Copolymerization of Propylene Oxide and Carbon Dioxide

the thesis submitted in the fulfilment of the
Award of Degree of

Doctorate of Philosophy

by

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CERTIFICATE

This is to certify that the thesis entitled "**Copolymerization of Propylene Oxide and Carbon Dioxide",** being submitted by Ms. Shilpa Narang in fulfillment of the requirements for the degree of **DOCTOR OF PHILOSOPHY** to the Thapar University, Patiala, is a record of the candidate's own work carried out by her under our supervision and guidance. The matter embodied in this thesis has not been submitted in part or full to any other university or institution for the award of any degree.

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PREFACE

The carbon dioxide (CO_2) is naturally present in earth's natural carbon cycle. Human beings are adding more and more CO_2 into the atmosphere and destroying natural sinks like forests that removes it. Increasing CO_2 emission has led to change in temperature level which is affecting the growth rate of various plants and other species. Thus, the necessity to reduce CO_2 emission has gained worldwide momentum and there are several international programs aimed at balancing CO_2 emission through control on emission and its sequestration. One of the possible means to reduce CO_2 involves its use as a raw material in synthetic chemistry which is of interest from the perspective of developing clean technologies for environmental protection. Although the process does not use large amounts of CO_2 but still gives a greener means for resource utilization since CO_2 is a nontoxic, non-flammable and inexpensive substance and is also present in abundance. In view of this there has been continued interest in CO_2 activation using different catalysts and its further use as a viable carbon source.

There are a number of reactions that can give value added products from CO_2. Amongst the most important green reactions and the subject of present thesis is the catalytic conversion of CO_2 into polycarbonates and cyclic carbonates by fixing it chemically with epoxides. The reaction products are value added commodities of immense economic importance and provide a methodology for preparation of polycarbonates under milder conditions unlike its traditional industrial preparation method which requires intense vigorous conditions. The aim of the present work has been to carryout copolymerization of propylene oxide and CO_2 to synthesize poly(propylene carbonate) and cyclic carbonate using different catalyst/co-catalyst systems.

This thesis embodies the subject matter resulting out of this study and is arranged in seven separate chapters. Chapter 1 discusses the background and introduction to the research problem. The chemistry of chemical fixation of propylene oxide and CO_2 is discussed in Chapter 2. Opening of epoxide ring by nucleophilic attack and corresponding insertion of carbon dioxide molecule has also been discussed in this chapter. The available literature on copolymerization of propylene oxide and carbon dioxide (CO_2) to poly(propylene carbonate) [PPC] and cyclic carbonate are summarized and critically assessed in Chapter 3. In view of the reports in literature, the present work has been planned to carry out copolymerization of

propylene oxide and CO_2 to poly(propylene carbonates) and cyclic carbonates in the presence of different Schiff base catalyst systems. The aim of the present work is to explore different achiral catalyst systems, investigate the relationship between effect of changing electron density around catalyst systems and corresponding polymerization and to optimize the reaction conditions with respect to pressure, temperature, monomer to initiator ratio, catalysts and reaction time.

Chapter 4 presents the details of different materials that have been used in the reactions and equipment, along with the procedure for the synthesis of poly(propylene carbonate) and cyclic carbonate. Grade and source of materials used, procedure adopted for distillation of propylene oxide, details of equipment and experimental procedures and various characterization techniques used for the quantification and analysis of the product.

Chapter 5 presents the details of the synthesis of different Schiff base ligands and their characterization. These have been used as catalysts/co-catalysts. Synthesis of cyclic carbonate and poly(propylene carbonate) and results of related studies are described in Chapter 6. The major conclusions derived on the basis of present work and scope of future work are summarized in Chapter 7.

References cited are listed at the end and Appendix I includes the list of publications/presentations based on the work presented in the thesis and Appendix II includes the NMR spectra of the ligand precursors used for the synthesis of catalysts.

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INTRODUCTION

CHAPTER-1 INTRODUCTION

1.1 Background

CO_2 is naturally present in earth's natural carbon cycle which is presently being altered by human activities. Increasing concentration of carbon dioxide (CO_2) in the atmosphere and the resultant greenhouse effect are adversely affecting environment through climate change and global warming. The amount of CO_2 in the environment is expected to double by 2065 [Rahman *et al.* (2011)]. In 2013, CO_2 accounted for about 82% of all U.S. greenhouse gas emissions [http://www.epa.gov/climatechange/ghgemissions/gases/CO_2.html, accessed on September 15, 2015]. Besides emission through various biological processes and combustion of carbonaceous fuels, CO_2 is also emitted as waste or by-product of large number of industries involved in the synthesis of ammonia, ethanol, urea, hydrogen, ethylene oxide etc. Around 3 million tons of CO_2 is released each year by 500 MW coal-fired power plant alone [Roth *et al.* (2013)]. Cement industries alone account for 5% of the total global CO_2 emissions [Ernst Worrell *et al.* (2001)]. The increasing CO_2 level has led to change in temperature level which in turn is affecting the growth rate of various plants and other species [Soon *et al.* (1999)]. Thus, the necessity to reduce CO_2 emission has gained momentum and there are several international programs aimed at balancing CO_2 emission and on increasing its sequestration [Weimer *et al.*, (1998); Aresta *et al.* (1999); Hjeresen *et al.* (2001); Poliakoff *et al.* (2001); Aresta *et al.* (2002); Anastas *et al.* (2002); Poliakoff *et al.* (2002)]. One of the possible means to reduce CO_2 involves its use as feed-stock in synthesis of chemicals and polymers through clean and green technologies for environmental protection [Allen *et al.* (2002)]. Although the process does not use large amounts of CO_2 but still permits use of a cleaner means for utilizing CO_2, a nontoxic, nonflammable and inexpensive substance available in abundance [Du *et al.* (2005)].

1.1.1 Value Added Products from CO_2

There are a number of reactions that can give value added products from CO_2. In metal-CO_2 complexes, CO_2 is capable of acting as a ligand, which can further facilitate CO_2 conversion to other valuable chemicals [Aresta *et al.* (2010)]. There have been efforts to convert CO_2 into formic acid [Musashi *et al.* (2000)]. Another large volume fixation of CO_2 is in the manufacture of urea from ammonia and CO_2, synthesis of methanol, dimethylether, and salicylic acid [Lu *et al.* (2012)]. Amongst the most important green reactions and the subject of the present thesis is the catalytic conversion of CO_2 into polycarbonates by fixing it chemically with epoxides [Darensbourg *et al.* (2005); Sugimoto *et al.* (2004); Ohkawara *et al.* (2014)]. The reaction products are value added commodities of immense economic importance and provide a methodology for preparation of polycarbonates under milder conditions unlike its traditional industrial preparation which requires intense vigourous conditions.

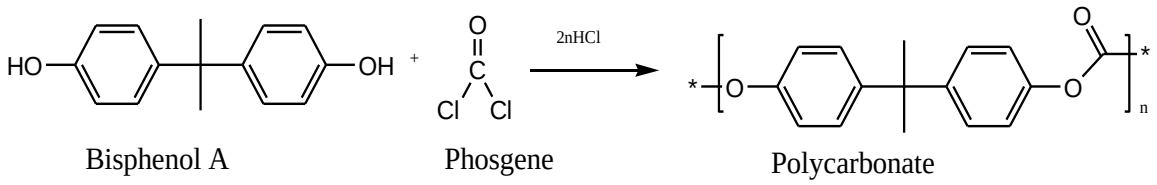
This process of synthesis of polycarbonates from CO_2 also provides an alternative to the the synthetic plastics that are formed from fossil fuels and poses a serious threat to the environment.

1.2 Polycarbonates

Polycarbonates are a class of thermoplastic polymers that contain carbonate linkages. They exhibit wide range of applications depending upon the glass transition temperature (T_g), which in turn depends on the starting monomer units used for their synthesis. They have high durability and can be easily moulded and thermoformed [https://en.wikipedia.org/wiki/Polycarbonate, accessed on 23 December, 2015]. They score over many commodities and engineering polymers with respect to properties like strength, lightness, heat and electrical resistances; and are easily processed and coloured. Beside this, polycarbonates can also be blended with various other polymers like polyethylene, liquid

crystalline polymers [Pisitak *et al.* (2013)], polyvinylchloride [Braun *et al.* (2011)], polydimethoxysiloxane rubber [Kumar *et al.* (2007)] etc to increase its mechanical properties.

Alfred Einhorn, a German scientist from the University of Munich, was the first to synthesize polycarbonate in 1898 but the product remained without commercialization even after 30 years of research. Later, Hermann Schnell of Farbenfabriken Bayer AG resumed the research and synthesized high molar mass polycarbonates in 1953 [Schnell. (1956)]. The polymer was based on bisphenol-A and phosgene (Figure 1.1). Since then, a number of polycarbonates based on bisphenol A (BPA) and other diphenols, aliphatic diols and epoxides have been synthesized [Sweileh. (2010)].



Bisphenol A Phosgene Polycarbonate

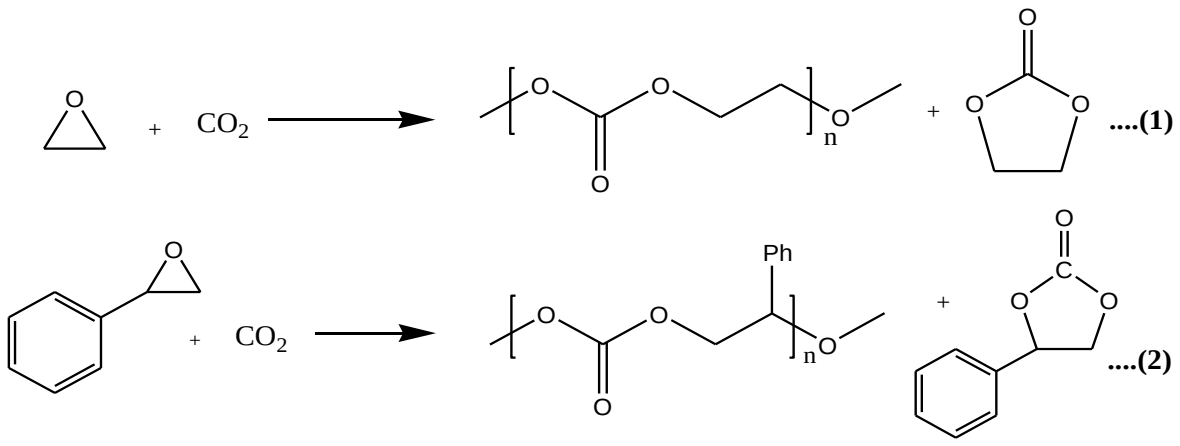
Figure 1.1: Reaction between bisphenol A and phosgene to give polycarbonate [Sweileh. (2010)]

1.2.1 Polycarbonates from Epoxides and CO_2

Synthesis of different type of poly(alkene carbonate)s from epoxides and CO_2 is of great interest since the process provides a greener method and an alternative to current industrial preparation of polycarbonates. The present industrial process which involves reactions between a dihydroxy compound and a carbonic acid diester in presence of a suitable catalyst, is carried out at elevated pressure and temperature, and is hazardous and expensive.

Chemical fixation of CO_2 with different epoxide units (such as ethylene oxide, propylene oxide, styrene oxide, cyclohexene oxide and oxetane etc) is helpful as the poly(alkene carbonates) obtained at the end of the reaction have different glass transition temperature (T_g) based on which their applications can be designed. For example, poly(ethylene carbonate) has a T_g of about 25^oC and thus has excellent oxygen barrier properties. It is integrated into

traditional packaging plastics that can help the food containers to have suitable structural and barrier properties [www.novomer.com/thermoplastics-overview, accessed on September 15, 2015]. Poly(propylene carbonate)s [PPC] have a T_g of about 35-40 ^oC and thermal degradation temperature about 250^oC. These properties make PPC suitable for adhesive based applications [Coates *et al.* (2004); Varghese *et al.* (2012); Okada *et al* (2011)]. Likewise, poly(cyclohexene carbonate) [PCHC] has a higher T_g of about 115^oC and thus posses material properties like that of polystyrene [Coates *et al.* (2004)]. The high thermal degradation temperature of PCHC (around 300^oC) allows it to favour melt processing. Thus, polymers from different monomer units lead to the synthesis of poly(alkene carbonate)s with different material properties. The scientists in various laboratories are attempting to develop new catalyst systems for epoxides/CO_2 copolymerization reactions through clean routes. The best part of this strategic route is that it is an environmentally friendly phosgene free route based on a cheap CO_2 monomer. Figure 1.2 shows the copolymerization of different epoxide monomers with CO_2 which leads to the resultant poly(alkene carbonate) bearing specific T_g thereby providing diverse nature of polymers with wide range of applications.



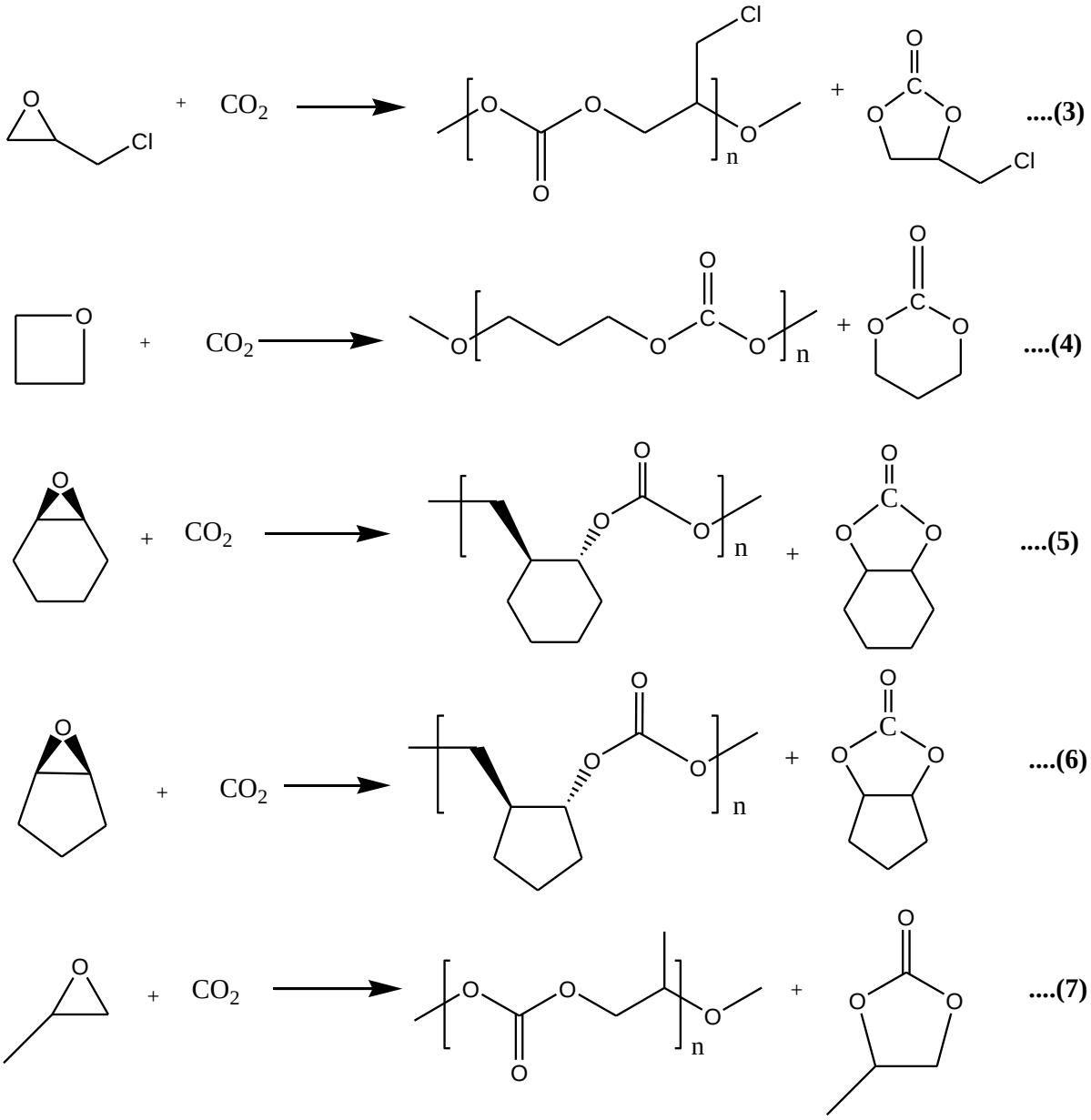


Figure 1.2: Copolymerization of different epoxides and CO_2. Respective epoxides used as monomers for the above reactions are (1) ethylene oxide (2) Styrene oxide (3) 2-chloromethyl oxirane (4) oxetane (5) cyclohexene oxide (6) cyclopentene oxide (7) propylene oxide

CHAPTER-2

CHEMISTRY OF POLY(PROPYLENE CARBONATE(S)) AND CYCLIC CARBONATE

CHAPTER-2 CHEMISTRY OF POLY(PROPYLENE CARBONATE(S)) AND CYCLIC CARBONATE

This chapter discusses the chemistry behind chemical fixation of propylene oxide and CO_2. Ring opening of epoxide ring by nucleophilic attack and corresponding insertion of carbon dioxide molecule has been discussed in this chapter. Further, possible regioisomers and stereoisomers of poly(propylene carbonate) [PPC] and applications of PPC and Cyclic carbonate has also been discussed.

2.1 Ring-opening of Epoxides

Epoxides have greater angle strain compared to larger ring cyclic ethers, thus they can undergo ring opening quite easily. Ring opening of the epoxides can proceed via two basic mechanisms: (A) Acid catalyzed ring opening of epoxides and (B) Base catalyzed ring-opening of epoxides. In the former case, the oxygen of an epoxide ring is protonated by an acid and then the nucleophile attacks at the most substituted position (Figure 2.1 (A)). It has also been observed that when nucleophilic attack occurs, the inversion of stereochemistry takes place at this position while no change of inversion occurs at other position. In the second case, base generally attacks the epoxide ring from the less hindered site as in case of SN^2 mechanism. This is then followed by the protonation of the resultant alkoxide (Figure 2.1 (B)) [http://www.masterorganicchemistry.com/2015/02/02/opening-of-epoxides-with-acid, accessed on September 15, 2015].

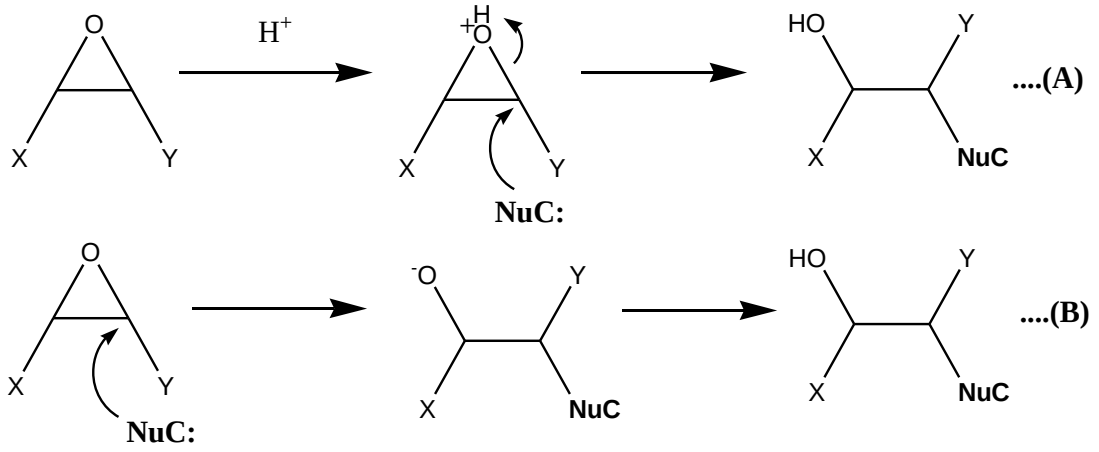


Figure 2.1: (A) Acid catalyzed ring opening of epoxides (B) Base catalyzed ring opening of epoxides

2.2 Copolymerization of Propylene Oxide and CO_2

Chemical fixation of propylene oxide and CO_2 is of immense interest since both the starting monomers are cheap and abundantly available and lead to the development of value added products i.e. poly(propylene carbonate) and cyclic carbonate. Propylene oxide has a strained three membered ring (with all angles of 60^o) which increases its reactivity towards catalysts for anionic and related nucleophilic polymerization. Due to its highly strained ring, it is relatively more reactive than its higher ring analogues. It is capable of undergoing bond cleavage at the methine-oxygen bond (α) or at methylene-oxygen bond (β) thereby leading to the ring opening (Figure 2.2) [Sugimoto *et al.* (2006)]. However, it is believed that the attack from β position is more likely to occur since it is sterically less hindered.

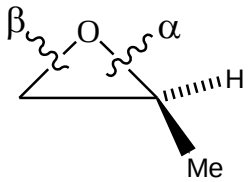


Figure 2.2: Ring-opening of Propylene Oxide

Many reactions based on carbon dioxide for the production of chemicals are known that require a metal catalyst (or acid-base catalyst). In the last few years, interests in the investigation of the interaction of CO_2 with metal systems and organic substrates have

increased remarkably [Aresta. (1999)]. Reactions with CO_2 can be reductive as well as non-reductive. With respect to atom economy, non-reductive reactions are more favourable for the chemical fixation of CO_2 since they retain oxygen atoms.

Chemical fixation of carbon dioxide and propylene oxide (Figure 2.3) to form an alternating copolymer i.e. poly(propylene carbonate) and cyclic carbonates is an example of non-reductive reaction (since oxygen is retained).

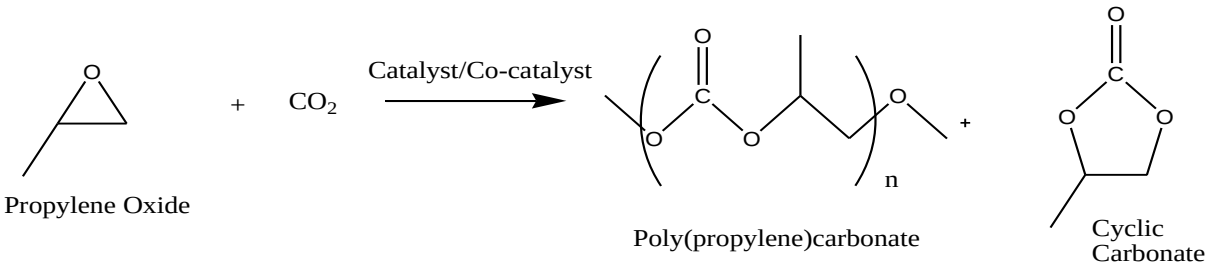


Figure 2.3: Copolymerization of CO_2 and Propylene Oxide

The presence of homo-ether or polyether linkages as a result of propylene oxide units joining together can be observed in some cases during reaction of propylene oxide and CO_2. Most systems can be tuned to favour CO_2 incorporation by catalyst selection and maintaining proper CO_2 pressure, monomer-to-catalyst ratio, propylene oxide concentration, and temperature. The energetically disfavoured simultaneous insertion of two molecules of CO_2 giving rise to dicarbonate linkages has not been reported till date [Coates *et al.* (2004)].

2.2.1 Applications of Poly(propylene carbonate) [PPC] and Cyclic Carbonate

PPC and cyclic carbonates are two products formed in the reaction between propylene oxide and CO_2. The polymeric product PPC has numerous applications where comparatively low glass transition temperature is required (between 30-45^{o}C). It is used for increasing the strength of some epoxy resins and as a sacrificial binder for the preparation of ceramics where it evaporates during–sintering. It is also appropriate for preparation of many electro-ceramic materials like dielectric materials and piezoelectric ceramics. PPC can be used in variety of ceramic processing techniques as dry pressing, tape casting, injection moulding,

extrusion and screen printing. In comparison to traditionally used binders like polyvinyl butyral and ethyl cellulose, PPC burns more cleanly in a uniform manner and at lower temperature with no harmful end products. Additionally, this polymer also provides better ceramic products with improved mechanical and electrical properties and uses less energy during manufacturing because of shorter sintering time and lower furnace temperature to remove the binder [http://www.novomer.com/ceramic-binder-materials, accessed on September 15, 2015]. Cyclic carbonates are used as polar aprotic solvent, electrolytic element in lithium ion secondary batteries, as starting material in the synthesis of various polycarbonates and as chemical intermediates in the preparation of agricultural chemicals and medicines [Du *et al.* (2005)]. They are also used as greener substitutes to phosgene which is toxic in nature and also as a substitute to dimethyl sulfate in many chemical reactions.

2.3 General Mechanism for Copolymerization of Propylene Oxide and CO_2

Based on the literature available on the copolymerization of propylene oxide and CO_2, a general mechanism can be written as shown in Figure 2.4. The nucleophilic group X of the ligand (catalyst) and the nucleophilic group of the co-catalyst opens up the ring of propylene oxide and then insertion of CO_2 takes place. This process continues to give rise to polycarbonate units.

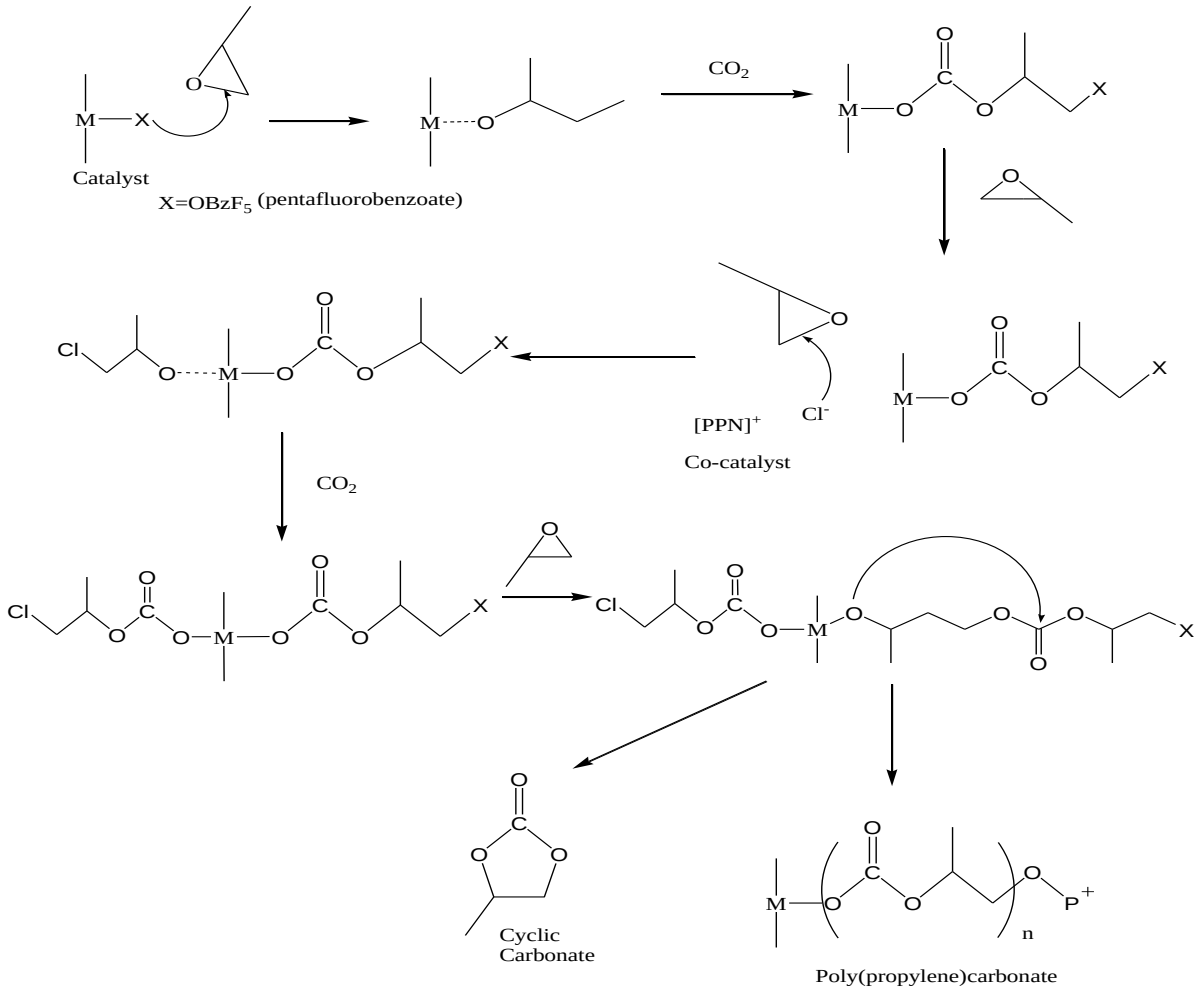


Figure 2.4: Proposed mechanism for the copolymerization reaction (M=metal, X= nucleophilic group)

The ring-opening of epoxide during copolymerization takes place via ion coordination mechanism which involves the complex of a metal (M) with ligand (L). This complex coordinates with the oxygen atom of the propylene oxide through an ionic bond. This is followed by an attack of the nucleophile at the metal site resulting in opening of the epoxide ring to give initiating species which propagate the chain through further addition of monomer and CO_2 (Figure 2.5)

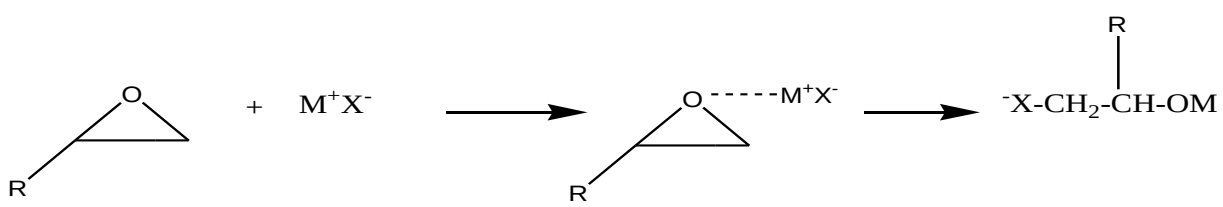


Figure 2.5: Coordinative polymerization of epoxides

2.4. Regioisomers and Stereoisomers of Poly(propylene carbonate)

2.4.1 Regioisomers

Based on the fact that whether the cleavage of the propylene oxide ring takes place from methine-oxygen bond (α) or at methylene-oxygen bond (β) (as in Figure 2.2), the alternating copolymerization of CO_2 and propylene oxide give rise to different type of regioisomers: **(A)** If one of the oxygen of carbonate group joins with methylene carbon and other oxygen of the carbonate joins with methine carbon of propylene oxide monomer, it give rise to head-to-tail linkage. **(B)** If both the oxygen atoms of carbonate group end joins with methylene carbon of propylene oxide monomer, it give rise to tail-to-tail linkage. **(C)** If both the oxygen atoms of carbonate group end joins with methine carbon of propylene oxide monomer, it give rise to head-to-head linkage [Lu *et al.* (2012); Liu *et al.* (2001); Meng *et al.* (2002)]. Respective regioisomers of poly(propylene carbonate) are shown in Figure 2.6.

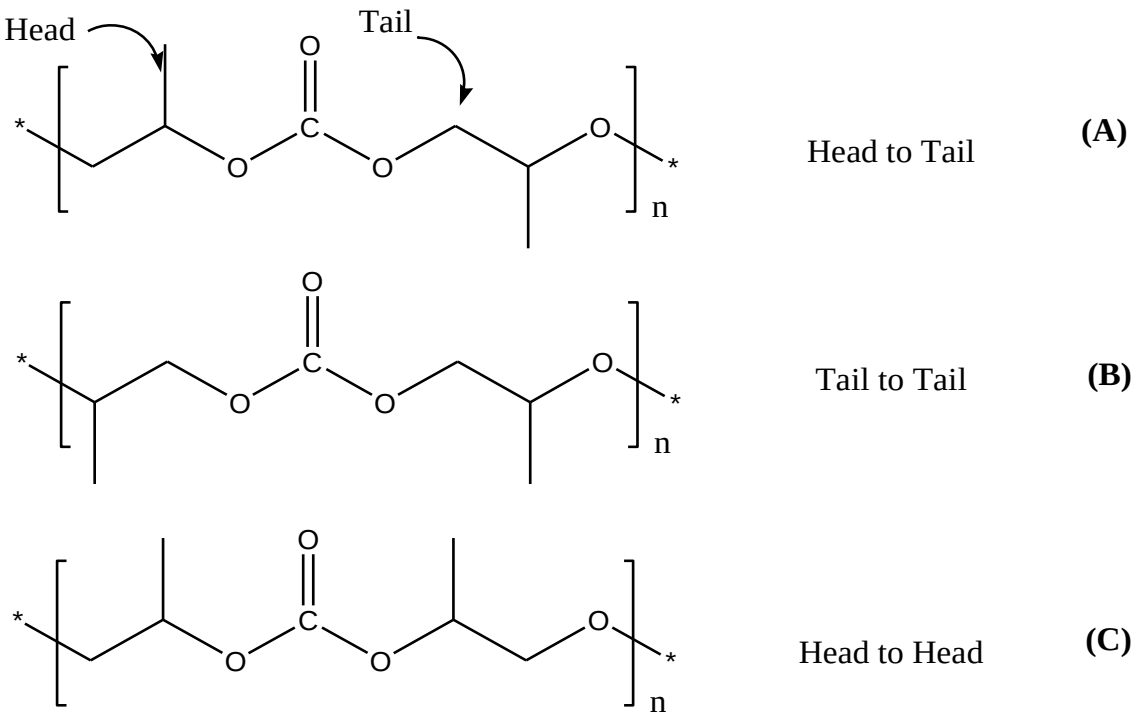


Figure 2.6: Regioisomers of Poly(propylene carbonate)

2.4.2 Stereoisomers

Based on the type of enantiomeric form of propylene oxide (i.e. R or S) as well the enantiomeric form of catalyst (R or S), the stereochemistry of the synthesized polymer is decided. The three major classes of stereoisomers that are formed in case of poly(propylene carbonate) majorly with head-to-tail linkages are: isotactic, syndiotactic and atactic. When the addition of propylene oxide units taking place in the polymeric chain bears alternating inverted configuration, it gives rise to syndiotactic polymer. When all the propylene oxide units adding in the polymeric chain bears same optical configuration, it give rise to isotactic polymer. When the optical configuration of the polymer is completely random due to the alternately adding propylene oxide units, it gives rise to atactic polymer [Lu *et al.* (2012)]. Corresponding stereoisomers for poly(propylene carbonate) are shown in Figure 2.7.

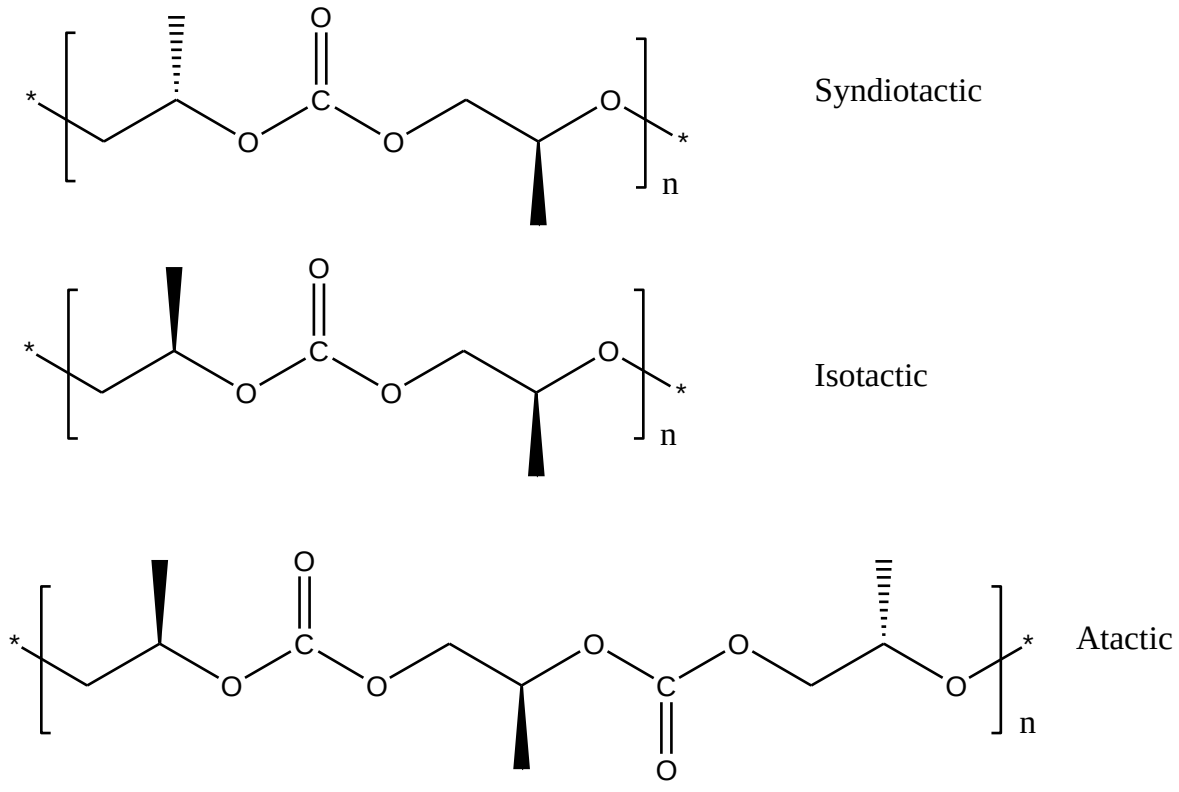


Figure 2.7: Stereoisomers of poly(propylene carbonate)

2.5. Commercial Aspects Regarding PPC

Although PPC was discovered long back in 1969 by Inoue and co-workers but due to the low catalytic activity, low molecular weight as well as long polymerization time, the commercialization was not very successful. It was also probably impeded greatly due to the properties of PPC since it was not meant to fit into existing market at that time. But, with the passage of time, applications of PPC and other poly(alkene carbonate) made from epoxides and CO_2 are being extensively explored. One of the reasons of increase in its production and demand is also its smooth biological degradation.

Around 1998, Prof Wang Xianhong of Changchun Institute of Applied Chemistry (CIAC), Chinese Academy of Sciences, developed rare earth ternary catalysts which gave high molecular weight PPC in short reaction time. Further, licenced by CIAC, Meng Xi High Tech Group in Ordos City, Innu, Mongolia and China National Offshore company is producing PPC through this route since 2004 [Xianhong *et al.* (2011)]. The latter has also established a production line of 5000 ton/year in 2009 in Dongfong city. PPC line of 10,000 tons/year has also been commissioned by China Blue Chemical Ltd [Luinstra *et al.* (2011)].

Empower Materials, New Castle, USA is the largest producer of PPC in the world. The company is also producing poly(cyclohexene carbonate), poly(ethylene carbonate) and poly(propylene/cyclochexene carbonate) and thus offers copolymers and terpolymers for wide range of applications. Novomer, New York, USA is also effectively producing PPC and PEC, polymer with upto 50% CO_2 by weight. There is still a considerable scope for the increase in level of its commercialization thereby giving more and more economic benefits. Some of the physical properties of PPC on the basis of which its applications can be explored are given in Table 2.1 [Luinstra *et al.* (2011)].

Table 2.1 Physical properties of poly(propylene carbonate) [Luinstra *et al.* (2011)]

S.No.	**Properties**	
1.	Hardness (H D)	74
2.	Refractive Index	1.4
3.	Density (g/ml)	1.26
4.	Dielectric constant	3
5.	Surface Energy (mJ/m^2)	42.9
6.	Permeability (cc mil/m^2 day atm)	
Oxygen		15-35
Nitrogen		10
Carbon Dioxide		120
Water		3-18

CHAPTER-3

LITERATURE REVIEW

CHAPTER-3 LITERATURE REVIEW

This chapter presents a review of the available literature on chemical fixation of propylene oxide and carbon dioxide (CO_2) to poly(propylene carbonate) [PPC] and cyclic carbonate. The efficacy of various inorganic, organometallic and ligand metal complexes as catalysts/co-catalysts has been discussed.

3.1. History of catalyst development

Catalytic sequestration of carbon dioxide with propylene oxide to obtain cyclic carbonates and polycarbonates has received attention of researchers during past few decades. Inoue *et al.* (1969) pioneered the development of diethylzinc/water based catalyst system capable of giving PPC but with broad molecular weight distribution. This group further explored the catalytic activity of diethylzinc with various protic sources like resorcinol [Kobayashi *et al.* (1971)], hydroquinone [Kobayashi *et al.* (1971)], α-pheneethylamine [Inoue *et al.* (1972)], meta-hydroxybenzoic acid [Kobayashi *et al.* (1973)] and isophthalic acid [Kobayashi *et al.* (1973)]. Subsequent studies in this area revealed that diethylzinc based system along with various dihydric and trihydric alcohols such as pyrogallol [Kuran *et al.* (1976); Rokicki *et al.* (1979)], 4-bromopyrogallol [Gorecki *et al.* (1985)], resorcinol [Kuran *et al.* (1976)] and phloroglucinol [Kuran *et al.* (1976)] are also capable of PPC production. It was found that when monoprotic reagents were used, the reaction became selective for cyclic carbonate production. Kuran *et al.* (1979) also elucidated the influence of diethylzinc along with heteroatom (m-HXC_6H_4XH where X=N or S) on this reaction. In 1991, his group investigated diethylzinc-oxygen catalysts based on condensed (based on catechol and saligenin) and non-condensed zinc species (based on phenol) [Kuran *et al.* (1991)]. Following the zinc based complexes developed by Inoue and Kuran many other zinc based complexes were developed after 1990. These complexes include zinc bis(β-diiminate) [Allen

et al. (2002)], zinc adipate [Sakharov *et al.* (2002); Tang *et al.* (2013)], zinc based double metal cyanide complexes [Dong *et al.* (2012); Zhang *et al.* (2012); Lu *et al.* (2013)] zinc fluorobenzoate complex [Darensbourg *et al.* (2002)] etc.

In addition to the above catalysts, numerous ligand metal based complexes such as metalloporphyrins and schiff base ligand metal complexes have also been explored since these were found to exhibit good catalytic activity for copolymerization with narrow molecular weight distribution. First ligand metal complexes based on tetraphenylporphyrin aluminium [(TPP)AlX where X=Cl, OMe, Me, OR, OAc] were also developed by Inoue *et al.* (1978). Since these early studies, many different inorganic, organometallic and ligand metal based catalysts have been used till date to initiate this copolymerization reaction. Although, all of these classes have been found to be active but better polydispersity (near to unity) has been achieved with ligand metal based complexes and organometallic catalysts. On the other hand, higher molecular weight has been achieved using inexpensive inorganic catalysts but in relatively longer time duration. Thus, both the types of catalyst systems have their own limitations and advantages.

3.2. Studies on copolymerization of propylene oxide and CO_2

Most of the available studies on copolymerization of propylene oxide and CO_2 have been done by mainly targeting the following objectives:

i. To synthesize an active catalyst for copolymerization and study the effect of catalysts and co-catalyst,
ii. To optimize the reaction conditions (parameters like pressure, temperature and time) and
iii. To increase the molecular weight of product polycarbonate.

The available information on operating pressure, temperature, molecular weight and poly-dispersity as reported by various workers who have investigated co-polymerization of CO_2 and propylene oxide is presented in Table 3.1.

Table 3.1: Copolymerization of CO_2 and propylene oxide using different catalyst and reaction conditions

S.No	Catalyst	Reaction Temp ^oC (K)	Pressure Bar (psi)	Time (h)	Maximum M_n* (g/mol) /PD/TON Yield (%)	References
1.	Planar tetradendate metal complexes/$[PPN]^+Cl^-$	60 (333)	20 (290)	12	39×10^3 PD=1.2	Ohkawara *et al.* (2014)
2.	SalenCoX/DMAP, SalenCrX/DMAP	40 (313)	40 (580)	40	37×10^3 PD=1.05	Xu *et al.* (2014)
3.	Multi metal cyanide catalysts from $ZnCl_2$, $NiCl_2$, $K_3[Fe(CN)_6]$	70 (343)	30 (450)	40	$M_n=37\times 10^3$ PD=2.2	Lu *et al.*(2013)
4.	Bifunctoinal porphyrin cobalt(III) based complexes	25 (298)	20 (290)	5	$M_n=48\times 10^3$ PD=1.2	Wu *et al.*(2013)
5.	Zinc Adipate/Tertiary amine	80 (353)	52 (750)	32	$M_n=2.59\times10^5$ PD=3.09	Tang *et al.*(2013)
6.	Double metal cyanide complexes	90 (363)	54 (780)	1	$M_n=15\times10^3$-25×10^4	Coates *et al.*(2012)
7.	Combinatorial catalysts from rare earth ternary metal complex and double metal cyanide $Zn_3[Co(CN)_6]$	70 (343)	40 (580)	10	$M_n=114\times10^3$ PD=4.64	Dong *et al.* (2012)

8.	Porphyrin-Cobalt(III) Chloride complexes (substituents=H,OMe,OEt,O^nPr,O^i	25 (298)	50 (725)	18	M_n=52.5×10^3 PD=1.26	Anderson *et al.* (2012)
9.	Mechanochemically synthesized double metal cyanide catalysts $Zn_3[Fe(CN)_6]$ and $Zn_3[Co(CN)_6]$	70 (343)	40 (580)	10	M_n=114×10^3 PD=4.64	Zhang *et al.*(2011)
10.	1,9-bis(2-oxidophenyl)dipyr rinate ligand metal complexes	60 (333)	20 (290)	12	M_n=28.5×10^3	Nakano *et al.*(2011)
11.	Inoganic Oxide Supported Rare Earth Ternary Catalyst $Y(CCl_3OO)_3$/glycerin/$ZnEt_2$ (Maximum molecular weight reported with Magnesium Oxide)	70 (343)	20-40 (290-580)	10	M_n=14.3×10^4	Lu *et al.*(2011)
12.	R,R Salen CoX complex X=$OOCF_3$,$OOCCl_3$,$OOCCH_3$	40 (313)	20 (290)	2	M_n=24.8×10^3	Liu *et al.*(2011)
13.	Dinuclear Co-Salen complexes	20-60 (293-363)	53 (742)	2	M_n=3.6×10^3	Nakano *et al.*(2010)
14.	Dimeric Cr(III) Salophen Catalysts	60 (333)	40 (580)	24	M_n=46×10^3 PD=3.3	Vagin *et al.*(2010)
15.	Cobalt (2,4-dinitrophenolate) Schiff base complex	65 (338)	20-40 (290-580)	2	M_n=11.5×10^3	Y Niu *et al.*(2009)
16.	N,N′-bis(salicylidene)-1,2-phenylenediaminechromiumX	30 (303)	15 (217)	1.5	M_n=12.4×10^3 PD=1.62	Niu *et al.*(2009)
17.	N,N′-bis(salicylidene)-1,2-phenylenediaminocobalt(III)X	45 (318)	10-40 (145-580)	24-30	M_n=34.7×10^3 PD=1.39	Liu *et al.*(2009)

18.	Quaternary ammonium ion tethered Salen Co (III)X complex (X=2,4-dinitrophenolate)	70 (343)	20 (290)	1	M_n=3.0×10^3	Min *et al.* (2009)
19.	Triphenylphosphine Cobalt(III)Chloride- DMAP system	40 (313)	50 (725)	24	M_n=9.0×10^3 PD=1.23	Sugimoto and Kuroda. (2008)
20.	Cobalt salen complex with piperidinium end	25 (298)	14 (200)	3	M_n=8.3×10^3	Nakano *et al.*(2006)
21.	Zinc glutarate complexes	60 (333)	20 (300)	40	M_n=14.3×10^4 PD=2.4	Kim *et al.*(2005)
22.	N,N′-bis(3,5-di-butylsalicylidene)-1,2-diaminocyclohexane)CoX	22 (295)	13.7-55.15 (200-800)	2	PD=1.15	Cohen *et al.* (2005)
23.	Co(III)salen / Lewis base	25 (298)	24.13 (350)	5	M_n=17.1×10^3 PD=1.05	Paddock *et al.*(2005)
24.	Ethylsulphinate containing zinc glutarate	60 (333)	40 (580)	40	M_n=1.91×10^5 PD=3.3	Eberhardt *et al.*(2004)
25.	Cobalt based ligands	25 (298)	57.14 (800)	8	M_n=2.1×10^3	Qin *et al.* (2003)
26.	Salen Cr complexes	75 (348)	13 (188)	4	M_n=16.7×10^3 PD=1.38	Robert Eberhardt *et al.* (2003)
27.	Zinc Adipate	25 (298)	80 (1160)	10	M_n=64×10^3	Sakharov *et al.* (2002)

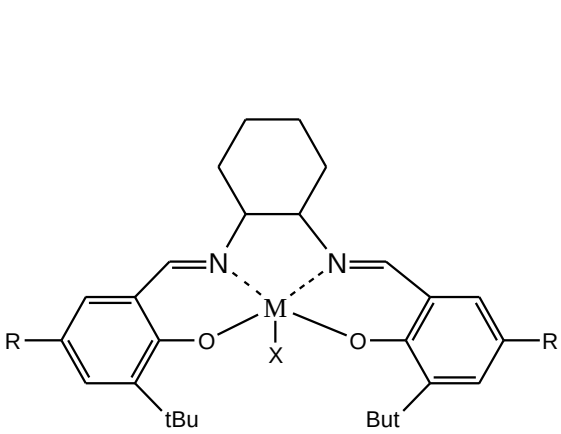
28.	[2,6-(diflourobenzoate)Zn_X] and [2,6-(dichlorobenzoate)Zn_x]	55 (328)	45-52 (650-700)	48	-	Darensbourg *et al.* (2002)
29.	Zinc bis(β-diiminate)complexes	10 (283)	20 (300)	-	M_n=1.0×10^4	Allen *et al.* (2002)
30.	Ln $(CCl_3COO)_3$ based catalyst	60 (333)	30 (435)	12	M_n=62.2×10^3	Liu *et al.* (2001)
31.	Tetraphenylporphinatoaluminium chloride	40 (313)	51 (720)	168	M_n=3.6×10^3 PD=1.31	Jung *et al.* (1999)
32.	Ternary rare earth metal coordination catalysts	60 (333)	27.5 (398)	12	TON=395	Tan *et al.* (1997)
33.	Aluminium complex[{η^3-Hb(3-Phpz)$_2$(5-Phpz)}$_2$]	60 (333)	51.7-82.7 (750-1200)	24	TON=50	Darensbourg *et al.* (1996)
34.	Organometallic compounds R=halogen, alkyl, acyl groups	50-70 (323)	(40-60) 560-840	24	-	Inoue *et al.* (1975)

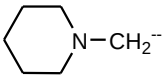
* M_n is the number average molecular weight, PD is the Polydispersity of the polymer.

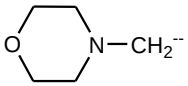
TON is the turn over number

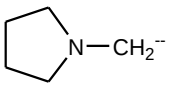
The successful results on copolymerization of propylene oxide and CO_2 to give poly(propylene carbonate)s and cyclic carbonates are based on salen-Cr(III) complexes [Paddock *et al.* (2001); Eberhardt *et al.* (2003); Niu *et al.* (2009); Xu *et al.* (2014)] and salen-Co(III) complexes [Qin *et al.* (2003); Paddock *et al.* (2005); Cohen *et al.* (2005); Nakano *et al.* (2006); Cohen *et al.* (2006); Chatterjee *et al.* (2013)]. Coates *et al.* (2003) reported that Co(III) based salen complexes were capable of producing poly(propylene carbonate) (PPC) with no detectable byproduct (like cyclic carbonate and polypropylene oxide) at the end of the reaction. The selectivity of the catalyst was found to be higher at high CO_2 pressure.

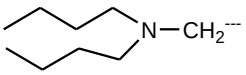
Further, Cohen *et al.* (2005) found that the chiralities of the monomer (i.e propylene oxide) as well as catalyst have considerable effect on the regiochemistry and stereochemistry of poly(propylene carbonate). To study this effect they carried out copolymerization using racemic , R and S propylene oxide as well as both racemic and R forms of salcy(Co)Br. It was observed that high CO_2 pressure around 800 psi and temperature at 22^{o}C gave yield of around 36% with 82% head to tail linkages using RR(salcy)CoBr as catalyst. By replacing racemic propylene oxide with R-propylene oxide the catalytic activity decreased to half value giving 20% yield and 43% head to tail linkages. Moreover PPC obtained was completely regiorandom. Copolymerization carried out with S-propylene oxide gave yield of upto 49% and about 93% head to tail linkages. The obtained polymer was also isotactic in nature.



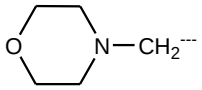
R=  X=Cl, 1a

R=  X=Cl, 1b

R=  X=Cl, 1c

R=  X=Cl, 1d

R= tert-butyl X=Cl, 1e

R=  $X=N_3$, 2b

R= tert-butyl $X=N_3$, 2e

Figure 3.1 (a): Structure of Salen Co(X=Cl/N_3) ligands with lewis basic moiety

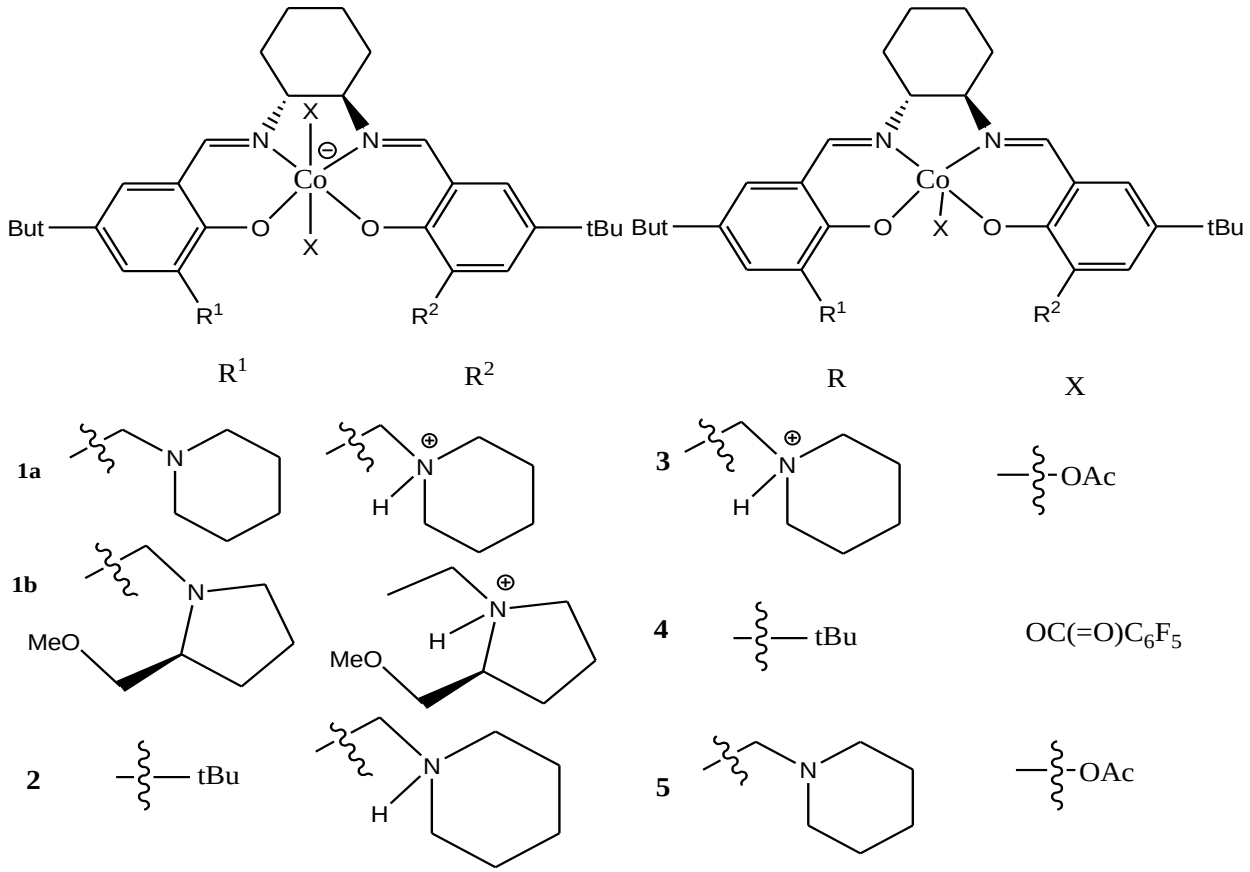


Figure 3.1 (b): Structure of Salen Co(X=OAc/ $OCOC_6F_5$) ligands with lewis basic moiety

Liu *et al.* (2009) studied the effects of Lewis base group attached to salen meoity on copolymerization (Figure 3.1(a)) and ratio of polypropylene carbonate and cyclic carbonate formed during the reaction was studied using IR spectroscopy. It was observed that all the ligand metal complexes were capable of giving poly(propylene carbonate) but Complex 1b (Figure 3.1(a)) was highly selective catalyst for the copolymerization giving 86% head to tail linkages with M_n=28.4×10^3 g/mol and PD=1.21. The results showed that the catalysts were capable of giving copolymer as the dominant product with nearly negligible amount of homopolmer. Nakano *et al* (2011) further explored the synthesis of stereo-controlled and stereo-gradient copolymers using salen cobalt complexes with different Lewis base substituents attached to it (Figure 3.1(b)). Copolymerization of propylene oxide and CO_2 were carried out at pressure of about 14 bar and temperature of 25^{o}C. It was observed that complex 1a (Figure 3.1(b)) gave moderate regioselectivity with 72% head to tail linkages and

no detectable enantioselectivity. Out of all the complexes studied, complex 1b gave 84% propylene oxide conversion with 99% selectivity for polycarbonate and 86% head to tail linkages. Studies were also carried out by replacing acetate group of Complex 5 (Figure 3.1(b)) with pentafluorobenzoic acid which gave highest regio and enatioselectivities.

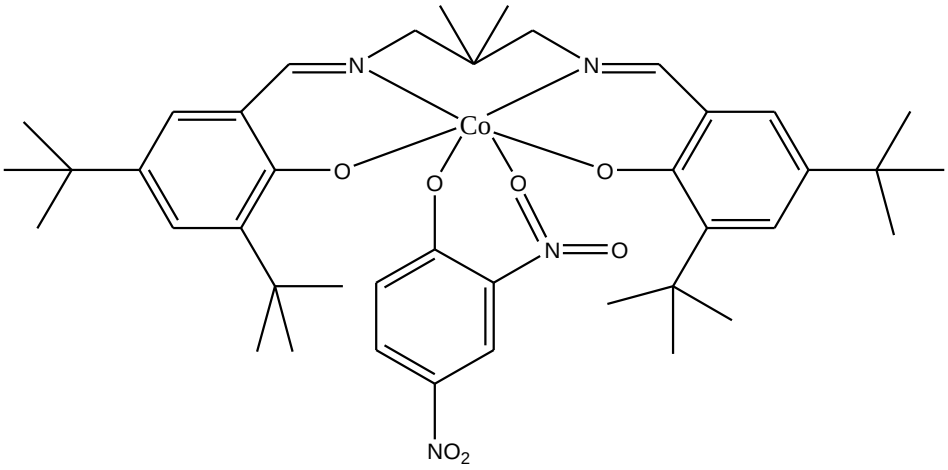


Figure 3.2: Schiff base ligand with cobalt metal center and 2,4-dinitrophenolate at axial position

Niu *et al.* (2009) investigated the activity of Lewis base additive at axial position X of the schiff base ligand (Figure 3.2). The catalyst was different from the previous studies since it carried dimethyl substituted propylenediamine backbone. The catalyst showed moderate activity towards polymerization with a maximum yield of around 24.5%. In order to get an insight of the role of co-catalysts copolymerization was carried out using 4-DMAP, tetrabutylammonium bromide and (triphenylphosphine)iminium chloride. Among these co-catalysts, 4-DMAP was found to be the most active with best activity that could be achieved at temperature 60^{o}C, pressure 20 bar and catalyst/co-catalyst ratio of 2:1. M_n of the obtained polymer was found to be 11.5 × 10^3 g/mol with narrow polydispersity near to 1 and head to tail linkages > 90%.

Double metal cyanide catalysts were explored by Zhang *et al.* (2011). $Zn_3[Fe(CN)_6]$ and $Zn_3[Co(CN)_6]$ were synthesized and the effect of mechano-chemical methods using liquid

assisted grinding methods on copolymerization was investigated. The method gave a greener way for the synthesis of catalyst at room temperature within minutes. Selectivity of catalysts was improved by this method. The catalyst morphology on the basis of solvent employed was divided into amorphous and crystalline. Polar solvents such as di-methyl sulfa oxide (DMSO), di-methyl forma-amide (DMF) and methanol gave low crystallanity in contrast to solvents of weak polarity such as cyclohexane, ethanol and chloroform which gave crystalline solids. DFP although being non polar gave largely amorphous double metal cyanide complexes the reason for which remained unresolved.

Dong *et al.* (2012) studied the effect of copolymerization in presence of combinatorial catalyst consisting of double metal cyanide complex along with rare earth ternary complex. Double metal cyanide complex $Zn_3[Co(CN)_6]$ and rare earth ternary complex from glycerin, $Y(CCl_3OO)_3$ and $ZnEt_2$ were combined together and used for copolymerization. It was observed that combinatorial catalyst thus synthesized gave interesting results in comparison to individual double metal cyanide catalyst and ternary rare earth metal complex. Lu *et al.* (2013), synthesized multi-metal cyanide catalysts using grinding methods. The effect of metal element on structure and catalyst efficiency was observed. Three different metal salts $ZnCl_2$, $NiCl_2$ and $K_3Fe(CN)_6$ were taken in different ratios and their effect on copolymerization was observed.

Liu *et al.* (2001) investigated and compared the effects of ternary catalysts system on copolymerization in comparison to binary catalyst system. It was found that yield of the copolymer increased significantly using $Nd(CCl_3COO)_3$-$ZnEt_2$-glycerol instead of $ZnEt_2$-gycerol binary catalyst. The effect of copolymerization was studied at different rare earth compound concentrations and it was observed that when the concentration of rare earth metal compound reached about 1.2×10^{-3} mol the polyether linkage nearly disappeared which also

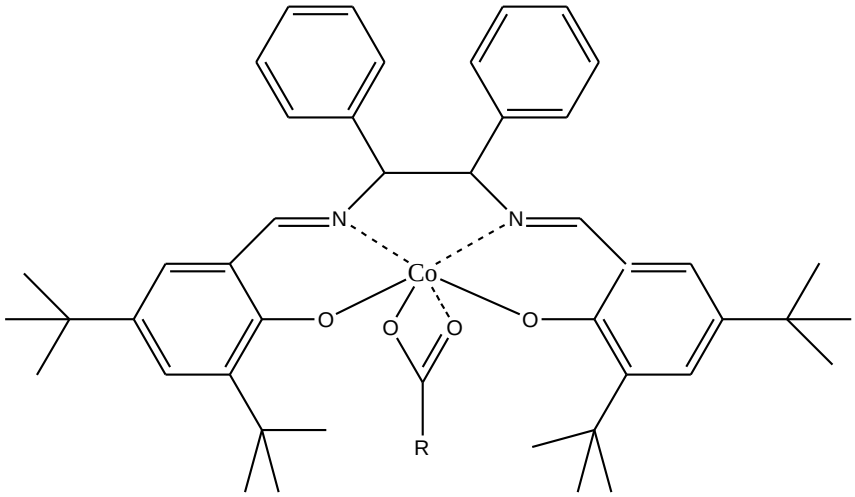
increased the intrinsic viscosity of the copolymer. Some polyether linkages were observed at higher catalyst concentration.

Meng *et al.* (2002) investigated the effect of zinc glutarate complexes on copolymerization of propylene oxide and CO_2. The complexes were prepared by three different routes: magnetic stirring, ultrasonication and mechanical stirring. It was found that catalysts synthesized by magnetic stirring method were very efficient in copolymerization because of their high crystallinity, small particle size and high surface area to volume ratio. This was followed by the catalyst prepared by mechanical stirring and then by that prepared using ultra-sonication.

Lu *et al.* (2011) studied the effect of $Y(CCl_3OO)_3$ / glycerin/ $ZnEt_2$ anchored to various supports on the propylene oxide and CO_2 copolymerization activity. The catalysts were prepared by two different methods. In the first method $ZnEt_2$ was added drop-wise to $Y(CCl_3OO)_3$ / glycerin/ support and in the second system $Y(CCl_3OO)_3$ / glycerin/ $ZnEt_2$ was anchored on supports as SiO_2, α-Al_2O_3, MgO and γ-Al_2O_3. In the later case, it was seen that catalytic activity increased from about 13 to 36% in all the catalyst systems with little change in the molecular weight. In the former case the catalytic activity was lower than $Y(CCl_3OO)_3$ /glycerin/$ZnEt_2$ system but there was a slight increase in the molecular weight of poly(propylene)carbonate. Other than this, the effects of nano- and micro-size silica were also seen where the molecular weight with all catalyst systems remained almost unchanged. The catalytic activity of the micro-size silica was found to be slightly lower than that of nano-size silica.

Eberhardt *et al.* (2004) reported ethylsulfinate modified zinc dicarboxylates for the synthesis of poly(propylene carbonate). They introduced different mol% (9, 17, 25, and 50) of ethylsulfinate groups into zinc glutarate and observed its activity as catalyst for chemical fixation of propylene oxide and carbon dioxide. It was observed that as the percentage of ethylsulfinate groups increased the polymerization activity of the catalyst also increased up to

17 mol% and then decreased. When ethylsulfinate groups were introduced on other higher and lower homologues of zinc dicarboxylates, the catalytic efficiency of the complexes was found to decrease.



Complex1. R=CF_3
Complex2. R=CCl_3
Complex3. R=CH_3

Figure 3.3: (R,R)-SalenCo(III)X [Salen = N,N'-bis(3,5-di-tert-butylsalicylidene)-1,2-di-phenylethylenediimine] complex

Li *et al.* (2011) investigated the effect of axial group of cobalt/Schiff base complexes (Figure 3.3) along with [PPN]Cl as co-catalyst on the copolymerization of propylene oxide and CO_2. It was found that Complex 1 was highly effective and selective for copolymerization giving > 99% selectivity for polycarbonate with M_n=24.8×10^3 g/mol and head to tail linkages of 95% when reaction was carried for 2 hrs at 40^{o}C with CO_2 pressure of 20 bar. The selectivity for poly(propylene carbonate) decreased in the order 1 > 2 > 3 (99% > 84% > 79%). Further studies concerning the effect of molar ratio of complex1/ [PPN]Cl were carried out which showed that molecular weight first increased with increase in molar ratio, reached to an optimum and then decreased with further increase. Furthermore, when the reaction time was increased upto 30 h polycarbonate with molecular weight up to 72.5×10^3 g/mol and 98% poly(propylene)carbonate selectivity could be obtained.

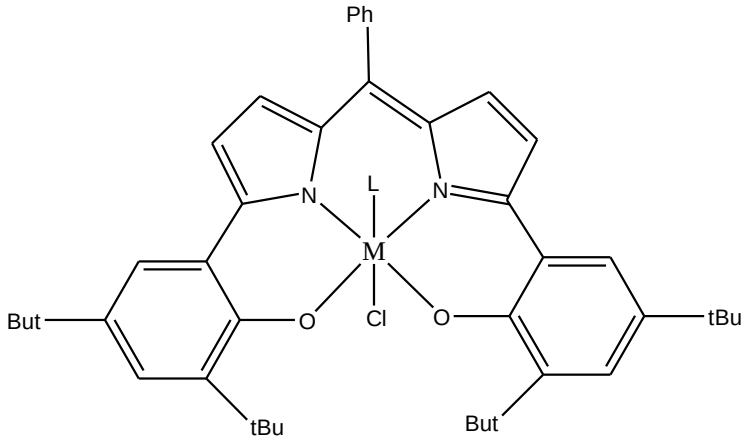


Figure 3.4: Tetravalent metal complex

Nakano *et al.* (2011) used the combination of a tetravalent metal ion, a trianionic [ONNO]-tetradentate ligand, with monoanionic ancillary ligand that was equally active like dianionic tetradentate (salen)MX complexes [or schiff base metal complexes] bearing a nucleophilic group at axial position for synthesizing copolymer. The tetravalent metal complexes (Figure 3.4) with a 1,9-bis(2-oxidophenyl) dipyrrinate ligand were synthesized and studied for copolymerization for the first time. The study was carried out for titanium, germanium, tin and zirconium metal ions and [PPN]Cl as co-catalyst. Out of these Ti and Ge were able to carry out copolymerization of propylene oxide and CO_2 whereas Sn and Zr gave significant amount of cyclic product. In case of germanium complex lower amount of [PPN]Cl and high CO_2 pressure resulted in higher PPC selectivity. When titanium was used as metal center, pressure had no effect on copolymerization but higher concentration of co-catalyst and temperature gave significant amount of cyclic product.

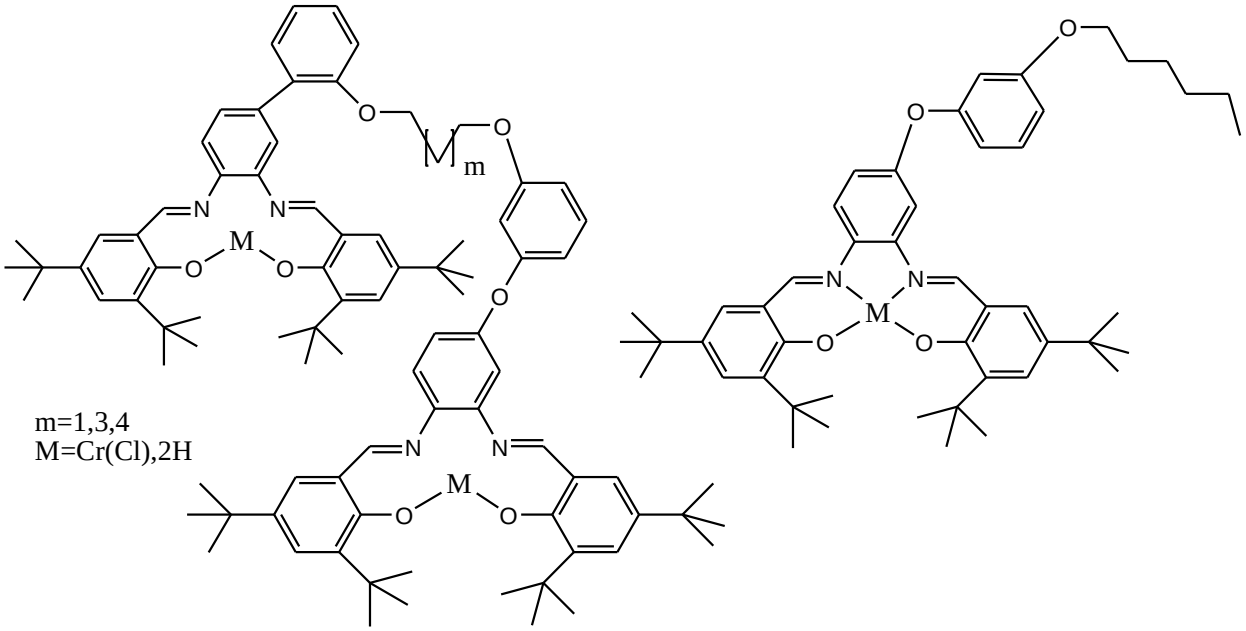


Figure 3.5: Dimeric and monomeric salophen ligands

Vagin *et al.* (2010) explored the activity of bi-functional and mono-functional Schiff base chromium (III) complexes (Figure 3.5) for carbon dioxide and propylene oxide copolymerization. It was observed that these bi-functional catalysts have relatively better activity in comparison to other Schiff base complexes. It is expected in such type of complexes that the growing chain at one metal center was capable of interacting with the activated monomer species at another chromium center and thus giving rise to higher molecular weight product.

Cooperative bimetallic catalysts have been used recently in asymmetric epoxide opening reactions displaying second-order kinetic dependency on catalyst where one metal is proposed to serve as Lewis acid for the activation of propylene oxide and another as counter ion for the nucleophile leading to increase in the rate of polymerization. Complexes that contain multiple metal centers with proper orientation are reported to provide improved reactivity compared to monometallic catalysts [Nakano *et al.* (2010), Ready *et al.* (2001)].

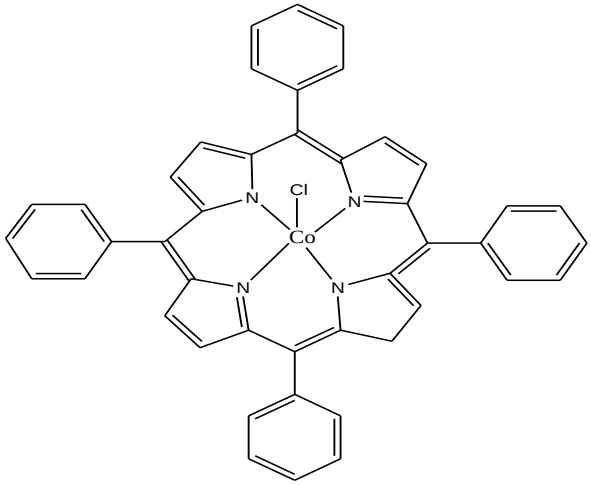


Figure 3.6: Structure of (TPP)CoCl

Sugimoto and Kuroda. (2008) studied the effect of cobalt porphyrin (TPP)CoCl (Figure 3.6) in combination with DMAP for alternating copolymerization of CO_2 and epoxide. The catalyst was unlike various other catalyst complexes since it was active for copolymerization of CO_2 with both propylene oxide and cyclohexene oxide. The catalyst was also active under mild conditions (P=1 atm and temperature=25^{o}C) though the highest molecular weight (M_n=9.0 ×10^3 g/mol) was obtained at 50 atm and 40^{o}C in 24 h.

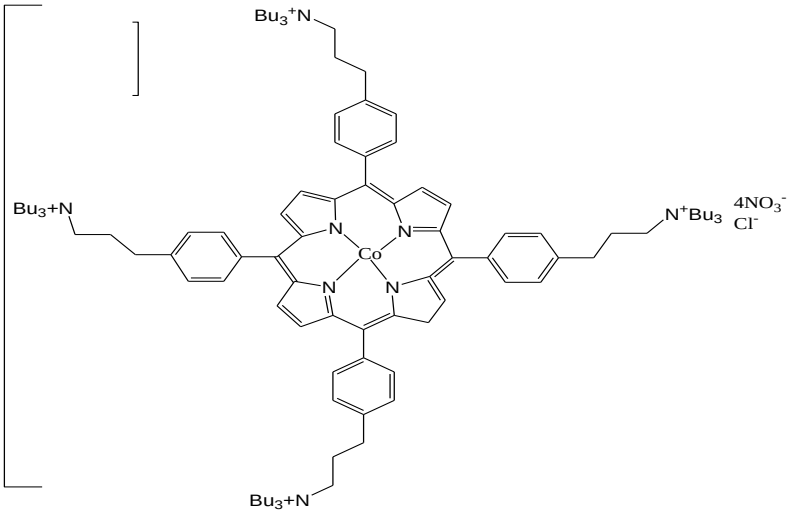


Figure 3.7: Bifunctional Porphyrin catalysts

Wu *et al.* (2013) synthesized bi-functional cobalt (III) porphyrin catalysts for the copolymerization of propylene oxide and CO_2. Two different types of porphyrin based catalysts were chosen for study, one bearing two quaternary ammonium cations (Complex 1)

and other bearing four quaternary ammonium cations (Complex 2, Figure 3.7) attached on the side moieties. It was observed that Complex 1 was more active for the copolymerization reaction in comparison to Complex 2. The Complex 1 was able to give poly(propylene carbonate) in 25% yield even at 25^{o}C and 1 atm but the copolymer obtained contained 85% carbonate linkages. At 40 atm the rate of copolymerization increased significantly with 99% carbonate linkages.

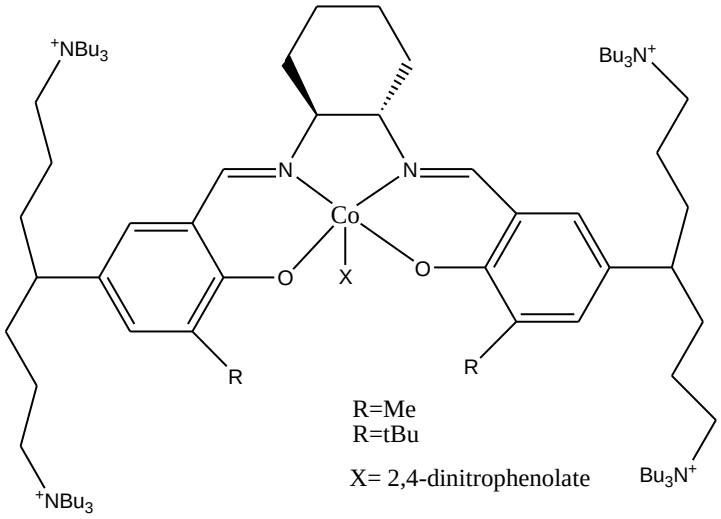


Figure 3.8: Quaternary ammonium ions tethered Salophen complex

Min *et al.* (2009) comprehensively investigated the effect of salen-Co(III) complexes tethered with four quaternary ammonium ions (Figure 3.8). It was observed that catalyst shows one of the best activities in the class of salen-CoX type catalysts. Lee and co-workers attempted a new and simple pathway for the synthesis of salen-CoX complexes tethered with quaternary ammonium ions. Such complexes were found to give completely alternating polymer from propylene oxide and CO_2 with M_n=3.0×10^5 g/mol and PD=1.31. This innovative catalyst had an advantage that it could be removed from the polymer mixture through filtration over a silica gel pad and thus can be used commercially.

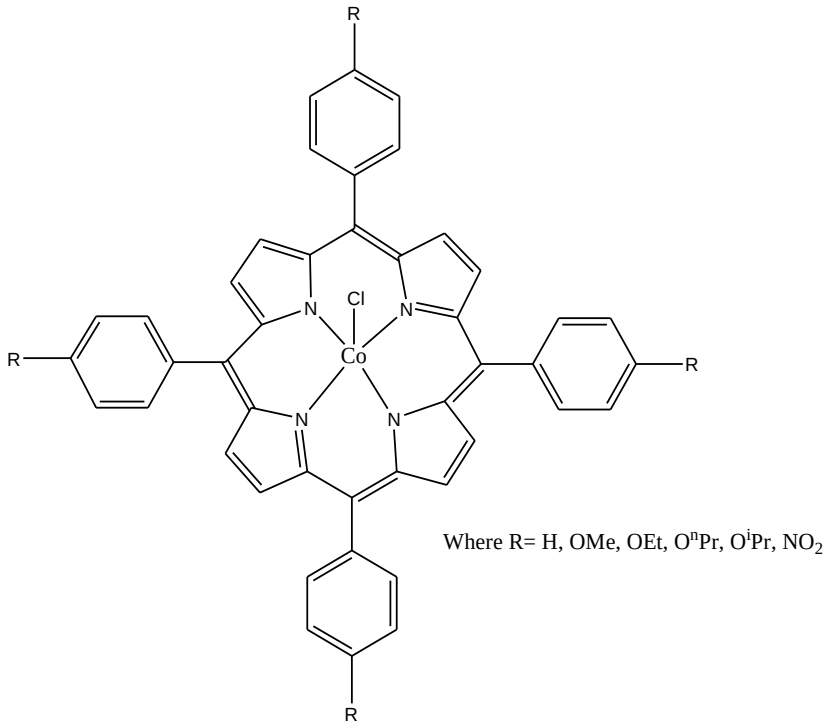


Figure 3.9: Porphyrin Cobalt(III)-chloride complexes

Anderson *et al.* (2012) explored the activity of cobalt based porphyrin complexes (Figure 3.9) towards copolymerization of propylene oxide and carbon dioxide. They systematically varied the substitution pattern around porphyrin complexes by various electron donating and electron withdrawing groups and explored the activity of the complexes. It was observed that catalysts bearing electron donating substituents favour PPC formation and the one bearing electron withdrawing substituents favours cyclic carbonate formation.

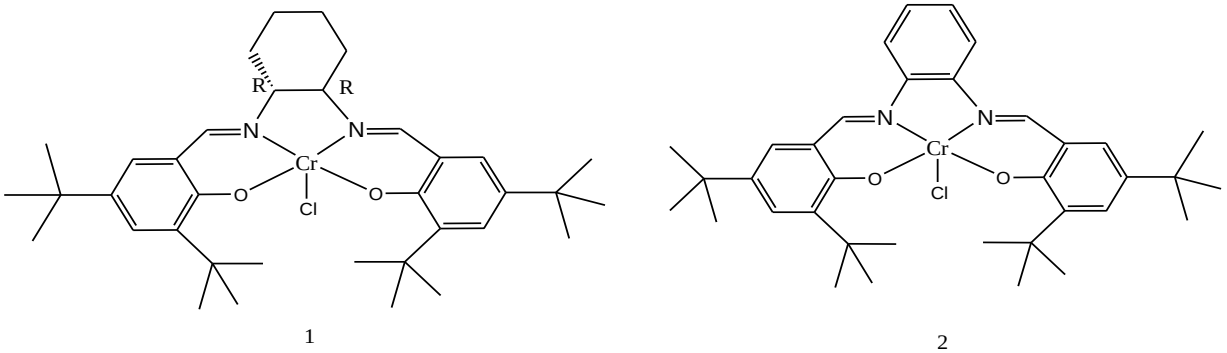


Figure 3.10: Chromium complexes with conjugated and non-conjugated backbone

Eberhardt *et al.* (2003) investigated the effect of conjugated and non-conjugated backbone (Figure 3.10) of salen-Cr(III) chloride complex on copolymerization. All the reactions were carried out using DMAP co-catalysts. It was found that the conjugated system was more effective for polycarbonate production. Although higher concentration of co-catalysts lead to cyclic carbonate formation but high polycarbonate selectivity could be obtained at lower concentration of 1 and 0.5 equivalents. It was further observed that complex containing non-conjugated diamine fragments in the backbone gave predominantly cyclic carbonate which might be due to easier dissociation of the alcoholate chain and more electron rich ligand structure.

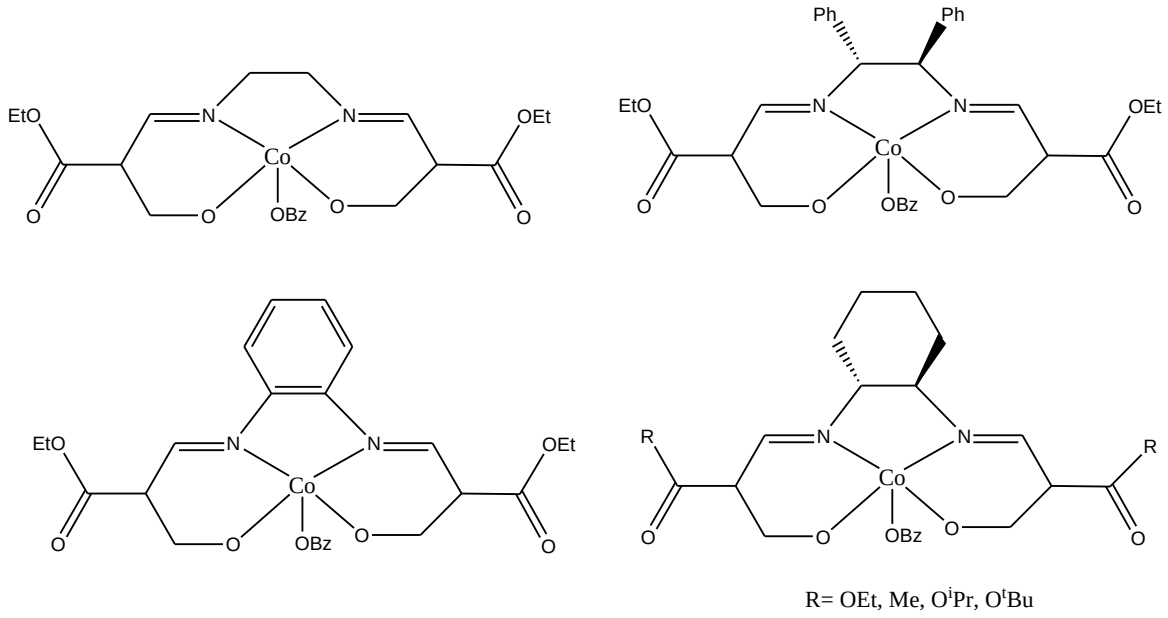


Figure 3.11: Di(ketoiminato)cobalt complexes

The class of different di(ketoiminato)cobalt complexes (Figure 3.11) had also been explored for copolymerization of propylene oxide and CO_2 by Yamada *et al.* (2010). This class of complexes has excellent activity and selectivity for polycarbonate synthesis without any ether linkages. Di(ketoiminato)cobalt complexes with different diamine meoity as ethylenediamine, trans-1,2-cyclohexanediamine, trans-1,2-diphenylethylenediamine and 1,2-phenylenediamine were used as catalysts for the copolymerization reaction. It was observed

that catalysts with trans-1,2-cyclohexanediamine backbone gave the best result in terms of reactivity and selectivity.

3.3 Effect of temperature, pressure and time

Several workers have investigated the effect of varying reaction conditions (pressure and temperature) and have reported a very significant effect on the product molecular weight and yield.

3.3.1 Temperature

Synthesis of polycarbonates and cyclic carbonates are competitive in nature. The difference in the activation energy required for cyclic carbonates and polycarbonates is very less and hence polycarbonate synthesis is a critical process. PPC conversion is affected by both kinetic and thermodynamic factors. It has been observed that the catalytic activity increases with an increase in polymerization temperature. The yield of copolymer with most of the catalyst systems increases with increasing temperature up to a certain temperature range (20 - 60^{o}C) and then decreases with a further temperature increase. This decrease of polymer yield at higher temperatures can be attributed due to the depolymerization reactions thereby favouring cyclic carbonate formation (Figure 3.12).

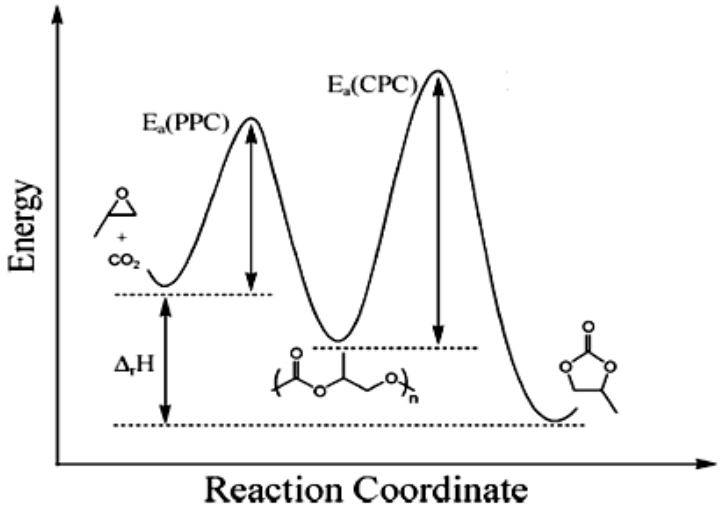


Figure 3.12: Reaction coordinate diagram for coupling of CO_2 and propylene oxide [Darensbourg *et al.* (2003)]

3.3.2 Pressure

Using CO_2 as a reagent in organic synthesis can be technically difficult and expensive if reactions are operated at high pressures. To overcome this limitation, it is necessary to develop a catalyst system that is capable of giving polycarbonate efficiently at low CO_2 pressures. It has been found that the molecular weight of polymer increases with an increase in pressure to a certain value and then decreases [Lu *et al.* (2004); Cohen *et al.* (2005); Liu *et al.* (2009)]. Use of low CO_2 pressures is attractive, as milder conditions are more amenable for reaction scale up. It is supposed that change in pressure will increase concentration of carbon dioxide and thereby will increase the conversion of the product. However, the increase in molecular weight with increase in pressure is not continuous rather it reaches a limiting value at some pressure. The average molecular weights of the product are dependent on individual rate constants of initiation, propagation and termination. Thus, when we change the catalyst/co-catalysts system it is expected that an optimum pressure, temperature and M_w trend will be different for different catalyst/co-catalyst systems depending on system conditions.

3.3.3 Time

The molecular weight increases with an increase in reaction time up to a certain value, after which it decreases slightly. It is expected that with increase in reaction time the yield of the polycarbonate product increases leading to an increase in the viscosity of the reaction system. The viscosity hinders the diffusion of the polymer. Probably, as the viscosity reaches a maximum value, the rate of chain transfer and decomposition for resulting copolymer in the presence of catalyst, exceeds that of the normal value and would result in a decrease in the molecular weight [Cohen *et al.* (2005); Liu *et al.* (2009)].

3.4 Catalysts and Co-catalysts

3.4.1 Catalyst

Literature search reveals that the catalysts with weak nucleophilic activity are found to be active for copolymerization of propylene oxide and CO_2. The major role of nucleophilic group of the catalyst is to open the propylene oxide ring. In the metal catalysed propylene oxide/CO_2 copolymerization, the axial group X (leaving nucleophilic group) of the complex, Lewis acid metal center and the substituents on the ligand exert a significant influence on the catalytic activity, polycarbonate/cyclic carbonate selectivity and the polymer head to tail linkages. Several workers have studied the effect of altering the electronic and steric environment around the metal center by changing the axial group X of the complex and the substituents on the ligand and observed the effect of these changes on the copolymerization reaction [Darensbourg *et al.* (2003); Lu *et al.* (2004); Cohen *et al.* (2006); Lu *et al.* (2011)]. It has been found that catalyst systems with poor nucleophilic activity lead to higher poly(propylene carbonate) selectivity in comparison to strong nucleophiles which form cyclic carbonates as the major reaction product. Stronger nucleophiles may enhance the back-biting reaction thereby leading to the formation of cyclic product. Further oxidation states of the catalysts have considerable influence on polycarbonate synthesis. Cobalt and chromium in +3 oxidation states are capable of producing polycarbonate successfully whereas their +2 oxidation states are found to be inactive for the same [Darensbourg *et al.* (2005)].

3.4.2 Co-catalyst

To optimize the reactivity of the catalyst system several research groups have studied the effect of catalyst to co-catalyst mole ratio [Cohen *et al.* (2005); Niu *et al.* (2009); Li *et al.* (2011)]. For the catalyst/co-catalyst systems, an increase in the molar ratio of co-catalyst to catalyst increases the yield initially, which reaches maximum and then decreases. This decrease is accompanied by a substantial decrease in the polymer molecular weight and the

concomitant formation of the cyclic carbonate. The addition of co-catalyst also helps to achieve poly(propylene carbonate) at lower pressure of CO_2. Cohen *et al.* (2005) has shown that (salen)-CoX is capable of giving polycarbonate at 800 psi whereas with the addition of co-catalysts like [PPN]Cl and [PPN]$OBzF_5$ polycarbonate conversion can be achieved at 200 psi only. The molar ratio of co-catalyst to catalyst also has a considerable effect on the yield, polycarbonate/cyclic carbonate selectivity and molecular weight of the polymer, but it does not influence the polydispersity of the product polymer [Cohen *et al.* (2005); Niu *et al.* (2009); Li *et al.* (2011)]. The cyclic polycarbonate formation is based on degradation reactions that take place at higher co-catalyst concentrations. Evidently, higher concentrations of co-catalyst assist in the shifting of the growing polymer chain from the catalyst to the additional initiating sites provided by the co-catalyst resulting in the shorter polymer chains and higher cyclic carbonate formation [Cohen *et al.* (2005)]. This chain degradation proceeds most likely by a backbiting reaction starting from an alcoholate chain-end. Nucleophilic attack of free alcoholate group at the nearby carbonate moiety yields a cyclic carbonate by a backbiting reaction and further a new alcoholate end-group (Figure 3.4).

3.5 Terpolymers based on CO_2 and Propylene Oxide

The present work deals only with the copolymer of CO_2 and propylene oxide. However, some reports have appeared in literature in which one further step has been incorporated in the reaction to synthesize terpolymers involving CO_2 and propylene oxide. Thus, a brief review of the following section has also been presented for the sake of completion of the literature review in this field.

The polycarbonate obtained from propylene oxide offers a number of advantages in various fields. Propylene oxide is one of the most easily available and inexpensive source that can be obtained for the synthesis of polycarbonates but one of the factor that still limits its benefits is

its low glass transition temperature <50^{o}C. The glass transition temperature of PPC is too low to be used as structural materials and too high to be used as soft film. Thus, the glass transition temperature of polycarbonate can be tuned (increased or decreased) by forming triblock polymer or terpolymer by using CO_2 and propylene oxide along with other epoxides. New type of polycarbonates can be synthesized with excellent properties and different glass transition temperature. The T_g can be varied and adjusted by varying the type and reactivity ratio of the two epoxides used in the reaction.

Aida *et al.* (1982) are among the first few researchers to find the catalysts for the terpolymer synthesis from carbon dioxide. They explored aluminium porphyrin complexes (TPP)AlCl for the synthesis of polyether-polycarbonate block copolymer. They synthesized a homolpolymer of propylene oxide and then carried out the block copolymerization by the reaction of this homopolymer with propylene oxide and CO_2, which was probably initiated by the living homopolymer. They further used the same catalyst system for the synthesis of phthalic anhydride and epoxide copolymerization. Aida *et al.* (1986) further explored aluminium porphyrin complex with organic salt a successful example of catalyst system that was capable of controlling the molecular weight of the polymer with narrow molecular weight distribution. They synthesized the copolymer from propylene oxide and carbon dioxide and further also prepared its block polymer by carrying out its reaction with phthalic anhydride.

Wu *et al.* (2012) synthesized block polymers from propylene oxide and styrene oxide and then coupling them with CO_2. The T_g was adjusted between 50 to 100^{o}C by varying the ratio of the two monomers which was found to be well above original glass transition temperature of PPC. But the reaction offers significant amount of poly(propylene carbonate) formation since the rate of reaction of propylene oxide is far higher than rate of reaction of styrene oxide.

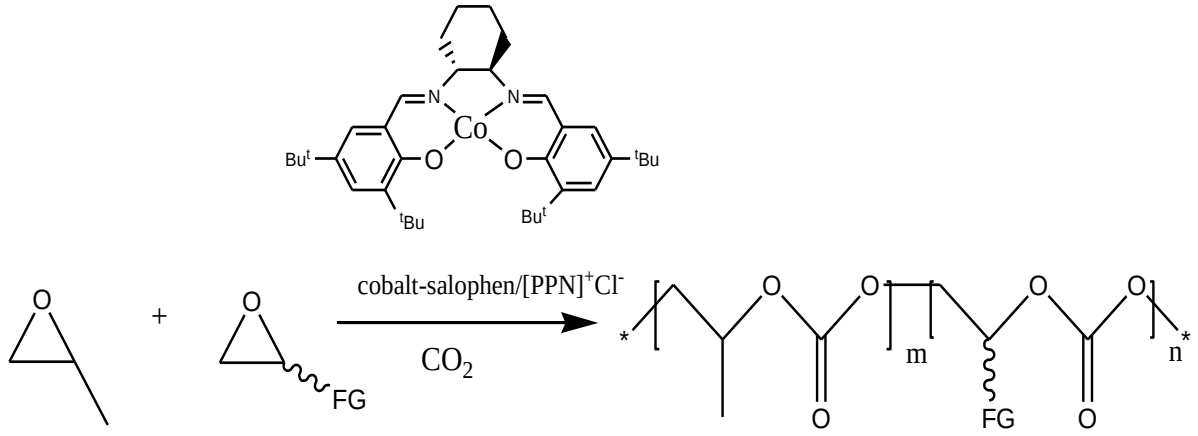


Figure 3.13: Polymerization of CO_2 with propylene oxide and another alkylene oxide (FG=with various functionalities) [Okada *et al.* (2011)]

Okada *et al.* (2011) further explored the first alternating polymerization of CO_2 with propylene oxide and another alkylene oxide (with various functionalities) randomly incorporating into the polymer chain (Figure 3.13). By controlling the length of the alkylene oxide with functionality, the polymer of different M_w was obtained. Since the rate of reaction of propylene oxide and CO_2 proceeded much faster relative to other oxide, different ratios of alkene oxides were taken with propylene oxide in excess. Thus, the obtained polymer carried greater amount of poly(propylene carbonate) linkages (since propylene oxide is in excess) relative to other poly(alkylene carbonate) units. It was observed that as the length of the alkylene oxide bearing functionality was increased, the corresponding glass transition temperature of the polymer decreased.

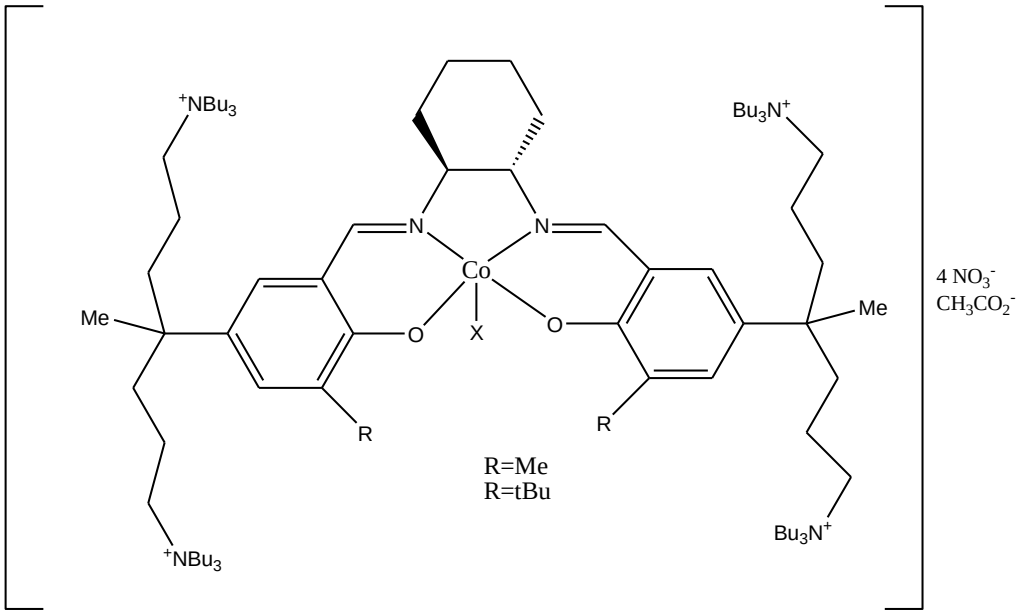


Figure 3.14: Quaternary ammonium ion tethered salen-CoX complex [Varghese *et al.* (2012)]

Varghese *et al.* (2012) further explored the quaternary ammonium ion tethered salen-Co(III)X catalysts (Figure 3.14) for tuning the properties of the synthesized polymer. They introduced the dual catalyst system of double metal cyanide (DMC) and above salenCo(III)X complex for the synthesis of the product polymer. Using DMC being active for homopolymer formation and salen-CoX complex being active for alternating PPC formation, they played with the ratio of two catalyst systems for the synthesis of the product polymer of different low T_g. Using the same catalyst Jeon *et al.* (2014) synthesized the terpolymers from propylene oxide/CO_2/phthalic anhydride. The process gave extremely high M_w polymer upto 3.81×10^5 g/mol with almost complete conversion of phthalic anhydride in the reaction. Depending upon the amount of phthalic anhydride used in the reaction, polymers of different T_g could be obtained.

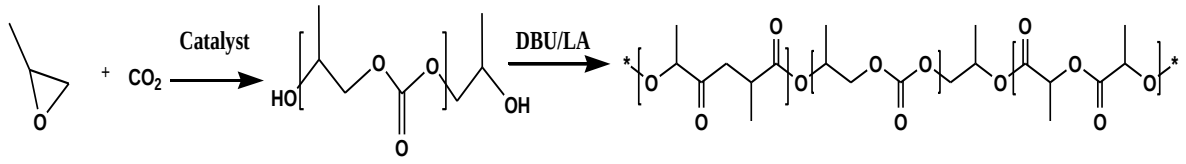


Figure 3.15: Triblock polymer from lactide, propylene oxide and carbon dioxide

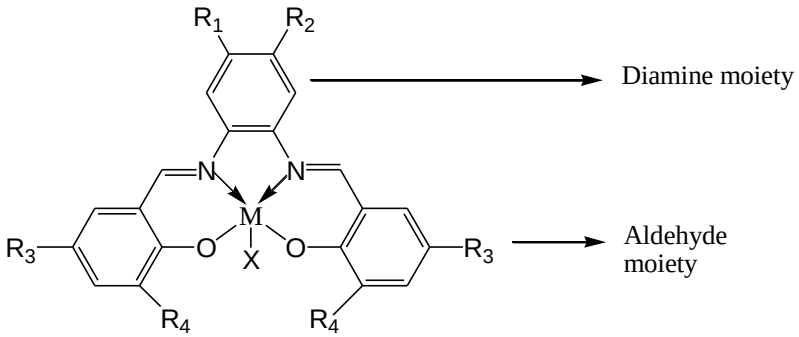
Darensbourg *et al.* (2013) synthesized triblock copolymer from lactide, propylene oxide and CO_2. Triblock copolymer was synthesized in two steps by synthesizing poly(propylene carbonate) from propylene oxide and CO_2 in the first step and then forming a block polymer by polymerizing it with lactide in the presence of DBU (1,8-diazabicyclo[5.4.0]undec-7-ene) catalyst in the second step. Water was used as a chain terminating reagent at the end of the first step leading to hydrolysis of poly(propylene carbonate) chain ends as well as that of catalyst, thereby confirming that the ends of polymer chain was capped with hydroxyl group. These polymer molecules are easily biodegradable. Thus, this methodology also lead to the synthesis of biodegradable and green block polymer with high glass transition temperature (Figure 3.15).

Binary electrophile -nucleophile cobalt-based catalyst systems have been found to be active for the alternating copolymerization of both propylene oxide and cyclohexene oxide with CO_2 separately at mild conditions. Binary catalyst system was first explored by Shi *et al.* (2006) for the terpolymerization of CO_2 with propylene oxide and cyclohexene oxide. It was found that the binary system of the complex and $[PPN]^+Cl^-$ could operate very efficiently at 25 °C and 1.5 MPa CO_2 pressure for the terpolymerization of CO_2 with propylene oxide (50 mol %) and cyclohexene oxide (50 mol %) and polycarbonate product so obtained had appreciable narrow polydispersity (M_w/M_n ratio) of 1.24.

3.6 Justification for the present work

In view of the above reports in literature, the present work has been planned to carry out copolymerization of propylene oxide and CO_2 to poly(propylene carbonates) and cyclic carbonates in the presence of different schiff base catalyst systems. In the previous years, an extensive research was devoted to CO_2 and epoxide copolymerization using chiral catalyst complexes while only few publications are available on their achiral analogues. It is believed that achiral catalysts can prove to be more cost effective for the reaction and can also provide rigid geometry that can efficiently influence the Lewis acidity of metal center and thus allow polymer chain growth effectively. The aim of the present thesis is to explore different achiral catalyst systems and investigate the relationship between effect of changing electron density around catalyst systems (Figure 3.16) and corresponding polymerization. The effect of different type of co-catalysts has also been explored. Additionally, comprehensive study on effects of parameters like monomer to catalyst ratio, catalyst/co-catalyst ratio, and reaction conditions like stirring rate, temperature, pressure of CO_2 on the molecular weight, yield and selectivity of poly(propylene carbonate) [PPC] over propylene carbonate are planned to be studied.

Most of the studies available in the literature on schiff base ligand metal complexes either deals with the effect of electron densities around aldehyde moiety of different chiral ligand metal complexes or catalysts with different type of diamine linkages attached to it [Paddock *et al.* (2005); Darensbourg *et al.* (2005); Liu *et al.* (2011)]. Some researchers have also studied the effect of various electrophilic metal center and axial nucleophilic groups [Nakano *et al.* (2011); Li *et al.* (2011); Niu *et al.* (2009)]. Thus, the present study has been performed to understand the effect of electron density on the diamine moiety of achiral salophen derivatives keeping the o-phenylenediamine and aldehyde moiety unchanged. Interesting results has been obtained in the above studies.



M=metal center
X=axial nucleophilicgroup

R_1=H,CH_3,Cl
R_2=H,Cl
R_3 , R_4=H, tert-butyl groups

Figure 3.16: Structure of catalyst representing diamine and aldehyde moiety

The materials used in the study and method adopted are explained in the successive chapter.

CHAPTER-4

MATERIALS AND METHODS

CHAPTER-4 MATERIALS AND METHODS

This chapter presents details of different materials and equipment that have been used in investigating the reactions along with the procedure for the synthesis of poly(propylene carbonate) and cyclic carbonate. Source and type of materials used and the procedure adopted for distillation of propylene oxide are given in Section 4.1. Details of equipment and experimental procedures are given in Section 4.2 and various characterization techniques used for the quantification and analysis of the product are described in Section 4.3.

4.1 Materials

Laboratory reagent grade o-phenylenediamine was obtained from Loba Chemical (India). Propylene oxide (reagent grade, purity >99%), $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium), 3,5-di-tert-butylsalicylaldehyde, lithium bromide, 4-chloro-phenylenediamine, 4,5-dichloro-phenylenediamine and 4-methyl-phenylenediamine were purchased from Sigma Aldrich (USA). Absolute alcohol was obtained from E Merck (Germany) and analytical reagent grade salts cobaltous acetate tetrahydrate, cobalt(II)chloride, ferric(III)chloride, tetrabutylammonium bromide, tetradecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide were obtained from Sd-Fine Chemicals (India). Calcium hydride (for drying) and pentafluorobenzoic acid were purchased from High Media, India. High purity CO_2 (99.99%) was obtained from Sigma gases and Lalit gases (India).

4.1.1 Distillation of Propylene Oxide

The racemic propylene oxide (reagent grade) was distilled over calcium hydride (CaH_2) before the polymerization. Since all the ring-opening polymerization reactions are sensitive to moisture, adequate care was taken to keep the monomer and the reaction kettle free from impurities such as water molecules. CaH_2 reacts with the water molecules and forms calcium hydroxide, and thereby removes moisture from the system.

4.1.2 Catalyst(s) and Co-catalyst(s)

Various schiff base ligand metal complexes with a nucleophilic group attached to it were used as catalysts in the reactions. Detailed synthesis procedure and the analysis of the catalysts has been given in Chapter 5. $PPN]^{+}Cl^{-}$ ($[PPN]^{+}$ = bis(triphenylphosphine)iminium), tetrabutylammonium bromide, tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide and DMAP (4-dimethylaminopyridine) were used as co-catalysts in the polymerization. Figure 4.1 shows simplified structure of catalyst and Table 4.1 lists the co-catalysts and their chemical structure.

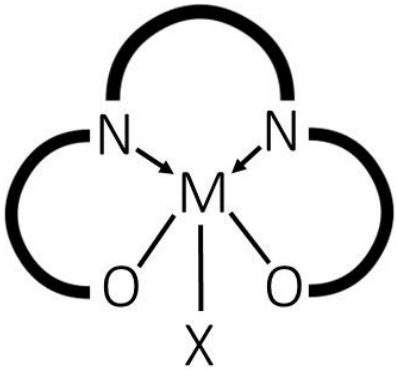
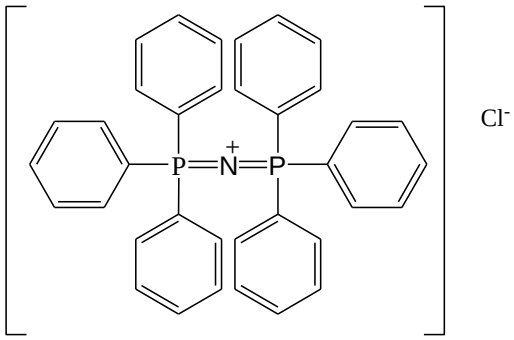
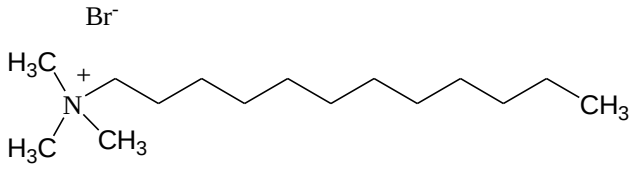
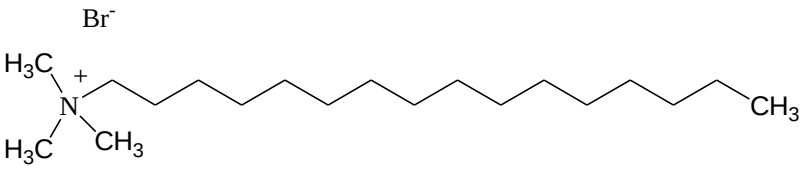
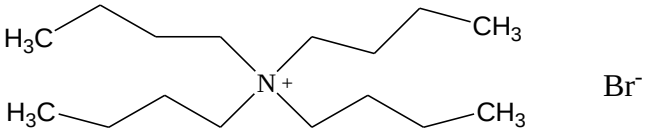
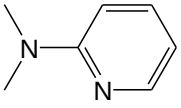


Figure 4.1: General structure of the catalyst

M=Metal center, X=nucleophilic group

Table 4.1: Structures of different co-catalysts used in the reaction

S.No.	Name of co-catalyst	Structure
1.	$[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium)	
2.	Tetradecyltrimethylammonium bromide	
3.	Hexadecyltrimethylammonium bromide	
4.	Tetrabutylammonium bromide	
5.	Dimethylaminopyridine, DMAP	

4.2. Equipment and Experimental Details

4.2.1 High Pressure Autoclave Reactor

High pressure autoclave reactor (made of stainless steel SS 316 and capacity 100 ml) was used to carry out the reactions. The reactor is rated for use upto a pressure of 350 bar and temperature of 250^o C. The photograph and schematic diagram of the unit used are shown in Figure 4.2 and 4.3, respectively. It was equipped with a mechanical stirrer having impeller blades inclined slightly in upward direction to facilitate vertical mixing. High purity carbon

dioxide gas used was passed through 4A molecular sieves before it was allowed to enter the reactor to make it free from moisture.

Figure 4.2: High pressure autoclave reactor

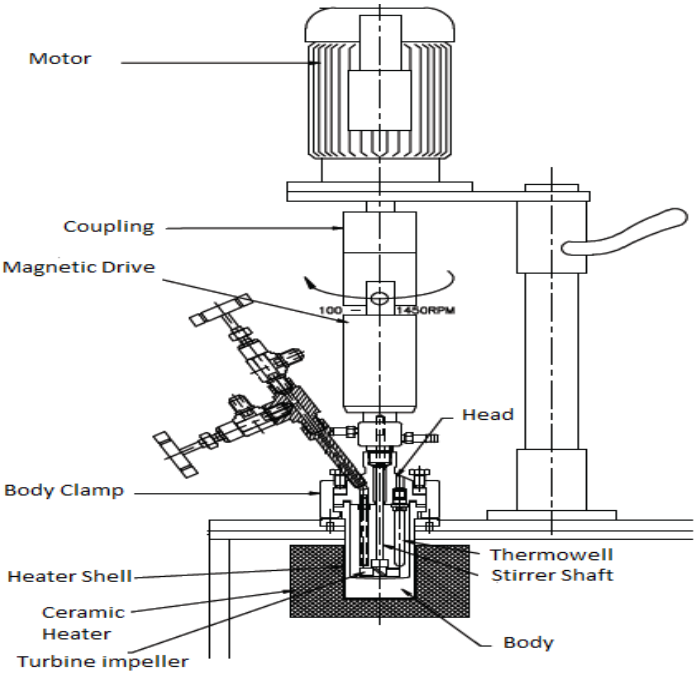


Figure 4.3: Internal construction of the reactor used to carry out synthesis of cyclic carbonates

4.2.2 Methodology

The autoclave reactor (100 mL capacity), was heated to about 80 °C under vacuum to flush out water and other volatile impurities and then cooled to room temperature. The process was carried out for *3 h*. A mixture of catalyst/co-catalyst dispersed in propylene oxide was added to the reactor. Dry CO_2 was then introduced at the desired pressure and the reaction was carried out at particular temperature. The mixture was stirred with a mechanical stirrer for required period, after that it was cooled and the remaining CO_2 was vented out to the atmosphere through a fume hood. After opening the reactor, the crude product was dissolved in small amount of dichloromethane and reaction was then terminated using 5% acidified methanol. At this stage a small aliquot of the mixture was taken for ^{1}H NMR analysis in order to find the conversion of propylene oxide to poly(propylene carbonate) and cyclic carbonate. Finally, PPC was precipitated by adding excess of methanol. The resultant polymer was dried under vacuum overnight at 50^{o}C.

4.3. Characterization Techniques

Several instrumental techniques were used to characterize catalysts and poly(propylene carbonate)/cyclic carbonate samples. In this work, ^{1}H-NMR, ^{13}C-NMR, ^{1}H-^{13}C HSQC NMR, COZY, FTIR, CHN, GPC and DSC techniques have been used for the analysis of the product as discussed below.

4.3.1 Nuclear Magnetic Resonance (NMR)

Nuclear magnetic resonance spectra (^{1}H NMR, ^{13}C NMR & ^{19}F NMR) of the product were recorded on a JEOL ECS-400 (400 MHz) spectrophotometer using $CDCl_3$ or DMSO as solvent and tertramethyl silane (TMS) as internal reference. Chemical shifts (δ) were expressed in parts per million (ppm). Spectra of few samples were also recorded on Bruker Advance II (400 MHz) spectrometer.

The Heteronuclear Single Quantum Coherence (HSQC) NMR technique was used for the characterization of product in order to correlate the chemical shift of proton with the chemical shift of the directly bonded carbon.

4.3.2 Fourier Transform Infrared Spectroscopy (FTIR)

FTIR spectroscopic measurements were carried out on Agilant Cary-660 spectrophotometer from 650 to 4000 cm^{-1} using KBr or ATR accessory. The FTIR spectroscopy is used mainly for the determination of the chemical structure (functional groups) of the compounds. In case of the synthesis of catalysts, the binding of the metal to the ligand and further the binding of nucleophilic group at axial position was investigated primarily using FTIR technique.

4.3.3 Size Exclusion Chromatography (SEC) or Gel Permeation Chromatography (GPC)

Gel permeation chromatography (GPC) measurements were carried out using a common instrument that consisted of a pump (Watrex, Czech Republic, flow rate 1 $mL.min^{-1}$ eluted with THF), an injection valve (Rheodyne, USA, Model 7105), a column (linear SHODEX GPC KF 806L, Japan) and an evaporative light scattering detector, ELSD (PL-Agilent, Model 1000, UK/USA). The sample volume used was 50 µL with an ambient temperature of about 22 °C.

M_w (weight average molar mass) and M_n (number average molar mass) of the poly(propylene carbonate) samples were calculated with the help of Clarity software from Data Apex, Czech Republic, using polystyrene standards for calibration.

4.3.4 Differential Scanning Calorimetry (DSC)

Glass transition temperature (T_g ^oC) of the obtained polymer was evaluated by differential scanning calorimetory (DSC). The heat flow behaviour of the obtained polymer was observed with respect to temperature to know the T_g and degradation temperature of the product polymer. The measurements were carried out using DSC 4000 Standard Single-Furnace

Differential Scanning Calorimeter at a heating rate of 10^{o}C/min under N_2 gas flow using differential type balance.

4.3.5 CHNS Analysis

The elemental analysis (detection of % age of carbon, hydrogen and nitrogen) of the synthesized ligands used for the catalyst synthesis was carried with the help of Thermo Scientific Flash 2000 Organic Elemental Analyzer equipped with thermal conductivity detector. The samples were added in tin capsules for analysis and introduced into a combustion reactor via an auto-sampler. Empty tin capsules were taken as blank and amino acids BBOT and methionine were taken as standards for CHNS analysis.

CHAPTER-5

SYNTHESIS OF CATALYSTS

CHAPTER-5 SYNTHESIS OF CATALYSTS

The synthesis of different schiff base ligand metal complexes which were used as catalysts for the chemical fixation of propylene oxide and CO_2 to poly(propylene carbonate) [PPC] and cyclic carbonate and results of their characterization are discussed in this chapter. All the synthesized catalysts were characterized using ^{1}H NMR, ^{13}C NMR, CHNS and FTIR spectroscopic techniques. The synthesized complexes are electrophile/nucleophile catalyst systems where the nucleophile moiety helps in opening up of the propylene oxide ring and the metal centre forms metal alkoxide bond with propylene oxide unit and thereby initiate the reaction. These catalysts were used for the synthesis of PPC and cyclic carbonates as detailed in Chapter 6. It was observed that the catalysts described in Section 5.1 were active for both PPC and cyclic carbonate synthesis whereas the catalysts described in Section 5.2 were active only for cyclic carbonate synthesis (no PPC formation was observed).

5.1 General procedure for the synthesis of R_1,R_2-salophenCoOBzF_5 (R_1=CH_3, H, Cl and R_2=H, Cl) catalysts

R_1R_2-salophen ligands were synthesized through the condensation of one equivalent of R_1R_2-phenylenediamine and two equivalents of 3,5-di-tert-butylsalicylaldehyde. The mixture was heated under reflux along with stirring for a required period of time and the progress of the reaction was observed using thin layer chromatography (TLC). At the end of the reaction, the solid precipitate was separated by filtration. For the complexation of the ligand with cobalt, the corresponding ligand and cobalt acetate tetrahydrate were taken in 1:1 molar ratio and refluxing along with stirring of the reaction mixture was carried out for a required time. For the binding of axial nucleophilic group, one equivalent of pentafluorobenzoic acid and one equivalent of ligand metal complex were taken in a 100 ml round bottom flask fitted with a Teflon stir bar. Toluene was added to the reaction mixture as solvent and it was stirred

open to air at room temperature for about 18 h. The general reaction scheme for the synthesis of R_1R_2-salophenCoOBzF_5 catalyst synthesis is given in Figure 5.1. Characterization of the synthesized ligand precursors was done by ^{1}H NMR, ^{13}C NMR, CHNS and FTIR while thereby binding with cobalt and pentafluorobenzoate was observed using shift in band frequency in case of FTIR spectra.

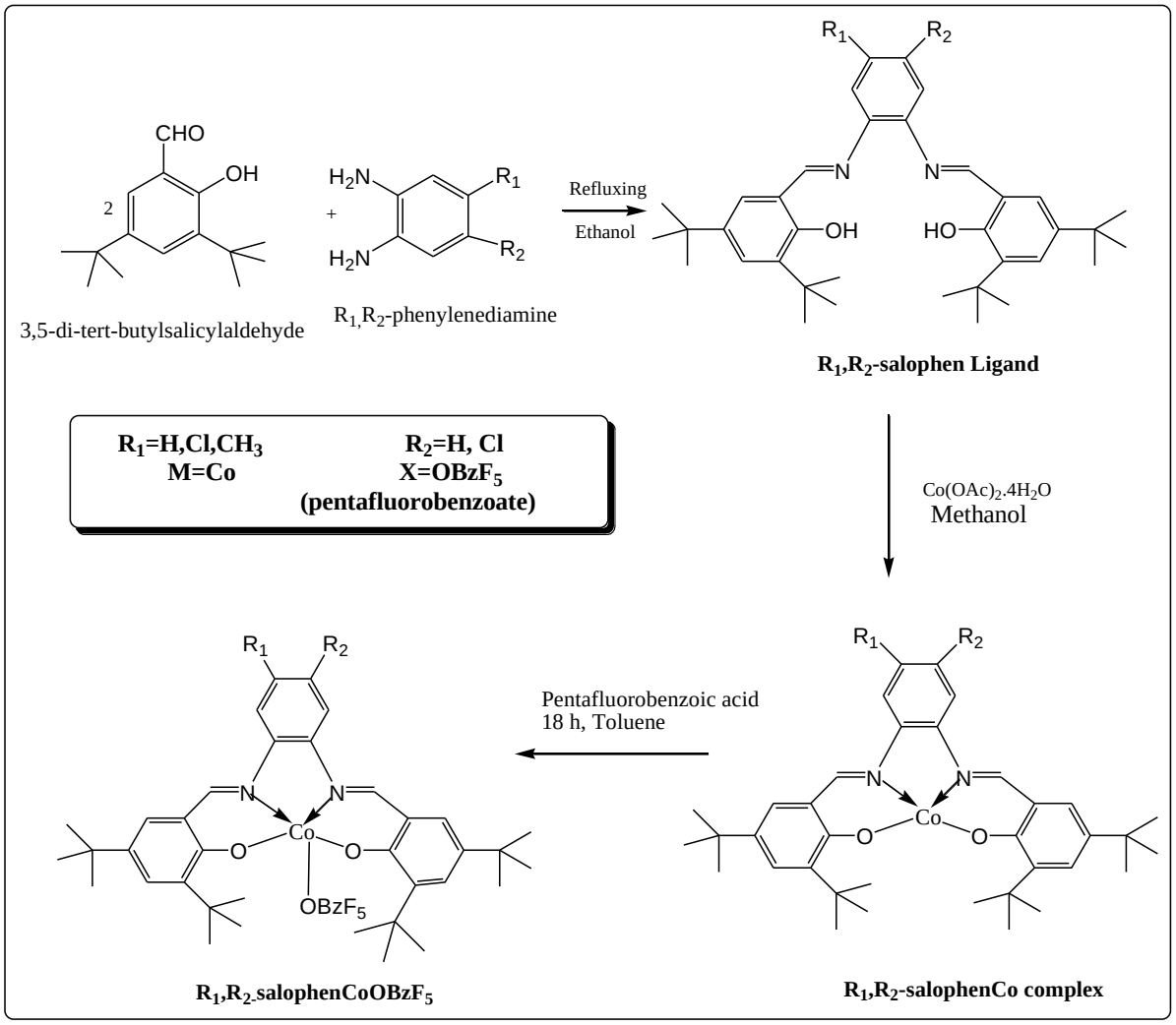


Figure 5.1: General reaction scheme for the synthesis of R_1,R_2-salophenCoOBzF_5 catalysts

Table 5.1: Various ligand precursors synthesized for the preparation of catalysts

Ligand	Diamine	Aldehyde	Reaction Time (h)	Colour of precipitate
N,N′-bis-(3,5-di-tert-butylsalicylidene)-phenylenediimine (salophen)	*o-phenylenediamine*	*3,5-di-tert-butylsalicylaldehyde*	*3*	*Yellow*
N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-methyl-o-phenylenediamine (salophen-CH_3)	*4-methyl-o-phenylenediamine*	*3,5-di-tert-butylsalicylaldehyde*	*3*	*Orange*
N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-chloro-o-phenylenediamine (salophen-$ClCoOBzF_5$)	*4-chloro-o-phenylenediamine*	*3,5-di-tert-butylsalicylaldehyde*	*8-9*	*Brown*
N,N′-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-o-phenylenediamine (salophen-$Cl_2CoOBzF_5$)	*4,5-dichloro-o-phenylenediamine*	*3,5-di-tert-butylsalicylaldehyde*	*8-9*	*Dull Green*

The ligand precursors and their corresponding ^{1}H NMR, ^{13}C NMR and CHNS results are given below. Their respective 1H & 13C NMR spectra are presented in Appendix II.

5.1.1. N,N′-(3,5-di-tert-butylsalicylidene)-phenylenediimine (salophen):

The ligand [N, N'-bis-(3,5-di-tert-butylsalicylidene)-phenylenediimine] (salophen) was prepared using o-phenylenediamine (0.230g, 0.002 mol) and 3,5-di-tert-butylsalicylaldehyde (1g, 0.004 mol) following the general procedure described in Section 5.1.

Bright yellow precipitates. **(^{1}H NMR, 400 MHz, $CDCl_3$)**: δ 8.6 (s, CH=N); 7.2-7.4 (m, Ar-H); 1.3 (s, 18 H, tert-butyl H), 1.42 (s, 18 H, tert-butyl H). **(^{13}C NMR, 100 MHz, $CDCl_3$)**: 164.78, 158.63, 142.82, 140.37, 137.25, 128.25, 127.38, 126.84, 119.87, 118.4, 36.18, 34.24, 31.54, 29.80. **CHNS**: Calculated for $C_{36}H_{48}N_2O_2$: **C**: 79.5; **H**: 8.9; **N**: 5.01, Found: **C**: 79.9; **H**: 9.03; **N**: 5.6.

5.1.2. N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-methyl-o-phenylenediamine (salophen-CH_3):

4-methyl-o-phenylenediamine (0.260g, 0.002 mol) and 3, 5-di-tert-butylsalicylaldehyde (1g, 0.004 mol) were mixed and general procedure was followed to synthesize salophen-CH_3 ligand.

Orange coloured precipitates. **(^{1}H NMR, 400 MHz, $CDCl_3$):** δ 8.64 (s, CH=N); 7.03-7.42 (m, Ar-H); 1.31 (s, 18 H, tert-butyl H), 1.42 (s, 18 H, tert-butyl H), 2.41 (s, 3H, CH_3) **(^{13}C NMR, 100 MHz, $CDCl_3$):** 164.62, 158.57, 142.63, 140.29, 137.45, 128.15, 126.82, 120.54, 119.50, 118.44, 35.19, 31.55, 29.50, 21.21. **CHNS:** Calculated for $C_{37}H_{50}N_2O_2$: **C**: 79.5; **H**: 8.9; **N**: 5.01, Found: **C**: 79.9; **H**: 9.03; **N**: 5.6

5.1.3. N,N′-bis-(3, 5-di-tert-butylsalicylidene)-4-chloro-o-phenylenediamine (salophen-Cl):

4-chloro-o-phenylenediamine (0.303g, 0.002 mol) and 3,5-di-tert-butylsalicylaldehyde (1g, 0.004 mol) were mixed and the mixture was allowed to react as per the procedure given in Section 5.1 to synthesize salophen-Cl.

Brown coloured product. **(^{1}H NMR, 400 MHz, $CDCl_3$):** δ 8.63 (s, CH=N); 7.15-7.44 (m, Ar-H); 1.26 (s, 18 H, tert-butyl H); 1.42 (s, 18 H, tert-butyl H); 11.63 (s, OH) **(^{13}C NMR, 100 MHz, $CDCl_3$):** 165.50, 158.65, 143.74, 140.62, 137.33, 132.54, 128.79, 127.11, 120.84, 118.22, 35.2, 34.26, 31.52, 29.48. **CHNS:** Calculated for $C_{36}H_{47}N_2O_2Cl$: **C**: 75.19; **H**: 8.18; **N**: 4.87, Found: **C**:74.8; **H**: 8.19; **N**: 5.08

5.1.4.N,N′-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-o-phenylenediamine (salophen-Cl_2):

4,5-dichloro-o-phenylenediamine (0.378g, 0.002 mol) and 3,5-di-tert-butylsalicylaldehyde (1g, 0.004 mol) were taken and the procedure described above was followed for the synthesis of catalyst.

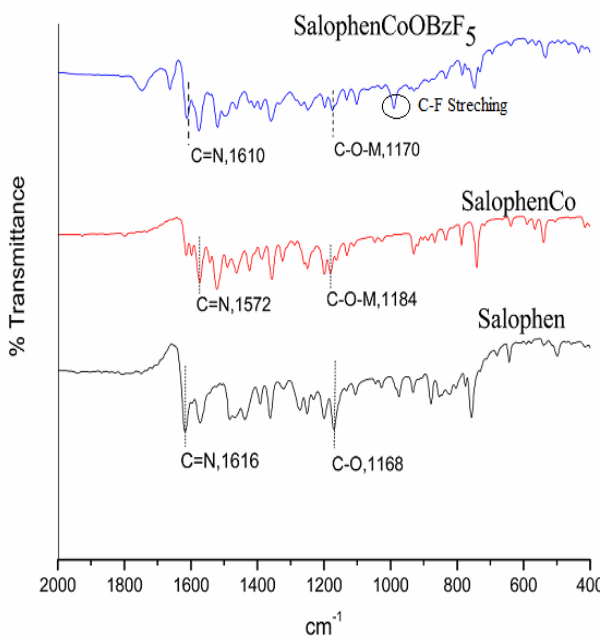
Dull green precipitates. **(^{1}H NMR, 400 MHz, $CDCl_3$):** δ 8.8 (s, 1H, CH=N); 9.9 (s, 1H, CH=N), 7.40-7,64 (m, Ar-H); 1.29 (s, 18 H, tert butyl); 1.38 (s, 18 H, tert butyl); 11.7 (s, 1H, OH); 13.1 (s, 1H, OH) **(^{13}C NMR, 100 MHz, $CDCl_3$):** 165.66, 157.08, 142.76, 140.26, 136.44, 131.14, 128.93, 127.82, 120.14, 118.50, 34.59, 33.97, 31.22, 29.25. **CHNS:** Calculated for $C_{36}H_{46}N_2O_2Cl_2$: **C**: 70.8; **H**: 7.7; **N**: 4.5, Found: **C**: 69.75; **H**: 7.51; **N**: 4.11

5.1.5. FTIR spectra of various R_1,R_2-salophenCoOBzF_5 complexes used as catalysts

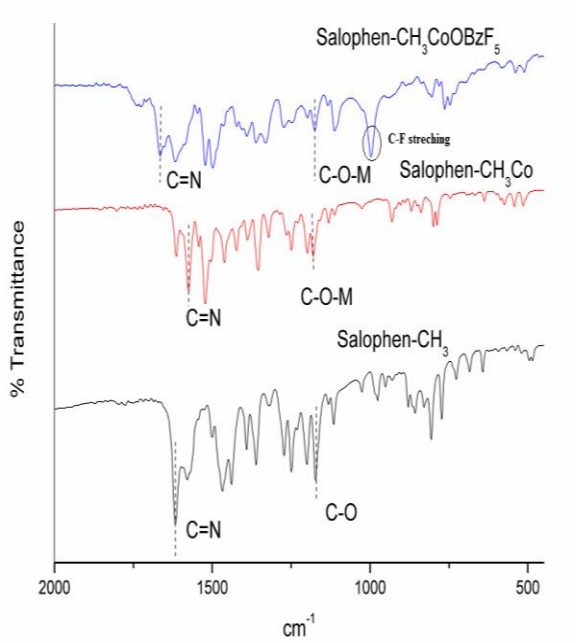
Synthesis of respective ligands, ligand metal complexes and their further binding with the axial nucleophilic groups (X) was confirmed using FTIR spectroscopy. The confirmation of the complex formation was done by observing the shift in characteristic bands of C=N, C-O and OH functional groups. The spectra of various catalysts are given in Figure 5.2 and the relevant data are summarized in Table 5.2.

Table 5.2: FTIR data of R_1,R_2-salophen, R_1,R_2-salophenCo and R_1,R_2-salophenCoOBzF_5

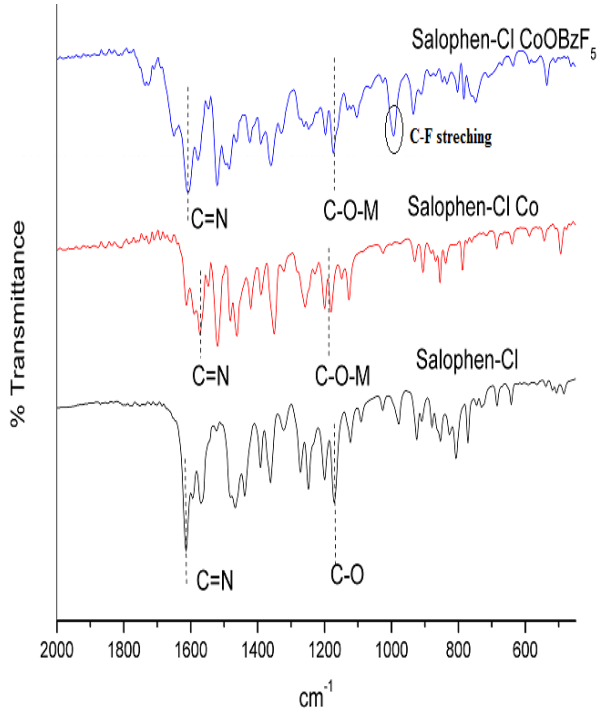
Complex	***C=N***	***C-O***	***-OH***
Salophen	*1616*	*1168*	*3465*
salophen Cobalt	*1572*	*1184*	*Disappearance of Band*
salophenCoOBzF5	*1610*	*1170*	
salophen-CH_3	*1616*	*1170*	*3470*
salophen-CH_3 Cobalt	*1574*	*1180*	*Disappearance of Band*
salophen-CH_3CoOBZF_5	*1662*	*1174*	
salophen-Cl	*1612*	*1162*	*3450*
salophen-Cl Cobalt	*1574*	*1191*	*Disappearance of Band*
salophen-Cl CoOBzF_5	*1607*	*1170*	
salophen-Cl_2	*1612*	*1130*	*3460*
salophen-Cl_2 Cobalt	*1600*	*1145*	*Disappearance of Band*
salopphen-Cl_2 CoOBzF_5	*1662*	*1120*	


SalophenCoOBzF5
C-F Streching
C=N,1610
C-O-M,1170
SalophenCo
C=N,1572
C-O-M,1184
Salophen
C=N,1616
C-O,1168
% Transmittance
2000 1800 1600 1400 1200 1000 800 600 400
cm-1

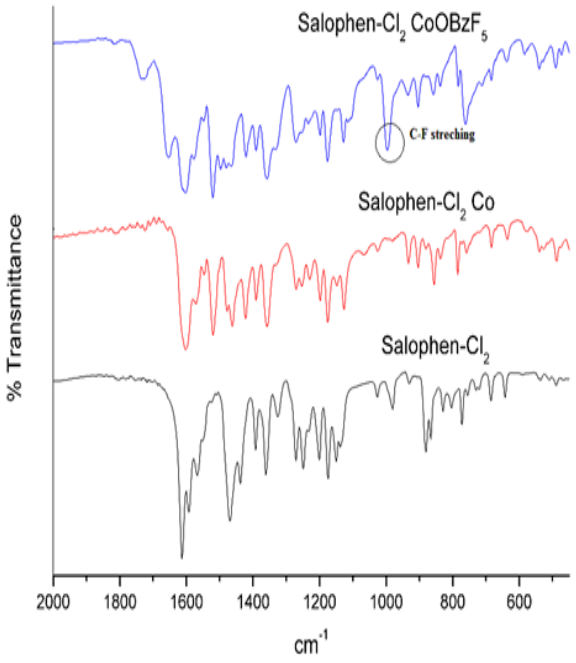
(A)


Salophen-CH3CoOBzF5
C-F streching
C=N
C-O-M
Salophen-CH3Co
C=N
C-O-M
Salophen-CH3
C=N
C-O
% Transmittance
2000 1500 1000 500
cm-1

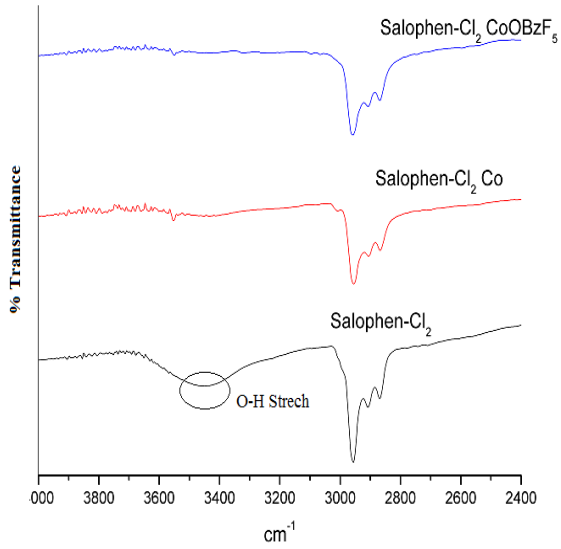
(B)


Salophen-Cl CoOBzF5
C-F streching
C=N
C-O-M
Salophen-Cl Co
C=N
C-O-M
Salophen-Cl
C=N
C-O
% Transmittance
2000 1800 1600 1400 1200 1000 800 600
cm-1

(C)


Salophen-Cl2 CoOBzF5
C-F streching
Salophen-Cl2 Co
Salophen-Cl2
% Transmittance
2000 1800 1600 1400 1200 1000 800 600
cm-1

(D)



(E)

Figure 5.2 FTIR spectra **(A)** Salophen, salophenCo and salophen $CoOBzF_5$ **(B)** Salophen-CH_3, salophen-CH_3 Co and salophen-CH_3 $CoOBzF_5$ **(C)** Salophen-Cl, salophen-Cl Co and salophen-Cl $CoOBzF_5$ **(D),(E)** Salophen-Cl_2, salophen-Cl_2 Co and salophen-Cl_2 $CoOBzF_5$

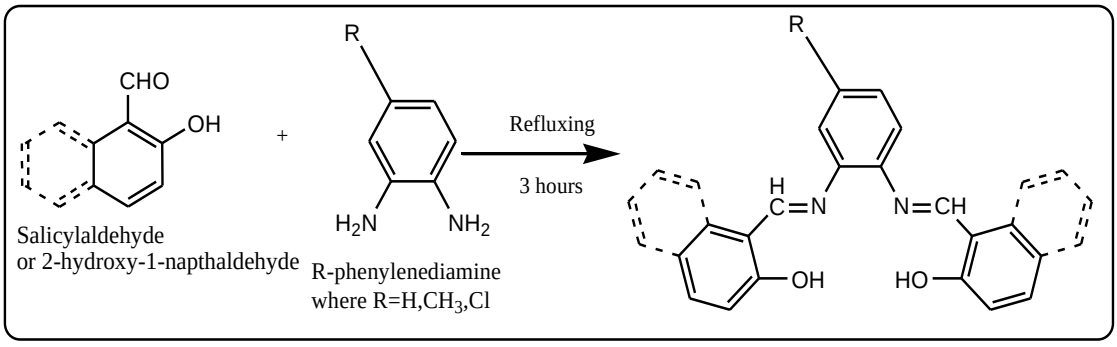
It is observed that the band due to -OH around 3460 cm^{-1} in case of salophen based ligand disappears when it is complexed with cobalt metal attached at the center. This clearly confirms the binding of cobalt metal with the ligand at this position. It is observed that the band around 1150 cm^{-1} in R_1,R_2-salophen ligand attributed to C−O strech is shifted to higher frequency by about 10-20 cm^{-1} in case of R_1,R_2-salophen cobalt complex which confirms the participation of oxygen in the C−O−M bond. This band again gets shifted to a lower frequency, almost to the same position as the ligand when pentafuorobenzoate binds to the axial position. The band for the ligand around 1610 cm^{-1} due to C=N stretching is shifted to a lower frequency around 1570 cm^{-1} when it was bind with cobalt metal. This band is again shifted to higher frequency when electron withdrawing pentafluorobenzoate gets attached to the complex. The band due to C-N at 1480 cm^{-1} is also shifted to a lower frequency by about 20 cm^{-1} (around 1460 cm^{-1}) further confirming the coordination of nitrogen with the metal.

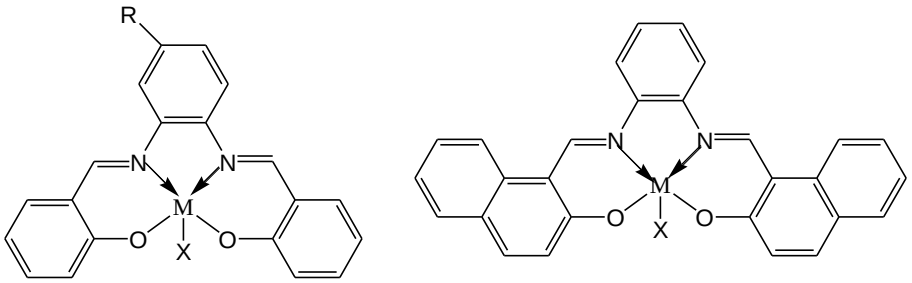
As per the shift in FTIR frequency due to C=N as well as C-O stretching, it can be confirmed that both oxygen and nitrogen are binding with the metal ion.

Synthesis of R_1,R_2-salophenCoOBzF_5 could also be confirmed clearly from the band around 990 cm^{-1} due to C-F stretching which is seen in all the complexes. This band is not observed in case of R_1,R_2-salophen cobalt complex. These results are also in agreement with those reported by Hostalek *et al.*(2015).

5.2 General synthesis of R-salenMX (R=H, CH_3, Cl) and napthenMX based catalysts [M=Co, Fe M=Co, Fe and X=SO_4^-,Cl^-,Br^-, $OBzF_5$]

One equivalent of R-phenylenediamine (R=H, CH_3 and Cl) and two equivalents of salicylaldehyde or napthaldehyde were dissolved in ethanol. The refluxing and stirring of the reaction was carried for 3-4 hours and then the mixture was cooled to room temperature. The precipitate thus obtained were filtered, washed with cold ethanol and finally dried in oven. The corresponding reaction scheme is shown in Figure 5.3. Complexation of salen was carried out separately with $CoSO_4$ and $FeCl_3$ by refluxing with continuous stirring a 1:1 molar mixture of above synthesized ligand and the corresponding salt dissolved in methanol for 3 h. The solid products thus obtained were filtered using vacuum filtration. Further, in order to synthesize salenCoOBzF_5 or salen-CH_3CoBr catalyst (employing pentafluorobenzoate or lithium bromide) similar procedure as described in Section 5.1 was followed by employing a salen ligand.





Salen **Napthen**

M=Co, Fe X=SO_4, $OBzF_5$, Br
R=H, CH_3, Cl

Figure 5.3: Synthesis of salen and napthen based ligands and structure of their respective complexes

Table 5.3: Ligand precursors synthesized for the preparation of catalysts

Ligand	**Diamine**	**Aldehyde**	**Reaction Time (h)**	**Colour of precipitate**
N,N'-bis-(salicylaldehyde)-o-phenylenediamine (salen)	*o-phenylenediamine*	*salicylaldehyde*	*3*	*Orange*
N,N'-bis-(salicylaldehyde)-4-methyl-o-phenylenediamine (salen-CH_3)	*4-methyl-o-phenylenediamine*	*salicylaldehyde*	*3*	*Orange*
N,N'-bis-(salicylaldehyde)-4-chloro-o-phenylenediamine (salen-Cl)	*4-chloro-o-phenylenediamine*	*salicylaldehyde*	*8*	*Brown*
N,N'-bis-(2-hydroxy-1-naphthyldehyde)-o-phenyleneldiamine (napthen)	*o-phenylenediamine*	*2-hydroxy-1-naphthaldehyde*	*3*	*Bright Yellow*

5.2.1. N,N'-bis-(salicylaldehyde)-o-phenylenediamine (salen)

Salicylaldehyde (0.86 ml, 8.0 mmol) and o-phenylenediamine (0.432 g, 4.0 mmol) were taken for the synthesis of ligand precursor and the catalyst was synthesized following the procedure given in Section 5.2.

Orange precipitates. **(^{1}H NMR, 400 MHz, $CDCl_3$):** δ 8.59 (s, CH=N); 6.9-7.5 (m, Ar-H); 11.02 (s, OH) **(^{13}C NMR, 100 MHz, $CDCl_3$):** 163.80, 161.41, 142.63, 133.47, 132.43, 127.81, 119.7, 119.3, 119.08, 117.63 **CHNS:** Calculated for $C_{20}H_{16}N_2O_2$: **C**: 75.0; **H**: 5.0; **N**: 8.75 Found: **C**: 76.39; **H**: 5.11; **N**: 9.04.

5.2.2. N,N'-bis-(salicylaldehyde)-4-methyl-o-phenylenediamine (salen-CH_3)

Salicylaldehyde (0.86 ml, 0.008 mol) with 3,4-diaminotoluene (0.5g, 0.004 mol) were used for synthesizing this ligand by employing the general procedure described in Section 5.2.

Bright orange precipitates. **(^{1}H NMR, 400 MHz, $CDCl_3$):** δ 8.61(s, CH=N); 6.88-7.38 (m, Ar-H); 11.01 (s, OH), 2.42 (s, 3H, CH_3) **(^{13}C NMR, 100 MHz, $CDCl_3$):** 163.67, 161.42, 142.56, 139.99, 133.38, 132.26, 128.40, 120.46, 119.03, 117.63, 21.23 **CHNS:** Calculated for $C_{21}H_{18}N_2O_2$: **C**: 75.4; **H**: 5.38; **N**: 8.38 Found: **C**:75.8; **H**: 5.49; **N**: 8.49

5.2.3. N,N'-bis-(salicylaldehyde)-4-chloro-o-phenylenediamine (salen-Cl)

For synthesizing this catalyst salicylaldehyde (0.86 ml, 0.008 mol) and 4-chloro-o-phenylenediamine (0.568g, 0.004 mol) were taken and the procedure given in Section 5.2 was followed.

Brown coloured product. **(^{1}H NMR, 400 MHz, DMSO):** δ 12.7 (s, CH=N); 7.0-8.06 (m, Ar-H); 13.3 (s, 1H, OH) **(^{13}C NMR, 100 MHz, DMSO):** 157.97, 152.96, 131.76, 126.31, 123.05, 122.49, 118.96, 117.34, 112.54, 111.14 **CHNS:** Calculated for $C_{20}H_{15}N_2O_2$: **C**:67.3; **H**: 4.2; **N**: 7.85, Found: **C**:65.8; **H**:3.88; **N**: 8.04

5.2.4. N,N'-bis-(2-hydroxy-1-naphthyldehyde)-o-phenyleneldiamine (napthen)

The precursors 2-hydroxy-1-naphthaldehyde (1g, 0.0058 mol) and o-phenylenediamine (0.313g, 0.0029 mol) were taken for the synthesis of the ligand using the general procedure described in Section 5.2.

Bright Yellow precipitates. **(^{1}H NMR, 400 MHz, DMSO):** δ 9.5 (s, CH=N); 6.86-8.9 (m, Ar-H); 15.1 (s, OH) **(^{13}C NMR, 100 MHz, DMSO):** 168.54, 157.22, 138.51, 136.65, 132.99,

128.92, 127.28, 126.84, 123.50, 121.42, 120.47, 119.61, 109.20 **Napthen**: Calculated for $C_{28}H_{20}N_2O_2$: **C**: 80.0; **H**: 4.76; **N**: 6.66 Found: **C**: 81.8; **H**: 4.86; **N**: 6.83.

5.2.5. FTIR spectra of various salen and napthen ligand metal complexes

Synthesis of ligands and their respective metal complexes was ascertained using FTIR spectroscopy. The characteristic bands of C=N, C-O and OH functional groups were observed for confirming the complex formation. The spectra of various catalysts are given in Figure 5.4 and the relevant data is given in Table 5.4

Table 5.4: FTIR spectra of the ligand precursors and their respective complexes used as catalysts active for cyclic carbonate formation

Complex	***C=N***	***C-O***	***-OH***
salen	*1613*	*1274*	*2500-3000*
salenCo	*1603*	*1309*	*Disappearance of band*
salenCoOBzF$_5$	*1625*	*1269*	
salenCoSO$_4$	*1604*	*1320*	
salenFeCl$_3$	*1608*	*1314*	
salen-CH$_3$	*1615*	*1265*	*2500-3100*
salen-CH$_3$Co	*1608*	*1300*	*Disappearance of band*
salen-CH$_3$CoOBzF$_5$	*1610*	*1293*	
salen-CH$_3$CoSO$_4$	*1605*	*1290*	
salen-CH$_3$CoBr	*1680*	*1400*	
salen-Cl	*1611*	*1246*	*2700-3200*
salen-ClCo	*1600*	*1260*	*Disappearance of Band*
salen-ClCoBr	*1617*	*1247*	
napthen	*1622*	*1325*	*3434*
napthenCoSO$_4$	*1614*	*1360*	*Disappearance of band*

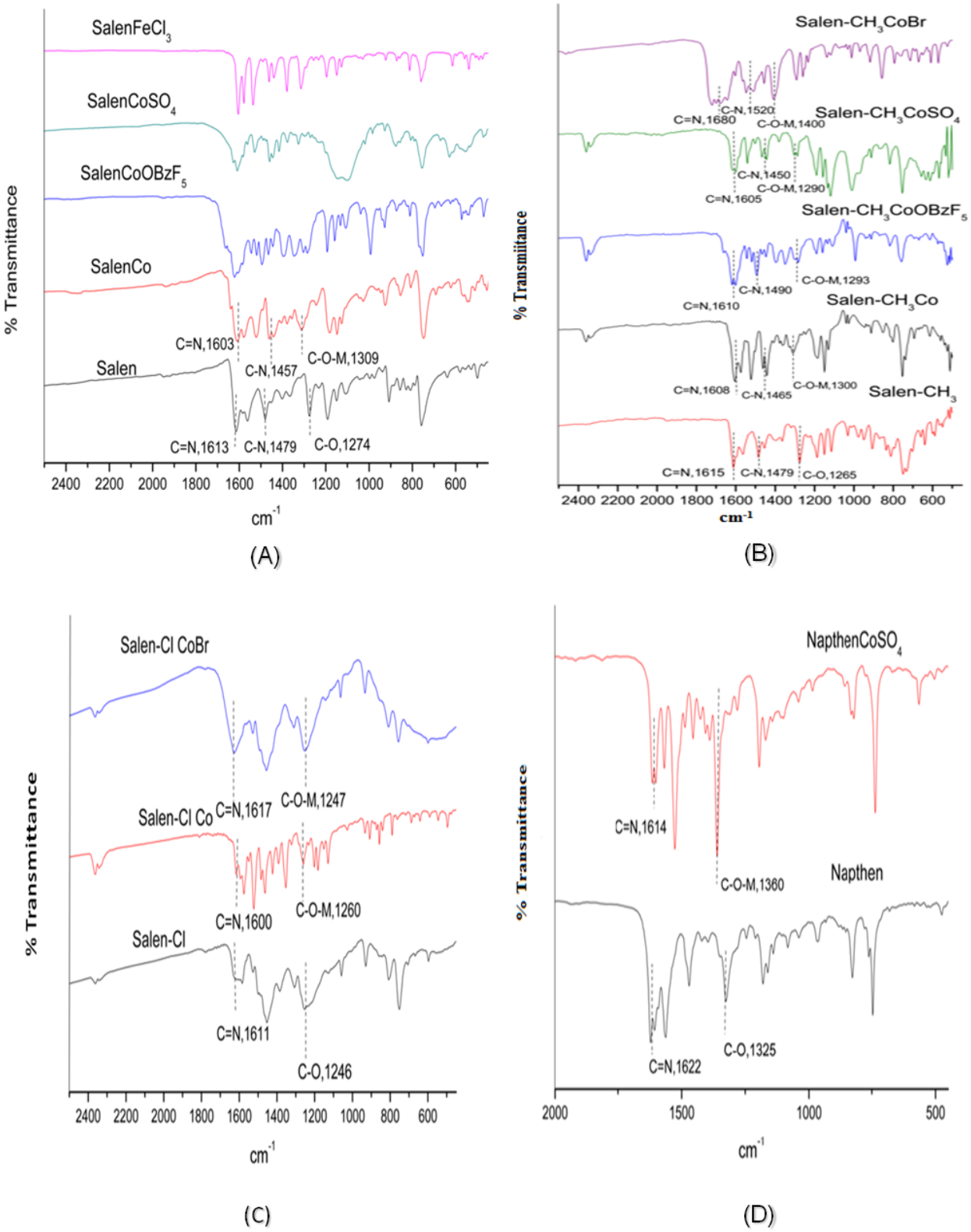


Figure 5.4: FTIR spectra **(A)** Salen, salenCo, salenCoOBzF_5, salenCoSO_4 and salenFeCl_3 **(B)** Salen-CH_3, salen-CH_3, salen-CH_3CoOBzF_5, salen-CH_3CoSO_4 and salen-CH_3CoBr **(C)** Salen-Cl, salen-Cl cobalt, salen-Cl CoBr **(D)** Napthen and napthenCoSO_4

It is observed that the band due -OH (around 3000 cm^{-1}approx) in the ligand disappears when the respective ligand metal complex is formed. This clearly confirms the binding of the corresponding metal with the ligand at this position. It is observed that the band around 1250 cm^{-1} in the ligand attributed to C−O is shifted to higher frequency by about 30-40 cm^{-1} in case of the ligand complex which confirms the participation of oxygen in the C−O−M bond. The band for the ligand around 1615 cm^{-1} due to C=N stretching is shifted to a lower frequency around 1600 cm^{-1}. The band due to C-N at 1480 cm^{-1} is also shifted to a lower frequency by about 20 cm^{-1} (around 1460 cm^{-1}) further confirming the coordination of nitrogen with the metal. Due to the shift in FTIR frequency of C=N as well as C-O stretching, it is confirmed that both oxygen and nitrogen are involved in the binding with the metal ion. During the formation of metal complex with pentafluorobenzoate at the axial position, the band at around 990 cm^{-1} due to C-F stretching is observed in the complexes.

The application of catalysts synthesized in this chapter has been explored for chemical fixation of propylene oxide and CO_2 in Chapter 6.

CHAPTER-6

SYNTHESIS OF POLY(PROPYLENE CARBONATE(S)) AND CYCLIC CARBONATE

CHAPTER-6 SYNTHESIS OF POLY(PROPYLENE CARBONATE(S)) AND CYCLIC CARBONATE

As mentioned earlier (Chapter 5) synthesis of cyclic carbonates and poly(propylene carbonate) [PPC] using various catalysts and co-catalyst systems has been studied and effects of various parameters such as monomer/catalyst molar ratio, catalyst/co-catalyst molar ratio, pressure, temperature, reaction time, and stirring on the molecular weight of the polymer and yield have been investigated. The results of these experiments and related pertinent observations are presented in this chapter.

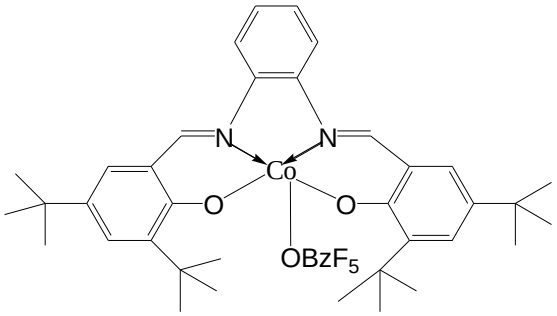
The first two sections (Section 6.1 and 6.2) of this chapter deal with the synthesis of PPC and cyclic carbonate using salophenCoOBzF_5 catalyst and $[PPN]^+Cl^-$ and tetrabytyl ammonium bromide as co-catalysts respectively. Further, the details of a comprehensive study involving effect of parameters such as catalyst to co-catalyst molar ratio, monomer to catalyst molar ratio, pressure, temperature, reaction time, and stirring on the yield and molecular weight of products are also included.

The results correlating the catalyst's electron density with polymer conversion and molecular weight are presented in the Section 6.3. Copolymerization of propylene oxide and carbon dioxide (CO_2) has been studied using different R-salophenCoOBzF_5 (OBzF_5=pentaflorobenzoate, R=CH_3, H, Cl, Cl_2) based catalysts. The central moiety of the catalysts R-salophenCoOBzF_5 has been kept the same and effect of changing electron density on the catalyst towards the copolymerization reaction has been investigated. The effects of different type of co-catalysts such as tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium), DMAP and tetrabutyl ammonium bromide have also been

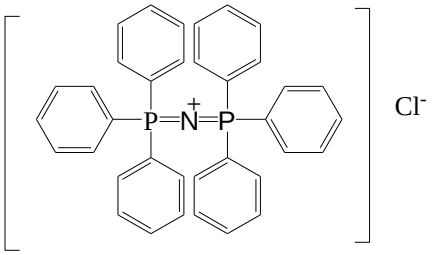
investigated. The following chapter 6.4 shows the characterization of PPC by ^{1}H NMR, ^{13}C NMR, ^{19}F NMR, HSQC and FTIR spectroscopy.

The last two sections of this chapter (Section 6.5 and 6.6) presents the results of those experiments where only cyclic carbonate formation has been observed. The basic salen and napthen based catalyst systems were used in the experiments for the chemical fixation of propylene oxide and CO_2. SalenCo(III)$OBzF_5$, salen-CH_3Co(III)$OBzF_5$, salen-CH_3Co(III)Br, salen-ClCo(III)Br, salen$CoSO_4$ and napthen$CoSO_4$ were used as catalysts along with tetradecyltrimethylammonium bromide, hexadecyltrimethylammonium bromide, $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium) and tetrabutylammonium bromide co-catalysts. All the catalyst/co-catalyst systems were found to be selective for cyclic carbonate formation and no poly(propylene carbonate) was formed in these reactions.

6.1. Synthesis of Poly(propylene carbonate) and Cyclic carbonate using salophenCoOBzF$_5$/[PPN]$^+$Cl$^-$ catalyst System



[N,N'-bis-(3,5-di-tert-butylsalicylidene)-phenylenediamine]cobalt pentafluorobenzoate
salophenCoOBzF$_5$



$[PPN]^+Cl^-$
($[PPN]^+$ = bis(triphenylphosphine)iminium)

Figure 6.1: SalophenCo$OBzF_5$/$[PPN]^+Cl^-$ catalyst/co-catalyst system

The present study deals with the synthesis of cyclic carbonate and poly(propylene carbonate) using an economical and simple achiral salophenCo(III)$OBzF_5$/$[PPN]^+Cl^-$ catalyst synthesized for this purpose (Chapter 5, Section 5.1.1). High polymer conversion using the catalyst has been achieved under mild conditions of temperature and pressure. The effect of stirring rate has also been studied. It has been observed that cyclic product was formed

below 800 rpm but further increase in the impeller speed upto 1100 rpm lead to PPC as the major product. It is shown that at higher impeller speed mass transfer is no longer the limiting parameter. The effect of monomer to catalyst ratio on the conversion and molecular weight of PPC has been critically analysed for the first time for such systems. Further, a comprehensive study involving the effect of parameters such as reaction time, pressure, temperature, as well as catalyst to co-catalyst ratio on the yield and molecular weight is also presented.

Table 6.1: Effect of various operating parameters on percent conversion

Operating	**Percent Conversion**		M_n **x10^3**	M_w**x10^3**	**PD**
Parameter	**PPC**	**Cyclic Carbonate**	**(g/mol)**	**(g/mol)**	
Effect of Reaction Time: P = 15 bar, T = 50 ^{o}C, M_o/I_o = 2000:1					
Time, h = 0.5	17.0	12.0	6.0	7.0	1.13
Time, h = 1.0	29.0	27.0	11.0	15.0	1.29
Time, h = 1.5	39.0	16.0	11.0	14.0	1.25
Time, h = 2.0	41.0	12.0	11.0	12.0	1.14
Time, h = 1.0*	25.0	25.0	11.0	13.0	1.14
Time, h = 2.0*	29.0	32.0	11.0	14.0	1.23
Effect of Agitation: P = 15 bar, T = 50 ^{o}C, M_o/I_o = 2000:1, Time: 2 h					
RPM =700$^{\#}$	-	-	-	-	-
RPM =1100$^{\#}$	-	-	-	-	-
RPM =700	-	50.0	-	-	-
RPM=800	11.0	45.0	8.0	10.0	1.30
RPM=900	41.0	14.0	8.0	9.0	1.14
RPM=1100	41.0	12.0	11.0	12.0	1.14

T=Reaction time studied at 70^{o}C*

RPM=1450	40.0	12.0	8.0	11.0	1.31

$T^{\#}$=Agitation speed at 25^{o}C

Effect of M_o/I_o : P = 15 bar, T = 50 ^{o}C, Time:2 h

M_o/I_o = 1500:1	17.9	43.0	8.0	10.0	1.13
M_o/I_o = 2000:1	41.0	12.0	11.0	12.0	1.13
M_o/I_o = 3000:1	37.0	8.0	14.0	16.0	1.08
M_o/I_o = 4000:1	33.0	19.0	4.0	4.0	1.08

Effect of Pressure: M_o/I_o = 2000:1, T = 50 ^{o}C, Time:2 h

P = 7 bar	7.0	8.0	10.0	13.0	1.24
P = 15 bar	41.0	12.0	11.0	12.0	1.14
P = 25 bar	56.0	12.0	13.0	15.0	1.16

Effect of Temperature: M_o/I_o = 2000:1, P = 15 bar, Time:2 h

T = 25 ^{o}C	-	-	-	-	-
T = 50 ^{o}C	41.0	12.0	11.0	12.0	1.14
T = 70 ^{o}C	29.0	31.0	11.0	14.0	1.23

Effect of Initiator/Co-Initiator Ratio [In/Co-in]:M_o/I_o = 2000:1, P = 15 bar, T = 5 ^{o}C, Time:2 h

In/Co-in = 0.5	20.0	41.0	11.0	14.0	1.29
In/Co-in = 1.0	41.0	12.0	11.0	12.0	1.14
In/Co-in = 2.0	29.0	41.0	5.0	6.0	1.13

Effects of individual parameters given in Table 6.1 and are discussed separately in the following sections.

6.1.1. Effect of Reaction Time

It has been observed that PPC conversion increases with reaction time. But, keeping the reaction time constant and increasing the temperature leads to decrease in PPC formation and increase in cyclic carbonate formation. However, at the same temperature the percentage conversion increases monotonically with an increase in reaction time. This is quite significant for ring-opening polymerization, where reproducibility of results is lower since the reaction can easily be terminated even with the presence of small amount (ppm level) of impurities and/or water. With regard to average molecular weights, except for the initial part of the reaction at 0.5 hour the M_n and M_w values do not change significantly. Interestingly, the molecular weight distribution as indicated by the value of polydispersity, ratio of M_w/M_n, is remarkably narrow.

6.1.2. Effect of Agitation

The polymerization reactions were carried-out at different impeller speeds. The results are shown in Table 6.1. Since the capacity of an autoclave reactor used was 100 ml with a minimum stirring volume of 20 ml, therefore to augment the contact surface between the monomers, i.e. propylene oxide and CO_2, only that much amount of propylene oxide was initially employed, which would break the upper surface of the liquid. At 25^{o}C and stirring speed of 700 rpm no product formation was obtained. Further, at 700 rpm and temperature of 50^{o}C conversion of propylene oxide to cyclic carbonate took place with no detectable PPC formation. At 800 rpm, around 11% PPC conversion was obtained which increased to about 40% at 900 rpm. Thus, it was observed that with an increase in agitation speed, the conversion of propylene oxide to PPC increased and the best combination of conversion and molecular weight was achieved at 1100 rpm. Therefore, in order to eliminate the mass transfer limitation, all further reactions were carried-out at 1100 rpm.

Clausius Clapeyron relation was used to know the physical state of the system. Though the relation is strictly applicable only to single constituent systems, we have employed it for polycarbonate synthesis with two reacting constituents (CO_2 and propylene oxide). It is estimated that at 15 bar, the boiling point of propylene oxide is around 160^{o}C, which is nearly three times higher than the reaction temperature. This clearly indicates that propylene oxide must exist in liquid state during the reaction. It is expected that at higher agitation speeds, the interfacial area for contact between propylene oxide and carbon dioxide will increase, thereby resulting in the availability of more and more propylene oxide for polymerization to provide higher PPC formation. The extremely narrow molar mass distribution of resulting PPC as evident from the PD (nearly unity , calculated from GPC data, Table 6.1) was obtained.

6.1.3. Monomer/Catalyst ratio

The reactions were carried out at different monomer to catalyst (M_o/I_o) ratios and at constant pressure of 15 bar and temperature of 50^{o}C (Table 6.1 and Figure 6.2). At the lowest M_o/I_o ratio of 1500:1, the molar mass and conversion are both low. At M_o/I_o of 2000:1, the conversion first increases and then decreases again with further increase in M_o/I_o ratio. It is expected that at lower M_o/I_o ratio (i.e. 1500:1), the amount of catalyst is relatively high, and hence probably a greater number of initiating sites are available for polymerization which will result in the formation of several shorter polymer chains along with large amount of oligomers (thereby giving rise to polymer with low molecular weight) or cyclic carbonate. Thus, it is interesting to note that at 1500:1, the reaction becomes more favourable for cyclic carbonate conversion. It is seen that increasing the M_o/I_o ratio to 2000:1 and 3000:1, leads to an increase in M_w of the polymer. It is estimated that at high M_o/I_o ratio, the amount of catalyst required for the reaction is relatively less and the number of initiating sites for polymer chain growth decreases resulting in longer polymer chains with high molar mass and conversion. Further increasing the M_o/I_o ratio to 4000:1 (with smaller amount of catalyst),

decreases the number of initiating sites and thus small number of propagating chains get terminated by the impurities and moisture present in the system (which will also have significant effect on the molar mass). The SEC results (Figure 6.3) show that at M_o/I_o ratio of 3000:1 the molar mass obtained is the highest thereby showing lowest retention volume and at ratio of 4000:1 molar mass obtained is lower with high retention volume.

The increase in M_n with increase in M_o/I_o can also be explained by the simple relation:

$$DP_n = 1 + \frac{M_o}{I_o}$$

here DP_n is the degree of polymerization. In the absence of detailed kinetic rate constants, the above relation can be applied for the ring-opening polymerization. This relation is strictly valid for the polymerization where initiation step is very fast and there is no termination. Thus for other situations this relation should be used only as an approximation and for qualitative estimates [Mehta *et al.* (2005); Mehta (2006)]. From this relation, one can see that as M_o/I_o increases the molecular weight will also increase until the termination effect becomes the controlling step.

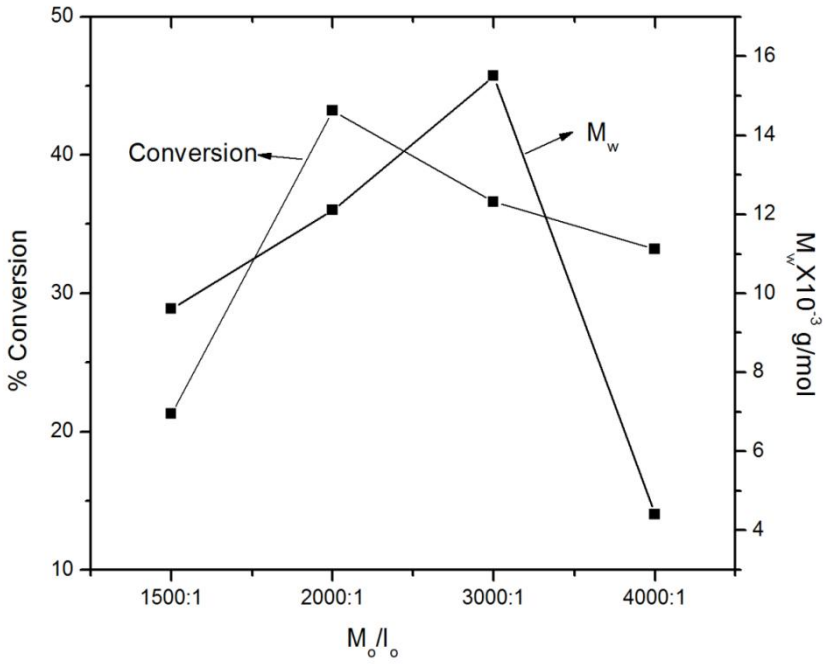


Figure 6.2: Effect of M_o/I_o ratio on PPC conversion and M_w

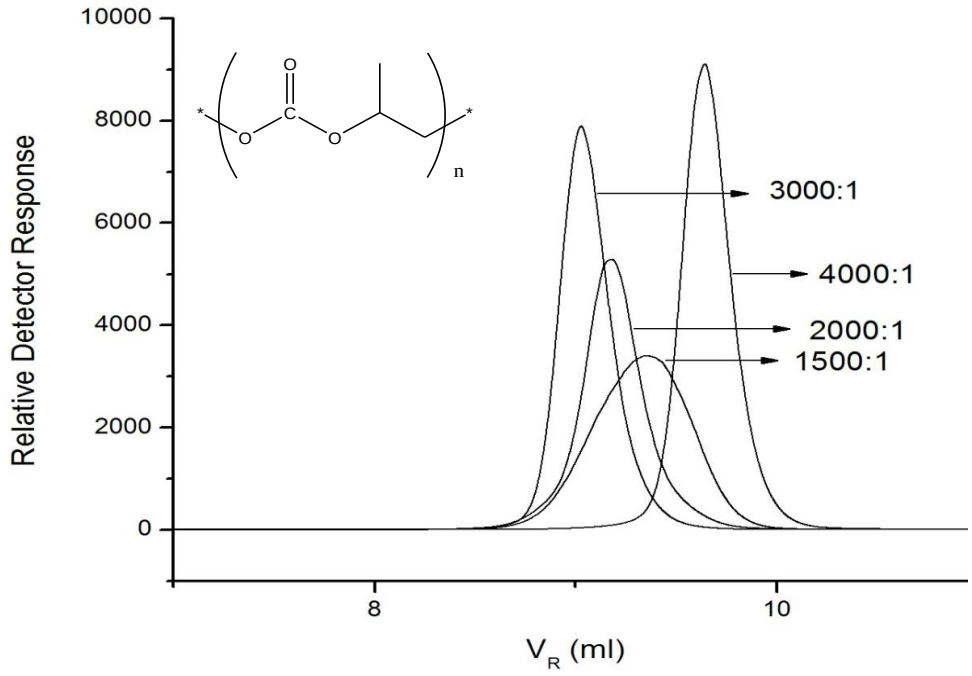


Figure 6.3: SEC chromatograms of PPC, Column:SHODEX GPC KF 806L, Detector: ELSD, Eluent: THF

6.1.4. Effect of Catalyst/Co-catalyst ratio

It is known that organic base and Lewis base co-catalysts increase the selectivity of PPC formation [Cohen *et al.* (2005); Qin *et al.* (2003)]. The co-catalyst attacks the epoxide from the vacant axial site, thereby opening the propylene oxide ring (Figure 2.4, Chapter 2) and thus assists in the polymer chain growth. In the present study, the amount of catalyst was kept fixed and the amount of co-catalyst was varied with three catalyst/co-catalyst ratios of 0.5, 1 and 2. It was observed that the selectivity for PPC first increased with an increase in the catalyst/co-catalyst ratio and then decreased with the further increase in this ratio (Table 6.1). Since the co-catalyst also increases the number of chain propagating sites, these results can be explained in the same way as the role of the catalyst at optimum M_o/I_o ratio (cf Section 6.1.3). Thus, the effect of catalyst as well as the co-catalyst leads to increase in polymer productivity [Vyas *et al.* (2010)]. However, higher amount of co-catalyst will lead

to increase in initiating sites for polymer chain growth giving PPC with low molecular weight and conversion.

6.1.5. Effect of Pressure

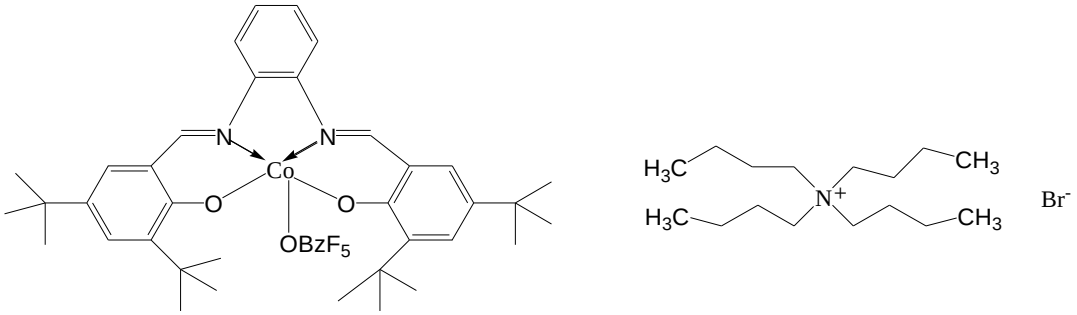
Effects of pressure on the percent conversion and M_w are shown in Table 6.1. It can be seen that for a given M_o/I_o ratio, the conversion changes appreciably with the change in pressure while there is only a little change in M_w values. The conversion is only around 6% at 7 bar which increases to around 41 % at 15 bar and 55% at 25 bar. Change in pressure, evidently increases concentration of carbon dioxide and thereby derives the reaction in the forward direction leading to an increase in the yield of the product. However, the increase in molecular weight with increase in pressure is not always continuous and it rather reaches a limiting value at a certain pressure. Since at a given monomer to catalyst ratio (i.e. 2000:1), the number of initiating sites for polymer chain growth is nearly the same at all pressures, there is only a little change in M_w with pressure. At the same time, the average molecular weight of the product is likely to depend on individual rate constants of initiation, propagation and termination. Thus, when the catalyst/co-catalyst system itself is changed, it is expected that the M_w trend will be different for different catalyst/co-catalyst systems (as the rate constants will be different) depending on system conditions.

6.1.6. Effect of Temperature

From Table 6.1 it can be seen that no conversion of propylene oxide occurs at 25^{o}C but on increasing the temperature to 50^{o}C, 41% conversion of PPC is observed. With further increase in temperature to 70^{o}C, the PPC conversion decreases and reaction becomes more favourable for the synthesis of cyclic carbonate. It probably happens due to the backbiting reaction that takes place at higher temperature. It has been observed that the polymerization temperature significantly affects the yield of the polymer but has little influence on the molar mass of polymer formed at 50 and 70^{o}C at constant M_o/I_o ratio. At a particular M_o/I_o ratio, the

number of initiating sites available for polymer chain growth remains the same, hence the average molar mass remains nearly constant. The PPC conversion is affected by kinetic and thermodynamic factors. The polymerization temperature affects only the yield of the PPC by shifting the equilibrium. But this trend can only be seen up to a limiting value, since the back biting of the polymer chain is expected to take place at higher temperature. The above trend may show a little variation with a change in catalyst/co-catalyst system where a significant change in molecular weight of PPC can be observed with change in temperature.

6.2. Synthesis of Poly(propylene carbonate) and Cyclic carbonate using SalophenCo(III)$OBzF_5$/$Bu_4^+Br^-$catalyst System



[N,N'-bis-(3,5-di-tert-butylsalicylidene)-phenylenediamine]cobalt pentafluorobenzoate
salophenCoOBzF$_5$

Tetrabutylammonium bromide

Figure 6.4: SalophenCo(III)$OBzF_5$/$Bu_4^+Br^-$catalyst System

Copolymerization of racemic propylene oxide with carbon dioxide is investigated in presence of economically inexpensive and effective achiral salophenCo(III)X [salophen = N,N'-bis(3,5-di-tert-butylsalicylidene)-phenylenediimine, X=pentaflorobenzoate] catalyst and tetrabutyl ammonium bromide as co-catalyst. The study is an extended set of experiments as discussed in Section 6.1 aiming to observe the effect of parameters on this co-polymerization reaction if catalyst system i.e. salophenCo$OBzF_5$ is kept constant and co-catalyst is changed from $[PPN]^+Cl^-$ to $Bu_4N^+Br^-$. Effects of different parameters like reaction time, monomer to catalyst ratio, catalyst/co-catalyst ratio, temperature, pressure of CO_2 on molecular weight, yield and selectivity of PPC have been investigated. The maximum M_w of 25.8×10^3 g/mol

has been obtained at 15 bar and 50^{o}C. All the samples were found to have excellent polydispersity near to 1.

Table 6.2: Effect of various operating parameters on percent conversion and molecular weight

Operating	**Percent Conversion**		M_n **x10^{-3}**	M_w**x10^{-3}**	**PD**
Parameter	**PPC**	**Cyclic Carbonate**	**(g/mol)**	**(g/mol)**	
		Effect of M_o/I_o : P = 15 bar, T = 50 ^{o}C			
M_o/I_o = 1500:1	12.1	48.1	13.3	17.2	1.29
M_o/I_o = 2000:1	46.5	20.4	13.2	15.2	1.14
M_o/I_o = 3000:1	27.1	37.5	22.2	25.8	1.16
M_o/I_o = 4000:1	17.9	19.2	5.5	6.0	1.08
		Effect of Reaction Time: P = 15 bar, T = 50 ^{o}C, *T=70^{o}C, M_o/I_o = 3000:1			
Time, h = 0.5	16.9	19.6	5.7	6.2	1.07
Time, h = 1.0	11.8	34.7	11.6	13.4	1.15
Time, h = 2.0	27.1	37.5	22.2	25.8	1.16
Time, h = 4.0	40.0	15.2	12.2	15.5	1.26
		Effect of Pressure: M_o/I_o = 3000:1, T = 50 ^{o}C			
P = 7 bar	12.0	17.6	8.1	10.5	1.28
P = 15 bar	27.1	37.5	22.2	25.8	1.16
P = 25 bar	42.0	15.5	15.0	19.0	
		Effect of Temperature: M_o/I_o = 3000:1, P = 15 bar			
T = 25 ^{o}C	-	-	-	-	-
T = 50 ^{o}C	27.1	37.5	22.2	25.8	1.16
T = 75 ^{o}C	-	25.2	-	-	-

Effect of Catalyst/Co-Catalyst Ratio [In/Co-in]: M_o/I_o = 3000:1, P = 15 bar, T = 50 ^oC

Cat/Co-cat = 0.5	29.6	6.2	13.4	16.6	1.23
Cat/Co-cat = 1.0	27.1	37.5	22.2	25.8	1.16
Cat/Co-cat = 2.0	32.6	24.1	10.9	15.2	1.38

It is seen that PPC conversion as well as the molecular weight increases with increase in reaction time. When the reaction was carried out for 0.5 h, around 16.9% of PPC conversion was obtained which increased to 27% and 40% after 2 and 4 h, respectively. As discussed in section 6.1.1, the product conversion is found to increase quite consistently with increase in reaction time and is rather noteworthy for ring opening polymerization reactions where reproducibility of product conversion is hardly seen as the reactions are easily terminated by even small amount of water molecules or impurities.

Further, when the reactions were carried out at different monomer to catalyst (M_o/I_o) ratios, it was observed that molecular weight first increased with increase in M_o/I_o ratio and then decreased with further increase in this ratio. This trend was also similar to that explained in Section 6.1.3. It is expected that at lower M_o/I_o ratio, greater number of initiating sites are present for growth of polymer chain (due to large amount of catalyst used) and thus initiation takes place at many different sites giving rise to polymer with shorter chain length. With increase in M_o/I_o ratio, the number of initiating sites decreases but chain length or molecular weight increases. Very less PPC formation was seen at M_o/I_o ratio of 1500:1 (12.1 % PPC conversion) and highest M_w was observed at 3000:1 with 27% PPC conversion and a M_w of 25.8 $\times 10^3$ g/mol. Figure 6.5 shows SEC chromatograms of PPC obtained at different M_o/I_o ratio with polymer obtained at 3000:1 with least retention volume and highest M_w.

Pressure effect on percent conversion and M_w is shown in Table 6.2. It has been observed that at a particular M_o/I_o ratio, conversion as well as M_w changes with pressure. The

conversion is around 12% at 7 bar which increases to about 42 % at the pressure of 25 bar. The trend of change in conversion with this catalyst system was similar to the one as observed with salophenCo(III)OBzF_5/[PPN]$^+$Cl$^-$ catalyst system (Section 6.1) but differ with respect to change in M_w. Using salophenCo(III)OBzF_5/$Bu_4N^+Br^-$ catalyst, significant change in M_w was observed with changing pressure where as no change in M_w was observed with salophenCo(III)OBzF_5/[PPN]$^+$Cl$^-$ catalyst system. This clearly shows that when combination of catalyst/co-catalyst system is changed, the M_w trend changes as polymer reactions depends on rate of initiation, propagation and termination and this rate will be different for different combination of catalyst/co-catalyst systems. Increase in pressure would probably also result in contact of greater amount of CO_2 with propylene oxide monomer and thus giving rise to greater PPC conversion. However, often the increase in conversion with an increase in CO_2 pressure might not be continuous and achieves a limiting value at some pressure.

Effect of co-catalysts on polymerization was studied by varying the amount of co-catalyst /catalyst (Co-cat/Cat) ratio as 0.5, 1 and 2. It has been observed that this co-catalyst/catalyst system is more selective for PPC conversion at the lowest co-catalyst concentration (co-cat/cat ratio = 0.5). Increase in the amount of co-catalyst changes the trend by becoming relatively favourable for cyclic carbonate production. As per the discussion in section 6.1.4, it is expected that increase in amount of co-catalyst will increase the number of initiating sites and will either give rise to large number of growing polymer chains of shorter chain length or formation of cyclic carbonate. Temperature for the copolymerization reaction was also found to have significant effect on PPC conversion. At 25^{o}C no conversion of propylene oxide to PPC or cyclic carbonate was observed. Increasing the temperature to 50^{o}C gave 27% PPC conversion. Further increasing in the temperature to 75^{o}C gave negligible PPC conversion and the reaction became more favourable for cyclic carbonate synthesis.

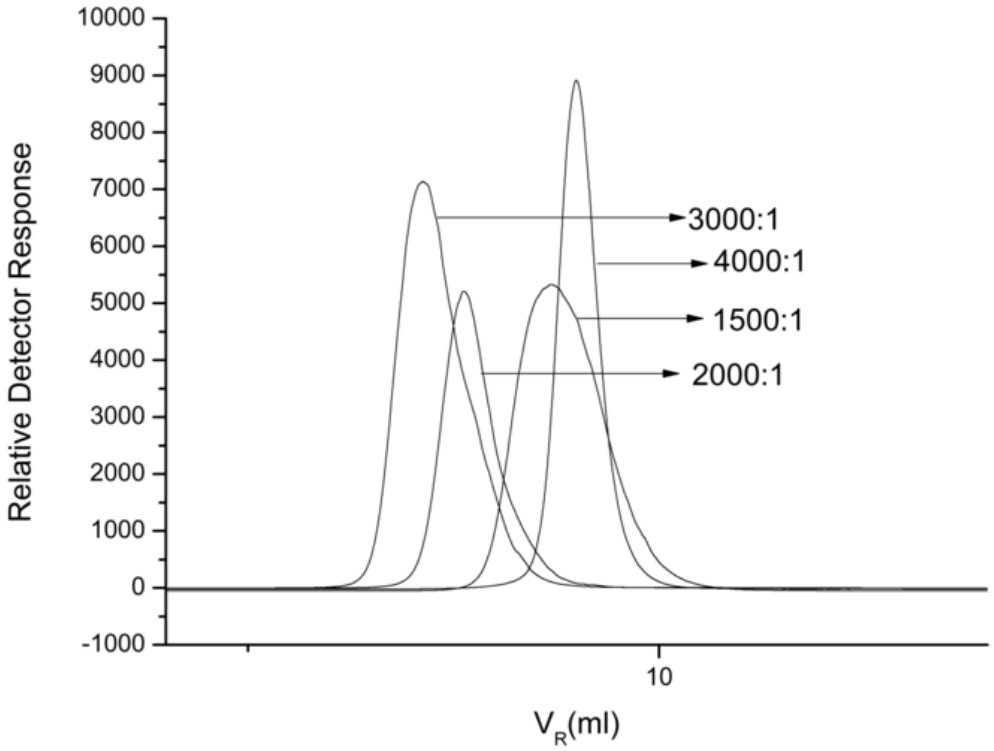
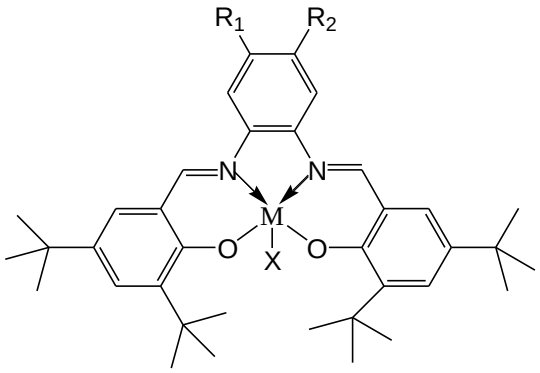


Figure 6.5: SEC chromatograms of PPC obtained using salophenCoOBzF_5/$Bu_4N^+Br^-$ catalyst/co-catalyst system

6.3 Effect of electron density on the catalysts for copolymerization of propylene oxide and CO_2

Copolymerization of propylene oxide and carbon dioxide (CO_2) has been studied using different R-salophenCoOBzF_5 (OBzF_5=pentaflorobenzoate, R=CH_3, H, Cl, Cl_2) based catalysts. The central moiety of the catalysts R-salophenCoOBzF_5 has been kept the same and effect of changing electron density on the catalyst has been studied on the copolymerization reaction. It has been explicitly observed in the present study that changing the electron density around diamine backbone (Figure 6.6) is one of the important key factors in controlling the yield and molecular weight of PPC product. It has been observed that introduction of electron withdrawing group (like Cl, Cl_2) on the o-phenylenediamine backbone moiety of the catalyst makes it more selective for PPC synthesis. On the other

hand, introduction of electron donating group (like CH_3) makes it more selective for cyclic carbonate formation. The effect of different type of co-catalysts has also been investigated using tetradecyltrimethylammonium bromide, hexadecyltrimethyl ammonium bromide, $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium), DMAP and tetrabutylammonium bromide.



Catalyst	R_1	R_2
6.6a	CH_3	H
6.6b	H	H
6.6c	Cl	H
6.6d	Cl	Cl

M=Co X=$OBzF_5$ (pentafluorobenzoate)

Figure 6.6: Catalyst systems with different electron densities

Reiger and co-workers (2008), explored the activity of achiral salophenCr(III)Cl on polymerization of racemic β-butyrolactone. The effect of electron density on o-phenylenediamine moiety of the catalyst was observed by introducing different groups i.e. H, Cl, Br, and F. It was observed that introduction of halogen groups to the original phenyl bridge lead to surprising improvement in the conversion and molecular weight. The study reports that there is no explanation for the substitution effect, if any, till then. Reiger *et al.* (2010), further explored salophenCr(III)Cl based complex comprehensively and observed the effect of substitution and possible electron density on o-phenylenediamine moiety of the catalyst on racemic β-butyrolactone polymerization. It was observed that introduction of methyl group lead to decrease in conversion while electron withdrawing group lead to an

increase in conversion. Recently, Hostalek *et al.* (2015) also reported that chloro substituted salophenCo(III)X complex (X=dinitrophenol, $OOCCl_3$) gave lower PPC formation in comparison to unsubstituted achiral salophenCo(III)X complex. It has been reported that introduction of electron withdrawing chlorine increases the Lewis acidity of cobalt metal to a considerable extent thus bonding strongly with the nucleophile. Reiger *et al.* (2012) also systematically varied the substitution pattern around cobalt based porphyrin complexes by various electron donating and electron withdrawing groups and explored the activity of the complexes (Figure 3.9). It was observed that catalysts bearing electron donating substituents favoured PPC formation and the one bearing electron withdrawing substituents favoured cyclic carbonate formation. The results obtained in the present study using schiff base complexes are completely different from the ones reported by Reiger *et al.* (2012) and that by Hostalek *et al.* (2015).

In all the above reported studies, there is no plausible explanation of the substitution effect on the catalysts in enhancing or decreasing its polymerization activity. In the present study, an attempt has been made to explain how the substitution on catalyst plays a role in increasing and decreasing the polymer conversion and molecular weight.

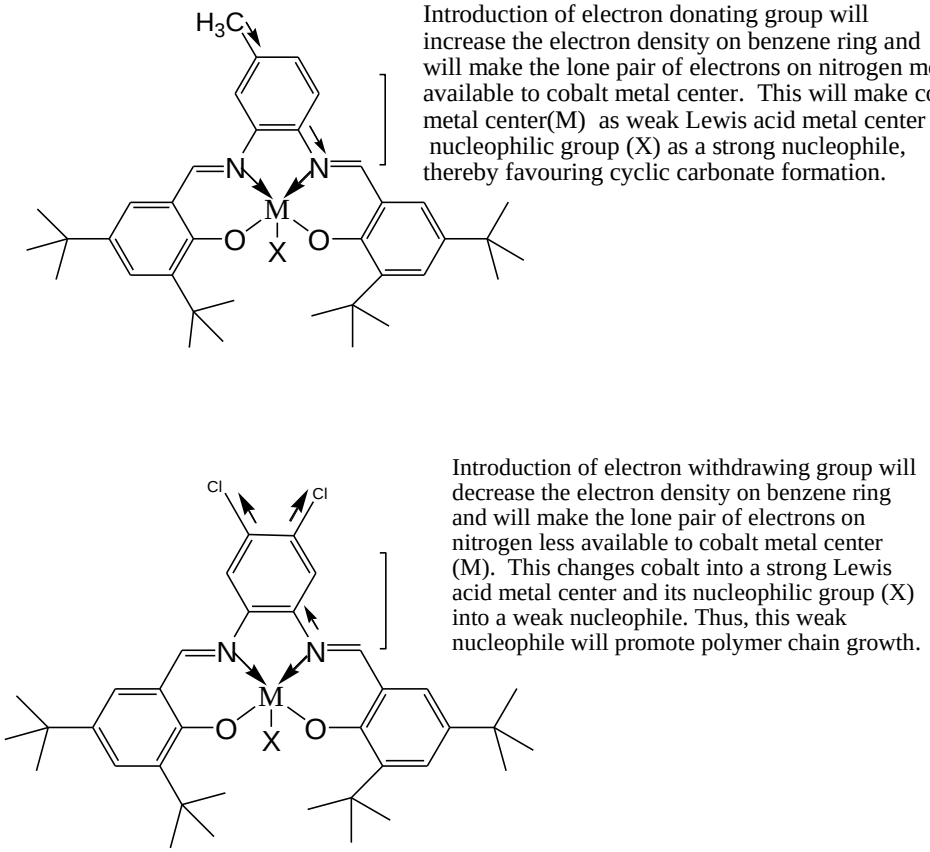


Figure 6.7: Effect of electron donating and electron withdrawing groups on the catalyst

It has been observed in the present study that electron density on the catalyst has considerable effect on the polymerization activity. Introduction of electron donating group (Figure 6.6(a) and Figure 6.7) on the catalyst decreases its polymerization activity and makes it more selective for cyclic carbonate formation. Increasing the electron density (by introduction of electron donating CH_3 group) will make cobalt a weaker electrophilic metal center by making the lone pair of electrons on nitrogen (of o-phenylenediamine moiety) more available to cobalt (Figure 6.5) and enhance the nucleophilic activity of the pentaforobenzoate chain end of the catalyst. This will in turn result in backbitting of the growing polymer chain leading to the cyclic carbonate formation (Table 6.3, Entry4). On the contrary, introduction of electron withdrawing groups like Cl and Cl_2 (Figure 6.6(c) and 6.6(d), Figure 6.7) on the catalyst, makes it more selective for PPC formation. Though, pentaflorobenzoate is itself a weak

nucleophile but introduction of electron withdrawing group like chlorine on o-phenylenediamine moiety of the catalyst (Figure 6.6(c) and 6.6(d)) makes cobalt an excellent electrophilic metal center and axial pentaflorobenzoate end a still further weak nucleophile. It is expected that when electron withdrawing groups (Cl and Cl_2) are attached on the catalyst, the lone pair of electrons present on nitrogen of o-phenylenediamine moiety of the catalyst (Figure 6.5) will be less available to the cobalt metal center and thus it will make cobalt a strong Lewis acid (or strong electrophile) and its conjugate pentaflorobenzoate end further a weaker nucleophile. By doing so, the catalyst becomes more selective for PPC conversion since a catalyst with weak nucleophilic chain end (i.e. pentaflorobenzoate) will probably resist the back-biting reaction (avoiding cyclic carbonate formation) and might favour the polymer chain growth (Table 6.3, Entry 2, 5 and 8, Figure 6.7). Additional increase of electron withdrawing effect (introduction of two chlorine atoms) on the catalyst further makes it more selective and efficient for PPC conversion (Table 6.3, Entry 3, 6 and 9). Since the nucleophilic activity of pentaflorbenzoate group attached on the axial position of the catalyst weakens to a considerable effect, the catalyst shows very little activity for cyclic carbonate formation.

The effect of temperature was also studied with all the catalysts possessing different electron densities. It was observed that all the catalysts showed similar trend towards the product formation. The optimum value for PPC selectivity for all the R-salophen based catalyst systems was observed at 50^{o}C (Table 6.3, Entry 4, 5 and 6). This result is in agreement with the results reported by several other researchers [Niu *et al* (2009); Liu *et al.* (2009); Li *et al.* (2011)]. It is expected that the increase in electron density probably decreases the activation energy of the reaction, as a result the salophenCH_3CoOBzF_5 catalyst shows polymerization activity even at a temperature as low as 30^{o}C (6.6(a), Table 6.3, Entry 1). No product formation was observed with salophenClCo(III)OBzF_5 (6.6(c), Table 6.3, Entry 2) at low

temperature. Further, with highly active salophenCl_2CoOBzF_5 (6.6(d), Table 6.3, Entry 3) PPC formation was observed. On increasing the temperature to 70°C salophenCH_3Co(III)OBzF_5 (6.6 (a), Table 6.3, Entry 7) exhibited high selectivity for cyclic carbonate with very little PPC conversion. Both complexes 6.6(c) and 6.6(d) at 70°C (Table 6.3, Entry 8 and 9) showed a decrease in PPC formation and relative increase in cyclic carbonate formation in comparison to the conversion observed at 50°C. At all three temperatures i.e. 30°C, 50°C and 70°C, salophenCl_2Co(III)OBzF_5 (6.6 (d), Table 6.3, Entry 3,6 and 9) was found to be more selective for PPC formation in comparison to other catalysts.

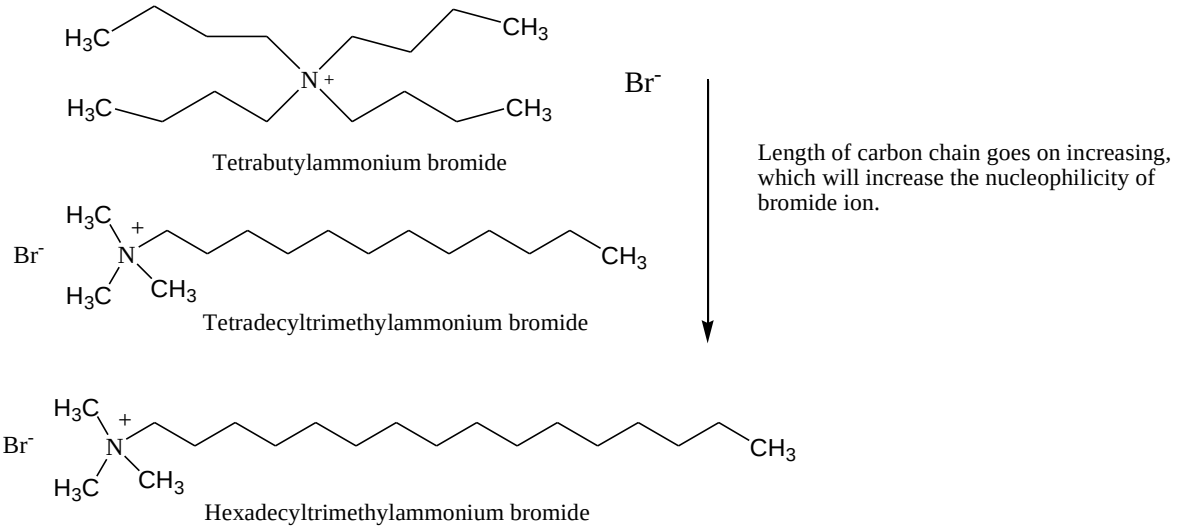


Figure 6.8: Different co-catalysts used for the reaction

Lu *et al.* (2004) explored propylene oxide and CO_2 copolymerization using chiral salenCoX catalysts (X=$OOCCH_3$, $OOCCl_3$, nitrophenoxy, dinitrophenoxy, trinitrophenoxy) with different co-catalysts. Lu *et al.* (2006) further reported the reaction using (R,R)-salcy Co(III)X (X=Cl, Br, NO_3, ClO_4, $OOCCl_3$, 2,4-dinitrophenoxy, pentafluorophenoxy) as catalyst along with different co-catalysts. In both the above studies, co-catalysts having same electropositive quaternary ammonium ion moiety and different nucleophilic moiety ($[PPN]^+Cl^-$, $[PPN]^+N_3^-$, $[PPN]^+ClO_4^-$) or ($Bu_4N^+Br^-$, $Bu_4N^+Cl^-$, $Bu_4N^+I^-$, $Bu_4N^+F^-$, $Bu_4N^+ClO_4^-$) were used. In the present study, we have explored a vice versa situation i.e. the nucleophilic groups have been kept unchanged and the effect of changing the length of

carbon chain around electropositive quaternary ammonium ion moiety has been observed (Figure 6.8). The effect of different co-catalysts was observed with the corresponding catalysts (Table 6.4, 6.6(a), 6.6(b), 6.6(c) and 6.6(d)). It was observed that introduction of either electron withdrawing or electron donating groups on the catalysts made the catalysts almost inactive towards different quaternary ammonium ions like tetradecyltrimethylammonium bromide and hexadecyltrimethylammonium bromide. SalophenCH_3CoOBzF_5 though showed little activity with $Bu_4N^+Br^-$ (Table 6.4, 6.6(a), Entry 3) but gave completely cyclic products with tetradecyltrimethylammonium bromide (Table 6.4, 6.6(a), Entry 2). This might be probably due to the fact that the carbon chain in the later case is long enough to make the bromide ion on the co-catalyst again a strong nucleophile and thus the combination of strong nucleophilic catalyst i.e. salophenCH_3Co(III)CoOBzF_5 (due to the presence of electron donating CH_3 group, which will make pentafluorobenzoate axial group as a strong nucleophile) and co-catalyst will lead to cyclic carbonate formation. It was expected that salophenCl_2CoOBzF_5 would show enhanced catalytic activity with corresponding ammonium ions but this did not happen. Using this catalyst again little activity was observed with all the three co-catalysts i.e. tetrabutylammonium bromide, tetradecyltrimethylammonium bromide and hexadecyl trimethylammonium bromide (Table 6.4, 6.6(d), Entry 10,11 and 12). Even in this case, using a combination of catalyst with extremely weak nucleophile at chain end (i.e pentafluorobenzoate) and co-catalyst with strongly nucleophilic anionic species might have resulted in the dominance of co-catalyst effect and thus cyclic carbonate formation. SalophenCo(III)OBzF_5 with balanced activity was found to be relatively more active with all the above three quaternary ammonium ions (Table 6.4, 6.6(b), Entry 4, 5 and 6). But, with $[PPN]^+Cl^-$ as a co-catalyst, the best catalytic activity and selectivity for PPC was observed with salophenCl_2CoOBzF_5 catalyst (since

pentafluorobenzoate acts as a weak nucleophile when electron withdrawing chlorine atoms are introduced on the catalyst) (Table 6.4, 6.6(d), Entry 9).

The effect of monomer to catalyst ratio (M_o/I_o) was also studied for salophenCl_2Co(III)OBzF_5 and it was observed that the catalyst showed almost negligible activity at higher and lower M_o/I_o ratio. For example, it was observed that at ratios 1500:1 and 3000:1, extremely low PPC conversion was obtained in comparison to the reaction carried out at ratio 2000:1 (Table 6.5). As discussed in Section 6.1 and 6.2, it is expected that at ratio of 1500:1, the amount of catalyst used is relatively high which will probably give rise to greater number of initiating sites for polymerization resulting in the formation of several short polymer chains with simultaneous formation of large number of oligomers. At the higher monomer to catalyst ratio of 3000:1, only a few initiating sites are available for polymer chain growth, which can undergo simultaneous termination with concomitant amount of impurities and moisture present in the system.

Table 6.3: Effect of temperature on the activity and selectivity of different catalysts and $[PPN]^+Cl^-$ co-catalyst

Catalyst		Temp (^oC)	Percent Conversion		$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	PD
			PPC	Cyclic carbonate			
6.6a	salophenCH_3 Co$OBzF_5$	30	11.4	2.2	3.56	4.07	1.14
6.6c	salophenCl Co$OBzF_5$	30	-	5.5	-	-	-
6.6d	salophenCl_2 Co$OBzF_5$	30	11.2	2.5	3.7	4.24	1.14
6.6a	salophenCH_3 Co$OBzF_5$	50	11.7	44.2	6.35	7.9	1.25
6.6c	salophenCl Co$OBzF_5$	50	43.2	12.3	8.94	11.1	1.24
6.6d	salophenCl_2 Co$OBzF_5$	50	45.6	6.3	10.2	12.3	1.28
6.6a*	salophenCH_3 Co$OBzF_5$	70	8.3	28.8	-	-	-

6.6c	salophenCl $CoOBzF_5$	70	14.0	36.0	3.80	4.47	1.17
6.6d	salophenCl_2 $CoOBzF_5$	70	19.7	21.1	4.13	4.81	1.16

Co-catalyst= $[PPN]^+Cl^-$, M_o/I_o= 2000:1, Reaction time=2 h, Initial pressure of CO_2= 15 bar

*Sample was unable to recover probably due to small amount of low molecular weight PPC formed at higher temperature that could not be precipitated

Table 6.4: Effect of different co-catalysts on activity of various catalysts

Catalyst		Co-catalyst	PPC	Cyclic carbonate	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	PD
6.6a	salophenCH_3 $CoOBzF_5$	$[PPN]^+Cl^-$	11.7	44.2	6.35	7.9	1.25
6.6a	salophenCH_3 $CoOBzF_5$	Tetradecyltrimethyl ammonium bromide	-	25.3	-	-	-
6.6a	salophenCH_3 $CoOBzF_5$	Tetrabutyl ammonium bromide ($Bu_4N^+Br^-$)	9.0	27.8	2.6	3.4	1.26
6.6b	salophen $CoOBzF_5$	Tetradecyltrimethyl ammonium bromide	45.0	9.0	5.91	6.82	1.15
6.6b	salophen $CoOBzF_5$	Tetradecyltrimethyl ammonium bromide*	14.0	14.5	6.86	8.0	1.16
6.6b	salophen $CoOBzF_5$	Hexadecyltrimethyl ammonium bromide	28.5	19.1	9.2	10.9	1.18
6.6b	salophen $CoOBzF_5$	DMAP	-	-	-	-	-
6.6b	salophen $CoOBzF_5$	Tetrabutyl ammonium bromide ($Bu_4N^+Br^-$)	46.5	20.4	13.2	15.2	1.14
6.6d	salophenCl_2 $CoOBzF_5$	$[PPN]^+Cl^-$	45.6	6.3	10.2	12.3	1.28
6.6d	salophenCl_2 $CoOBzF_5$	Tetradecyltrimethyl ammonium bromide$^{\#}$	5.2	28.0	-	-	-
6.6d	salophenCl_2 $CoOBzF_5$	Hexadecyltrimethyl ammonium bromide$^{\#}$	3.7	24.8	-	-	-
6.6d	salophenCl_2 $CoOBzF_5$	Tetrabutyl ammonium bromide ($Bu_4N^+Br^-$)$^{\#}$	6.0	33.3	-	-	-

M_o/I_o= 2000:1, Time=2 h, Temperature=50^oC, Pressure of CO_2= 15 bar

Samples could not be recovered either due to small amount of low molecular weight PPC present that could not be precipitated or due to the presence of low M_w PPC oligomers along with cyclic carbonate and polypropylene oxide.

Table 6.5: Effect of M_o/I_o ratio on salophenCl_2CoOBzF_5/[PPN]$^+Cl^-$ catalyst/co-catalyst system

M_o/I_o ratio	PPC	Cyclic carbonate	$M_n \times 10^{-3}$ (g/mol)	$M_w \times 10^{-3}$ (g/mol)	PD
1500:1	6.5	10.6	6.35	7.9	1.25
2000:1	45.6	6.3	10.2	12.3	1.28
3000:1	-	4.0	-	-	-

6.4.Characterization of Poly (propylene carbonate) (PPC)

6.4.1. ^{1}H NMR, ^{13}C NMR, HSQC, COZY, FTIR spectroscopy and DSC analysis

Figure 6.9 shows the ^{1}H NMR spectra of product, PPC obtained after precipitation from the crude mixture and cyclic carbonate. In case of ^{1}H-NMR spectra of PPC the shift at 1.3 ppm corresponds to CH_3 protons of PPC and at 4.2 and 4.8 ppm to CH_2 and CH protons, respectively. In case of ^{13}C-NMR (Figure 6.10) the shift around 154 ppm corresponds to carbonyl carbon of PPC and at 16, 69 and 72 ppm to CH_3, CH_2 and CH carbons, respectively. The ^{13}C-NMR also helps in explaining the regio-chemistry of PPC (Figure 6.11). The shift at 153.8 ppm corresponds to head-to-head linkage and at 154.2 and 154.7 ppm to head-to-tail and tail-to-tail linkages. The diagramatic representation of these linkages is shown in Figure 2.6 (Chapter 2). Most of the synthesized samples show abundance of head-to tail linkages (>90%). Heteronuclear single quantum coherence (HSQC) spectroscopy (Figure 6.12) clearly shows the correlation between ^{1}H and ^{13}C NMR spectra. In case of ^{1}H NMR spectra of the polymeric product, it was expected that since -CH_2 protons have –CH protons in their neighbourhood and they should give a doublet in ^{1}H NMR but probably due to the jump coupling in case of CH_2 protons a multiplet (i.e.small peaks on the side of middle intense

peak) is observed (Figure 6.13). The multiplet around 4.2 ppm due to $-CH_2$ protons shows that some protons of $-CH_2$ are in different environment then the other, thereby giving rise to the jump coupling by different types of interaction with the neighbouring –CH protons. This result is further found to be in agreement with the HSQC results which shows the presence of no additional protons and carbons around the region (4.0-4.2 ppm). Figure 6.14 shows ^{1}H NMR (COZY) of PPC sample. The COZY spectra clearly shows the coupling of –CH protons with $-CH_2$ and $-CH_3$ protons of PPC.

The FTIR spectrum of PPC is shown in Figure 6.15 which shows the band at 1246 cm^{-1} and 1740 cm^{-1} corresponding to C-O stretching and C=O stretching of PPC.

The DSC analysis of the polymer sample (obtained using salophenCoOBzF_5/$[PPN]^+Cl^-$) shows the glass transition and thermal degradation temperature of the polymer to be around 36^oC and 246^oC, respectively (Figure 6.16). Polymer obtained starts degrading around 210^oC and almost complete degradation is observed at 246^oC which clearly shows that the product has structural regularity and is thus an alternating polymer.

6.4.2. PPC End Group Analysis

In order to understand the reaction mechanism on a broader perspective, PPC end-group analysis of polymer obtained by salophenCoOBzF_5/$[PPN]^+Cl^-$ catalyst/co-catalyst system was done using ^{19}F NMR and EDS analysis. In case of ^{19}F NMR, the spectrum exhibited resonances at δ -140.49, -148.5, -155.7, -157.1 and -160.7 ppm (Figure A17, Appendix II) which were consistent with a $OBzF_5$ (pentafluorobenzoate) moiety on the PPC. EDS analysis also showed the atomic % of various elements as C=52.2, O=46.5, F=0.44 and Cl=0.27 (Figure A18, Appendix II). Thus, the presence of fluorine (from nucleophilic group of catalyst) and chlorine (from nucleophilic group of co-catalyst) in the results clearly indicates that catalyst and co-catalyst both are playing a role in initiating the reaction. It is expected that one end of the polymer chain is either attached to pentafluorobenzoate or chlorine

nucleophile while the other end of the chain is attached to the hydroxyl group since the termination of the reaction was carried out using acidified methanol (Figure 6.17).

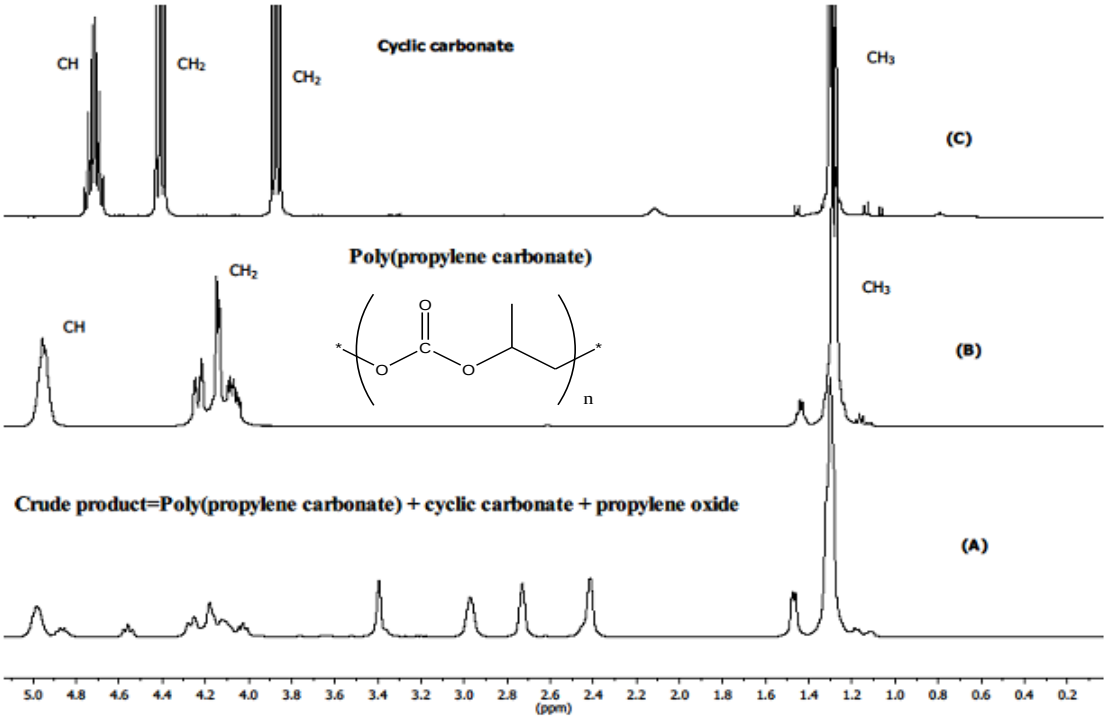


Figure 6.9: ^{1}H NMR spectra of **(A)** Crude product (where the chemical shift at 3.4 is a sharp peak due to methanol since polymerization was terminated with acidified methanol). For propylene oxide the shift around 2.4 and 2.7 is due to CH_2 protons and that around 2.9 ppm is due to CH protons **(B)** Poly(propylene carbonate) obtained after separation from reaction mixture and **(C)** cyclic carbonate

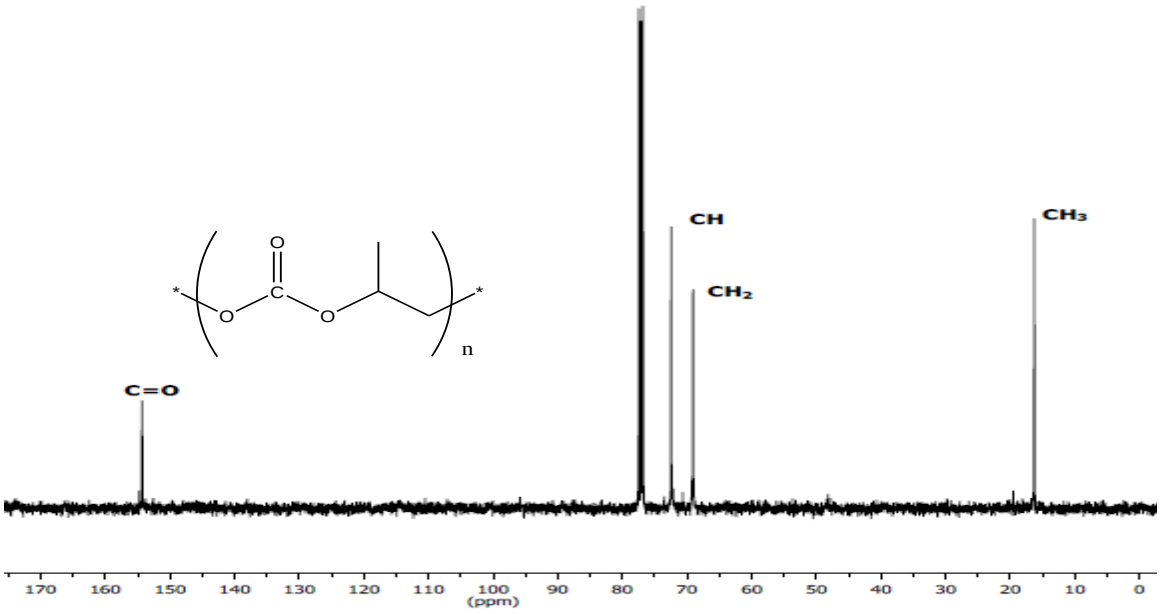


Figure 6.10: ^{13}C NMR of poly(propylene carbonate)

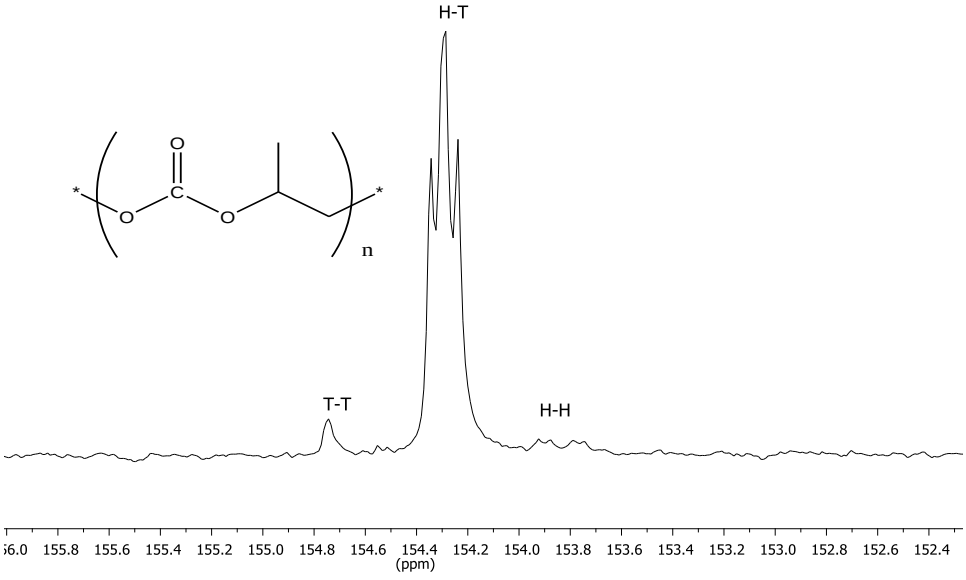


Figure 6.11: Regiochemistry of poly(propylene carbonate) determined by ^{13} C NMR

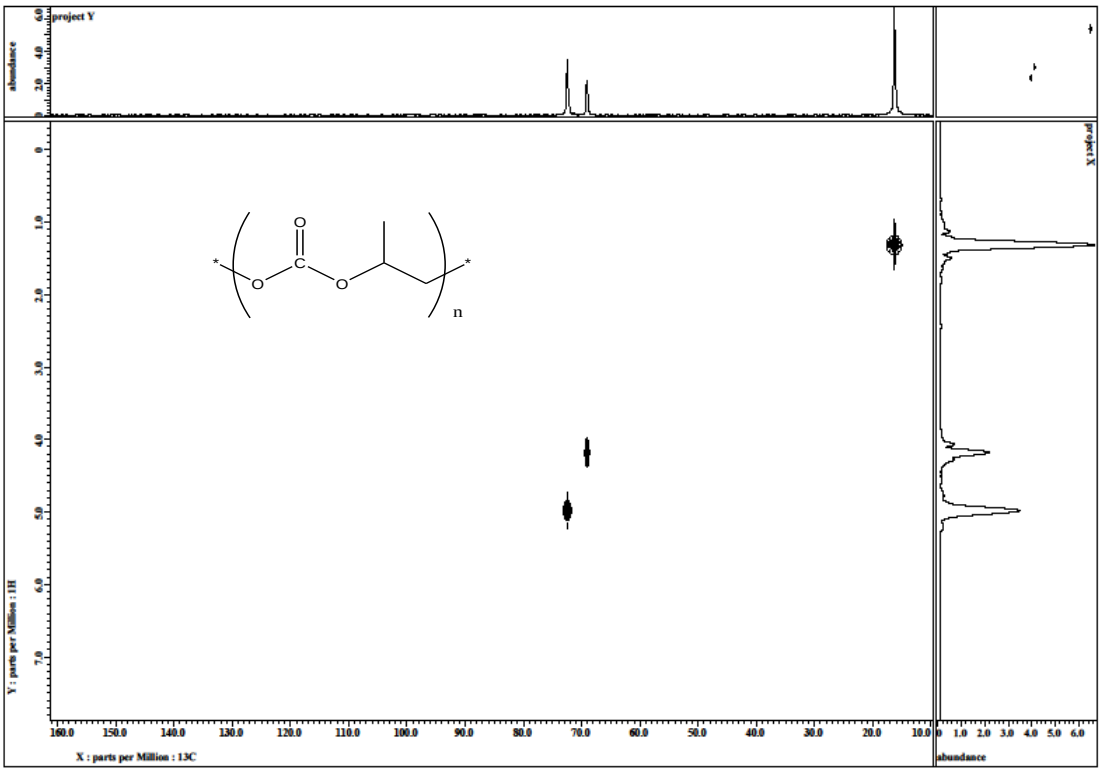


Figure 6.12: HSQC spectra of poly(propylene carbonate)

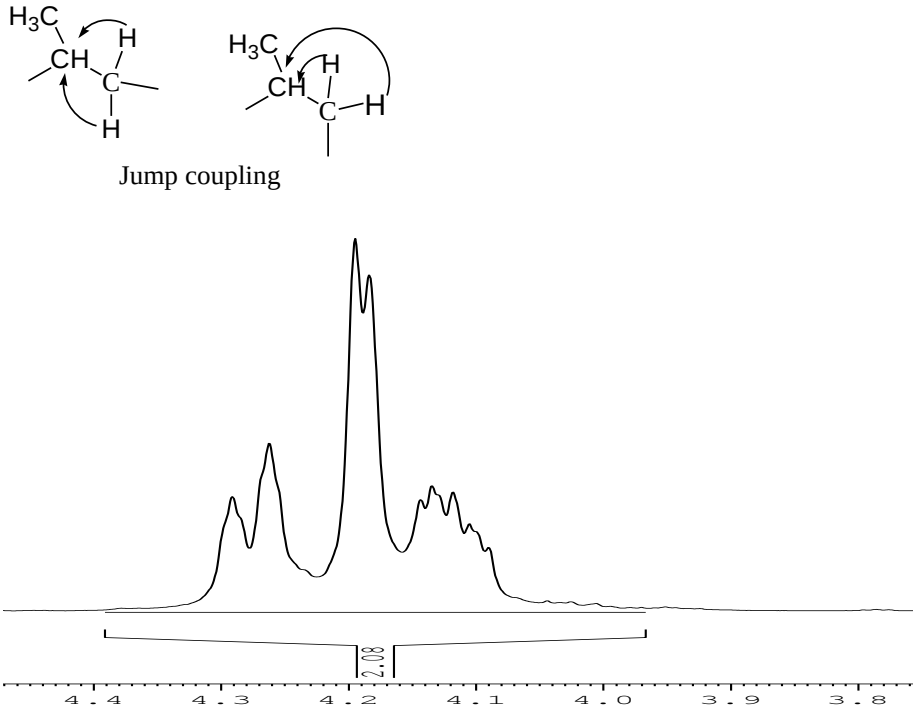


Figure 6.13: Jump coupling pattern of Poly(propylene carbonate) due to $-CH_2$ protons

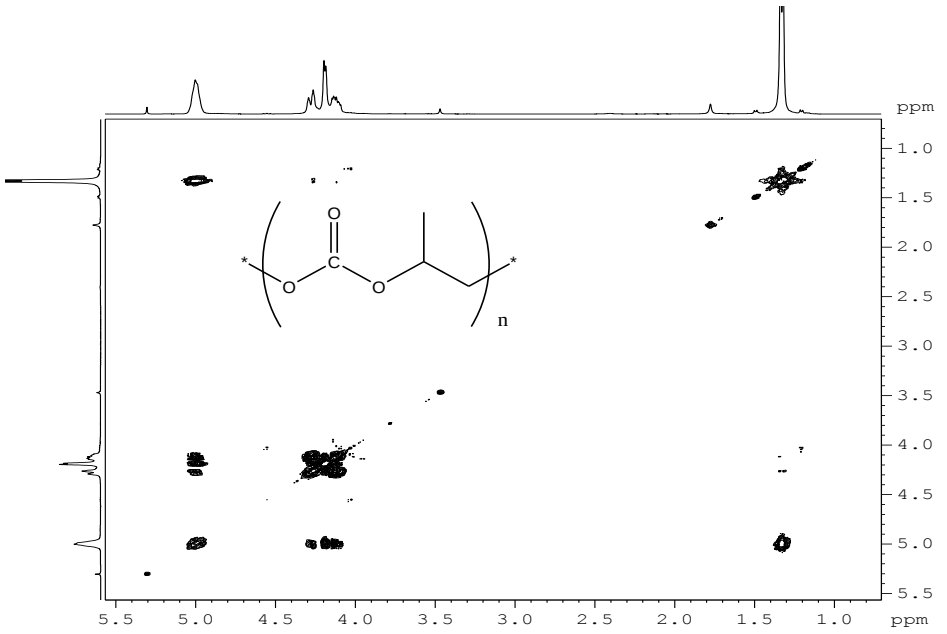


Figure 6.14: COZY (Correlation spectroscopy) of Poly(propylene carbonate) product

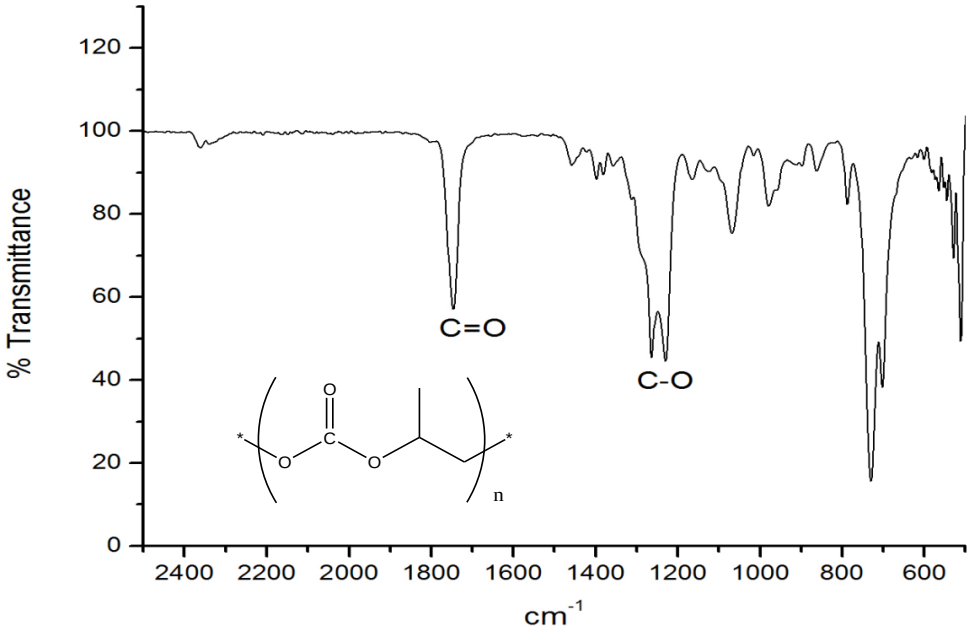


Figure 6.15: FTIR spectra of poly(propylene carbonate)

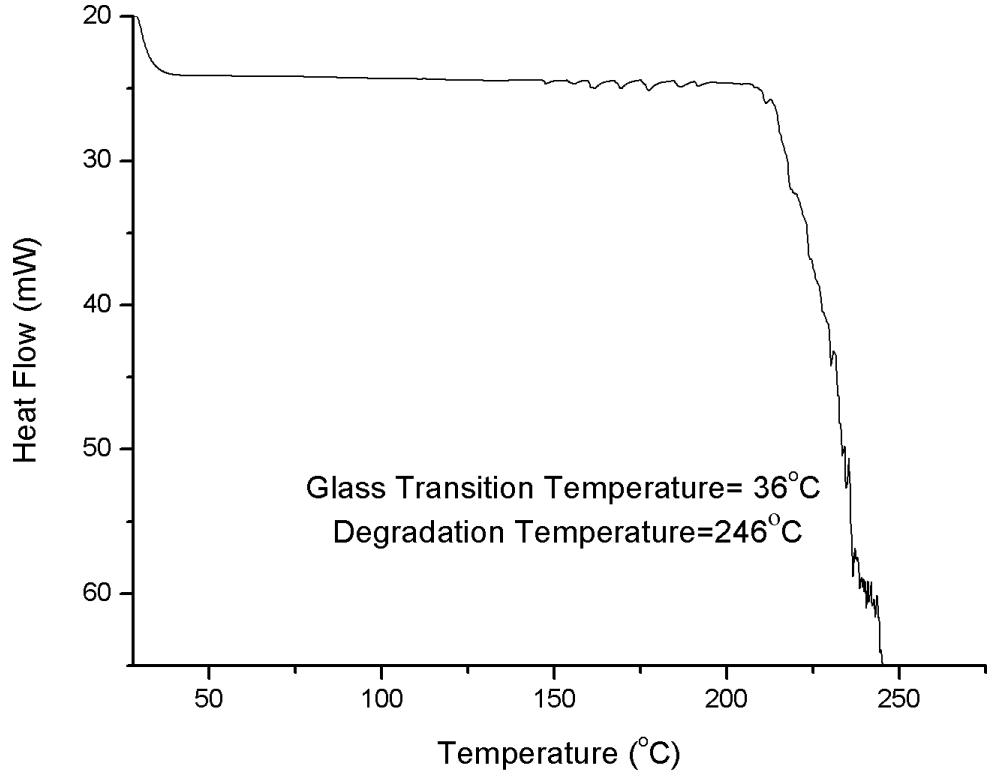
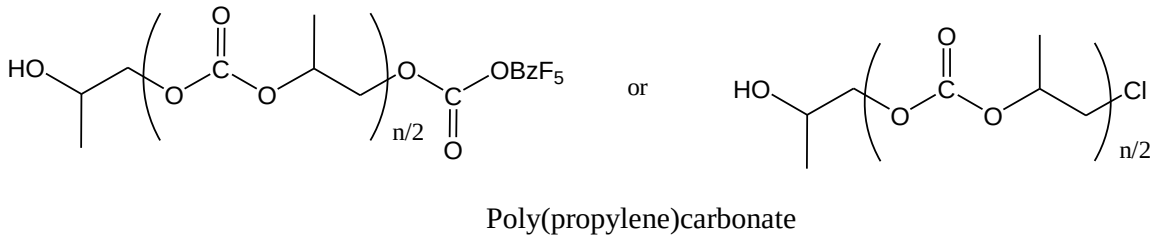


Figure 6.16: DSC analysis of synthesized poly(propylene carbonate)



Poly(propylene)carbonate

Figure 6.17: Possible end groups for Poly(propylene carbonate)

6.5. Synthesis of Cyclic carbonates from Propylene Oxide and CO_2

This section deals with the set of experiments involving catalyst/co-catalyst systems where only cyclic carbonate formation was observed. These catalyst/co-catalyst systems are expected to be relatively strong nucleophile in comparison to the R-salophenCo(III)X based catalysts discussed in previous sections and thus give rise to cyclic carbonate formation.

Table 6.6 gives conversion of propylene oxide and CO_2 to cyclic carbonate using various catalyst/co-catalyst systems. The actual state of monomers under high pressure and temperature conditions should be known before attempting to analyse the reaction data. As mentioned earlier (Section 6.1.2), using the Clausius-Clapeyron equation, it can be easily shown that at CO_2 pressure of 20 bar and temperature of 100^oC, the boiling point of propylene oxide is more than 200^oC which is nearly two times higher than the reaction temperature hence propylene oxide must exist in liquid state during the reaction though its boiling point at atmospheric pressure is 35^oC. Thus, it is expected that at polymerization temperatures of 60, 80 and 100^oC, propylene oxide will exist in liquid state under high pressure. The reaction between propylene oxide and CO_2 with salen$CoSO_4$/$Bu_4^+Br^-$ and napthen$CoSO_4$/$[PPN]^+Cl^-$ as catalyst systems (Table 6.6, Entry 1,2, 15 & 16) shows that on increasing the temperature the conversion to cyclic carbonate increases. It has been observed that DMAP as a co-catalyst does not give any conversion with either salen$CoSO_4$ or napthen$CoSO_4$ (Table 6.6, Entry 3, 4 and 14). Among the explored catalysts salen-CH_3CoBr/ $[PPN]^+Cl$ was found to be the most active catalyst (Table 6.6, Entry 17). It was observed that the conversion value increased from 40% to around 50% on increasing the pressure from 10 to 20 bar at a constant reaction time (Table 6.6, Entry 11 and 12). Respective conversions with salen $CoOBzF_5$/$Bu_4^+Br^-$ were found to increase with an increase in reaction time from 56.8% in 2 h to 67.3% conversion in 4 h (Table 6.6, Entry 8 and 9).

In order to study the steric effect on the catalyst, electron donating group was introduced on the ligand salen-CH_3 Co(III)$OBzF_5$ and its effect on the reaction was investigated. It is thought that methyl substituent will increase the electron density on the ligand and thereby will decrease the Lewis acid character of the Co(III) metal center by making the lone pair of electrons on nitrogen more available to cobalt and enhance the Lewis base or nucleophilic character of the axial nucleophilic pentafluorobenzoate group attached to it. Thus, it was

observed that salen-CH_3CoBr bearing electron donating methyl group and relatively better nucleophile as bromide ion was able to enhance activity of the catalyst and gave 67.0% conversion with $[PPN]^+Cl^-$ as co-catalyst (Table 6.6, Entry 17). The obtained conversion was found to be significant in comparison to the conversion obtained with salen $Co(III)OBzF_5$ catalyst for the same reaction time of 2h (Table 6.6, Entry 13). Further, introduction of electron withdrawing group decreased the electron density on the ligand by making the lone pairs of electrons on nitrogen of diamine moiety less available to cobalt metal center. This turns cobalt metal into a strong Lewis acid metal center and its conjugate bromide into a relatively weak nucleophile and thus decreases the conversion of propylene carbonate (Table 1, S.No. 18 and 19).

Table 6.6: Reactions between Propylene oxide and CO_2 using different catalyst/co-catalyst systems

Entry	Catalyst/Co-catalyst	Temperature (^oC)	Reaction Time (h)	% Conversion
1.	$SalenCoSO_4$/ $Bu_4N^+Br^-$	60	2	24.4
2.	$SalenCoSO_4$/ $Bu_4N^+Br^-$	100	2	50.7
3.	$SalenCoSO_4$/DMAP	60	2	No conversion
4.	$SalenCoSO_4$/DMAP	80	2	No conversion
5.	$SalenCoSO_4$/$[PPN]^+Cl^-$	60	2	13.6
6.	$SalenCH_3$-$CoSO_4$/$[PPN]^+Cl^-$	100	2	19.1
7.	$SalenCoSO_4$/Hexadecyl ammonium bromide	80	2	50.0
8.	$SalenCo(III)OBzF_5$/ $Bu_4N^+Br^-$	80	2	56.8
9.	$SalenCo(III)OBzF_5$/ $Bu_4N^+Br^-$	80	4	67.3
10.	$SalenCo(III)OBzF_5$/Tetradecyltri methylammonium bromide	80	2	36.3

11.	SalenCo(III)OBzF_5/$[PPN]^+Cl^-$	80	2	50.2
12.	#SalenCo(III)OBzF_5/$[PPN]^+Cl^-$	80	2	40.9
13.	SalenCo(III)OBzF_5/$[PPN]^+Cl^-$	100	2	55.6
14.	NapthenCoSO_4/DMAP	60	2	No conversion
15.	NapthenCoSO_4/$[PPN]^+Cl^-$	60	2	No Conversion
16.	NapthenCoSO_4/ $[PPN]^+Cl^-$	100	2	51.8
17.	SalenCH_3-Co(III)Br /$[PPN]^+Cl^-$	100	2	67.0
18.	SalenCl-Co(III)Br/$[PPN]^+Cl^-$	100	2	20.0
19.	SalenCl- Co(III)Br/ $Bu_4N^+Br^-$	100	2	23.0

M_o/I_o =2000:1, Pressure=20 bar, % Conversion has been calculated through ^{1}H NMR.

 # Pressure= 10 bar,*M_o/I_o =1000:1

6.6. ^{1}H NMR, ^{13}C NMR , HSQC and FTIR of cyclic carbonates:

^{1}H NMR spectra of propylene carbonate confirms the formation of cyclic carbonates in all the samples (Figure 6.18). A doublet around 1.5 ppm corresponds to methyl protons, triplets around 4.0 and 4.5 ppm correspond to CH_2 protons, and multiplet at about 4.8 ppm refers to CH protons. The multiplet at 4.8 ppm confirms the coupling of CH with both methyl and methylene hydrogens.

The ^{13}C NMR spectrum of propylene carbonate is shown in Figure 6.19. The chemical shift around 19 ppm corresponds to primary carbon and those at around 70 and 73 ppm correspond to secondary and tertiary carbons, respectively. The shift due to carbonyl carbon appears at around 155 ppm. The HSQC spectrum further clearly confirms the formation of propylene carbonate (Figure 6.20). The shift around 1.5 ppm corresponds to CH_3 carbon at 19 ppm. The shift around 4.2 and 4.5 ppm corresponds to CH_2 carbon at 70 ppm and the one around 4.8 ppm corresponds to CH carbon at 73 ppm.

The product propylene carbonate was also characterized by FTIR giving bands due to C=O at around 1790 cm^{-1} and C−O stretching at about 1180 cm^{-1} which are the characteristic bands of propylene carbonate and thereby confirm the formation of the product (Figure 6.21).

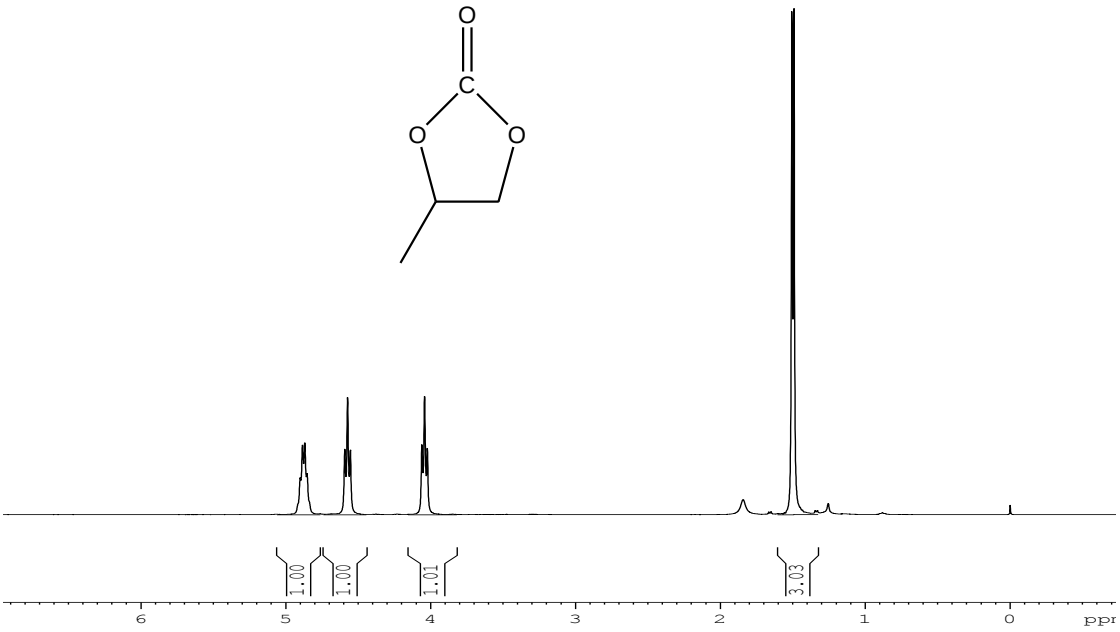


Figure 6.18: ^{1}HNMR of cyclic carbonate

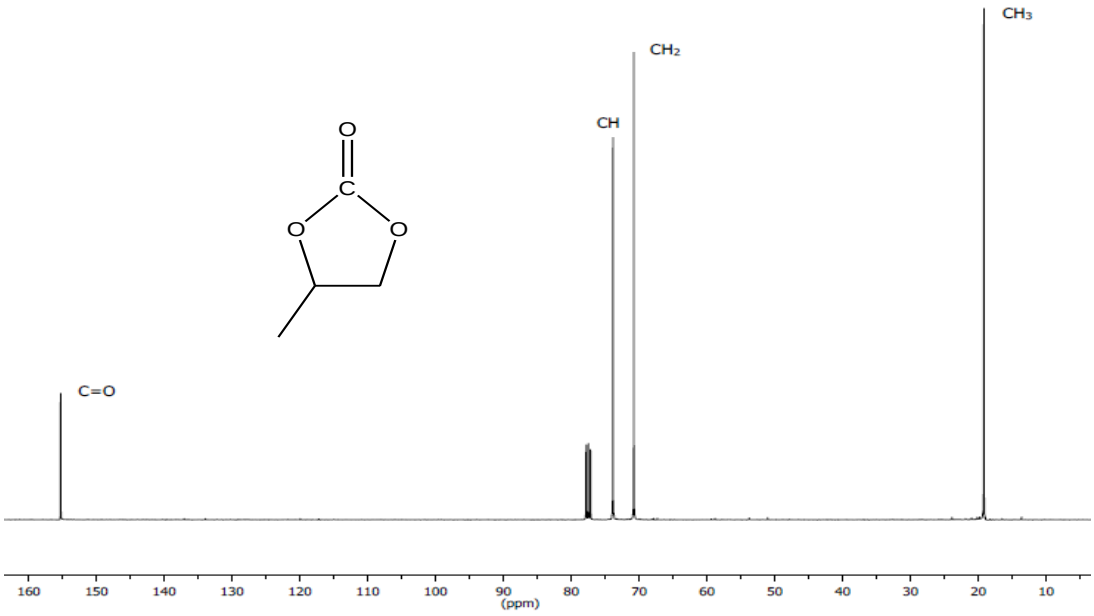


Figure 6.19: ^{13}C NMR spectra of cyclic carbonate

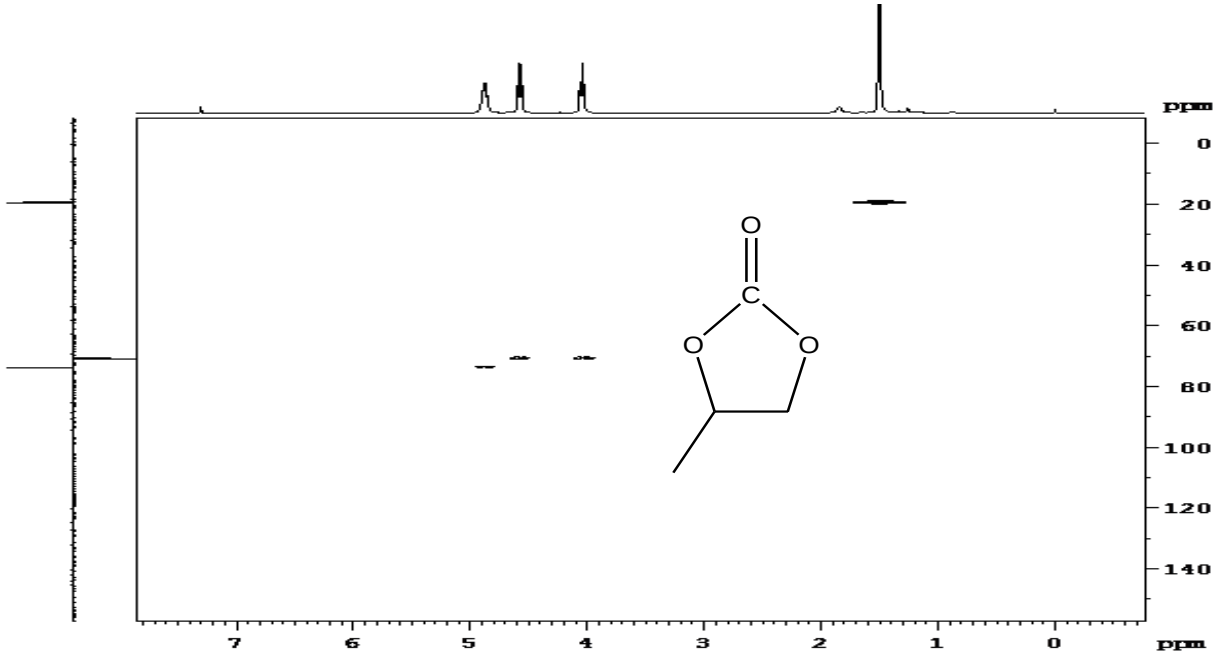


Figure 6.20: HSQC spectra of cyclic carbonate

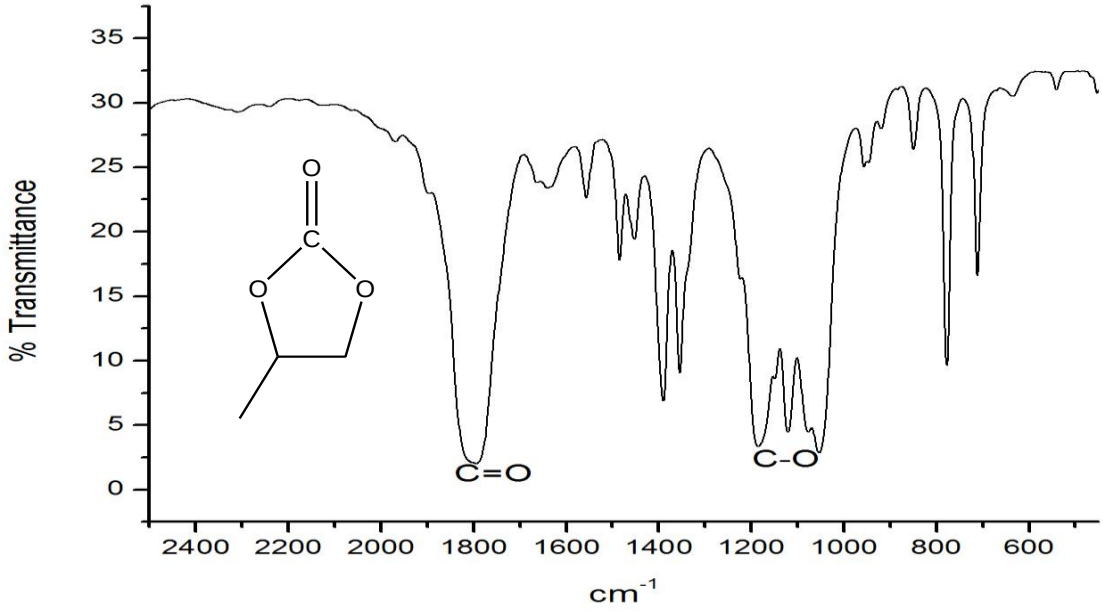


Figure 6.21: FTIR spectra of pure cyclic carbonate

CHAPTER-7

CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

CHAPTER-7 CONCLUSIONS AND RECOMMENDATIONS FOR FUTURE WORK

In the present thesis, work was carried out on the preparation of various ligand metal complexes as catalysts and their application in the chemical fixation of propylene oxide and CO_2. Various types of co-catalyst were also used in the reactions. Based on the nucleophilic activity, some catalysts were found to be selective for poly(propylene carbonate) [PPC] formation while some were found to be active only for cyclic carbonate formation. Additionally, a comprehensive study on the effects of parameters like monomer to catalyst ratio, catalyst/co-catalyst ratio, stirring rate and reaction conditions like temperature and pressure of CO_2 on the molecular weight, yield and selectivity of PPC over propylene carbonate was conducted. The major conclusions based on this work are summarized below:

7.1.1. Copolymerization using salophenCoOBzF_5 catalyst

- Chemical fixation of propylene oxide and CO_2 to PPC and cyclic carbonate was carried out under milder conditions (Figure 7.1). Poly(propylene carbonate) (PPC) was successfully synthesized using an inexpensive achiral salophenCoOBzF_5 (Figure 7.2) as catalyst with $[PPN]^+Cl^-$ and tetrabutyl ammonium bromide as co-catalysts.

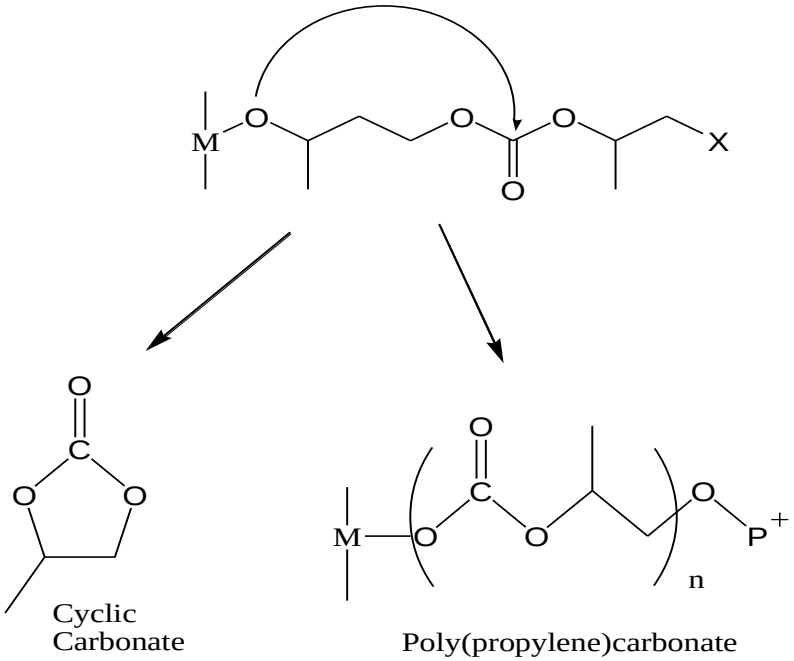


Figure 7.1: Possible poly(propylene carbonate) and cyclic carbonate formation

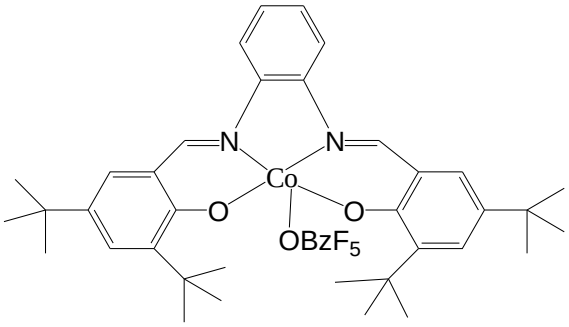


Figure 7.2: SalophenCoOBzF_5 catalyst system

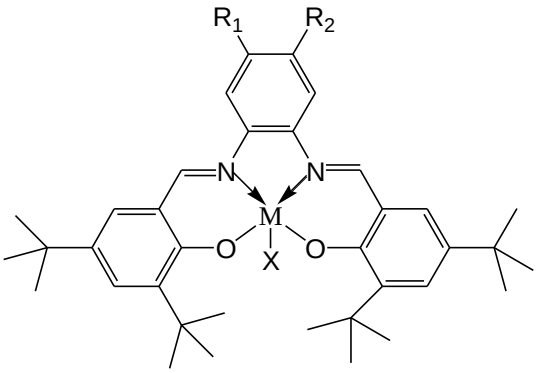
- The reaction mediated by salophenCoOBzF_5 catalysts showed a complex dependence on the ratios of propylene oxide and the amount of catalyst taken. It was observed that the conversion and the M_w of the polymer increased with increase in monomer to catalyst ratio and then decreased with its further increase. Excellent conversion and M_w was achieved at 2000:1 and 3000:1. Using salophenCoOBzF_5/$[PPN]^+Cl^-$ catalyst/co-catalyst system maximum conversion of PPC (upto 41%) was achieved at 2000:1 though maximum M_w of 14×10^3 g/mol was achieved at 3000:1. When salophenCo(III)OBzF_5/$Bu_4N^+Br^-$ was employed

as the catalyst/co-catalyst system, highest M_w of 25.8 $\times 10^3$ g/mol was obtained at 3000:1. It was observed that the ratio of catalyst/co-catalyst also had considerable effect on PPC conversion. The results showed that for the fixed amount of monomers, higher amount of catalyst or the co-catalyst increased the number of initiating sites and favours polymer with low M_w or cyclic carbonate formation.

- The polymerization temperature and pressure of CO_2 had significant effect on the yield of the polymer. PPC conversion was found to increase with an increase in temperature (up to 50^oC) though the backbiting reaction affected it at higher temperature (around 70^oC). It was observed that PPC conversion increased with increase in the pressure of CO_2. Change in pressure, evidently increased concentration of carbon dioxide and thereby drove the reaction in the forward direction leading to an increase in the yield of the product.
- The effect of stirring rate had been studied using salophenCoOBzF_5/$[PPN]^+Cl^-$ catalyst/co-catalyst system. Interestingly, that cyclic product was formed below 800 rpm and increasing the impeller speed to 1100 rpm led to PPC formation as the major product. It was seen that at impeller speed of 1100 rpm or more, mass transfer was no longer the limiting parameter.
- The polydispersity of all PPC samples was found to be close to unity as calculated from SEC results.

7.1.2. Effect of electron density on salophenCoOBzF_5 catalysts

- Copolymerization of propylene oxide and carbon dioxide (CO_2) was studied using different R-salophenCoOBzF_5 (OBzF_5=pentafluorobenzoate, R=CH_3, H, Cl, Cl_2) based catalysts, which were also synthesized (Fig 7.3).



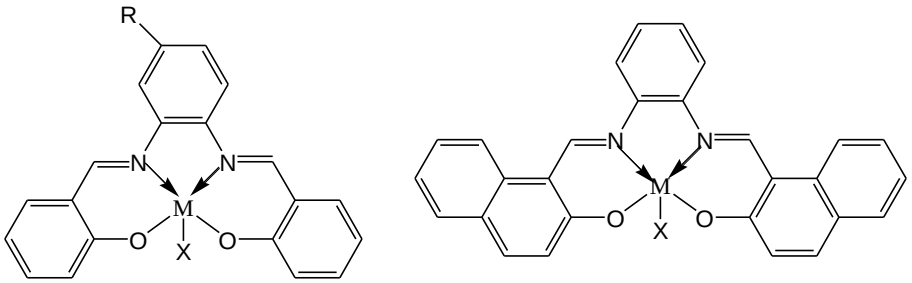
M=Co X=$OBzF_5$ (pentafluorobenzoate)

R_1= H, CH_3, Cl R_2=H, Cl

Figure 7.3: Effect of different electron donating (CH_3) and withdrawing groups (Cl, Cl_2) on PPC formation

- When R-salophenCoOBzF_5 catalyst was used with $[PPN]^+Cl^-$ as co-catalyst for the polymerization reaction, it was observed that increasing the electron density on the catalyst by introduction of CH_3 group on salophenCoOBzF_5 changed it into a strong nucleophile giving higher cyclic carbonate conversion. On the other hand, introduction of an electron withdrawing group (such as Cl and Cl_2) on the o-phenylenediamine moiety of salophen based catalyst decreased the electron density on the catalyst and changed it into a weaker nucleophile, thereby making it more active and selective for PPC conversion.
- The activity of the above catalysts with different electron density was also studied with various co-catalysts. Tetradecyltrimethylammonium bromide, hexadecyl trimethylammonium bromide, $[PPN]^+Cl^-$ ($[PPN]^+$ = bis(triphenylphosphine)iminium), DMAP and tetrabutylammonium bromide were used as co-catalysts in the reaction. It was observed that when the combination of salophenCl_2CoOBzF_5 catalyst with extremely weak nucleophilic activity and quaternary ammonium ions (i.e. tetradecyltrimethyl ammonium bromide, hexadecyltrimethylammonium bromide and tetrabutyl ammonium bromide) with strong nucleophilic activity were employed for the reaction, the effect of co-catalyst predominates and the reaction becomes favourable for cyclic carbonate formation.

7.1.3. Synthesis of cyclic carbonate



Salen **Napthen**

M=Co, Fe X=SO_4, $OBzF_5$, Br
R=H, CH_3, Cl

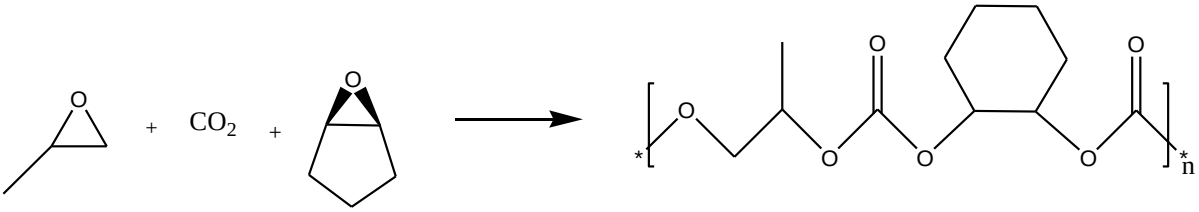
Figure 7.4: Salen and napthen based catalysts

- Various catalysts such as salenCoOBzF_5, napthenCoSO_4, salenCH_3CoBr, salenCl CoBr gave cyclic carbonate as the major product. The catalyst/co-catalyst systems are expected to be relatively strong nucleophile in comparison to R-salophenCo(III)X based catalysts, thus giving rise to cyclic carbonate formation.
- It is observed that increase in temperature and pressure favors cyclic carbonate formation.
- Salen based catalysts gave entirely different results in comparison to salophen based catalysts (in terms of conversion), i.e. introduction of electron withdrawing group as chlorine on o-phenylenediamine moeity of salen based catalysts (salenCl CoBr) lead to decrease in cyclic carbonate conversion whereas introduction of electron donating group as CH_3 (i.e. salen-CH_3CoBr) lead to increase in cyclic carbonate conversion.

  These results showed that catalyst with weak nucleophilic activity favored PPC formation whereas catalyst with strong nucleophilic activity favoured cyclic carbonate formation.

7.2. Recommendations for Future Work

- It would be interesting to synthesise different type of polycarbonates from various epoxides (such as ethylene oxide, cyclopentene oxide, styrene oxide, oxetane etc) and CO_2 giving rise to polymer with different range of glass transition temperature T_g.
- Synthesis of terpolymers can be attempted using two different epoxides and CO_2. This can probably increase the T_g of the synthesized polymer. Further, the T_g of the synthesized polymer can also be adjusted by varying the ratio of the two epoxides taken. Thus, this can give the possibility to tune the properties of the synthesized polymer. For example, the terpolymer synthesized from cyclohexene oxide, propylene oxide and CO_2 can be synthesized.



- Efforts should be made to explore other inexpensive achiral ligand metal complexes for such polymerization which could give high M_w polymer.

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APPENDIX-I

The results incorporated in this thesis are fully documented. Following publications in peer reviewed SCI journals have come out of the work carried out so far. Some of the work has also been presented at national/international conferences/seminars.

The work was also recognized at national level and awarded the **Joint Runners up Award** at the **5th National Award for Technology Innovation-2014** by the Ministry of Chemicals & Fertilizers, Department of Chemicals & Petrochemicals, Govt of India, in the category of Research in the Field of Polymer Science & Technology for the Innovation in **"Chemical Fixation of Carbon dioxide and Propylene Oxide to Poly(propylene carbonate) and Cyclic carbonate"**.

Publications:

1. Narang, S.; Mehta, R.; Upadhyay, S.N. Polyethylene Glycol and Montmorillonite Clay Anchored Schiff Base Ligand−Metal Complexes. *Ind. Eng. Chem. Res*, 2013, 52, 3967−3973.
2. Narang, S.; Mehta, R.; Upadhyay, S.N. Copolymerization of Propylene Oxide and Carbon Dioxide *Current Organic Chemistry*, 2015, 19, 2344-2357.
3. Narang, S.; Macova, E.; Berek, D.; Upadhyay, S.N.; Mehta, R. Synthesis of Poly(propylene carbonate) from Highly Active, Inexpensive Achiral (Salph) Co(III)X as Catalyst and Bis(Triphenyl Phosphine) Iminium as Co-catalyst. *Journal of Applied Polymer Science*, 2015 (DOI:10.1002/app43099).
4. Narang, S.; Berek, D.; Upadhyay, S.N.; Mehta, R. Chemical Fixation of Propylene Oxide and CO_2 using Achiral Salophen Co(III) pentaflourobenzoate and tetrabutyl ammonium bromide as catalysts. *Journal of Macromolecular Science, Part A*, 2015. (Accepted)

5. Narang, S.; Berek, D.; Upadhyay, S.N.; Mehta, R. Effect of Electron Density on Catalysts for Chemical Fixation of Propylene Oxide and CO_2. *Journal of Polymer Research,* 2015. (Accepted)
6. Narang, S.; Mehta, R.; Upadhyay, S.N. Synthesis of Ligand Metal complexes for the Chemical Fixation of CO_2 and Propylene Oxide to Cyclic Carbonates. *Synthesis and Reactivity in Inorganic, Metal-Organic and Nano-Metal Chemistry,* 2015. (under review)

Conferences:

- Narang, S.; Mehta, R.; Upadhyay, S.N. Synthesis of Polycarbonates from Carbon Dioxide and Propylene Oxide. *Polychar-19*, Kathmandu, Nepal, 2011.
- Narang, S.; Mehta, R.; Upadhyay, S.N. Chemical Fixation of CO_2 and Propylene Oxide to Polycarbonates and Cyclic Carbonates. *Polymers on the Frontiers of Science and Technology*. Chandigarh, APA, 2013.
- Narang, S.; Mehta, R.; Upadhyay, S.N. Synthesis of Polycarbonates and Cyclic Carbonates by Chemical Fixation of CO_2 and Propylene Oxide. *National Conference for Innovative Molecules for Sustainable Future.* Thapar University, Patiala, 2013

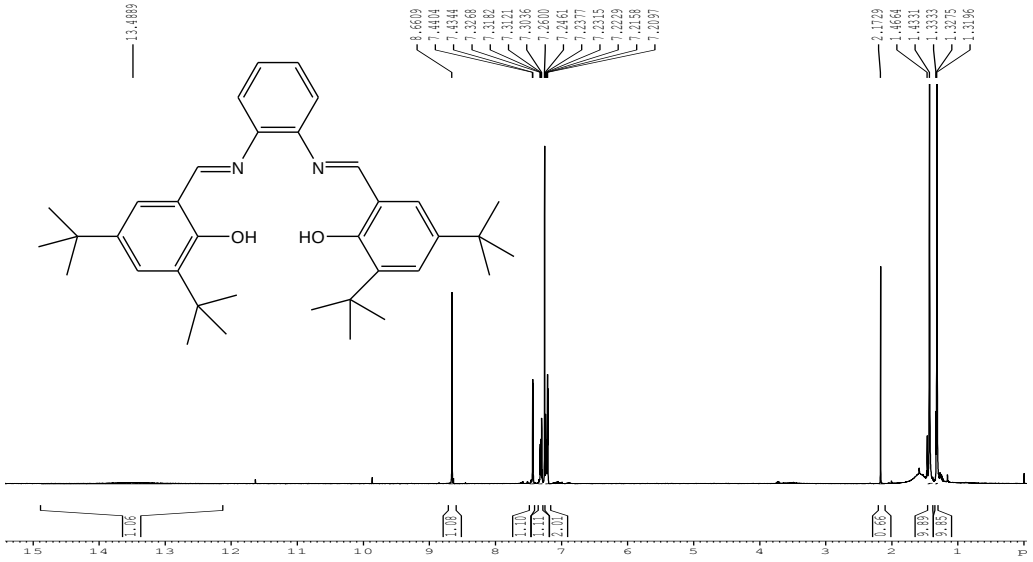

Figure A1: ^{1}H NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-methyl-o-phenylenediamine (salophen)

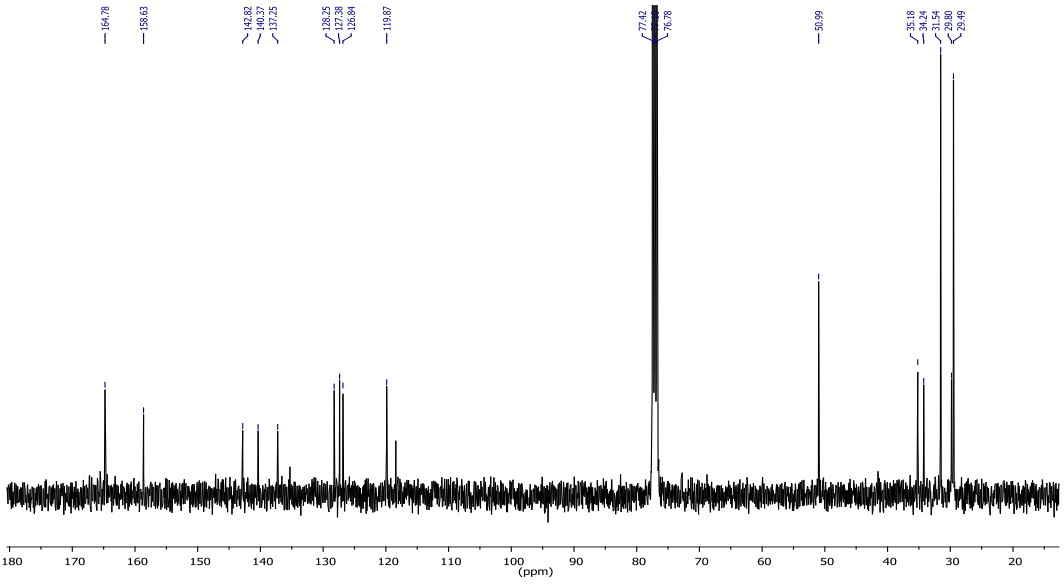

Figure A2: ^{13}C NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-methyl-o-phenylenediamine (salophen)

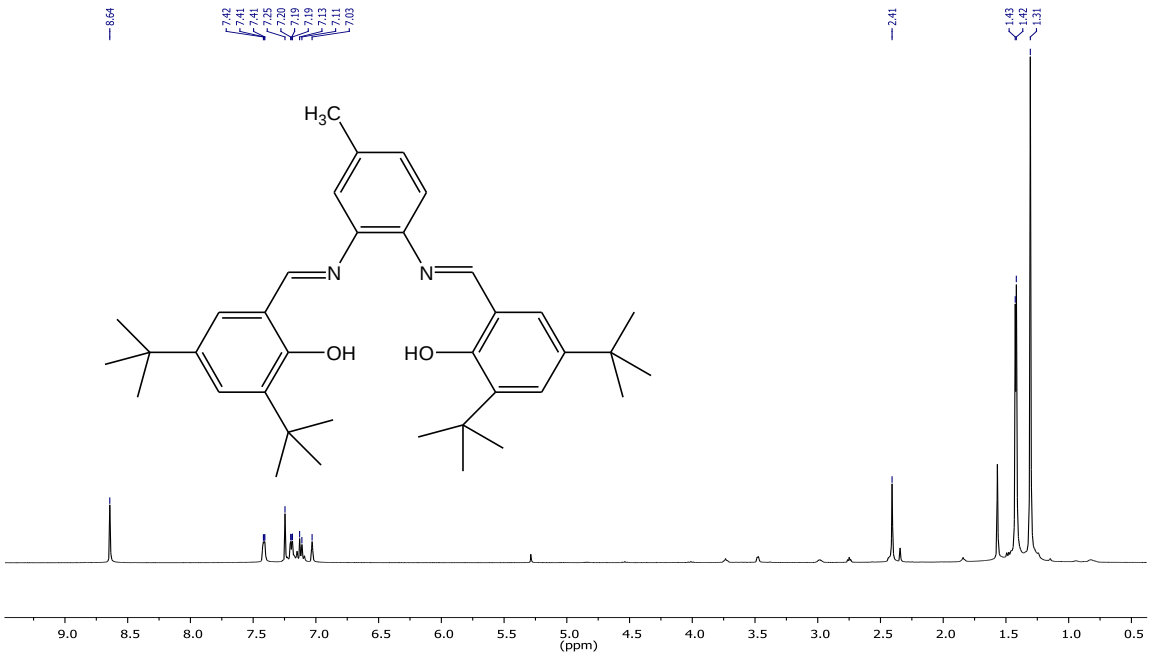

Figure A3: ^{1}H NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-methyl-o-phenylenediamine (salophen-CH_3)

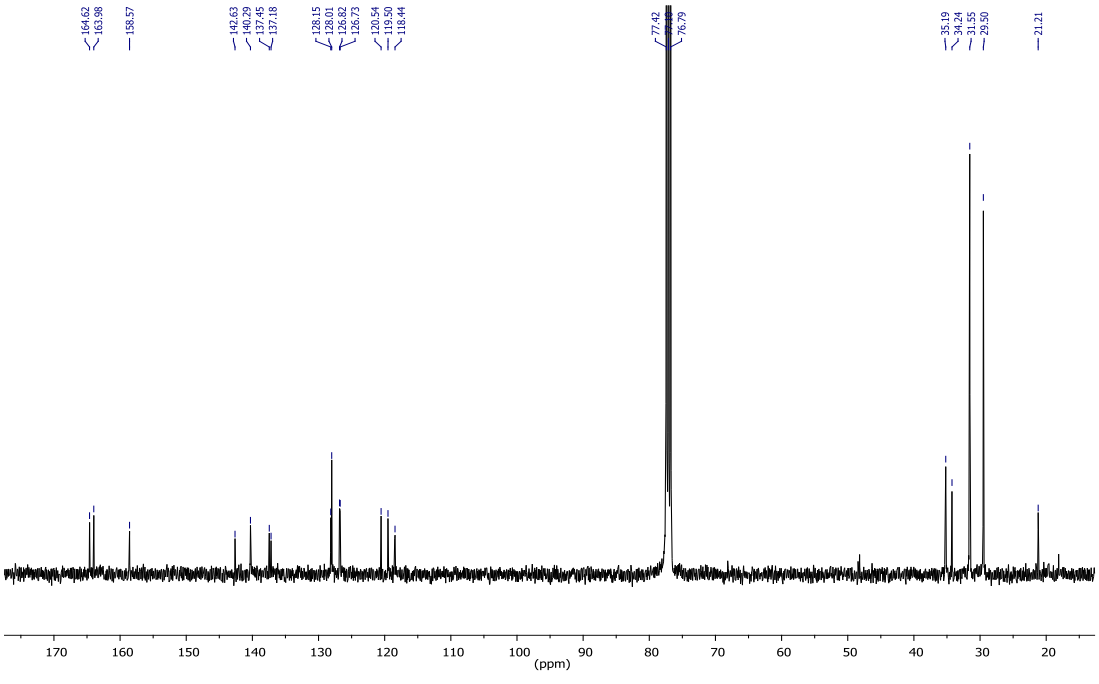

Figure A4: ^{13}C NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-methyl-o-phenylenediamine (salophen-CH_3)

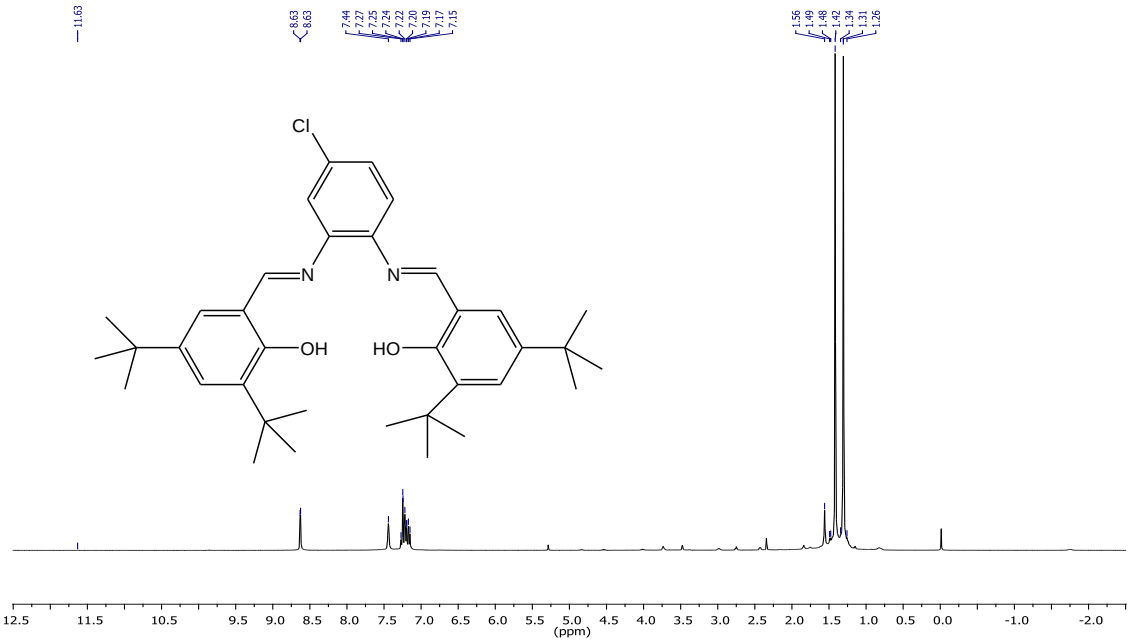

Figure A5: ^{1}H NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-chloro-o-phenylenediamine (salophen-Cl)

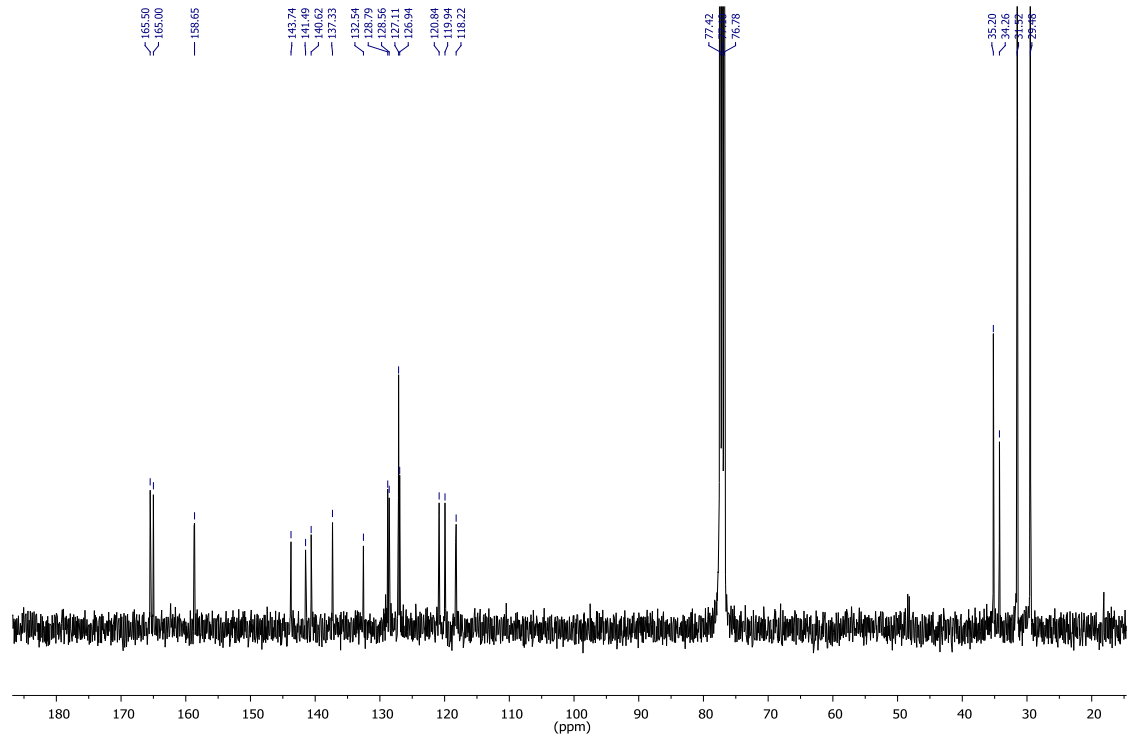

Figure A6: ^{13}C NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4-chloro-o-phenylenediamine (salophen-Cl)

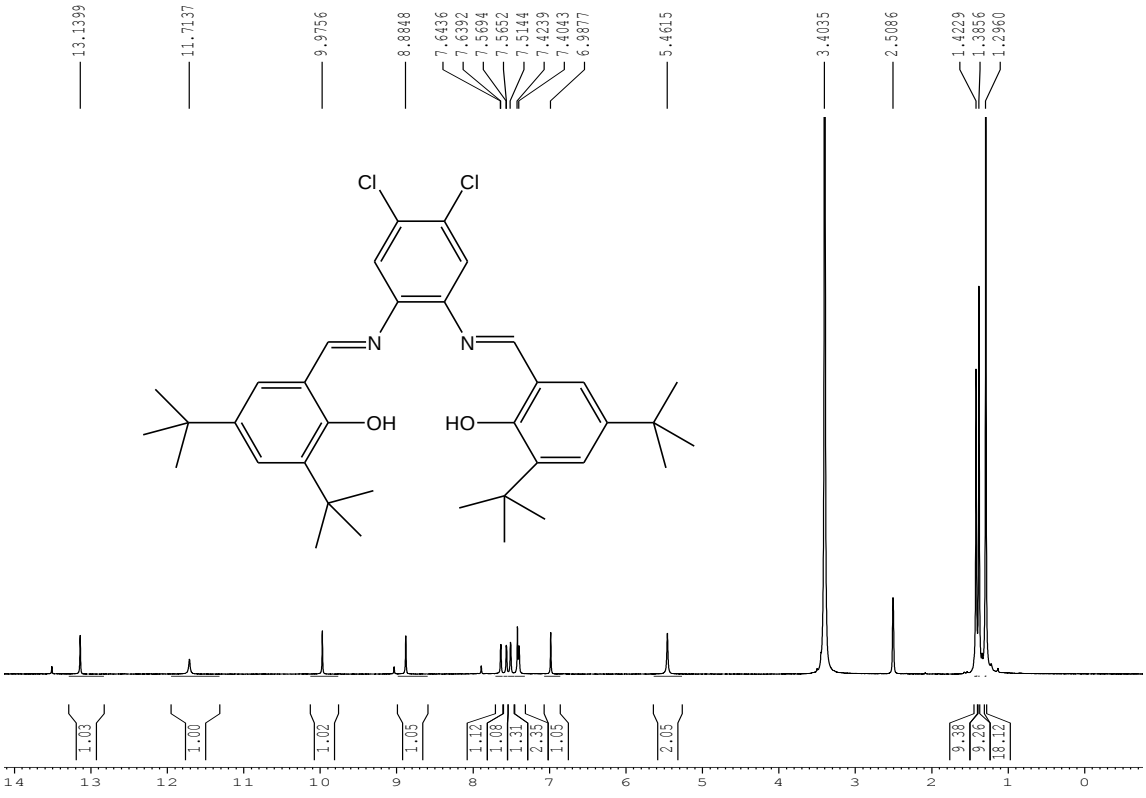

Figure A7: ^{1}H NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-o-phenylenediamine (salophen-Cl_2)

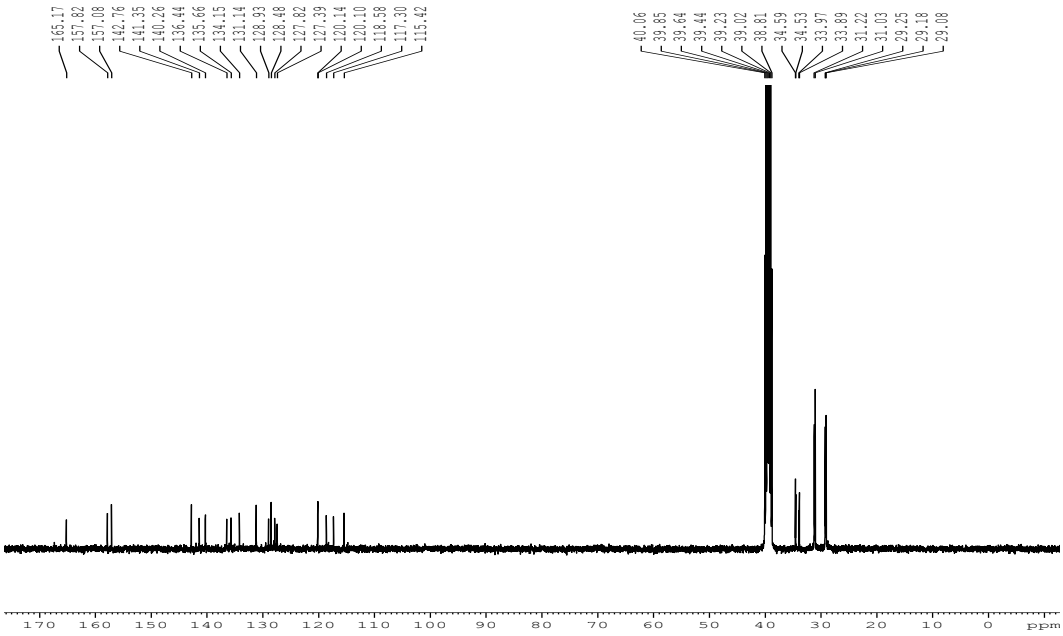

Figure A8: ^{13}C NMR of N,N′-bis-(3,5-di-tert-butylsalicylidene)-4,5-dichloro-o-phenylenediamine (salophen-Cl_2)

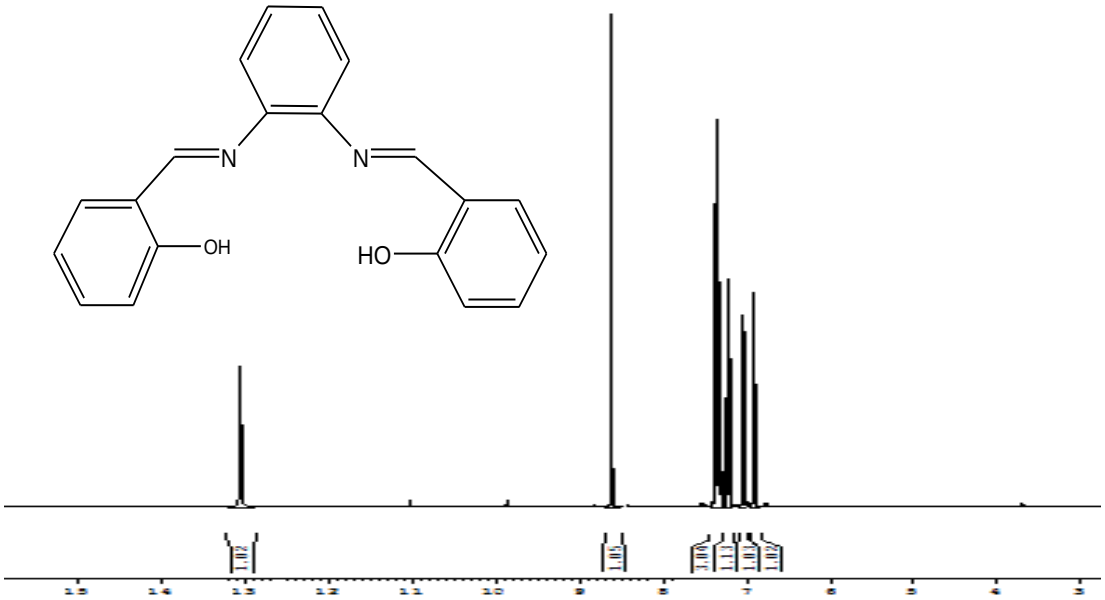

Figure A9: ^{1}H NMR of N,N′-bis-(salicylaldehyde)-o-phenylenediamine (salen)

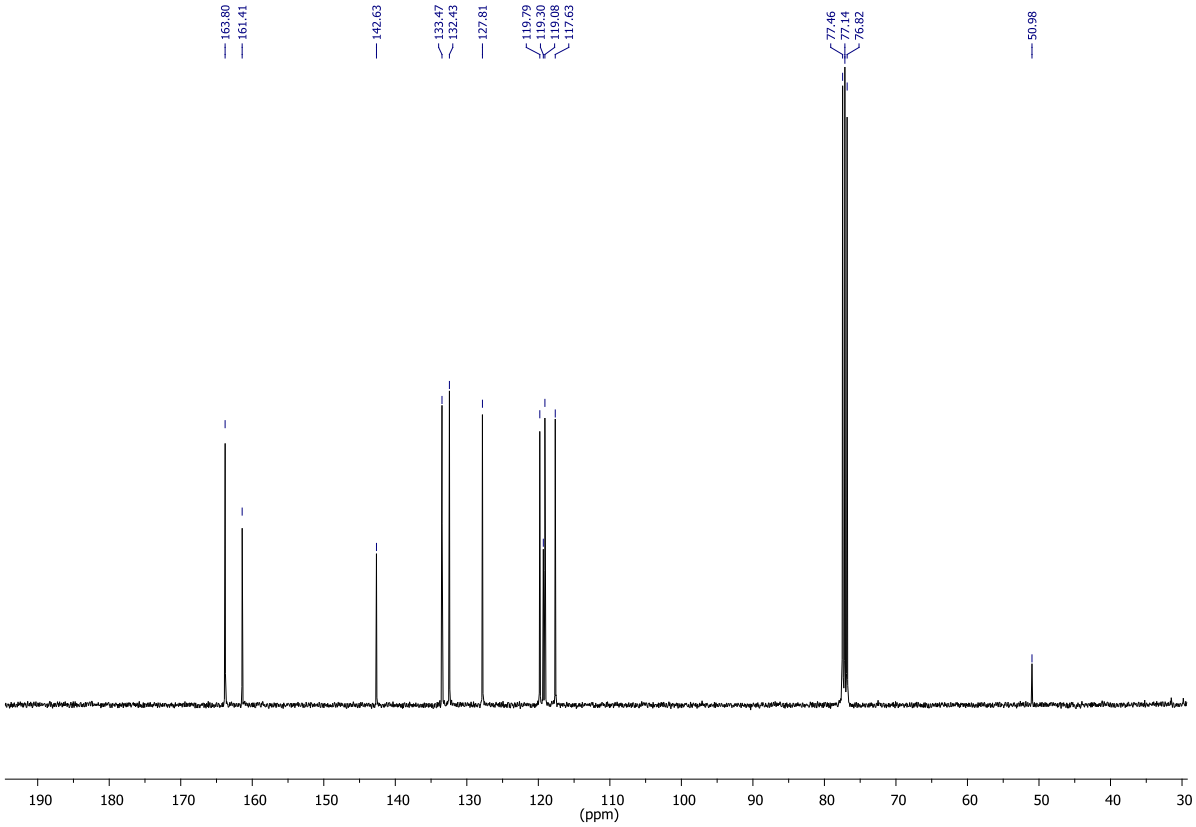

Figure A10: ^{13}C NMR of N,N′-bis-(salicylaldehyde)-o-phenylenediamine (salen)

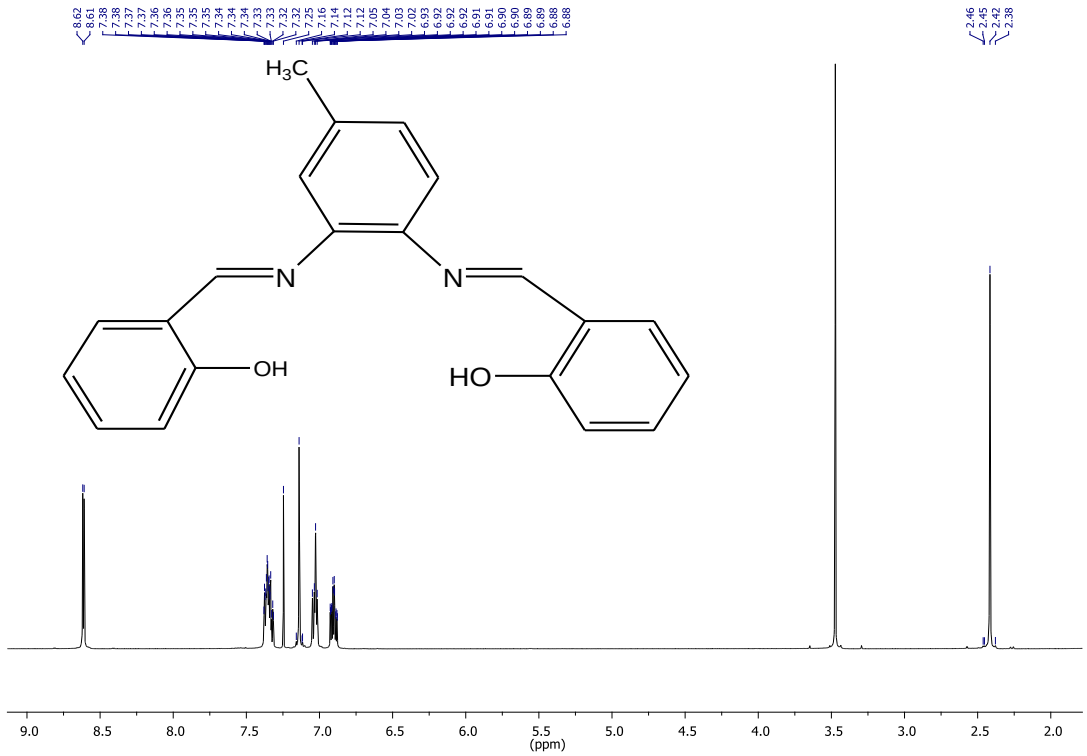

Figure A11: ^{1}H NMR of N,N′-bis-(salicylaldehyde)-4-methyl-o-phenylenediamine (salen-CH_3)

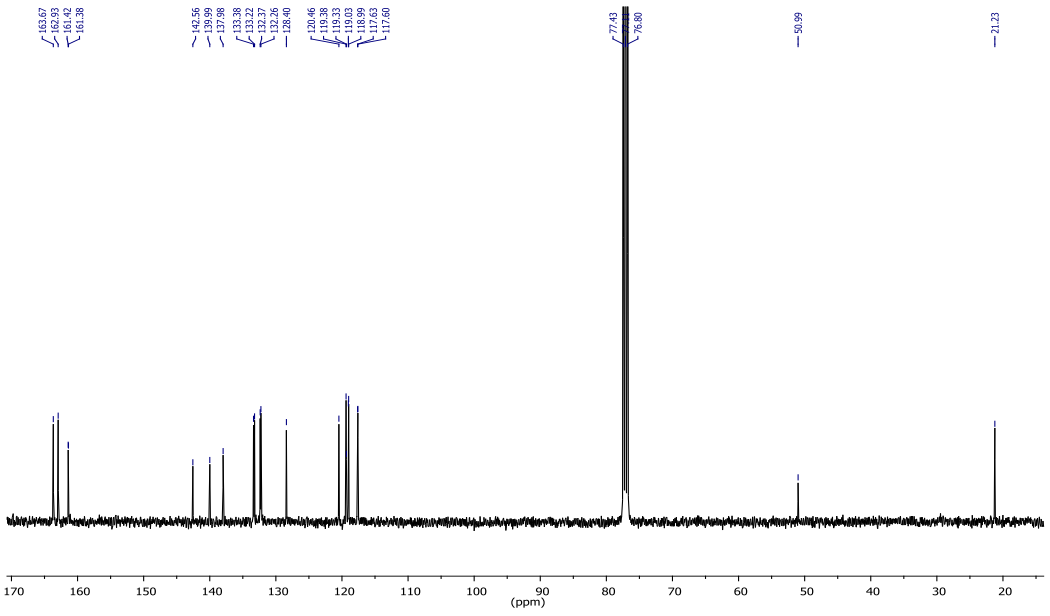

Figure A12: ^{13}C NMR of N,N′-bis-(salicylaldehyde)-4-methyl-o-phenylenediamine (salen-CH_3)

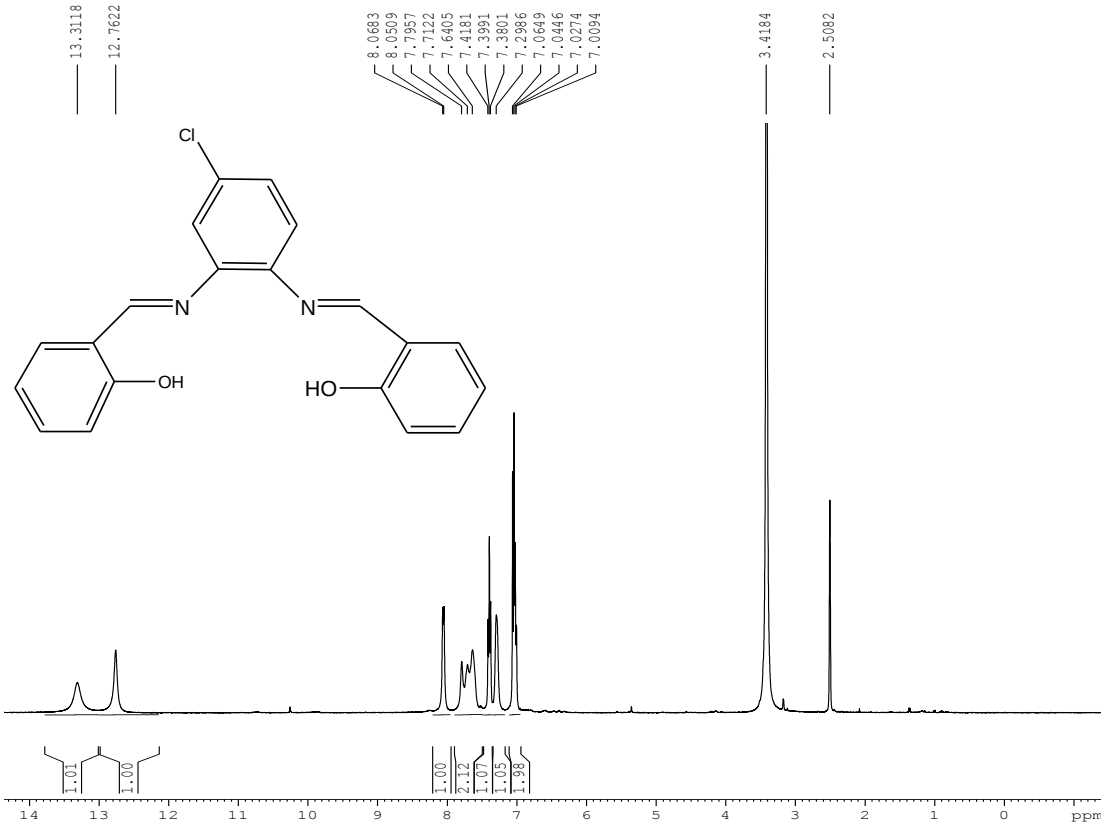

Figure A13: ^{1}H NMR of N,N′-bis-(salicylaldehyde)-4-chloro-o-phenylenediamine (salen-Cl)

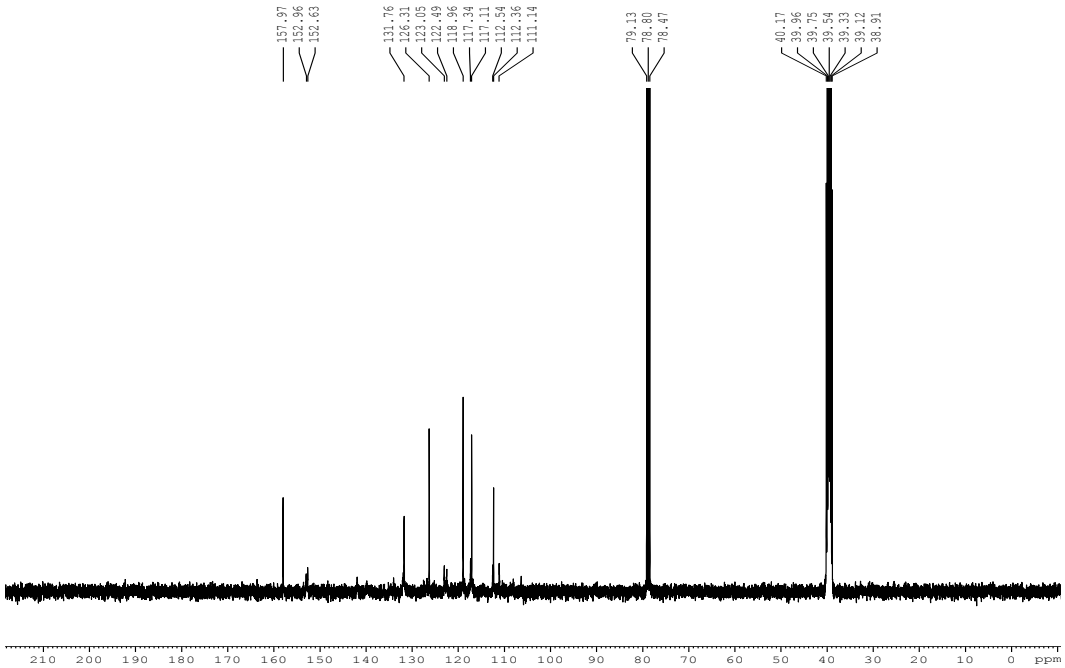

Figure A14: ^{13}C NMR of N,N′-bis-(salicylaldehyde)-4-chloro-o-phenylenediamine (salen-Cl)

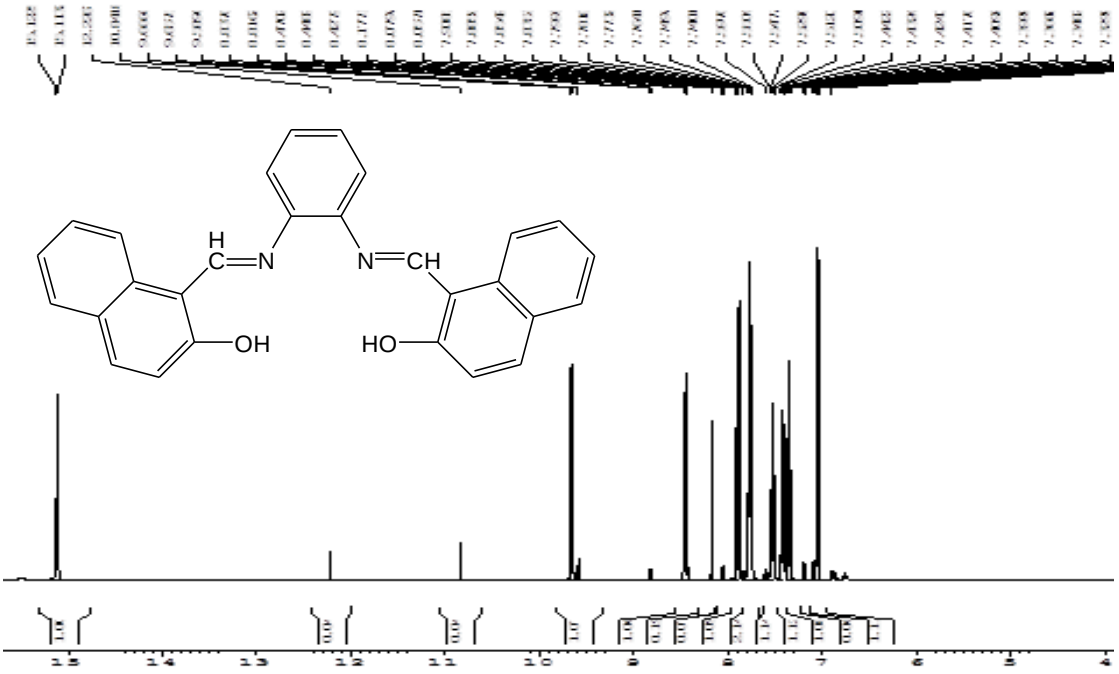

Figure A15: ^{1}H NMR of N,N′-bis-(2-hydroxy-1-naphthyldehyde)-o-phenyleneldiamine

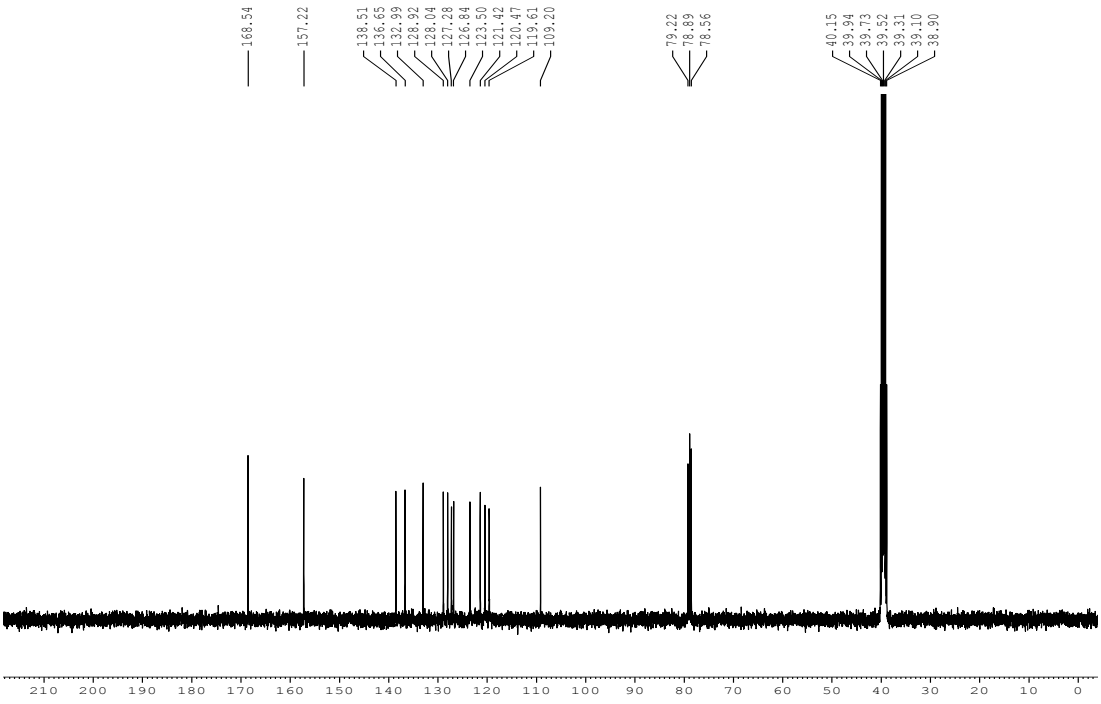

Figure A16: ^{13}C NMR of N,N′-bis-(2-hydroxy-1-naphthyldehyde)-o-phenyleneldiamine

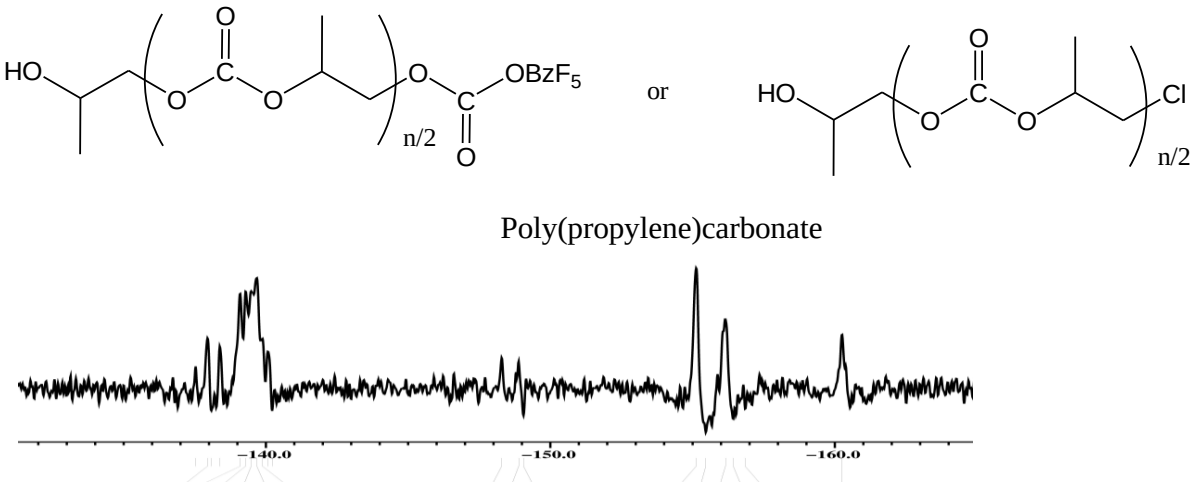

Figure A17: ^{19}F NMR of Poly(propylene carbonate) [resonance around δ -140, 148, 155, 157, 160 ppm]

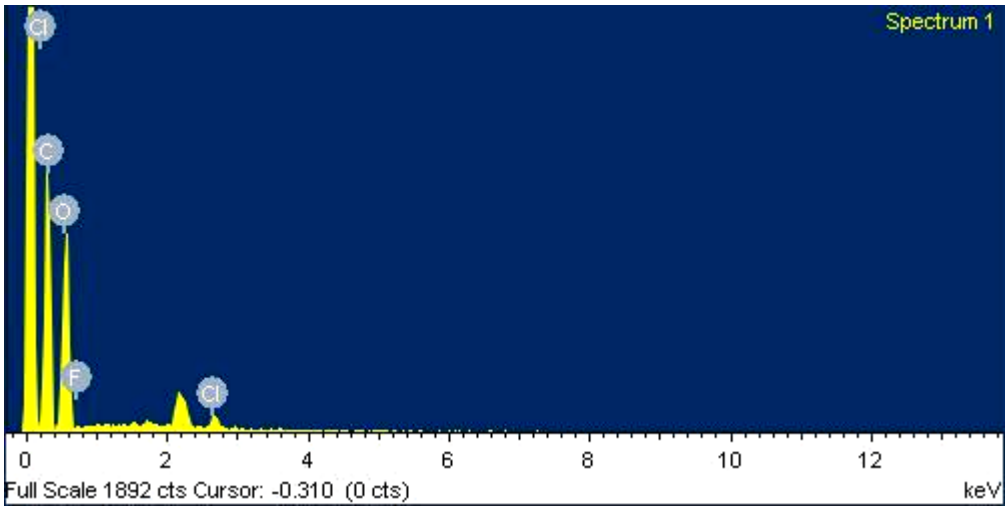

Figure A18: EDX analysis of Poly(propylene carbonate) showing the presence of fluorine and chlorine (i.e. nucleophilic groups of catalyst and co-catalysts)