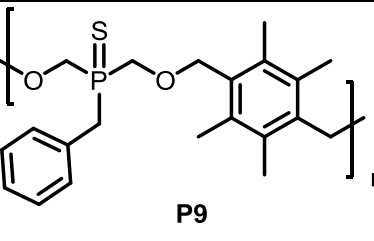
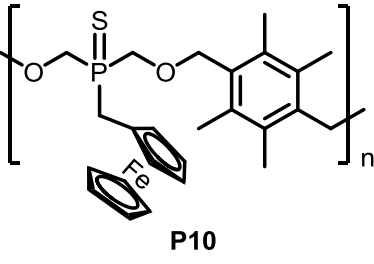
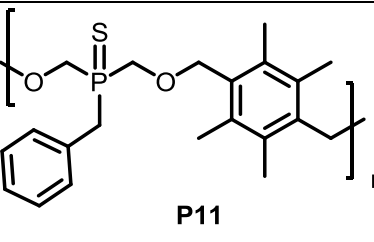
Since the presence of phosphorus would provide much needed conformational flexibility, mechanical stability and flame retardancy to the polymers, it was desired to synthesize polyethylene oxide (PEO) based polyethers with phosphate pendant group. The presence of phosphate bulky groups could prevent efficient packing of polymer chains thereby superstructure would be created for lithium-ion mobility. Therefore, the ROP of epoxides, in which phosphates attached as pendant groups, were carried out using complexes **1-4** as catalysts in the presence of tetrabutylammonium bromide (TBAB). These polymerizations proceeded following a “monomer activated anionic ring opening polymerization” mechanism. These living like polymerizations also progressed according to “formation of polymer chain per initiator” model. The solid-state lithium-ion conductivities of these polymers were examined using LiTFSI. The conductivity of one of the solid polymer electrolyte **SPE3** with 40 wt% of LiTFSI was $5.2 \times 10^{-5} \text{ S cm}^{-1}$ at room temperature and $2.9 \times 10^{-4} \text{ S cm}^{-1}$ at 80 °C. The polymers obtained (**P2**, **P3** and **P5-P7**) have high glass transition temperature compared to polycaprolactone and they can operate in a wider temperature range whereas their lithium-ion conductivity is still not attractive for the potential application. This is probably because, the presence of more flexible units (PEO) could not provide sufficient fixed perpetual free volume through which lithium-ion would move.

An alternative approach to obtain a fixed perpetual free volume could be the polymers with repetitive combination of flexible monomers and steric rigid co-monomers. The copolymerization reactions of ferrocenylmethyl bis(hydroxymethyl)phosphine sulphide or benzyl bis(hydroxymethyl)phosphine sulphide with dibromo monomer were successfully carried out to produce novel intrinsic porous polyethers. These polymers are obtained by nucleophilic substitution reactions. This strategy enabled to achieve the conductivity of $8.9 \times 10^{-4} \text{ S cm}^{-1}$ at room temperature and $5.3 \times 10^{-3} \text{ S cm}^{-1}$ at 80°C in benzyl bis(hydroxymethyl)phosphine sulphide based SPE (**SPE9**, Chapter 6) with 40 wt% of LiTFSI. The facile Li-ion conductivity by these polymers was explained (Chapter 6) by the intrinsic porous polymer framework that generated by the inefficient packing of polymer chains while assemblage generates free volume (or empty space). These facile transports of Li-ion demonstrated the significance of structural arrangement of polymer framework.

Altogether, we have prepared ten SPEs and studied their Li-ion conductivities at varying temperatures. The Table 7.1 displays the room temperature conductivities of these SPEs with varying salt loadings. The conductivities varied from the order of 10^{-9} to $10^{-4} \text{ S cm}^{-1}$. Highest conductivity was achieved by the **SPE9** made from the polymer **P9** (chapter 6) with 40 wt% LiTFSI. To the best of our knowledge, this is the best conductivity achieved so far in all solid state polymer electrolytes. Only few polymers like polysiloxane, polyphosphazene have been shown as a potential candidate for lithium-ion polymer electrolytes; however, both were liquids at room temperature. The synthesized phosphorous containing polyethers were highly stable polymers, solids at room temperature and completely amorphous in nature. Thus, the SPE having good lithium-ion conductivity with potential flame retardant property has been achieved. They can be utilized as solid polymer electrolyte in automobile lithium ion batteries.

Table 7.1. Structures of **P1-P11** and comparison of room temperature conductivities of **SPE1 (10%-40%)-SPE11 (10%-40%)**

Polymer	SPE	Conductivity at different wt% of LiTFSI			
		σ (S cm ⁻¹) at RT			
		10%	20%	30%	40%
 P1	SPE1	2.1×10^{-6}	4.9×10^{-6}	1.6×10^{-5}	
 P2	SPE2	2.68×10^{-9}	2.90×10^{-9}	5.02×10^{-8}	4.22×10^{-6}
 P3	SPE3	2.7×10^{-6}	3.3×10^{-6}	5.3×10^{-6}	5.2×10^{-5}
 P5	SPE5	3.9×10^{-9}	2.5×10^{-8}	7.7×10^{-7}	4.8×10^{-5}
 P6	SPE6	1.2×10^{-8}	4.0×10^{-8}	2.7×10^{-7}	9.8×10^{-7}

 P7	SPE7	2.2×10^{-9}	3.1×10^{-8}	4.5×10^{-8}	5.0×10^{-8}
 P8	SPE8	2.1×10^{-6}	4.2×10^{-6}	1.6×10^{-5}	4.5×10^{-4}
 P9	SPE9	8.7×10^{-7}	1.1×10^{-6}	1.8×10^{-6}	8.9×10^{-4}
 P10	SPE10	2.0×10^{-5}	2.9×10^{-5}	7.4×10^{-5}	1.4×10^{-4}
 P11	SPE11	7.7×10^{-7}	1.1×10^{-6}	2.8×10^{-5}	7.7×10^{-5}

List of Publications

Publications from thesis

1. “Zn(II), Cd(II) and Cu(II) complexes of 2,5- bis{N-(2,6-diisopropylphenyl)imino methyl}pyrrole: synthesis, structures and their high catalytic activity for efficient cyclic carbonate synthesis”,
Heeralal Vignesh Babu and Krishnamurthi Muralidharan, *Dalton Transactions*, 2013, **42**, 1238-1248.
2. “Intrinsic porous polymer framework: A new generation of solid polymer electrolyte”,
Heeralal Vignesh Babu and Krishnamurthi Muralidharan (under review).
3. “Polyethers with phosphate pendant groups by monomer activated anionic ring opening polymerization: Syntheses, characterization and their lithium-ion conductivities”,
Heeralal Vignesh Babu and Krishnamurthi Muralidharan (under review).
4. “Versatile metal complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl} pyrrole for epoxide-CO₂ coupling and ring opening polymerization of ϵ -caprolactone”,
Heeralal Vignesh Babu and Krishnamurthi Muralidharan (under review).
5. “Polymerization behavior of alkyl/aryl substituted bis(hydroxymethyl)phosphine oxides and sulfides: Phosphorus containing polyethers for Li-ion conductivities”,
Heeralal Vignesh Babu and Krishnamurthi Muralidharan (manuscript under preparation).

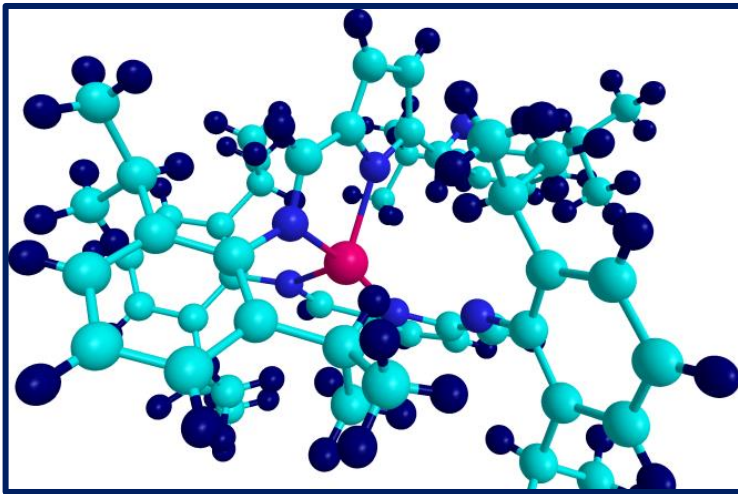
Publications

6. “Tandem ring opening and oximation of Ethyl 3-aryl-1-cyano-4-hydroxy-2,4,6-triarylcyclohexanecarboxylate by hydroxylamine”,
S. Saravanan, Heeralal Vignesh Babu and S. Muthusubramanian, *Synthetic Communications*, 2007, **37**, 3635-3648.
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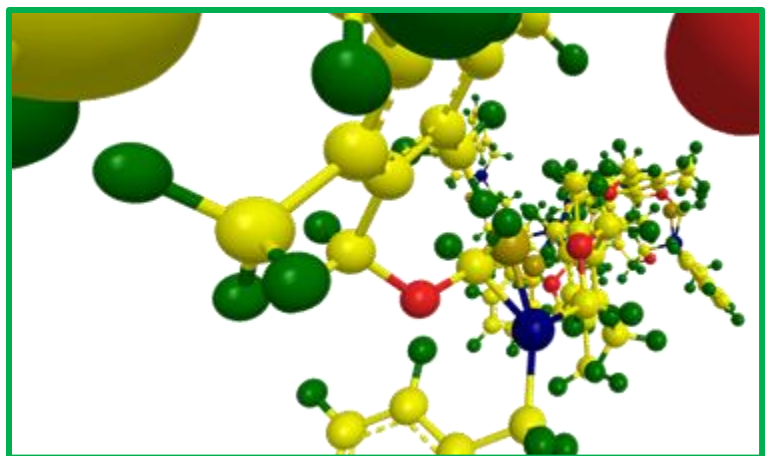
7. “Process for the preparation of carbapenem antiobiotic”,
U. P. Senthilkumar, S. Mohan and Heeralal Vignesh Babu, *US Patent Application*,
US 2010/0311984A1, 2010.
 8. “Process for the preparation of carbapenem antiobiotic”,
U. P. Senthilkumar, S. Mohan and Heeralal Vignesh Babu, *EP Patent Application*,
EP 2209787A1, 2010.
 9. “Process for the preparation of carbapenem antiobiotic”,
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8293924B2, 2012.
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Poster and Oral Presentations

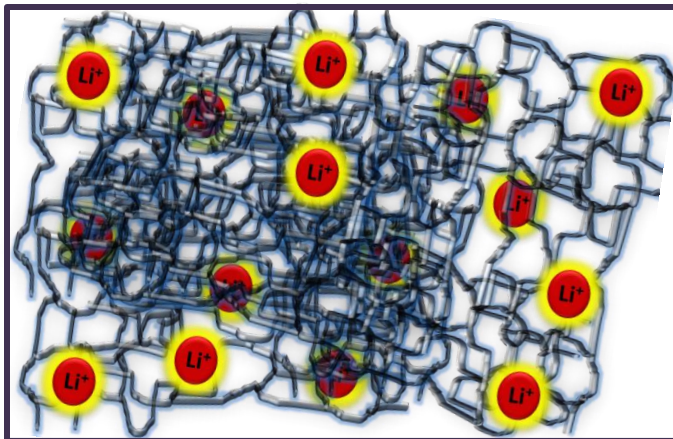
1. **Heeralal Vignesh Babu** and Krishnamurthi Muralidharan, “Synthesis and properties of novel phosphorous containing polyethers” presented a poster in ‘Frontiers in Chemical Sciences (FICS – 2010)’ held at Department of Chemistry, Indian Institute of Technology Guwahati on Dec 3-4, 2010.
 2. **Heeralal Vignesh Babu** and Krishnamurthi Muralidharan, “Synthesis and properties of novel phosphorous containing polyethers” presented a poster in In-house symposium, School of Chemistry, University of Hyderabad on Feb 7-8, 2011.
 3. **Heeralal Vignesh Babu** and Krishnamurthi Muralidharan, “Lithium-ion conducting phosphorus containing polyethers: synthesis, characterization and their ion conducting properties” presented a poster in ‘Modern Trends in Inorganic Chemistry (MTIC-2012)’ held at University of Hyderabad, on Feb 13-14, 2012.
 4. **Heeralal Vignesh Babu** and Krishnamurthi Muralidharan, “Synthesis of cyclic carbonates from atmospheric pressure carbon dioxide using Zn(II)iminomethyl pyrrolyl complex as catalyst” presented a talk and poster at In-house symposium, School of Chemistry, University of Hyderabad on Mar 03-04, 2012.
 5. **Heeralal Vignesh Babu** and Krishnamurthi Muralidharan, “Zn(II), Cd(II) and Cu(II) complexes of 2,5-bis{N-(2,6-diisopropylphenyl)iminomethyl}pyrrole: synthesis, structures and their high catalytic activity for efficient cyclic carbonate synthesis” presented a poster in ‘National Symposium on Frontiers in Organic Chemistry’ held at University of Hyderabad on Oct 11-12, 2013.
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Catalysis



Polymer



*Solid Polymer
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