博士論文

Study on Copolymerization Reactions of Epoxide Focusing on the Oxidation State of Metal-Salen Catalysts

（金属-サレン型触媒の酸化状態に注目した、エポキシドの共重合反応に関する研究）

東京大学大学院　工学系研究科

化学生命工学専攻　野崎研究室

畑澤　匡広

Table of Contents

List of Abbreviations

Ac	**acetyl**
Ar	**aryl**
ata	**atactic**
atm	**atmosphere(s)**
BDI	**β-diiminate**
BPA	**2,2-bis(4-hydroxyphenyl)propane (bisphenol A)**
Bu	**butyl**
CCHC	**cyclic(cyclohexene carbonate)**
CHO	**cyclohexene oxide**
CPC	**cyclic propylene carbonate**
d	**doublet(spectral)**
DFT	**density functional theory**
DMAP	**4-dimethylaminopyridine**
equiv.	**equivalent**
ESI	**electrospray ionization**
Et	**ethyl**
FG	**functional group**
G	**Gibbs free energy**
***i*-Pr**	**isopropyl**
iso	**isotactic**
LMCT	**ligand metal charge transfer**
m	**meso**

M_n	**number average molecular weight**
M_w	**weight average molecular weight**
PA	**phthalic anhydride**
PC	**polycarbonate**
PCHC	**poly(cyclohexene carbonate)**
PCHO	**poly(cyclohexene oxide)**
PEC	**polyethylenecarbonate**
PO	**propylene oxide**
PPC	**poly(propylene carbonate)**
PPN	**Bis(triphenylphosphoranylidene)ammonium**
PPO	**poly(propylene oxide)**
psi	**pound per square inch**
ROCOP	**ring-opening copolymerization**
s	**singlet(spectral)**
Salan	**N,N'-bis(o-hydroxybenzyl)-1,2-diaminoethane**
Salcy	**N,N'-bissalicylidene-1,2-cyclohexanediamine**
Salen	**N,N'-bissalicylidene ethylenediamine**
Salphen	**N,N'-bissalicylidene-1,2-phenylenediamine**
t	**triplet(spectral)**
TPP	**tetraphenylporphyrin**

Chapter 1
Introduction

1-1 Production and reactivity of epoxide

1-1-1 Production and availability of epoxide

Epoxides, also known as “oxiranes”, are defined as the following structure (Figure 1-1).

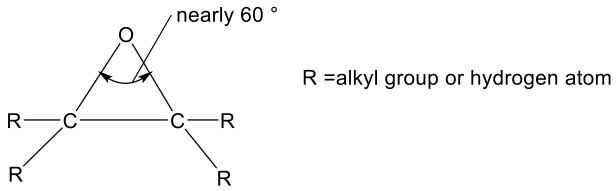
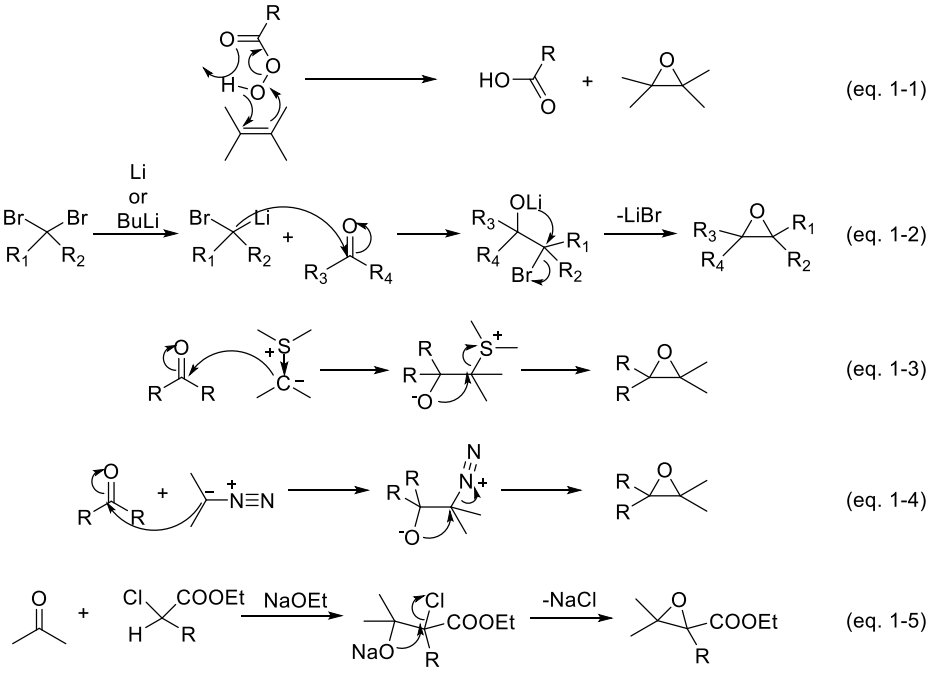


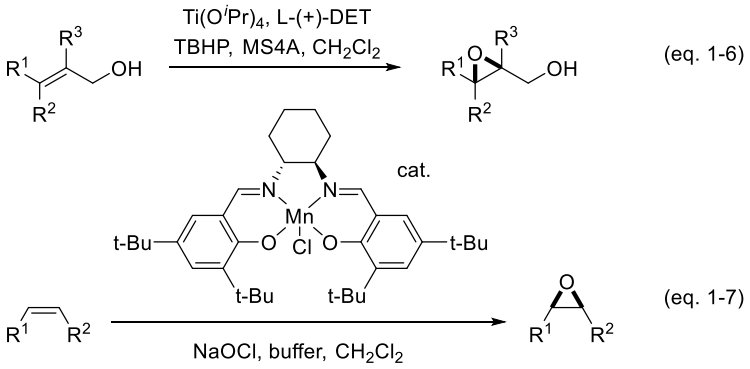
Figure 1-1: Structure of epoxide.

The bond angles of C–O–C and O–C–C are nearly 60 °.[1] These quite small bond angles make epoxides very reactive with various kinds of nucleophiles in the presence of appropriate catalysts (See the section 1-1-2). Because of this high reactivity, many researchers have extensively investigated the epoxide syntheses and their transformations. In this section, I briefly review general synthetic methods and some industrial processes to synthesize the epoxides. In laboratory scale, direct oxidation of alkene by peroxide (eq. 1-1),[2] reaction of carbonyl compound with halo-organometallic compound (eq. 1-2), sulfur ylide (eq. 1-3), diazo alkane (eq. 1-4) and α-halo ester (eq. 1-5)[3] have been known as the most common methods (Scheme 1-1).



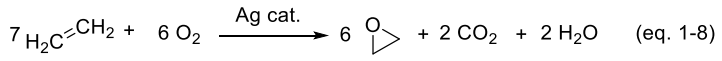
Scheme 1-1: Representative examples for epoxide formations.

Enantioselective syntheses of epoxides have also been reported; for example, Sharpless-Katsuki epoxidation (eq. 1-6)[4] and Jacobsen-Katsuki (eq. 1-7)[5] epoxidation have been known as one of the most common methods to synthesize epoxides, enantioselectively (Scheme 1-2).



Scheme 1-2: Examples of enantioselective epoxide formations.

The most common epoxides used industrially have been ethylene oxide and propylene oxide. In particular, production amount of ethylene oxide is about 20 million tons per year in the world.[6] Recently, ethylene oxide have been synthesized via a direct oxidation of ethylene by oxygen with a heterogeneous silver catalyst. The oxidation reaction is shown in below eq. 1-8.[7]

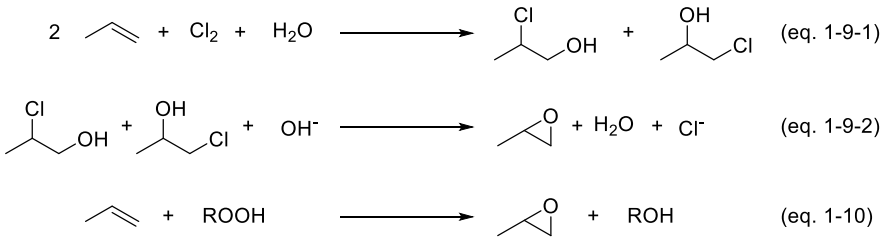


Scheme 1-3: Industrial process for the production of ethylene oxide.

It is noted that only water and carbon dioxide are produced as side products with efficiency up to 85.7%. Union Carbide has first developed this process, whose process were modified by Scientific Design and Shell. However, this process has not been able to be applied for the production of propylene oxide because the allylic C–H bond of propylene is more reactive than the C=C bond under reaction conditions.

Recently, propylene oxide has been synthesized by two different processes. One is the propylenechlorohydrin formation and the following dehydrochlorination (Scheme 1-4, eq. 1-9-1

and 1-9-2). The other is the oxidation of propylene by using peroxide (eq. 1-10). In 2009, Dow and BASF have started up a propylene oxide production plant using hydrogen peroxide as the oxidant.[8] It is noted that only water is produced as a side product.

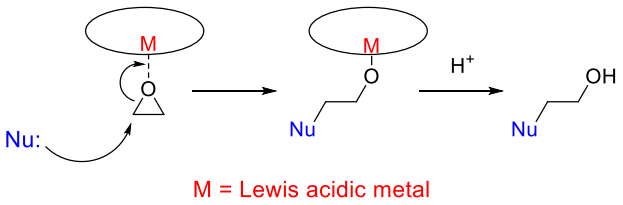


Scheme 1-4: Industrial processes for the synthesis of propylene.

Examples of other industrially important epoxides are epichlorohydrin, 1,2-epoxydodecane, mono- and di-epoxidized soybean oil, and styrene oxide. Those are mainly used for the epoxide-resin synthesis, plasticizers, and stabilizers for plastic materials.[9]

1-1-2 Selective ring-opening reaction mediated by Lewis acidic metal catalysts

Nucleophiles can attack the epoxide in the presence of appropriate Brønsted or Lewis acid catalysts such as boron trifluoride and metal complexes by the mechanism shown in Scheme 1-5.[9,10] Oxygen atom is coordinated to the Lewis acid center. Due to this coordination the carbon atom next to the oxygen become more electrophilic making the nucleophile possible to attack the activated carbon center effectively. The ligand of Lewis acidic catalyst controls the position of the nucleophilic attack.



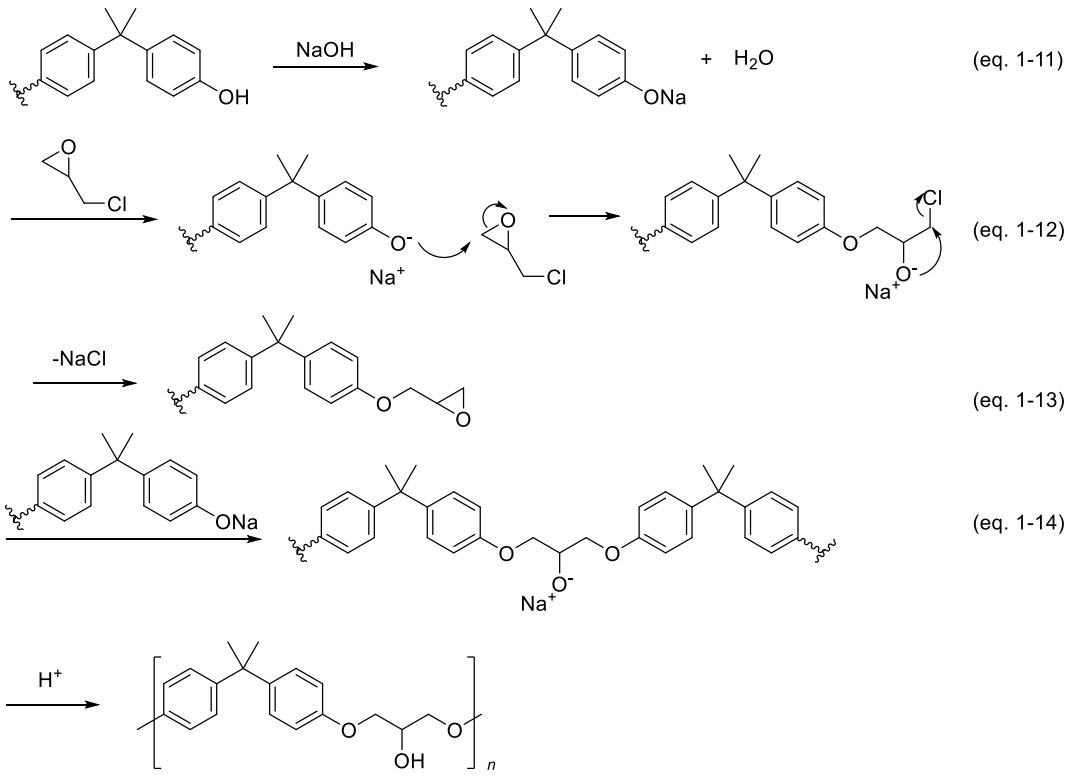
Scheme 1-5: Reaction mechanism of Lewis-acidic metal mediated ring-opening reaction of epoxide.

Actually, the above ring opening reaction has often been used for syntheses of complex molecules[11] and various kinds of metal precursors with chiral ligands have been used. For example,

lanthanoid metals[12,13], Al[14], Ti[15,16], Zr[17], Cr[18-20], Co[21-23], Rh[24], Zn[25,26], Si[27,28], and Ga[29] have been used extensively with substituted binaphthols, chiral salens, chiral diols and chiral aminoalcohols as the Lewis-acidic metals and chiral ligands respectively. In particular, metal–salen catalysts and their derivatives have used for this reaction because of its high activity, enantioselectivity, and wide substrate scope.[30]

1-1-3 Condensation polymerization for the synthesis of epoxy resin

By using the ring-opening reaction of epoxide, one can carry out condensation polymerization of diols with epoxides. For example, a raw material for epoxy resins can be synthesized from bisphenol A and epichlorohydrin as shown in Scheme 1-6.



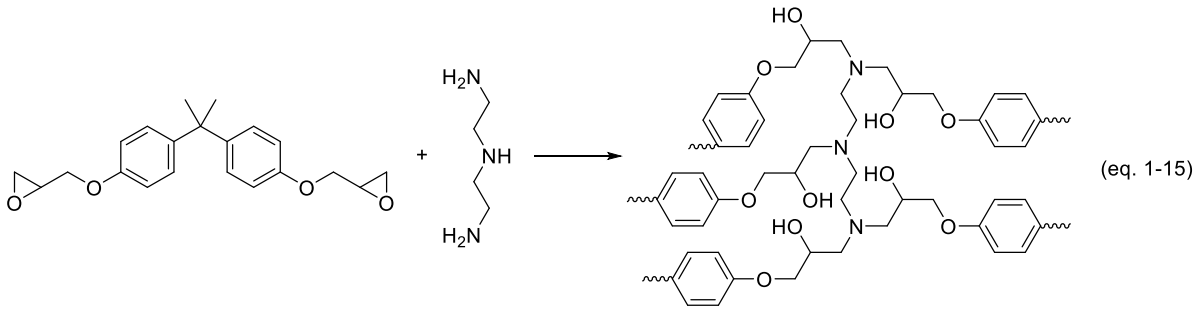
Scheme 1-6: Reaction mechanism of epoxy resin formation.

Reactions start from the exchange of the phenolic hydrogen with Na^+ (eq. 1-11). Phenolate group undergoes the ring-opening reaction with epichlorohydrin (eq. 1-12), followed by the ring

closure via the nucleophilic substitution of chloride by the alkoxide (eq. 1-13). The resulting epoxide can be attacked by another phenolate group (eq. 1-14). By repeating these steps, a simple linear polymer of bisphenol A and epichlorohydrin. This linear polymer is called “liquid epoxy resins”. Depending on the degree of polymerization, viscosity and softening temperature change dramatically.

In order to improve chemical and heat resistivity of the raw epoxy resin with, the linear epoxy resin is treated with suitable curatives, mostly diamines or triamines, to form three-dimensional cross-linked thermoset structures.

When catalytic amount of sodium hydroxide was used for the reaction in Scheme 1-6, we can obtain the product of eq. 1-13, which can further react with a hardener such as diethylenetriamine to form a network polymer (eq. 1-15 in Scheme 1-7). The network compound has been used as the solid epoxy resin. The strength of material depends on the feed ratio of monomer/hardener. Various solid epoxy resins have been produced in a industrial scale in different combinations of monomers and hardners.



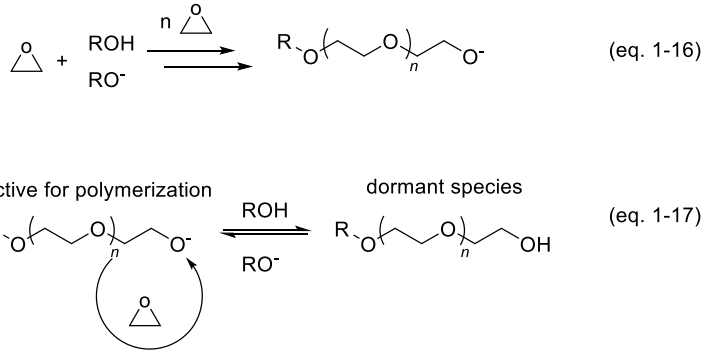
Scheme 1-7: Epoxy resin network formation by a triamine hardener.

1-1-4 Step-grow ring-opening polymerization of epoxide and properties of poly(epoxide)s

In addition to the condensation polymerization, epoxide can also be polymerized via step-grow ring-opening polymerization. In this polymerization, it is possible to control the polymerization degree and microstructure. There are three kinds of step-grow polymerization: namely, anionic polymerization, cationic polymerization, and coordination polymerization. Here I briefly introduce the anionic and cationic polymerization of epoxides, properties of the

resulting polymers and their application. Coordination polymerization of epoxide will be discussed in the next section.

Polyether have generally been synthesized by homopolymerization of epoxide. Among them, PEO and PPO have been highly important as industrial products. Anionic polymerization of ethylene oxide was reported for the first time by Wurtz and co-workers in 1863 by using alkali metal hydroxide.[31] Since then, various kinds of epoxide polymerizations have been reported by anionic polymerization. In 1929, Staudinger and Schweitzer reported relationship between the viscosity of PEO and its molecular weight. Already in 1930s, the polyethylene oxide was produced in an industrial scale and commercialized.[32] The process was almost the same as the current one. That is, ethylene oxide was mixed with a base catalyst and water or oligomer of ethylene oxide as an initiator. Molecular weight was controlled by the ratio of ethylene oxide/initiator. In 1940, Flory suggested the mechanism of base-initiated polymerization of the ethylene oxide.[33] He assumed that the molecular weight distribution of PEO given by living polymerization obeys a Poisson-type distribution. Reaction mechanism is shown in Scheme 1-8.

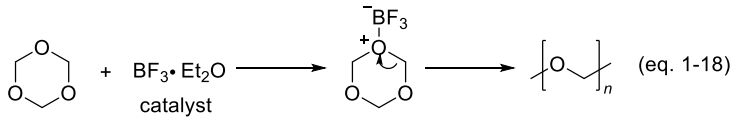


Scheme 1-8: Anionic polymerization of ethylene oxide.

After the ring-opening reaction initiated by the nucleophilic attack of alkoxide to the epoxide, the resulting alkoxide terminal undergoes the continuous ring-opening reaction (eq. 1-16). In the presence of an appropriate amount of protic solvent, alkoxide terminal shows the protonation-deprotonation equilibrium shown in eq. 1-17. A protonated terminal can act as a dormant species and the deprotonated one can act as an active species for this polymerization reaction.

When the ratio of this active/dormant species is appropriate, living anionic polymerization of epoxide proceeds. Recently, this very classical anionic polymerization method is still used as the major method to synthesize PEO or PPO. To achieve the highly-controlled polymerization, ultimately dehydrated condition is required.

Cationic ring-opening polymerization of cyclic ether has played an important role in an industrial process of many important polyethers. For example, cationic polymerization of 1,3,5-trioxane can produce poly(oxomethylene) (eq. 1-18 in Scheme 1-9).[34]



Scheme 1-9: Cationic polymerization of trioxane to produce poly(oxomethylene).

However, the cationic polymerization is rarely applied to polymerization of epoxide such as ethylene oxide and propylene oxide because cyclic ethers are produced as side products inevitablly.[35,36]

PEG or PEO has been known as a standard biocompatible polymer often employed for pharmaceutical, cosmetic, and medical applications. Due to its water solubility and controllable viscosity, they have been used for a tremendous number of materials.[37,38] Commonly, the polymer from ethylene oxide with higher molecular weight is called PEO and one with lower molecular weight, normally below 30 000 g/mol, is called PEG. PEG-modified polymers, called PEGylated polymers, have also played important roles to improve water soluble or biocompatible properties.[39-41] Syntheses of PEGylated polymers [42,43] and the PEO with very high molecular weight[44] have been investigated in detail and reviewed in reference.

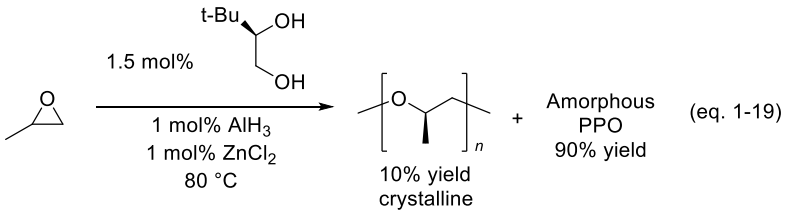
PPO, often designated as PPG for lower molecular weights, has been synthesized by the ring-opening reaction of propylene oxide. The product is water-insoluble solid that has very low glass transition temperature (ca. -70 °C).[45] PPO and PPG have been used as the lubricants, rheology modifiers, softeners and nonionic surfactants.[32]

Other polyethers such as poly butylene oxide (PBO) have been used as surface coating agent and additives for other polymers. Their high hydrophobicity is very useful as a coating agent for water unstable polymer such as polyurethane.

1-2 Metal-mediated homopolymerization of epoxide for the synthesis of polyethers

1-2-1 Monometallic catalysts for controlled ring-opening reaction

Compared with anionic polymerization, smaller numbers of investigations have been carried out for metal-mediated ring-opening polymerization. For the stereo- and enantioselective polymerization and copolymerization of epoxides, metal catalysts have been used to take advantage of their molecular weight controllability and high enantio- and stereoselectivity.[46,32] In 1949, Pruitt and Baggett in Dow Chemical Co. found the homopolymerization of propylene oxide by using iron(III)chloride as a catalyst.[47] In 1956, Natta and Price showed first example of partially *iso*-selective polymerization of epoxide.[48,49] In the early stage investigation, heterogeneous catalysts such as trialkylaluminum with H_2O and dialkyl zinc with H_2O have commonly been employed. These catalysts have not shown high regio regularity. When a chiral alcohol or a chiral amino alcohol was used as the initiator, highly *meso*-rich PPO has been partially obtained as crystalline material (eq. 1-19 in Scheme 1-10).[50]



Scheme 1-10: Isoselective PPO production by using a chiral alcohol initiator.

Various kinds of Lewis acidic metals with tri- or tetradentate planner ligand have often shown activity for the controlled epoxide polymerization. Al, Zn and Co have been the representative examples of the metal species and salen, porphyrins and chiral aminoalcohols have been the commonly used ligands. Representative complexes are shown in below Figure 1-2.

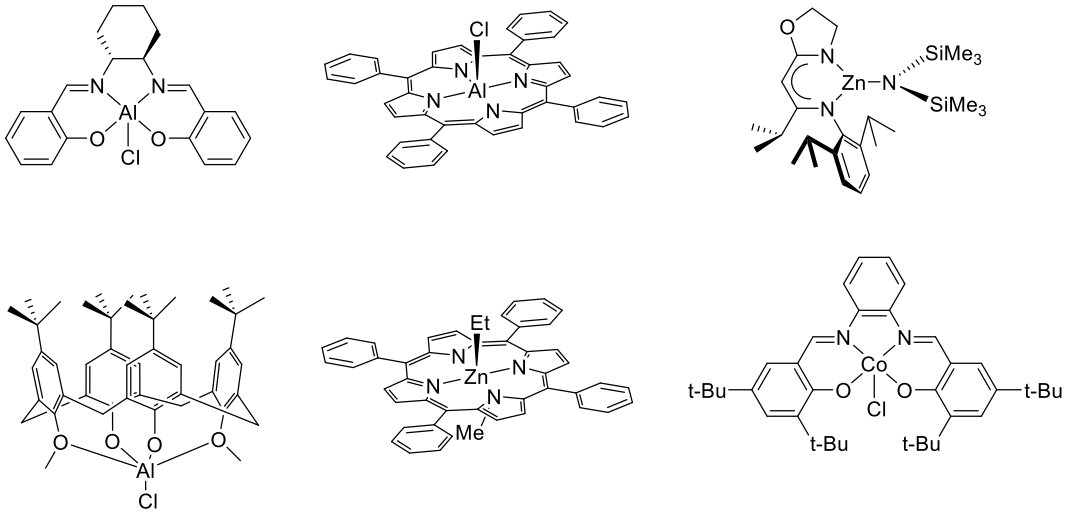
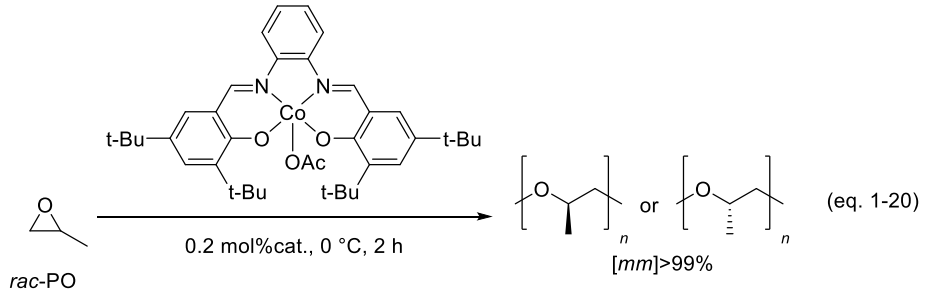


Figure 1-2: Representative catalysts for the stereocontrolled epoxide polymerization.[50]

These complexes have shown higher tacticity control than anionic polymerization of epoxide.

1-2-2 Bimetallic catalysts for controlled ring-opening reaction

Ajiro, Coates, and their co-workers have reported the highly *iso*-selective homopolymerization of *rac*-propylene oxide by using Co(III)-Salphen-OAc complex (eq. 1-20 in Scheme 1-11).[51,52]



Scheme 1-11: Isotactic polymerization of *rac*-propylene oxide by Co(III)-salphen-OAc.

This complex has not had the stereogenic center, but *mm* triad ratio was higher than 99%. To know the origin of this high tacticity, X-ray analysis of methoxy coordinated Co(III)-Salphen complex have been carried out. This complex has been a model compound of epoxide coordinated Co(III)-Salphen complex (Figure 1-3).

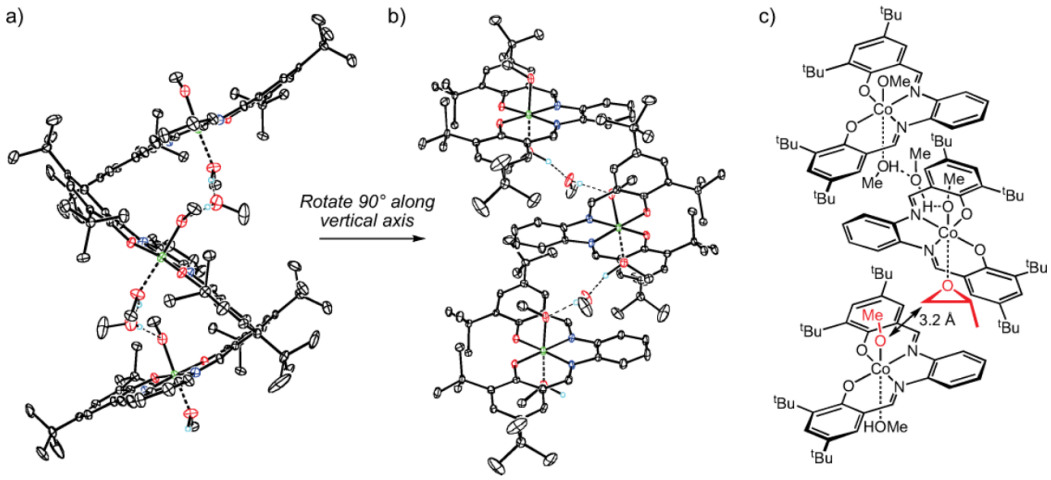


Figure 1-3: Crystal structure of Co(III)-salphen-OMe

It has been found that the oxygen atom of a methoxy group was coordinated by two cobalt centers and this coordination structure was infinitely accumulated. From this result, bimetallic ring opening mechanism have been strongly suggested (Figure 1-3, (c)). Therefore, bimetallic Co-Salen complex have attracted much attention. Since 2008, the same authors reported highly active and enantioselective bimetallic Co-Salcy complexes shown in Figure 1-4. Two Co-salen complexes were tethered by a biphenyl or a binaphthyl group.

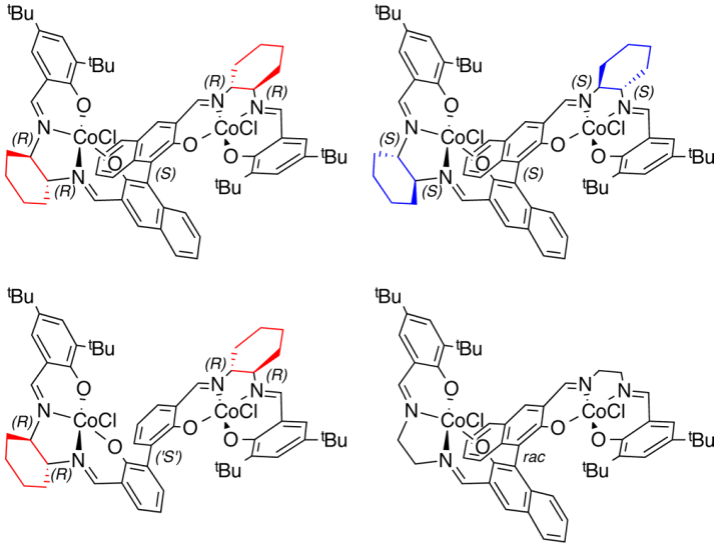


Figure 1-4 Bimetallic Co-Salen complexes synthesized by Coates and co-workers.

For various kinds of terminal epoxides, these bimetallic complexes have shown high enantioselectivity (k_{rel} value is higher than 200), high regioselectivity (>98% *mm* ratio), and high activity.[53-55] A bimetallic mechanism have also been strongly supported by DFT calculations.[55]

1-3 Copolymerization of epoxide with CO_2 for the synthesis of aliphatic polycarbonate

1-3-1 Background of aliphatic polycarbonate

Syntheses and properties of aromatic polycarbonate

Although aliphatic polycarbonate is the major topic in this thesis, I would like to overview the syntheses and properties of aromatic polycarbonates since they have been more commonly used in society. In 1898, the first aromatic polycarbonate was synthesized by Einhorn by the polycondensation of phosgene with resorcinol or hydroquinone. Products, aromatic polycarbonates have usually shown high melting temperature (190 °C for resorcinol, 280 °C for hydroquinone).

In 1953, Fox at General Electric Company discovered 2,2-bis(4-hydroxyphenyl)propane (bisphenol A) polycarbonate (Figure 1-5).

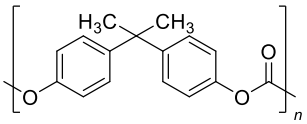


Figure 1-5: Chemical structure of BPA-PC.

This polycarbonate had optical transparency, high toughness, and heat distortion resistance. In 1958, Farbenfabriken Bayer started to produce BPA-PC in industrial scale. Nowadays, BPA-PC have been known as the economically most important polycarbonate.

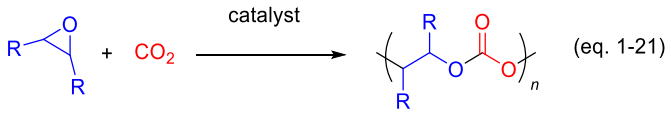
Synthesis and properties of aliphatic polycarbonate

The first aliphatic polycarbonates have been reported by Carothers. He has obtained products by the reaction of diethyl carbonate with glycols. Products have had the intermediate melting temperature (lower than 100 °C) and transparency between PMMA and BPA-PC.[56] Most primitive pathway for the synthesis of aliphatic polycarbonate have been the polycondensation reaction of diols with carbonate or phosgene. In order to avoid the usage of toxic phosgene, some other methods have been developed so far such as transesterification of carbonates[57], ring-opening polymerization of cyclic carbonate,[58] and copolymerization of epoxide with CO_2. Among them, direct transformation of CO_2 and epoxide to polycarbonate has been extensively studied by many researchers as one of the most promising utilization of CO_2. Recently, Sugimoto, Tomishige, and their co-workers have reported the condensation copolymerization of CO_2 with diols as an alternative method to produce the aliphatic polycarbonates.[59]

Copolymerization of epoxide with CO_2

Copolymerization of epoxide with CO_2 is the reaction that can produce aliphatic polycarbonate from the epoxide and CO_2 (eq. 1-21 in Scheme 1-12). The resulting polymer contains significant amount of CO_2 as the building block, namely up to equimolar amount to the

epoxide. A unique feature of the copolymer is its easy degradation at very low temperatures. When most commonly synthesized aliphatic polycarbonates, PEC and PPC undergo the thermal decomposition, resulting cyclic carbonates easily evaporate at the decomposition temperature of those polycarbonates. Because of these characters, this reaction has attracted many attention since its discovery in 1969.[60]



Scheme 1-12: General scheme of copolymerization of epoxide with CO_2.

For this reaction, a combination of Lewis acidic metal species with nucleophilic co-catalysts have been known as an effective catalyst system. A proposed reaction mechanism is shown in Figure 1-6. [6162]

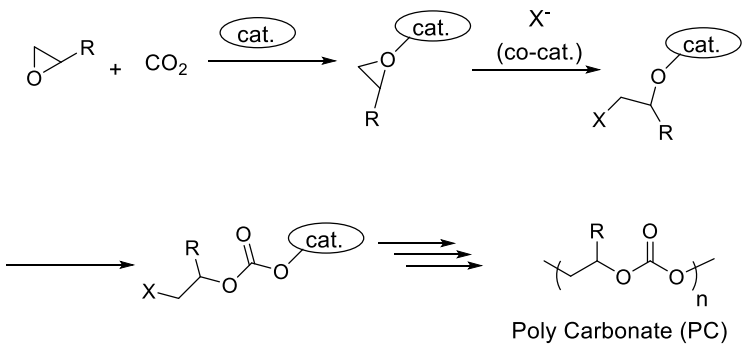


Figure 1-6: Reaction mechanism of copolymerization of epoxide with CO_2.

This reaction is started by the epoxide coordination to the Lewis acidic metal to make the carbon atom next to the oxygen electrophilic. Either the metal-coordinated or externally added nucleophilic initiators attack on the less substituted site of epoxide to induce the ring opening reaction forming a metal-alkoxide bond. After the ring-opening reaction, CO_2 insertion into metal-alkoxide bond takes place to form metal-carbonate. This carbonate terminal group undergoes the subsequent ring-opening reaction of another epoxide. The continuous alternating reaction provides aliphatic polycarbonate from epoxide and CO_2. Possible side products of this

reaction are cyclic carbonate which originates from the backbiting from the carbonate chain-end and polyether produced by the continuous ring-opening of epoxide. The production rates of these products vary depending on the catalyst.

In the next section, I introduce metal catalysts for this copolymerization.

1-3-2 Monometallic catalysts for copolymerization of epoxide with CO_2

In the early stage investigation, many kinds of heterogeneous metal species have been investigated as the catalyst. As representative examples, heterogeneous species have synthesized from $ZnEt_2$ and its derivatives. [26,60,63,64] The copolymerization activity and polycarbonate selectivity of these heterogeneous catalysts have been low. The first homogeneous catalyst was reported by Inoue and co-workers in 1986.[65] By using tetraphenyl porphyrin(TPP)-Al-Cl with $EtPh_3PBr$ combination, the first example of controlled copolymerization of epoxide with CO_2 was accomplished. The next breakthrough of homogeneous catalyst in the field was the discovery of zinc-diiminate catalysts in 1998 (Figure 1-7).[66]

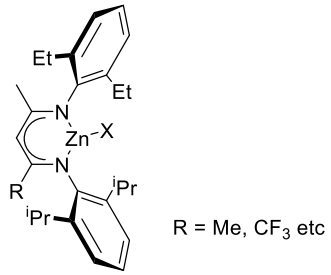


Figure 1-7: Zinc-diiminate complex

This catalyst has exhibited quite high activity for the copolymerization of epoxides with CO_2. Even at 20 °C, under 100 psi (ca. 0.7 MPa) CO_2 pressure condition, the catalyst which has CF_3 group at the R position has shown the TOF of 235 h^{-1} for the copolymerization of cyclohexene oxide. This catalyst have also been used for the copolymerization of less reactive epoxides such as limonene oxide.[67,68]

Since 2000's, many metal-Schiff bases especially salen complexes have been reported as catalysts for the copolymerization owing to its easy synthesis and modification (Figure 1-8).

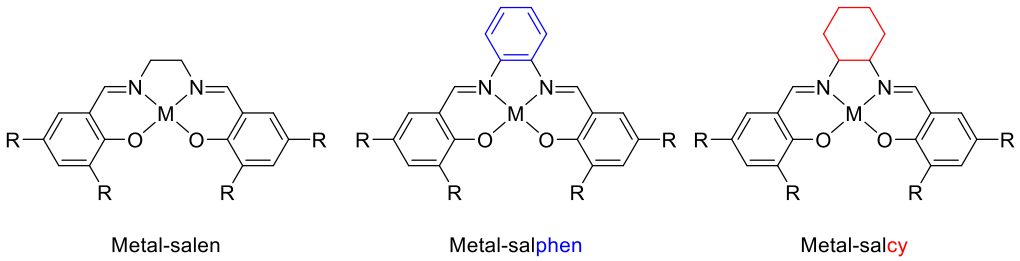


Figure 1-8: Metal-Salen complexes.

In 2001, Darensbourg and co-workers reported the CHO/CO_2 copolymerization by using a Cr(III)-Salcy-Cl complex.[69] The mechanism written in Figure 1-3 was proposed in their study. Notably, this Cr(III)-Salcy-Cl have produced cyclic carbonate predominantly when it was used for the copolymerization of PO/CO_2, although Cr(III)-Salphen-Cl have been a good catalyst for the copolymerization.[70]

In 2004, Xiao-Bing Lu found that Co(III)-salcy-DNP type complex with tetrabutylammonium chloride co-catalyst shows >99% PPC selectivity and TOF of 371 h^{-1} for the copolymerization of propylene oxide with CO_2 at 25 °C, under 4.0 MPa CO_2.[71] In 2005, Coates and co-workers investigated many kinds of Co(III)-salcy complexes which have various kinds of co-catalysts and axial ligands. And found that copolymerization of propylene oxide with CO_2 by using Co(III)-salcy with pentafluorobenzoate axial ligand and bis(phosphoranylidene)iminium chloride resulted in TOF of 630 h^{-1} for PPC and >95% PPC selectivity.[72] Nowadays, Co-salcy complex with bis(triphenylphosphine)iminium salt co-catalyst have been known as a benchmark catalyst for copolymerization of epoxide with CO_2 (Figure 1-9).

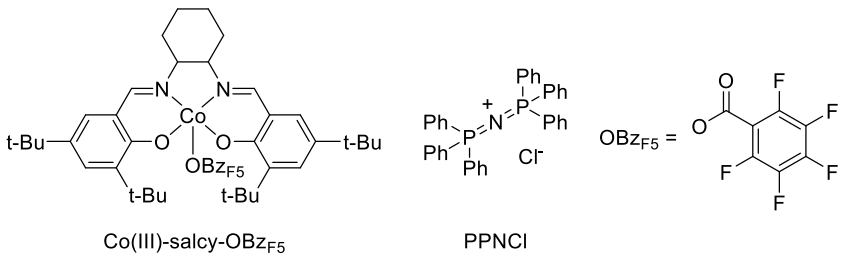


Figure 1-9: Benchmark catalyst system for copolymerization of PO/CO_2.

In 2006, Otsuka, Sugimoto, and Inoue reported that Salphen-Al-Me with tetraethylammonium acetate co-catalyst showed moderate activity and high selectivity for copolymerization of CHO/CO_2.[73]

In 2006, Nozaki and co-workers reported highly active piperidinium attached Co-Salcy complex (Figure 1-10, **a**). High PPC selectivity at high monomer conversion was attributed to the contribution of the neighboring ammonium group.[74] In 2011, the same group reported stereo-gradient propylene carbonate synthesis by using piperidinium attached Co-Salcy complex (Figure 1-10 **b**).[75]

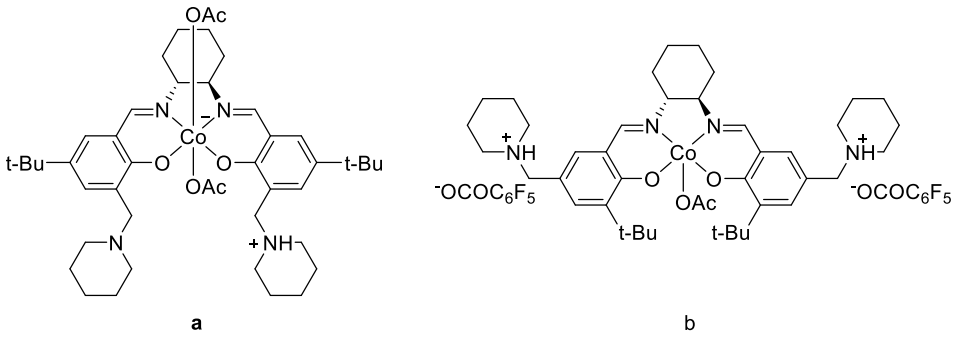


Figure 1-10: Benchmark catalyst system for copolymerization of PO/CO_2.

The ammonium arm attached Co-salen type complexes have been then further explored. In 2008, Bun-Youel Lee and co-workers reported 4 ammonium group attached Co-salen complex(Figure 1-11).[76]

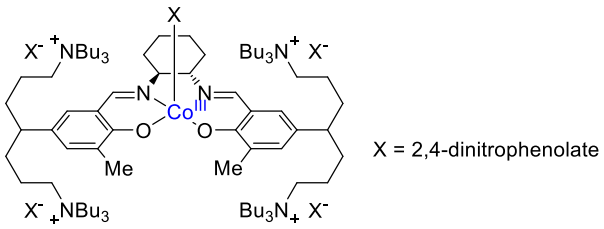


Figure 1-11: Four ammonium arms attached Co-salcy complexes.

This have shown the highest activity ever reported (TOF = 26000 h^{-1} at 80 °C) for the copolymerization of epoxide with CO_2 as a monometallic catalyst system thus far reported. For these Co(III)-salen type catalysts, partial contribution of bimetallic mechanism have been proposed in some reports.[52] In the next section, I review the recent advance of bimetallic type catalyst systems.

1-3-3 Bimetallic catalysts for copolymerization of epoxide with CO_2

Up to now, several bimetallic or multi-metallic catalyst systems have been reported for the copolymerization of epoxide with CO_2. Many researchers have predicted that the copolymerization would proceed via the concerted mechanism of the two metal species (Figure 1-12).[77]

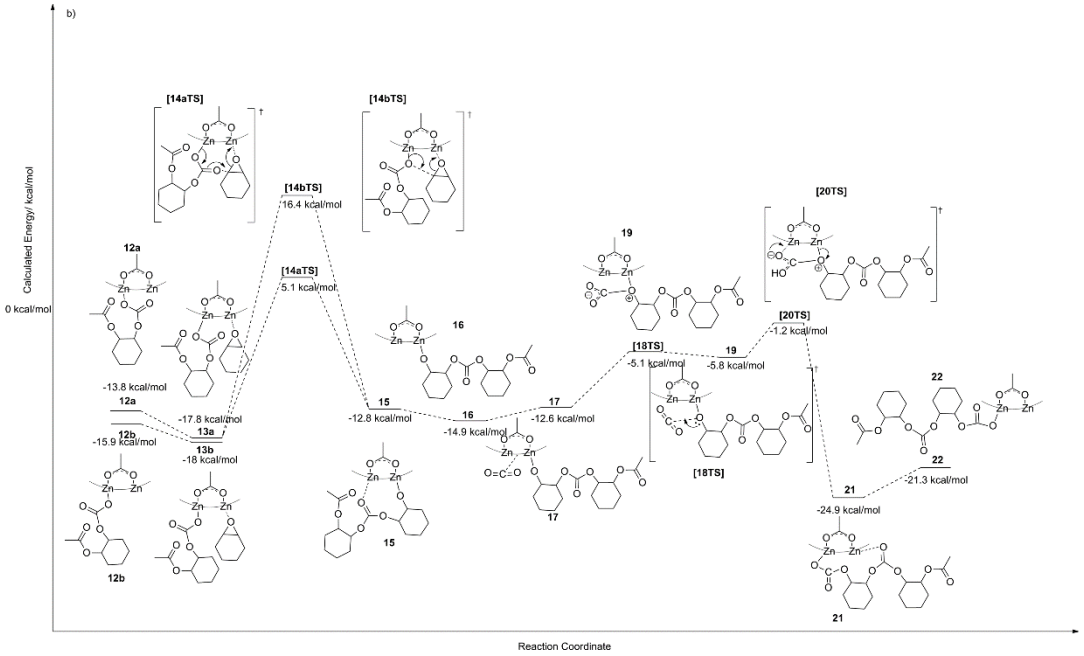


Figure 1-12: Proposed concerted mechanism of bimetallic Zn complexes.[77]

Figure 1-12 shows the energy diagram of the copolymerization of CHO with CO_2 mediated by the bimetallic zinc catalyst of Williams. They have carried out the DFT calculation for the polycarbonate propagation step. In the transition states of ring-opening reaction and of CO_2 insertion reaction, two metals have been suggested to act in a concerted manner. Acceleration of the polymerization have been expected as a result of this bimetallic reaction mechanism.

The first bimetallic homogeneous catalyst have been Zn-BDI type catalyst that was reported by Coates and co-workers in 1998.[66] This catalyst have shown moderate activity (TOF = 247 h^{-1} for the copolymerization of CHO/CO_2 at 50 °C) and carbonate selectivity. In this catalyst, metal centers have not been fixed at a specific distance. Kinetic study has revealed that reaction rate constant order in Zn was 1.8, which implies the contribution of a bimetallic mechanism.[78] Bimetallic type catalysts have been extensively researched since the discovery of bimetallic anilido-aldimine zinc complexes in 2005 by Bun-Yeoul Lee and co-workers.[79] They have synthesized bimetallic catalyst series which have various combinations of functional groups (Figure 1-13).

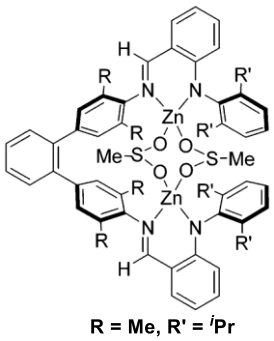


Figure 1-13: Bimetallic Zn complexes synthesized by Lee and co-workers.

Complex in Figure 1-13 have shown very high activity and molecular weight for the copolymerization of CHO and CO_2, TON of 2980 and nearly 300000 molecular weight. These values have been the highest values at that time. They have found that the loosely tethered Zn catalyst could accelerate the copolymerization reaction. Based on this observation, Rieger and co-workers have reported that extremely highly active bimetallic catalyst (Figure 1-14).[80]

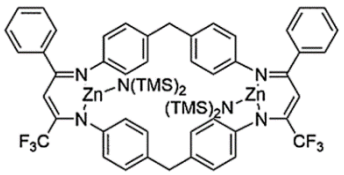


Figure 1-14: Bimetallic Zn complexes synthesized by Rieger and co-workers.

The TON of this catalyst have been 6740 in 2.6 min. for the copolymerization of CHO/CO_2 at 100 °C under 3.0 MPa CO_2 pressure. Although this TOF have been extremely high, the carbonate linkage selectivity has stayed up to 88%, possibly because the reaction was too fast for CO_2 molecules to disperse into the solution.

Williams and co-workers have independently developed homo- and hetero bimetallic salan catalysts. And they have found that the hetero-bimetallic system showed higher activity than the homo-bimetallic system (Figure 1-15).[81]

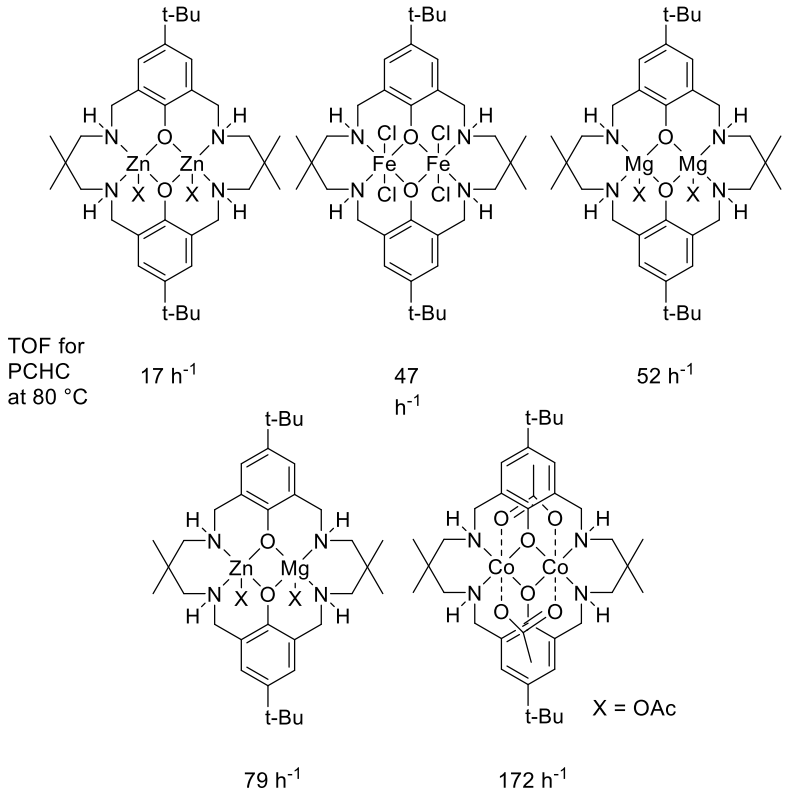


Figure 1-15: Bimetallic complexes synthesized by Williams and co-workers.

The activity of tethered Co-salen type catalyst have been also investigated extensively. In 2010, Nozaki and co-workers reported tethered Co-salen type catalyst.[82] They observed that tethered a bimetallic Co-salen complex showed higher activity than the corresponding monometallic complex in a diluted condition. In 2014, Xiao-Bing Lu and co-workers used biphenol group tethered bimetallic complex, originally invented by Coates *et al*., for the copolymerization of cyclopentene oxide(CPO)/CO_2 and 3,4-epoxytetrahydrofurane/CO_2.[83] They observed highly enantioselective polymerization and investigated the crystallization property of the resulting highly isotactic polycarbonate. Further studies on the stereocomplex formation of enantiomeric aliphatic polycarbonate have been recently reported using this bimetallic complex.[848586]

1-4 Copolymerization of epoxide with diacid anhydride for the synthesis of polyester

1-4-1 Background of polyesters

History of polyester synthesis

Polyester is one of the most commonly used polymer series in the modern society. Polyesters with widely varying properties can be produced depending on the starting materials and polymerization conditions. Since its discovery in 1940, various kinds of polyester have been synthesized and nowadays, aromatic polyesters (Vectran®), semi-aromatic polyesters (polyethylene terephthalate(PET) and polybutylene terephthalate(PBT)), and aliphatic polyesters (polyglycolic acid, polylactic acid (PLA), and polybutylene succinate(PBS)) have been produced in industrial scales (Figure 1-16).[87]

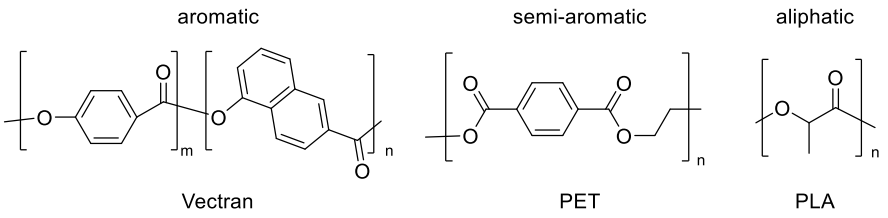
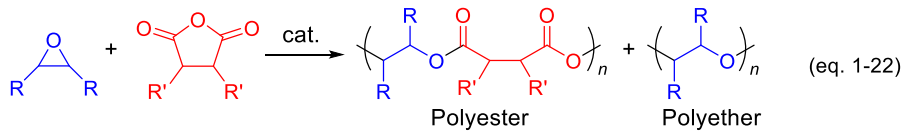


Figure 1-16: Representative examples of polyesters.

Most of the polyesters have been synthesized via polycondensation of diacids with diols. Very high molecular weight polyester has been synthesized via interfacial polymerization method. Aliphatic polyester such as polylactic acid and polycaprolactone have been synthesized by ring-opening reactions.[88]

To achieve the controlled polymerization, metal mediated ring-opening polymerization is very effective. While ring-opening polymerization of lactones (cyclic esters) is the most standard pathway for aliphatic polyester synthesis, the alternating ring-opening copolymerization of epoxide with diacid anhydride can also produce various types of aliphatic or semi-aromatic polyesters because there are many combinations of epoxides and diacid anhydrides. Here I briefly introduce the copolymerization of epoxide with diacid anhydride. General reaction scheme is shown in Scheme 1-13.



(eq. 1-22)

Scheme 1-13: General reaction scheme of copolymerization of epoxide with diacid anhydride.

This copolymerization reaction was first reported by Fischer in 1960.[89] In the first report, phthalic anhydride was copolymerized with epichlorohydrin and allyl glycidyl ether by using an amine as an initiator. Since this report, various metal catalyzed copolymerizations of epoxides with diacid anhydrides have been reported. Examples of commonly used diacid anhydride have been phthalic anhydride, succinic anhydride, and maleic anhydride. Other examples were summarized in Figure 1-17.[90]

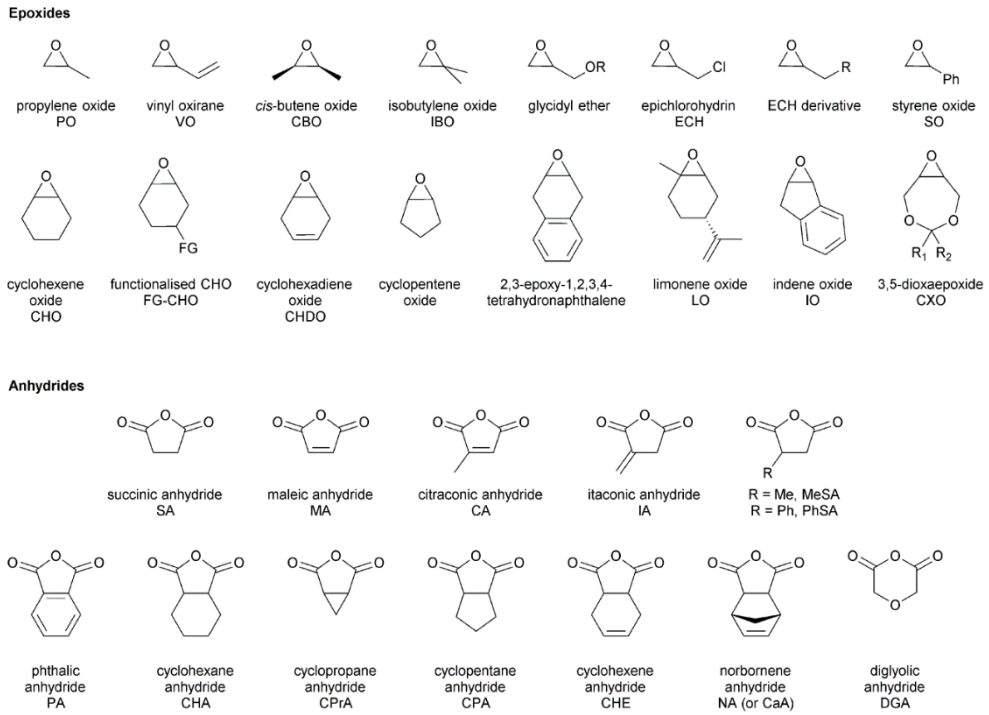


Figure 1-17: Examples of epoxide and diacid anhydride used for copolymerization.

Reaction mechanism is shown below (Figure 1-18).

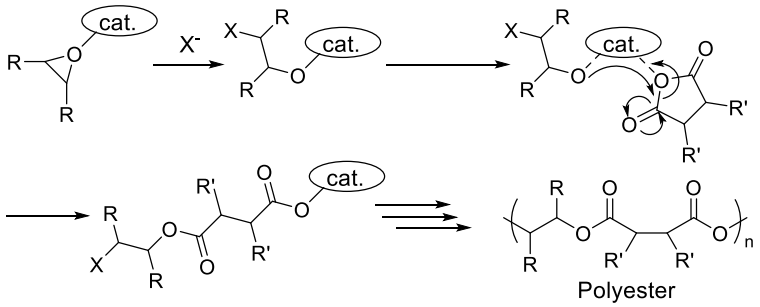


Figure 1-18: Reaction mechanism of copolymerization of epoxide with diacid anhydride.

Reaction mechanism is almost the same as the copolymerization of epoxide with CO_2, that means, Lewis acidic metal catalysts used for the copolymerization of epoxide with CO_2 are also effective for this copolymerization reaction as will be shown in the next section. In the same way as the copolymerization of epoxide with CO_2, possible side reaction is ether linkage formation via homopolymerization of epoxides. High polyester linkage selectivity is one of the requirements for a good catalyst.

1-4-2 Monometallic catalysts for copolymerization of epoxide with diacid anhydride

The same kinds of catalysts as used in the copolymerization of epoxide with CO_2 have been employed for the copolymerization of epoxide with diacid anhydride. Thus, here I emphasize the substrates scope of this copolymerization reaction. A detailed review have been reported by Williams and co-workers.[90]

Metalloporphyrin

In the earliest stage of homogeneous catalyst investigation, metalloporphyrin complexes have been firstly investigated. Porphyrin complexes of Al, Cr, Co and Mn have been extensively examined for the copolymerization of PO, CHO, SO and BO with SA, CPrA, CPA, PA. Chisholm and co-workers have reported that Cr(III)-Porphyrin complex with PPNCl co-catalyst showed higher activity than other type metalloporphyrin complexes.[91] Duchateau and co-workers have reported that Cr(III)-porphyrin-Cl with DMAP showed higher activity and polyester selectivity than Cr(III)-Salphen-Cl complexes with DMAP for the copolymerization of cyclohexene oxide with phthalic anhydride.[92] Thus, as the monometallic complexes, metalloporphyrin complex have been known as the best catalyst system for the copolymerization of epoxide with diacid anhydride.

Zinc-diiminate complex

Zinc-diiminate type complexes have been extensively investigated by Coates and co-workers. This catalyst has shown high activity for the copolymerization of VCHO, LO, PO, CBO and IBO with DGA.[93] However, this complex has shown low polyester selectivity for the copolymerization of MA with PO accompanied by significant production of polyether linkage(86% selectivity).[94]

Metal-salen complexes

Metal-salen complexes have been widely applied to the copolymerization of epoxide/diacid anhydride. Combination of Al(III), Mn(III), Co(III) and Cr(III) with salcy and salphen ligands have been extensively examined by Darensbourg, Coates and Duchateau. Among them, Co or Cr-salcy complexes have been mainly used for the regioselective polymerization at very low temperature. Generally speaking, comparison of the catalyst activity is very difficult because various metal-ligand combinations have been applied to different epoxide-anhydride combination. Nevertheless, Cr(III)-porphyrin complex and Cr(III)-salphen complex have been most widely used for this types of copolymerization and at present, Cr(III)-salphen-Cl complex with DMAP or PPNCl co-catalyst have been known as the benchmark catalyst of metal-salen catalysts.[95] For the copolymerization of CHO/PA, TOF of Cr(III)-salphen-Cl with DMAP co-catalyst have been 243 h^{-1}.

1-4-3 Bimetallic catalysts for copolymerization of epoxide with diacid anhydride

As was the case for monometallic complexes, the same bimetallic complexes applied to copolymerization of epoxide with CO_2 have been used for the epoxide/diacid anhydride copolymerization. I briefly introduce examples of highly active bimetallic catalysts. Williams and co-workers have reported that bimetallic Zn-salan complex and Mg-salan complex showed relatively high activity for the copolymerization of CHO with PA.[96] TOF of Mg bimetallic salan complex have been 97 h^{-1} at 100 °C. Very recently, Xiao-Bing Lu and co-workers have reported Al, Co, Cr bimetallic salcy complexes (Figure 1-19).[97]

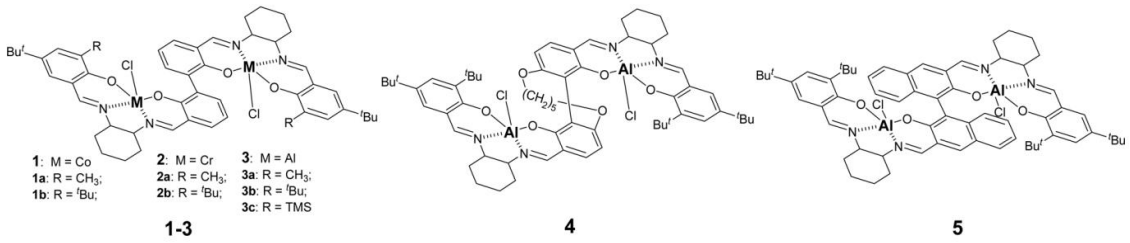


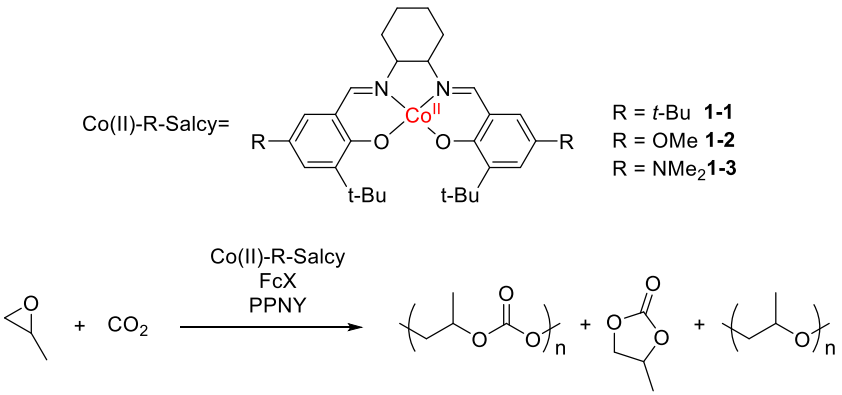
Figure 1-19: Bimetallic complexes synthesized by Lu and co-workers.

They have observed that R group in Figure 1-19 had strong effect for the activity of these complexes. And they have found that *t*-Bu group attached Al-bimetallic complex (**3b** in Figure 1-19) showed high activity, TOF of 750 h^{-1} for copolymerization of CHO/PA at 50 °C. This activity has been the highest value so far. They have also tried more rigid ligand structure complexes (**4** and **5** in Figure 1-19) but these were less active for this copolymerization reaction.

1-5 Purpose of this thesis

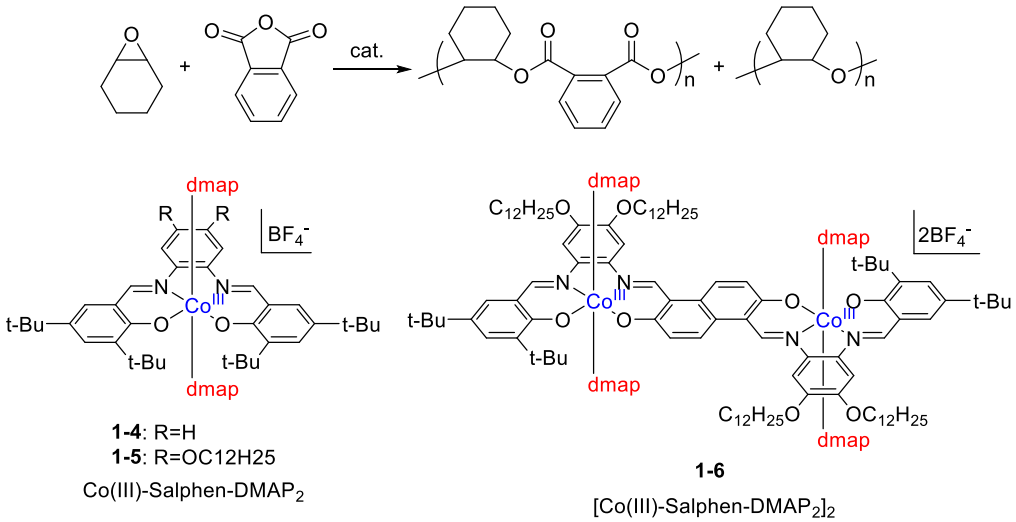
As summarized above, there are tremendous amount of reports about polymerization and copolymerization of epoxides. However, there are only limited number of reports about the relationship between the activity of metal catalyst with electronic state of the metal complex. For example, although electron-withdrawing group effect on the activity of Co-salen complex was investigated for the copolymerization of epoxide with diacid anhydride,[98,99] there is no report of EWG attached Co-salen complex for the copolymerization of epoxide with carbon dioxide. Furthermore, EDG attached Co-salen complex is difficult to synthesize while Okawara et al. recently suggested possible activity improvement by introduction of electron-donating group(s) on the ligands, especially salcy ligands.[62]

It should be noted that electronic state such as the electron transfer between metal with ligand is extensively investigated for the porphyrin and salen catalyst.[100] Especially electronic state of Co-salcy complex is reported very recently.[101] Accordingly, I decided to focus my research interest on the relationship between activity of Co-Salen catalyst for copolymerization of epoxide and the electronic state of Co-salen catalyst in chapter 2. To overcome the synthetic difficulty, I evaluated the activity for the copolymerization of PO with CO_2 by using *in situ* oxidized Co(III) complexes. I found that methoxy group attached Co-Salcy complex (**1-2**) showed higher activity than *t*-Bu group attached complex (**1-1**) while dimethylamino group attached complex (**1-3**) showed almost no activity.



Scheme 1-13: General scheme in chapter 2.

In chapter 3, I paid my attention on the axial ligand which works as an initiator for the copolymerization epoxides with diacid anhydrides. I expected the more nucleophilic the initiator is, the higher activity would be achieved. In fact, higher activity was accomplished using Co(III)-Salphen-DMAP2 (**1-4**). In addition, rather unexpectedly, I found bimetallic complex **1-6** showed higher catalytic activity for CHO/PA copolymerization when compared to its corresponding monometallic analog **1-5**.



Scheme 1-14: General scheme in chapter 3.

1-6 Reference

(1) Parker, R. E.; Isaacs, N. S. *Chem. Rev.* **1959**, *59* (4), 737–799.

(2) In *March's Advanced Organic Chemistry*; John Wiley & Sons, Inc.: Hoboken, NJ, USA; pp 999–1250.

(3) In *March's Advanced Organic Chemistry*; John Wiley & Sons, Inc.: Hoboken, NJ, USA; pp 1251–1476.

(4) Katsuki, T.; Sharpless, K. B. *J. Am. Chem. Soc.* **1980**, *102* (18), 5974–5976.

(5) Zhang, W.; Loebach, J. L.; Wilson, S. R.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1990**, *112* (7), 2801–2803.

(6) Stanford Research Institute *Ethylene Oxide*; *Chemical Economics Handbook*; Stanford Research Institute,

(7) Bloch, H. P. *Compressors and Modern Process Applications*; John Wiley & Sons, Inc.: Hoboken, NJ, USA, 2006.

(8) http://www.dow.com/propyleneoxide/news/20090305a.htm brows in November 29, 2016

(9) Sienel, G.; Rieth, R.; Rowbottom, K. T. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(10) May, C. *Epoxy Resins: Chemistry and Technology, Second Edition*, Second Edi.; CRC Press, 1987.

(11) Crotti, P.; Pineschi, M. *Epoxides in Complex Molecule Synthesis*; 2006.

(12) Hou, X.-L.; Wu, J.; Dai, L.-X.; Xia, L.-J.; Tang, M.-H. *Tetrahedron: Asymmetry* **1998**, *9* (10), 1747–1752.

(13) Sekine, A.; Ohshima, T.; Shibasaki, M. *Tetrahedron* **2002**, *58* (1), 75–82.

(14) Pakulski, Z.; Pietrusiewicz, K. M. *Tetrahedron: Asymmetry* **2004**, *15* (1), 41–45.

(15) Hayashi, M.; Kohmura, K.; Oguni, N. *Synlett* **1991**, *1991* (11), 774–776.

(16) Sagawa, S.; Abe, H.; Hase, Y.; Inaba, T. *J. Org. Chem.* **1999**, *64* (13), 4962–4965.

(17) Nugent, W. A. *J. Am. Chem. Soc.* **1992**, *114* (7), 2768–2769.

(18) Martinez, L. E.; Leighton, J. L.; Carsten, D. H.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1995**, *117* (21), 5897–5898.

(19) Hansen, K. B.; Leighton, J. L.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1996**, *118* (44), 10924–10925.

(20) Jacobsen, E. N. *Acc. Chem. Res.* **2000**, *33* (6), 421–431.

(21) Annis, D. A.; Jacobsen, E. N. *J. Am. Chem. Soc.* **1999**, *121* (17), 4147–4154.

(22) Breinbauer, R.; Jacobsen, E. N. *Angew. Chemie* **2000**, *39* (20), 3604–3607.

(23) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277* (5328), 936–938.

(24) Chan, A. S. C.; Coleman, J. P.; Parshall, G. W.; Nugent, W. A.; Osakada, K.; Obana, M.; Kariya, T.; Saburi, M.; Yoshikawa, S.; Yamashita, H.; Fiorini, M.; Marcati, F.; Giongo, G. M.; Imai, H.; Nishiguchi, T.; Fukuzumi, K.; Konig, W. A.; Benecke, I.; Sievers, S. *J. Chem. Soc. Chem. Commun.* **1991**, *4* (7), 535.

(25) Yamashita, H.; Mukaiyama, T. *Chem. Lett.* **1985**, *14* (11), 1643–1646.

(26) Nozaki, K.; Nakano, K.; Hiyama, T. *J. Am. Chem. Soc.* **1999**, *121* (47), 11008–11009.

(27) Denmark, S. E.; Barsanti, P. A.; Wong, K.-T.; Stavenger, R. A. *J. Org. Chem.* **1998**, *63* (8), 2428–2429.

(28) Tao, B.; Lo, M. M.-C.; Fu, G. C. *J. Am. Chem. Soc.* **2001**, *123* (2), 353–354.

(29) Iida, T.; Yamamoto, N.; Sasai, H.; Shibasaki, M. *J. Am. Chem. Soc.* **1997**, *119* (20), 4783–4784.

(30) *Aziridines and Epoxides in Organic Synthesis*; Yudin, A. K., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, FRG, 2006.

(31) Wurtz, C. A. *Ann. Chim. Phys.* **1863**, *69*, 317–354.

(32) Herzberger, J.; Niederer, K.; Pohlit, H.; Seiwert, J.; Worm, M.; Wurm, F. R.; Frey, H. *Chem. Rev.* **2015**, acs.chemrev.5b00441.

(33) Flory, P. J. *J. Am. Chem. Soc.* **1940**, *62* (6), 1561–1565.

(34) Okamura, S.; Higashimura, T.; Tomikawa, M. *J. Soc. Chem. Ind. Japan* **1962**, *65* (5), 712–716.

(35) Penczek, S.; Cypryk, M.; Duda, A.; Kubisa, P.; Słomkowski, S. *Prog. Polym. Sci.* **2007**, *32* (2), 247–282.

(36) Dubois, P.; Coulembier, O.; Raquez, J.-M. *Handbook of ring-opening polymerization*; Wiley-VCH, 2009.

(37) Hargreaves, A. E. *Chemical Formulation: An Overview of Surfactant Based Chemical Preparations Used in Everyday Life*; RSC Paperbacks; Royal Society of Chemistry: Cambridge, 2003.

(38) Dingels, C.; Schömer, M.; Frey, H. *Chemie unserer Zeit* **2011**, *45* (5), 338–349.

(39) Fruijtier-Pölloth, C. *Toxicology* **2005**, *214* (1), 1–38.

(40) Klein, R.; Wurm, F. R. *Macromol. Rapid Commun.* **2015**, *36* (12), 1147–1165.

(41) Kjellander, R.; Florin, E. *J. Chem. Soc. Faraday Trans. 1 Phys. Chem. Condens. Phases* **1981**, *77* (9), 2053.

(42) Knop, K.; Hoogenboom, R.; Fischer, D.; Schubert, U. S. *Angew. Chemie Int. Ed.* **2010**, *49* (36), 6288–6308.

(43) Pelegri-O'Day, E. M.; Lin, E.-W.; Maynard, H. D. *J. Am. Chem. Soc.* **2014**, *136* (41), 14323–14332.

(44) Dimitrov, I.; Tsvetanov, C. B. In *Polymer Science: A Comprehensive Reference*; Elsevier, 2012; pp 551–569.

(45) Dai, S.; Tam, K. C. *Langmuir* **2004**, *20* (6), 2177–2183.

(46) Childers, M. I.; Longo, J. M.; Van Zee, N. J.; LaPointe, A. M.; Coates, G. W. *Chem. Rev.* **2014**, *114* (16), 8129–8152.

(47) Baggett, J. M.; Pruitt, M. E. Catalysts for the polymerization of olefin oxides. US2706181, April 12, 1955.

(48) Price, C. C.; Osgan, M.; Hughes, R. E.; Shambelan, C. *J. Am. Chem. Soc.* **1956**, *78* (3), 690–691.

(49) Natta, G.; Corradini, P.; Dall, A. *Atti Accad. Naz. Lincei, Cl. Sci. Fis., Mat. Nat., Rend.* **1956**, *20*, 408.

(50) Coates, G.; Allen, S.; Ajiro, H. In *Stereoselective Polymerization with Single-Site Catalysts*; CRC Press, 2007; pp 627–644.

(51) Peretti, K. L.; Ajiro, H.; Cohen, C. T.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127* (33), 11566–11567.

(52) Ajiro, H.; Peretti, K. L.; Lobkovsky, E. B.; Coates, G. W. *Dalt. Trans.* **2009**, No. 41, 8828.

(53) Thomas, R. M.; Widger, P. C. B.; Ahmed, S. M.; Jeske, R. C.; Hirahata, W.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2010**, *132* (46), 16520–16525.

(54) Widger, P. C. B.; Ahmed, S. M.; Hirahata, W.; Thomas, R. M.; Lobkovsky, E. B.; Coates, G. W. *Chem. Commun. (Cambridge, U. K.)* **2010**, *46* (Copyright (C) 2016 American Chemical Society (ACS). All Rights Reserved.), 2935–2937.

(55) Ahmed, S. M.; Poater, A.; Childers, M. I.; Widger, P. C. B.; Lapointe, A. M.; Lobkovsky, E. B.; Coates, G. W.; Cavallo, L. *J. Am. Chem. Soc.* **2013**, *135* (50), 18901–18911.

(56) Abts, G.; Eckel, T.; Wehrmann, R. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2014; pp 1–18.

(57) Freitag, D.; Fengler, G.; Morbitzer, L. *Angew. Chemie Int. Ed. English* **1991**, *30* (12), 1598–1610.

(58) Mindemark, J. *Functional cyclic carbonate monomers and polycarbonates: synthesis and biomaterials applications*; Acta Universitatis Upsaliensis, 2012.

(59) Tamura, M.; Ito, K.; Honda, M.; Nakagawa, Y.; Sugimoto, H.; Tomishige, K. *Sci. Rep.* **2016**, *6*, 24038.

(60) Inoue, S.; Koinuma, H.; Tsuruta, T.; Vol, P. L.; Carbon, C. D. *J. Polym. Sci. Part B Polym. Lett.* **1969**, *7*, 287–292.

(61) Darensbourg, D. J.; Yeung, A. D. *Polym. Chem.* **2014**, 3949–3962.

(62) Ohkawara, T.; Suzuki, K.; Nakano, K.; Mori, S.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136* (30), 10728–10735.

(63) Tao, Y.; Wang, X.; Zhao, X.; Li, J.; Wang, F. *Polymer (Guildf).* **2006**, *47* (21), 7368–7373.

(64) Sugimoto, H.; Inoue, S. *Pure Appl. Chem.* **2006**, *78* (10), 1823–1834.

(65) Aida, T.; Ishikawa, M.; Inoue, S. *Macromolecules* **1986**, *19*, 8–13.

(66) Cheng, M.; Lobkovsky, E. B.; Coates, G. W.; V, C. U.; York, N. *J. Am. Chem. Soc.* **1998**, *120* (II), 11018–11019.

(67) Byrne, C. M.; Byrne, C. M.; Allen, S. D.; Allen, S. D.; Lobkovsky, E. B.; Lobkovsky, E. B.; Coates, G. W.; Coates, G. W. *Acs Symp. Ser.* **2004**, No. complex 2, 11404–11405.

(68) Li, C.; Sablong, R. J.; Koning, C. E. *Eur. Polym. J.* **2015**, *67*, 449–458.

(69) Darensbourg, D. J.; Yarbrough, J. C. *J. Am. Chem. Soc.* **2002**, *124* (22), 6335–6342.

(70) Eberhardt, R.; Allmendinger, M.; Rieger, B. *Macromol. Rapid Commun.* **2003**, *24* (2), 194–196.

(71) Lu, X. B.; Wang, Y. *Angew. Chemie - Int. Ed.* **2004**, *43* (27), 3574–3577.

(72) Cohen, C. T.; Chu, T.; Coates, G. W.; Cohen, C. T.; Chu, T.; Chu, T.; Coates, G. W.; Coates, G. W.; Cohen, C. T.; Chu, T.; Chu, T.; Coates, G. W.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127* (31), 10869–10878.

(73) Sugimoto, H.; Ohtsuka, H.; Inoue, S. *J. Polym. Sci. Part A Polym. Chem.* **2005**, *43* (18), 4172–4186.

(74) Nakano, K.; Kamada, T.; Nozaki, K. *Angew. Chemie - Int. Ed.* **2006**, *45* (43), 7274–7277.

(75) Nakano, K.; Hashimoto, S.; Nakamura, M.; Kamada, T.; Nozaki, K. *Angew. Chemie - Int. Ed.* **2011**, *50* (21), 4868–4871.

(76) S, S.; Min, J. K.; Seong, J. E.; Na, S. J.; Lee, B. Y. *Angew. Chemie - Int. Ed.* **2008**, *47* (38), 7306–7309.

(77) Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K. *Macromolecules* **2012**, *45* (17), 6781–6795.

(78) Moore, D. R.; Cheng, M.; Lobkovsky, E. B.; Coates, G. W. *J. Am. Chem. Soc.* **2003**, *125* (39), 11911–11924.

(79) Bun, Y. L.; Heon, Y. K.; Su, Y. L.; Sung, J. N.; Han, S. I.; Yun, H.; Lee, H.; Park, Y. W. *J. Am. Chem. Soc.* **2005**, *127* (9), 3031–3037.

(80) Kissling, S.; Lehenmeier, M. W.; Altenbuchner, P. T.; Kronast, a.; Reiter, M.; Deglmann, P.; Seemann, U. B.; Rieger, B. *Chem. Commun.* **2015**, *51* (22), 4579–4582.

(81) Saini, P. K.; Romain, C.; Williams, C. K. *Chem. Commun.* **2014**, *50* (32), 4164–4167.

(82) Nakano, K.; Hashimoto, S.; Nozaki, K. *Chem. Sci.* **2010**, *1* (3), 369.

(83) Liu, Y.; Ren, W.-M.; He, K.-K.; Lu, X.-B. *Nat. Commun.* **2014**, *5*, 5687.

(84) Liu, Y.; Ren, W.-M.; Zhang, W.-P.; Zhao, R.-R.; Lu, X.-B. *Nat. Commun.* **2015**, *6*, 8594.

(85) Liu, Y.; Wang, M.; Ren, W.-M.; Xu, Y.-C.; Lu, X.-B. *Angew. Chemie Int. Ed.* **2015**, n/a-n/a.

(86) Liu, Y.; Ren, W.-M.; Wang, M.; Liu, C.; Lu, X.-B. *Angew. Chemie Int. Ed.* **2015**, *54* (7), 2241–2244.

(87) Köpnick, H.; Schmidt, M.; Brügging, W.; Rüter, J.; Kaminsky, W. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(88) *Handbook of Thermoplastic Polyesters*; Fakirov, S., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, FRG, 2002.

(89) Fischer, R. F. *J. Polym. Sci.* **1960**, *44* (143), 155–172.

(90) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. *Chem. Commun.* **2015**, *51*, 6459–6479.

(91) Bernard, A.; Chatterjee, C.; Chisholm, M. H. *Polym. (United Kingdom)* **2013**, *54* (11), 2639–2646.

(92) Huijser, S.; Hosseininejad, E.; Sablong, R.; Jong, C. De; Koning, C. E.; Duchateau, R. *Macromolecules* **2011**, *44* (5), 1132–1139.

(93) Jeske, R. C.; DiCiccio, A. M.; Coates, G. W. *J. Am. Chem. Soc.* **2007**, *129* (37), 11330–11331.

(94) Diciccio, A. M.; Coates, G. W. *J. Am. Chem. Soc.* **2011**, *133* (28), 10724–10727.

(95) Hosseini Nejad, E.; Van Melis, C. G. W.; Vermeer, T. J.; Koning, C. E.; Duchateau, R. *Macromolecules* **2012**, *45* (4), 1770–1776.

(96) Saini, P. K.; Romain, C.; Zhu, Y.; Williams, C. K. *Polym. Chem.* **2014**, *5* (20), 6068–6075.

(97) (1) Li, J.; Liu, Y.; Ren, W.-M.; Lu, X.-B. *J. Am. Chem. Soc*. **2016**, *138* (36), 11493–11496.

(98) Longo, J. M.; Diciccio, A. M.; Coates, G. W. *J. Am. Chem. Soc.* **2014**, *136* (45), 15897–15900.

(99) DiCiccio, A. M.; Longo, J. M.; Rodríguez-Calero, G. G.; Coates, G. W. *J. Am. Chem. Soc.* **2016**, *138* (22), 7107–7113.

(100) Lyons, C. T.; Stack, T. D. P. *Coord. Chem. Rev.* **2013**, *257* (2), 528–540.

(101)Kurahashi, T.; Fujii, H. *Inorg. Chem.* **2013**, *52* (7), 3908–3919.

1-7 Authorization

Figure 1-3 is reprinted from *Dalt. Trans.* **2009**, No. 41, 8828–8830. with permission from the Royal Society of Chemistry

Figure 1-4 is is reprinted form *J. Am. Chem. Soc.* **2013**, *135*, 18901 with permission from the American Chemical Society

Figure 1-12 is reprinted from *Macromolecules* **2012**, *45*, 6781–6795. with permission from the American Chemical Society

Figure 1-13 is reprinted from *J. Am. Chem. Soc.* **2005**, *127*, 3031–3037. with permission from the American Chemical Society

Figure 1-14 is reprinted from *Chem. Commun.* **2015**, *51*, 4579–4582. with permission from the Rooyal Society of Chemistry

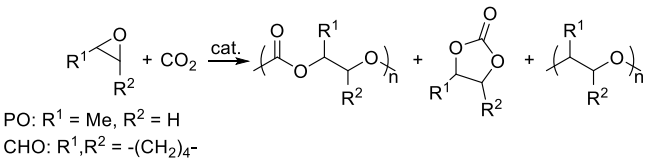
Figure 1-17 is reprinted from *Chem. Commun.* **2015**, *51*, 6459–6479. with permission from the Royal Society of Chemistry

Figure 1-19 is reprinted from *J. Am. Chem. Soc*. **2016**, *138*, 11493–11496. with permission from the American Chemical Society

Chapter 2
Investigation of Electron Donating Group Effect on the Activity of Co(III)-Salcy Complex for Copolymerization of Epoxide with CO_2

2.1 Introduction

Since its discovery in 1969,[1] various metal complexes were investigated as catalysts for copolymerization of epoxide with carbon dioxide (Scheme 2-1).[23] In the last decades, Salen complexes of trivalent metal ions, especially Co(III)–Salcy and Cr(III)–salphen complexes such as Co(III)-^{t}Bu-Salcy (**2-1**) and Cr(III)-^{t}Bu-salphen (**2-3**) in Figure 2-1 have been well studied owing to their high catalytic activities for the copolymerization.[456789] Usually, these metal(III) complexes are synthesized via the two steps; namely, salen complex formation with metal(II) species and subsequent oxidation of the central metal(II) to metal(III). The two-step process is especially advantageous for Co complexes, since Co(III) species are not suited for complexation compared with Co(II). For example, $CoCl_3$ easily decompose to $CoCl_2$ and Cl_2.[10] For the subsequent oxidation of Co(II) or Cr(II) to Co(III) or Cr(III), the use of oxidants such as O_2/AcOH,[11] $AgPF_6$,[12] $AgBF_4$,[12] $AgSbF_6$,[13] $[Cp_2Fe(III)]PF_6$,[14] and $[Cp_2Fe(III)]BF_4$[15] were reported in literature.



Scheme 2-1. Copolymerization of Epoxide with CO_2.

Introduction of substituents at the *para*-positions of phenolic oxygens in the salen complexes is one of the most common approaches to tune the electronic nature of the metal center. For example, Darensbourg *et al.* reported that MeO-substituents on the salphen complex, Cr(III)-OMe-salphen (**2-4**) enhanced the activity for the copolymerization of cyclohexene oxide (CHO) with CO_2 when compared to the ^{t}Bu-substituted complex **2-3** (Figure 2-1).[16] In a related Ge(IV) system bearing an ONNO-tetravalent trianionic ligand, improvement of activity by introduction of methoxy groups onto the ligand was also reported for copolymerization of propylene oxide (PO) with CO_2.[17] Furthermore, electronic nature of salen ligands were eagerly investigated from

the view point of the non-innocent ligand.[1819] For the redox active metal, such as Mn,[1819] Ni, [19] Co,[20] salen ligand can carry out ligand metal charge transfer(LMCT).The effect of this non-innocent nature of the salen ligand for the polymerization activity of the metal complex is also very interesting and undiscovered topic.

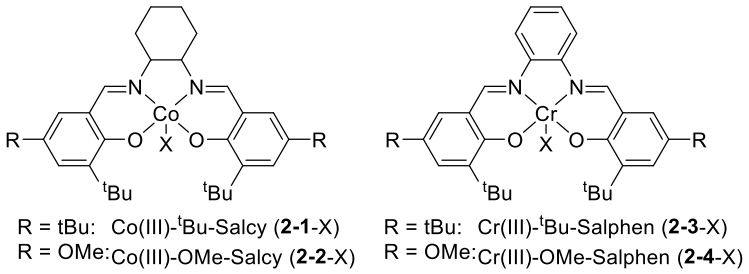


Figure 2-1. Co(III)- and Cr(III)- salen type complexes. X stands for the anionic ligand.

On the other hand, the activity of methoxy or other electron donating group substituted Co(III)–Salcy complex (Co(III)–MeO-Salcy (**2-2**)) have not been investigated, possibly because the electron-donating substituents on the Co(III)–Salcy complexes often cause lower stability of the Co(III) species under the standard oxidation conditions for Co(II) to Co(III). For example, the O_2/acid oxidation of Co(II)–Salcy species, is not applicable to the preparation of Co(III)–MeO-Salcy possibly due to the over oxidation of Co(III)–MeO-Salcy (**2-2**). As an alternative oxidation method to form Co(III)–MeO-Salcy, milder oxidants such as $AgSbF_6$[+] [1320] were reported to be effective, but the Co(III) complex thus prepared has never been applied to the epoxide/CO_2 copolymerization.

In this Chapter, I report the copolymerization of epoxide with CO_2 by using *in situ* generated Co(III)–Salcy complexes. PO was selected as the epoxide since it is the most easily available epoxide for industrial application. A simple admixture of Co(II)–Salcy complexes with $[Cp_2Fe(III)]PF_6$ resulted in reproduction of the results with isolated Co(III)–Salcy complexes. A higher catalytic activity was achieved with Co(II)–MeO-Salcy complex (**2-6**) than with

conventional Co(II)–tBu-Salcy complex (**2-5**) when bis(triphenylphosphoranilydene)ammonium 2,4-dinitrophenolate (PPNDNP) was used as a cocatalyst (Figure 2-2).

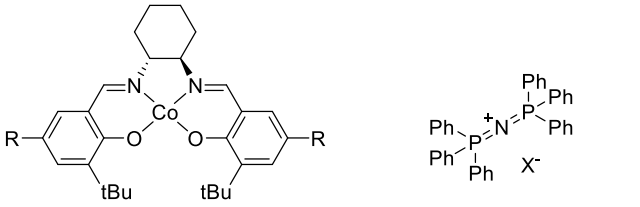
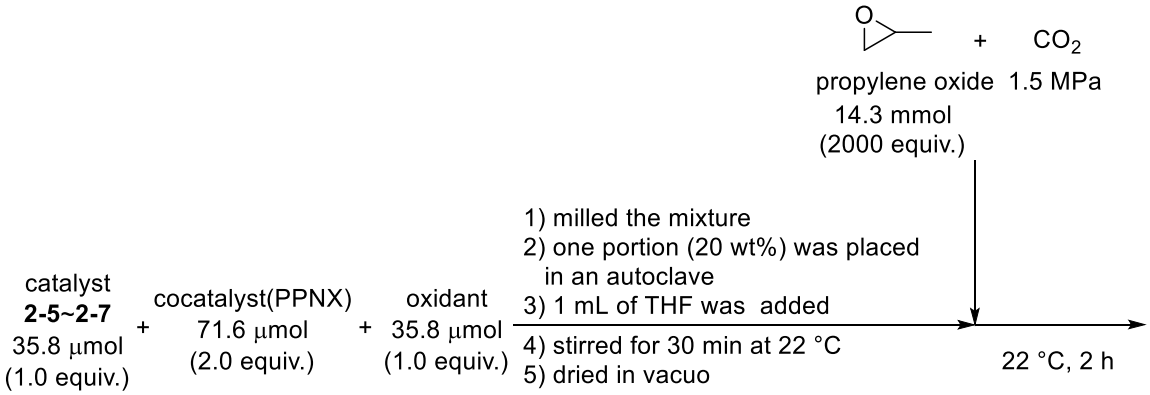


Figure 2-2. Synthesized Co(II) complexes and PPN salt.

2.2 Results and Discussion

Table 2-1. Copolymerization result by using *in situ* method.[a]



entry	Complex (R =)	PPNX (X =)	oxidant	TON for PPC[bc]	TON for CPC[bc]	MW(kg/mol)[c]	Mw/Mn[d]
1	**2-5**	Cl	$FcPF_6$	695±33	20±2	32.1±0.7	1.1
2	**2-6**	Cl	$FcPF_6$	729±43	22±1	28.9±1.6	1.2
3	**2-1-PF$_6$**	Cl	--	712±36	30±1	23.5±2.5	1.1
4	**2-2-PF$_6$**	Cl	--	703±1	20±2	18.7±0.4	1.1
5[e]	**2-6**	DNP	$AgPF_6$	-	-	-	-
6	**2-6**	Cl	$FcBF_4$	627±28	15±1	21.0±1.1	1.1
7	**2-6**	Cl	$FcBAr^F$	664±11	18±1	21.6±0.1	1.1
8	**2-5**	DNP	$FcPF_6$	802±26	0	32.4±2.8	1.2
9	**2-6**	DNP	$FcPF_6$	976±18	0	32.1±1.4	1.2
10[f]	**2-6**	DNP	$FcPF_6$	949±35	0	38.2±2.2	1.2
11	**2-7**	DNP	$FcPF_6$	2±1	1±0	-	-
ref-1[g]	**2-1-Cl**	Cl	-	860	<9[h]	35.4	1.1

a All copolymerization was performed at 22 °C, under 1.5 MPa of CO_2 pressure for 2 hours. For entries 1 to 5 and 6, the same reaction was repeated for three times and five times respectively. The average data are described here. See section 2.5 for details. b TON determined by ^{1}H NMR analysis. c I calculated average value and standard deviation for each entry's 3 or 5 runs and the described standard deviation as "+/-" d Determined by size-exclusion chromatography (SEC) analysis using THF as an eluent and polystyrene as a standard. e No polymeric compound was observed in ^{1}H NMR analysis. f Catalyst/Substrate ratio is 1/4000. 14.3 mmol of PO was used. g Catalyst was pre-isolated and mixed with one equivalent of PPNCl. h CPC amount was reported as <1%

Copolymerization of PO and CO_2 with *in situ* generated catalysts was examined in the procedure described in Table 1: A Co(II)-Salcy complex was first finely milled with two equivalents of cocatalyst PPNX and one equivalent of oxidant. A portion was placed in an autoclave, dissolved in THF, and stirred for 30 min at 22 °C to allow the Co(II) species to be oxidized to Co(III). After removal of the solvent, the residue was used as the catalyst for copolymerization. Three Co(II)-Salcy complexes were examined for the reaction, namely, the ones having *tert*-Bu, MeO and NMe_2 groups (**2-5**, **2-6** and **2-7**) at the *para*-positions of the phnoxy-oxygen. As a co-catalyst, PPNCl and PPNDNP were examined. The results are summarized in Table 1. The reported values with isolated Co(III)-^{t}Bu-Cl (**2-1-Cl**) are listed at the bottom of Table 1 as a reference (entry ref-1).

First, the Co(II) species oxidized *in situ* with ferrocenium salts $[Cp_2Fe(III)]X$(=FcX) were successfully applied to the copolymerization without any purification process. In entries 1 and 2, copolymerization reaction was carried out using complexes generated by *in situ* oxidation of **2-5** and **2-6** with $FcPF_6$ in the presence of PPNCl co-catalyst. The results were compared with the data using isolated Co(III) complexes **2-1-PF$_6$** and **2-2-PF$_6$**. Those Co(III) complexes were prepared by oxidation of **2-5** and **2-6** with $AgPF_6$, removal of silver particles, and reprecipitation from hexane. As shown, the TONs with *in situ* generated species and isolated species were comparable, those are, 695 with **2-5** and 712 with **2-1-PF$_6$** (entries 1 and 3), and 729 with **2-6** and 703 with **2-2-PF$_6$** (entries 2 and 4).[21] On the other hand, the molecular weight tended to be lower when the isolated complexes were employed (entries 3 and 4). This molecular weight change could be derived from the water contamination in the reaction system with isolated complexes, as follows. In all entries, the SEC charts showed bimodal profiles due to the coexistence of two initiators, the anion X of cocatalyst PPNX and water contaminant. Such molecular weight decrease by water was previously reported in literature.[22] While the molecular

weights described in Table 1 are the average of the bimodal peaks, I also analyzed the two peaks separately to prove that the molecular weight initiated by water (M_{water}) is double the molecular weight initiated by X (M_x). Thus, an ideal molecular weight M_{ideal} without water contamination could be calculated as $M_{ideal} = M_x + \alpha(M_{water})$ where α is defined as the area ratio of (water initiated polymer)/(X-initiated polymer). Notably, the M_{ideal} is constant for the *in situ* generated species and for the isolated complexes (See section 2.6 for details).

I also tried *in situ* oxidation of **2-6** by using $AgPF_6$ salt (entry 5). In this case, neither polymeric material nor cyclic carbonate was obtained. This result indicate that remained silver salt or silver particle inhibited the polymerization by a Co(III) catalyst.

Counter anion of the ferrocenium salt hardly affected the polymerization results, as the use of PF_6^-, BF_4^- and BAr^{F-} for **2-6** resulted in TON for PPC of 729, 627 and 664 (entries 2, 6, and 7). In contrast, the counter anion of the PPN was more influential as the use of PPNDNP (DNP = 2,4-dinitrophenolate) in place of PPNCl resulted in higher TON for PPC of 802 for **2-5** and 976 for **2-6** (compare entries 1 and 8, 2 and 9). Furthermore, with PPNDNP, formation of CPC was not detected unlike the results with PPNCl. This difference may be attributed to the higher leaving ability of chloride than 2,4-dinitrophenolate, that is, the nucleophilic ring opening of PO by chloride followed by insertion of one CO_2 molecule has higher chance to form CPC than the initiation by DNP. In all entries, any signal of the polyether linkage was detected in ^{13}C NMR analysis. It is notable that the TON of 976 accomplished by a combination of **2-6**, $FcPF_6$, and PPNDNP (entry 9) is higher than the value of 860 (entry ref-1) reported by Coates *et al.* with **2-1**-Cl and PPNCl[23], which is generally cited as a benchmark reaction for the copolymerization with Co(III)-Salcy system. This high TON value of **2-6** was maintained when I tried copolymerization by half amount of catalyst loading (entry 10).

Here I explain why electron donating group accelerate the copolymerization reaction. I estimated the reason based on the calculation reported by Nozaki and co-workers (Figure 2-3).[17]

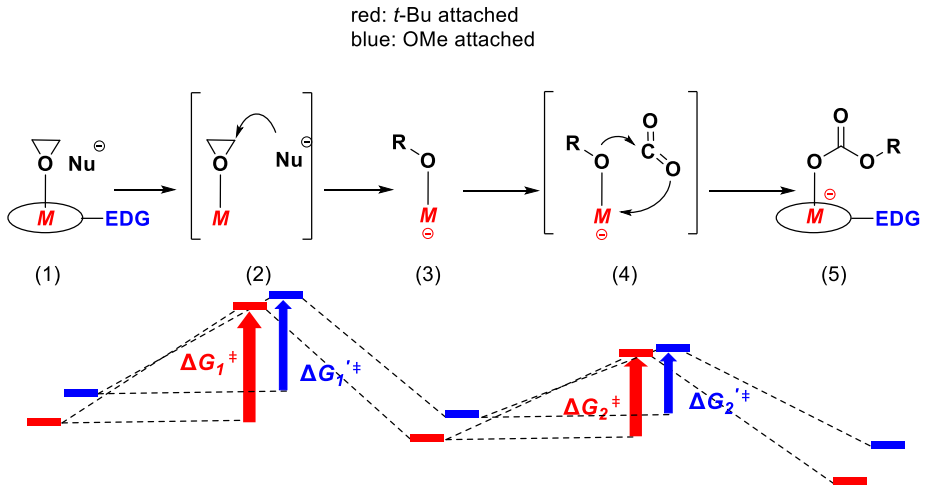


Figure 2-3: Estimated energy diagram of copolymerization of epoxide with CO_2. Red: *t*-Bu substituted complex Blue: OMe substituted complex

When methoxy substituted complex **2-6** was used for the copolymerization reaction, the transition state of ring-opening reaction and CO_2 insertion (state (2) and (4)) were destabilized by the effect of the electron donation from methoxy group. On the other hand, the energy of intermediate states(state (1), (3), and (5)) were further destabilized by the electron donating group. As a result of these electron donating group effect, activation energy $\Delta G_1'^{\ddagger}$ and $\Delta G_2'^{\ddagger}$ become lower than $\Delta G_1^{\ddagger}$ and $\Delta G_2^{\ddagger}$.

For further investigation of the electron donating substituent effect, I also attempted the copolymerization reaction by using species given by *in situ* oxidation of Co(II)-salen **2-7** bearing dimethylamino groups (entry 11). I found that the mixture of **2-7** with $FcPF_6$ and PPNDNP showed very low activity. TON for PPC was 2 and for CPC was 1. This result suggests that this copolymerization reaction needs appropriate electron donating groups at the salen ligand *para*-positions of the hydroxyl groups.

The equilibrium between Co(III)/L and Co(II)/$L^{+\bullet}$ could be involved in the reactions with **2-6** and **2-7**.[24] Fujii *et al.* reported that methoxy group attached Co-Salcy complex **2-2-OTf** have the equilibrium between Co(III)-Salcy and Co(II)-$Salcy^{+\bullet}$. [20] The stronger electron donating nature of the dimethylamino groups could have increased the contribution of radical cationic species

Co(II)-Salcy$^{+\bullet}$. Since divalent Co metal have no activity for PPC synthesis,[25] this could be the reason for the low reactivity of Co(II)-NMe_2-Salcy **2-7**.

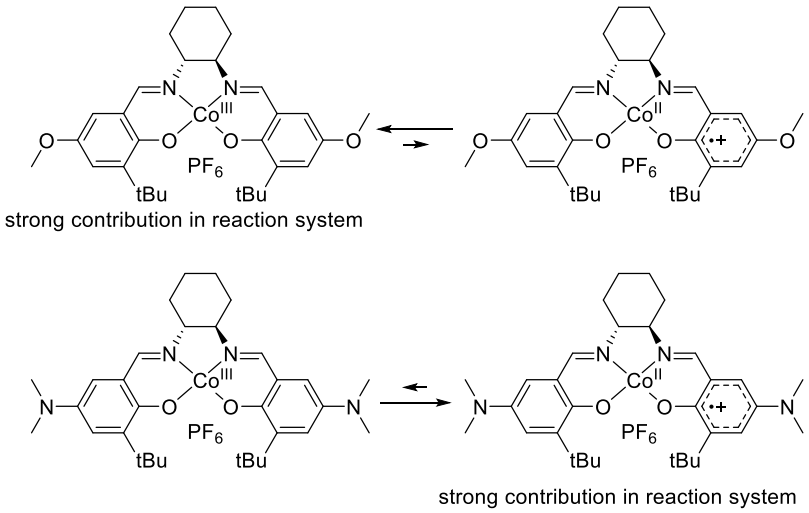


Figure 2-4. Proposed contribution of radical cationic species for Co(III) species.

The equilibrium between Co(III)-NMe_2-Salcy and Co(II)-NMe_2-Salcy$^{+\bullet}$ was supported by comparisons of UV-Vis-NIR absorption spectrum of **2-7** and oxidized **2-7** (Figure 2-5 and 2-6). Oxidized **2-7** was prepared by the reaction of **2-7** with $FcPF_6$ followed by reprecipitation from hexane to remove the generated ferrocene. For oxidized **2-7**, very weak and broad absorption was observed from 800 nm to 1500 nm while **2-7** shows no absorption above 800 nm. Similar broad absorption around 1200 nm for Co(III)-OMe-Salcy-OTf (**2-2**-OTf) was reported by Fujii *et al*. They attributed this absorption to ligand metal charge transfer (LMCT).

I carried out EPR measurement of Co(II)-NMe_2-Salcy and Co(III)-NMe_2-Salcy in the toluene/DCM solvent (Figure 2-7). As a result, I could observe an EPR signal in the Co(III)-NMe_2-Salcy solution. It strongly suggested the large contribution of Co(II) radical cationic state in the Co(III)-NMe_2-Salcy. This type of strong radical contribution was not observed in the Co(III)-OMe-Salcy complex.[20] From this result, the relationship between electron donating ability of substituted group and activity of Co(III)-Salcy complex was further supported.

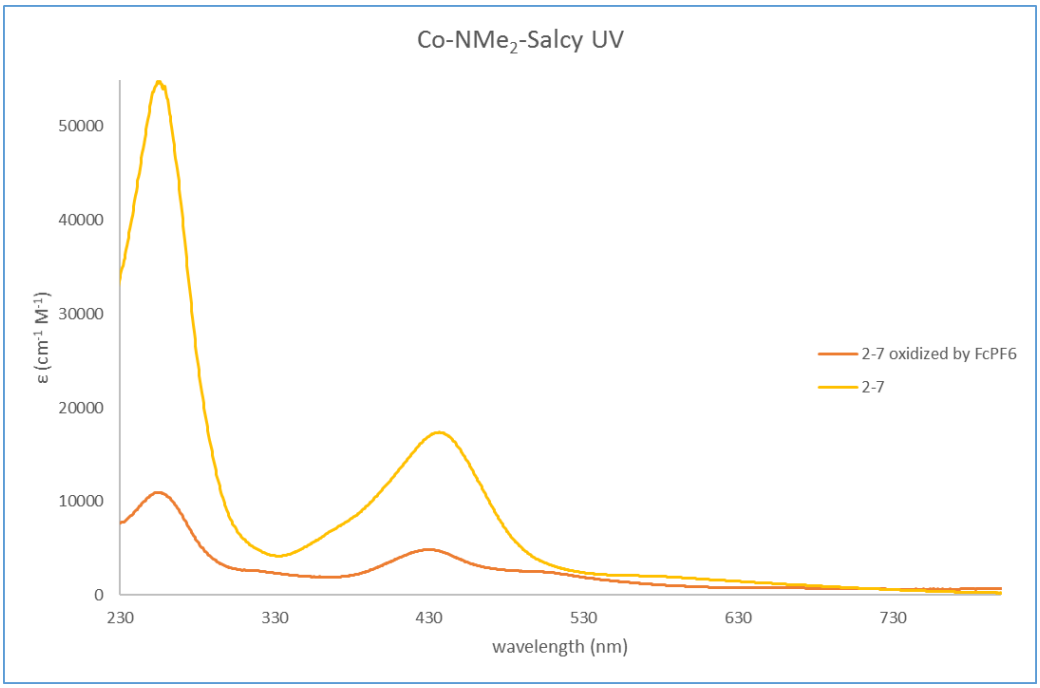


Figure 2-5: UV-Vis absorption spectrum of Co(II)-NMe_2-Salcy (**2-7,** 5.0×10^{-5} M) and Co(III)-NMe_2-Salcy (**2-7** oxidized by $FcPF_6$, after reprecipitation, 5.4×10^{-5} M) in CH_2Cl_2.

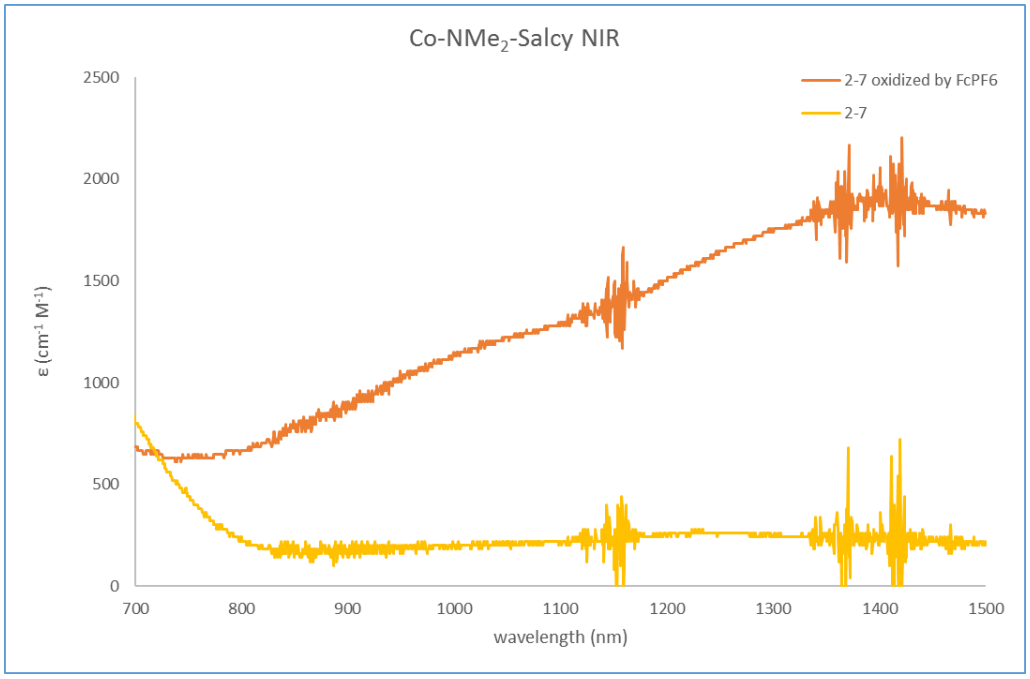


Figure 2-6: NIR region absorption of Co(II)-NMe_2-Salcy (**2-7,** 5.0×10^{-5} M) and Co(III)-NMe_2-Salcy (**2-7** oxidized by $FcPF_6$, after reprecipitation, 5.4×10^{-5} M) in CH_2Cl_2.

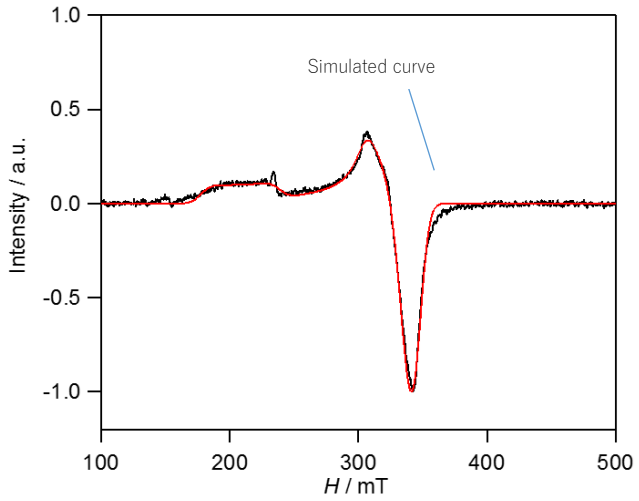


Figure 2-7: ESR spectrum and simulated curve of Co(III)-NMe_2-Salcy (**2-7** oxidized by $FcPF_6$ after reprecipitation 3.3×10^{-4} M) in CH_2Cl_2 40% in toluene solution. Measurement was carried out at 100 K. Simulation was carried out by anisotropic *g*-tensols of $g_1 = 3.105$, $g_2 = 1.988$, and $g_3 = 1.917$ and anisotropic hyperfine interactions (A_i) of $A_1 = 119$ G, $A_2 = 45$ G, and $A_3 = 18$ G on ^{59}Co ($I = 7/2$).

2.3 Conclusions

In conclusion, I developed a novel *in situ* oxidation method to generate Co(III)-Salcy complexes and applied them to the copolymerization of propylene oxide with CO_2. When $FcPF_6$ was used as the oxidant of Co(II) complexes, Co(II)-*t*-Bu-Salcy (**2-5**) and Co(II)-OMe-Salcy (**2-6**) showed the catalytic activity and selectivity for the polypropylene carbonate synthesis, with comparable TON and selectivity for PPC with isolated Co(III) complexes **2-1-PF$_6$** and **2-2-PF$_6$**. By the screening of ligand, oxidant, and counter anion of PPN salt, Co(II)-OMe-Salcy (**2-6**) with $FcPF_6$ and PPNDNP showed the highest activity and selectivity for PPC production; TON value was ca.980 and no cyclic carbonate was observed. When a more electron rich Co(II)-NMe_2-Salcy (**2-7**) was used with $FcPF_6$ and PPNDNP, quite a low TON for PPC was observed.

This indicates that appropriate electron donating power is important for the activity of Co-Salcy type catalysts.

2.4 Experimental Section

NMR spectra were recorded on Bruker Ascend 500 (^{1}H: 500 MHz and ^{13}C: 126 MHz) spectrometer or a JEOL−ECS400 spectrometer (^{1}H 400 MHz; ^{13}C 101 MHz) with residual protiated solvent for ^{1}H and deuterated solvent for ^{13}C{^{1}H}. Size-exclusion-chromatography (SEC) analyses were carried with two columns (Shodex KF-804L) using tetrahydrofuran as an eluent at 40 °C at 1 mL/min. The molecular weight was calibrated against standard polystyrene samples. Elemental analyses were performed at The University of Tokyo. UV spectrum was taken by Shimadzu UV-3100.

All manipulations involving air- and/or moisture-sensitive compounds were carried out using the standard Schlenk technique under argon purified by passing through a hot column packed with BASF catalyst R3-11 or in a glove box under argon atmosphere. Analytical thin-layer chromatography was performed on a glass plates coated with silica gel (thickness: 250 μm; mean particle size: 10-12 μm) containing a fluorescent indicator (Merck, #1.05715.0001). All the solvents used for reactions were distilled under argon after drying over an appropriate drying reagent or passed through solvent purification columns (Glass Contour solvent purification system). Most of reagents were purchased from Aldrich Chemical Co. or Kanto Kagaku Co., Ltd., and were used without further purification unless otherwise specified.

Complexes (*R*,*R*)-*N*,*N*'-Bis(3-methoxy-5-*tert*-butyl-salicylidene)-1,2-cyclohexanediaminato]cobalt(II)[13], (*R*,*R*)-*N*,*N*'-Bis(3-dimethylamino-5-*tert*-butyl-salicylidene)-1,2-cyclohexanediaminato]cobalt(II)[26], (*R*,*R*)-*N*,*N*'-Bis(3,5-di-*tert*-butyl-salicylidene)-1,2-cyclohexanediaminato]cobalt(II)[27], Ferrocenium tetrakis[(3,5-trifluoromethyl)phenyl]borate[28] were synthesized according to the literatures. Propylene oxide was distilled under argon after drying over calcium hydride.

PO/CO_2 copolymerization by *in situ* oxidation of Co(II) complexes

A mixture of Co(II)-complex (35.8 μmol), co-catalyst (71.5 μmol) and oxidant (35.8 μmol) were milled in the glove box until mixture became homogeneous powder. One-fifth weight of powder and 1 mL THF were added to the 50 mL autoclave (pre-heated at 150 °C for 2 h and cooled down in a glove box) equipped with a Teflon stir bar and stirred for 30 min. After removal of THF in vacuo, autoclave was take out from glove box and propylene oxide (1.0 mL, 14.3 mmol) was added to the autoclave under Ar atmosphere. The autoclave was pressurized to 1.5 MPa of CO_2 and was left to stir at 22 °C for 2 h. The reactor was vented at 22 °C. After the reaction, resultant polymerization mixture was vacuumed to remove the residual propylene oxide. The remaining mixture was then dissolved in methylene chloride (10 mL) and quenched with 1M HCl solution (0.2 mL). Then, phenanthrene (ca. 0.15 mmol) was added as the internal standard for ^{1}H NMR. ca. 1 mL of solution was sampling for the ^{1}H NMR and SEC analysis.

PO/CO_2 copolymerization by isolated Co(III) complexes

A mixture of Co(III)-complex (35.8 μmol) and co-catalyst (35.8 μmol) were milled in the glove box until mixture became homogeneous powder. One-fifth weight of powder was added to the 50 mL autoclave (pre-heated at 150 °C for 2 h and cooled down in a glove box) equipped with a Teflon stir bar. Then, propylene oxide (1.0 mL, 14.3 mmol) was added to the autoclave under Ar atmosphere. The autoclave was pressurized to 1.5 MPa of CO_2 and was left to stir at 22 °C for 2 h. The reactor was vented at 22 °C. After the reaction, resultant polymerization mixture was vacuumed to remove the residual propylene oxide. The remaining mixture was then dissolved in methylene chloride (10 mL) and quenched with 1M HCl solution (0.2 mL). Then, phenanthrene (ca. 0.15 mmol) was added as the internal standard for ^{1}H NMR. ca. 1 mL of solution was sampling for the ^{1}H NMR and SEC analysis.

Oxidation of 7 with $FcPF_6$ for the UV-Vis-NIR observation and ESR measurement.

A mixture of 7(34.9 mg, 60.4 μmol) and $FcPF_6$(20.0 mg, 60.4 μmol) were added to the flask equipped with a Teflon stir bar. THF (5 mL) was added to this mixture and stirred for 30 minutes. Then, 50 mL of hexane was added to this mixture and precipitates were filtered and

collected. After dried in vacuo, 37.4 mg of reddish green powder was obtained. This powder was directly used for the UV-Vis-NIR observation and ESR measurement.

2.5 All copolymerization data

Table 2-2. All copolymerization detail result by using *in situ* method.

	Catalyst	PPNX	oxidant	TON for PPC	TON for CPC	MW (kg/mol)(PDI)
1-1				673	20	31.5 (1.15)
1-2	2-5	Cl	$FcPF_6$	653	16	31.3 (1.12)
1-3				760	23	33.5 (1.13)
2-1				674	23	25.7 (1.16)
2-2	2-6	Cl	$FcPF_6$	700	23	30.4 (1.14)
2-3				814	21	30.5 (1.15)
3-1				703	23	18.0 (1.13)
3-2	2-1-PF6	Cl	-	701	16	19.0 (1.13)
3-3				706	22	19.1 (1.13)
4-1				643	30	19.6 (1.13)
4-2	2-2-PF_6	Cl	-	764	32	28.2 (1.15)
4-3				729	27	22.6 (1.14)
5-1				0	0	-
5-2	2-6	Cl	$AgPF_6$[c]	0	0	-
5-3				0	0	-
6-1				608	18	22.9 (1.14)
6-2	2-6	Cl	$FcBF_4$	591	15	19.1 (1.13)
6-3				681	13	21.1 (1.13)
7-1				677	17	21.7 (1.14)
7-2	2-6	Cl	$FcBAr^F$	643	20	21.6 (1.14)
7-3				673	16	21.4 (1.14)
8-1				803	0	30.3 (1.16)
8-2	2-5	DNP	$FcPF_6$	756	0	29.0 (1.16)
8-3				846	0	38.0 (1.16)
9-1[b]				709	0	21.1 (1.15)
9-2				1034	0	31.0 (1.16)
9-3	2-6	DNP	$FcPF_6$	982	0	31.3 (1.16)
9-4				988	0	33.1 (1.16)
9-5				944	0	35.8 (1.17)
9-6				933	0	29.3 (1.16)
10-1				900	0	35.6 (1.17)
10-2	2-6	DNP	$FcPF_6$	971	0	38.2 (1.17)
10-3				977	0	40.9 (1.17)
11-1				1	1	-
11-2	2-7[c]	DNP	$FcPF_6$	3	1	-
11-3				2	1	-

a **Reaction condition are written in main text.** ***b*** **9-1 was taken as an outlier. When I calculated the average of TON, I did not include this entry value.** ***c*** **Molecular weight was not measured because no polymeric material was observed.** ***d*** **In all entries, GPC profiles observed as the bimodal.**

2.6 Relationship between molecular weight and water initiation ratio

Water initiation ratio was calculated from the GPC profile. Water initiated polymer have twice molecular weight of the PPNX initiated polymer (Figure 2-8). The area was calculated by the curve fitting of the SEC profile.

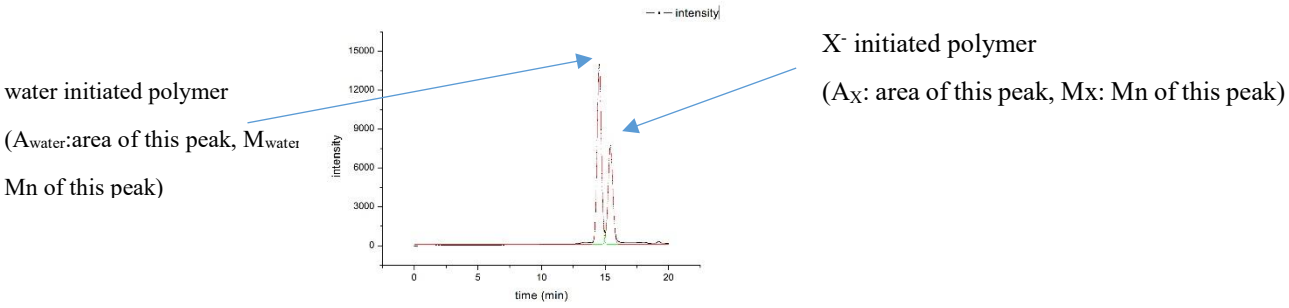


Figure 2-8: SEC profile of PPC polymerized by Co(III)-tBu-PF_6 with PPNCl.

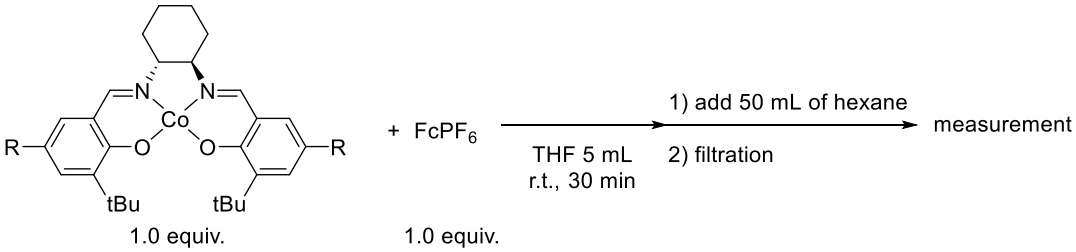
Table 2-3: Water initiation ratio and normalized Mn for all entries.

Catalyst	FcX (X=)	PPNX (X=)	TON for PPC	Mn (kg/mol) From PPNX (M_X)	Mn (kg/mol) From water (M_{water})	Mw/Mn	Area ratio of A_{water}/A_X (α)	M_{ideal}[a] (kg/mol)
Co(III)-OMe-PF_6	-	Cl	643	13.5	26.8	1.13	1.632	57.2
			764	21.2	42.5	1.15	0.969	62.4
			729	15.8	31.3	1.14	1.501	62.8
Co(III)-tBu-PF_6	-	Cl	703	12.4	24.6	1.13	1.647	52.9
			701	12.9	25.6	1.13	1.762	58.0
			706	13.0	25.8	1.10	1.745	58.0
Co(II)-OMe	PF_6	Cl	674	20.0	40.8	1.16	0.752	50.7
			700	24.8	50.8	1.14	0.576	54.1
			814	23.6	47.8	1.15	0.804	62.0
Co(II)-tBu	PF_6	Cl	673	27.4	56.3	1.13	0.345	46.8
			653	27.7	57.1	1.12	0.292	44.4
			760	29.2	59.4	1.13	0.368	51.1
Co(II)-OMe	BF_4	Cl	608	16.5	33.1	1.12	1.220	56.9
			591	13.0	25.5	1.11	1.679	55.8
			681	14.6	28.9	1.10	1.616	61.3
Co(II)-OMe	BAr^F	Cl	677	15.2	30.0	1.11	1.436	58.3
			643	15.6	31.0	1.12	1.235	53.9
			673	15.0	29.7	1.11	1.430	57.5
Co(II)-tBu	PF_6	DNP	803	23.2	48.0	1.16	0.834	63.2
			756	22.1	45.8	1.15	0.835	60.3
			846	31.0	66.1	1.16	0.542	66.8
Co(II)-OMe	PF_6	DNP	1034	23.0	47.6	1.16	1.005	70.8
			982	23.4	48.6	1.16	0.967	70.4
			988	24.6	51.2	1.16	1.001	75.9
			944	27.6	58.1	1.15	0.800	74.1
			933	21.2	43.5	1.16	1.151	71.3
Co(II)-OMe	PF_6	DNP	900	27.3	58.3	1.17	0.792	73.5
			971	31.0	67.4	1.17	0.545	67.7
			977	34.1	75.5	1.17	0.459	68.8

[a] $M_{ideal} = Mx + \alpha(Mwater)$

2.7 UV-Vis absorption spectra of Co(II) complexes and Co(III) complexes
Oxidation method

A mixture of Co-Salcy complex and oxidant (1.0 equiv. to Co-Salcy complex) were added to the flask equipped with a Teflon stir bar. 5 mL of THF was added to this mixture and stirred for 30 minutes. Then, 50 mL of hexane was added to this mixture and precipitate were filtered and collected. This powder was directly used for the UV-Vis-NIR observation.



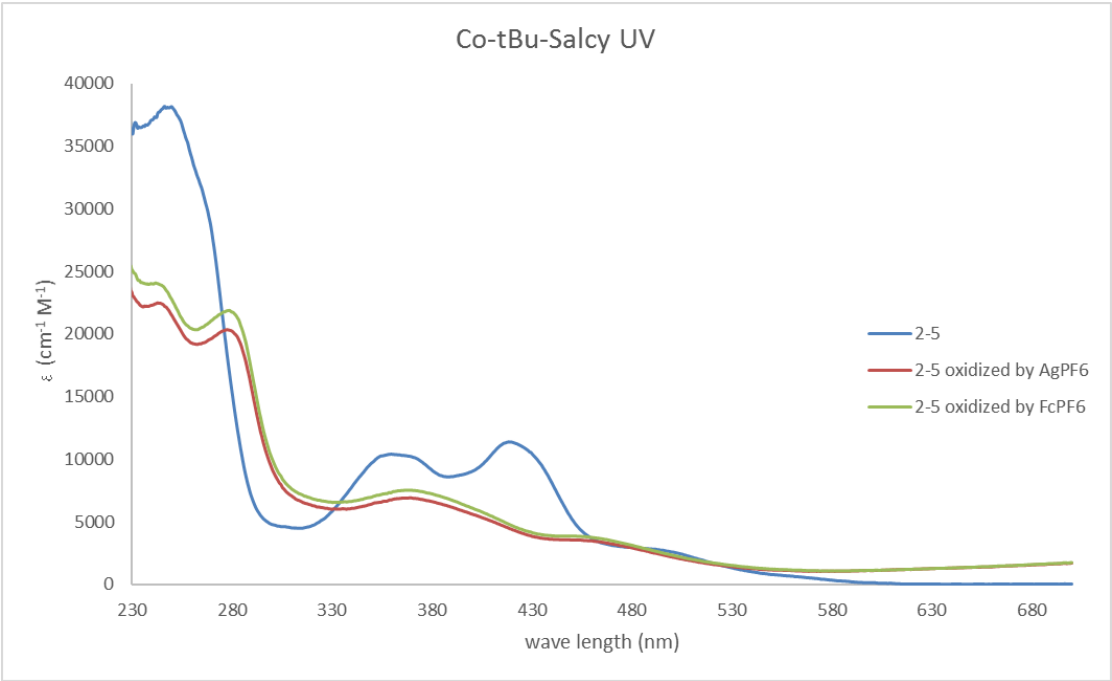


Figure 2-9: UV spectrum of Co(II)-^{t}Bu-Salcy (2-5, 5.4×10^{-5} mol/L) and Co(III)-^{t}Bu-Salcy (2-5 oxidized by $AgPF_6$, after reprecipitation, 5.3×10^{-5} mol/L and 2-5 oxidized by $FcPF_6$, after reprecipitation, 5.6×10^{-5} mol/L) in CH_2Cl_2.

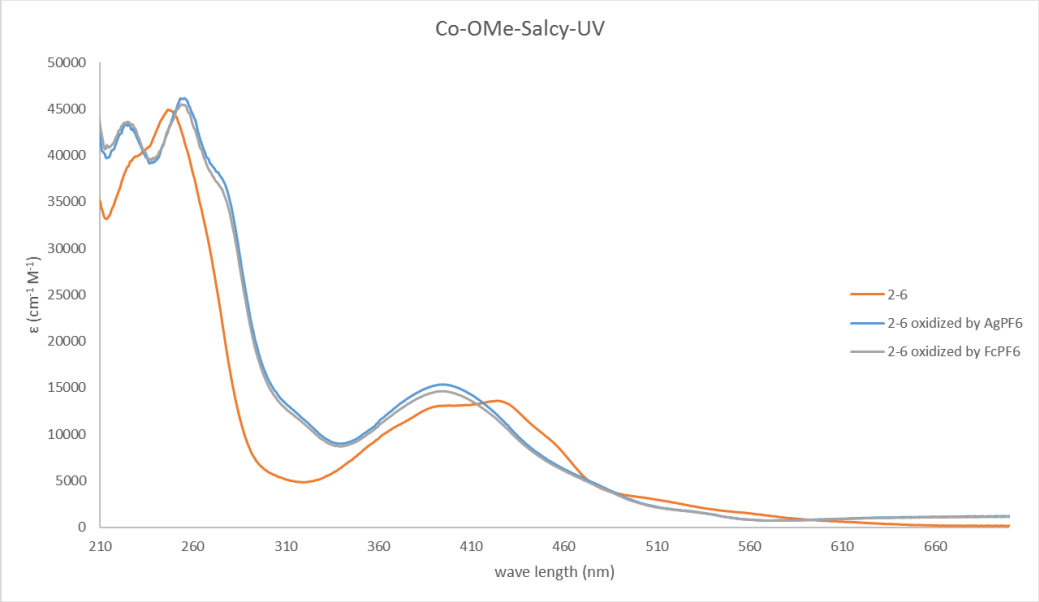


Figure 2-10: UV spectrum of Co(II)-OMe-Salcy (2-6, 4.7×10^{-5} mol/L) and Co(III)-OMe-Salcy (2-6 oxidized by $AgPF_6$, after reprecipitation, 5.2×10^{-5} mol/L and 2-6 oxidized by $FcPF_6$, after reprecipitation, 5.3×10^{-5} mol/L) in CH_2Cl_2.

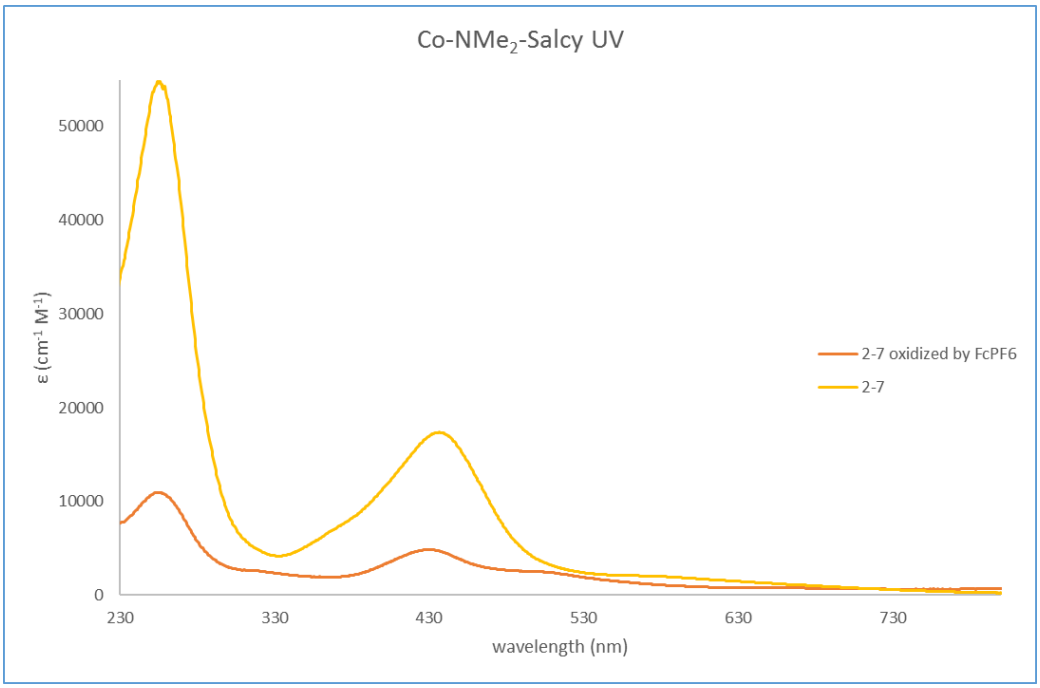


Figure 2-11: UV spectrum of Co(II)-NMe_2-Salcy (2-7, 5.0×10^{-5} mol/L) and Co(III)-NMe_2-Salcy (2-7 oxidized by $FcPF_6$, after reprecipitation, 5.4×10^{-5} mol/L) in CH_2Cl_2.

2.8 NIR absorption spectra of Co(II) complexes and Co(III) complexes

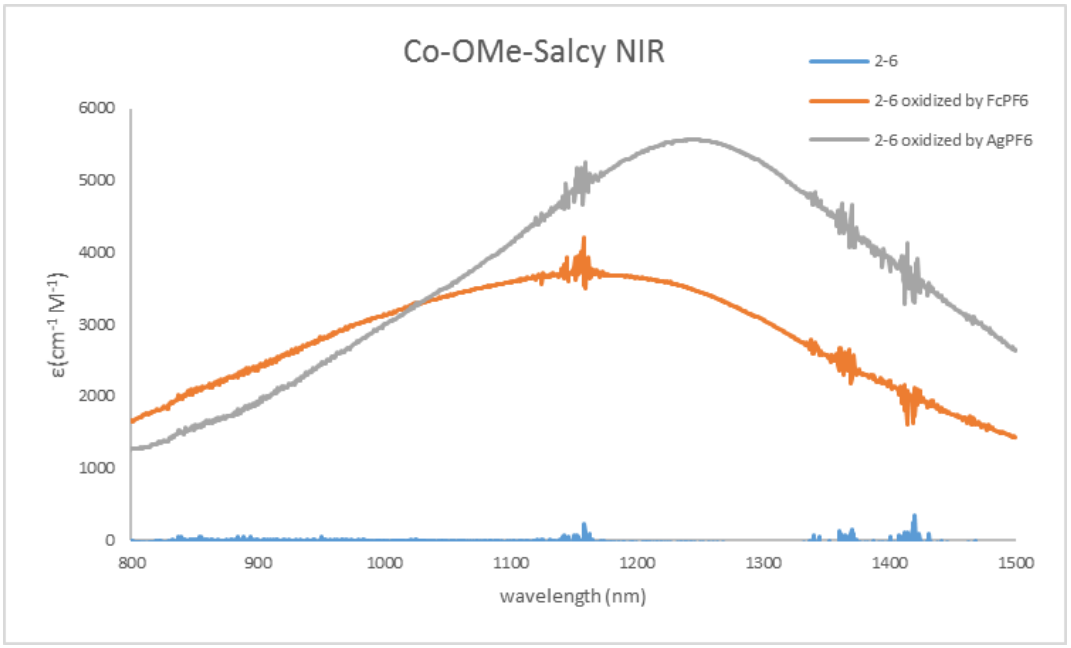


Figure 2-12: NIR spectrum of Co(II)-OMe-Salcy (2-6, 4.7×10^{-5} mol/L) and Co(III)-OMe-Salcy (2-6 oxidized by $AgPF_6$, after reprecipitation, 5.2×10^{-5} mol/L and 2-6 oxidized by $FcPF_6$, after reprecipitation, 5.3×10^{-5} mol/L) in CH_2Cl_2.

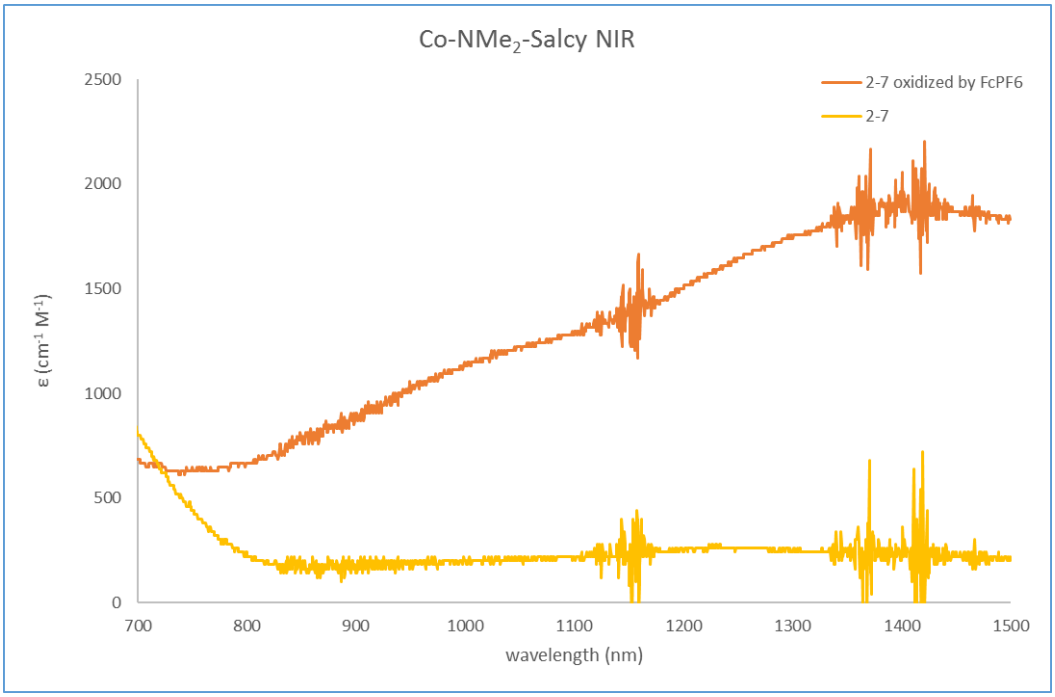


Figure 2-13: NIR spectrum of Co(II)-NMe_2-Salcy (2-7, 5.0×10^{-5} mol/L) and Co(III)-NMe_2-Salcy (2-7 oxidized by $FcPF_6$, after reprecipitation, 5.4×10^{-5} mol/L) in CH_2Cl_2.

2.9 Time dependent UV-Vis-NIR measurement

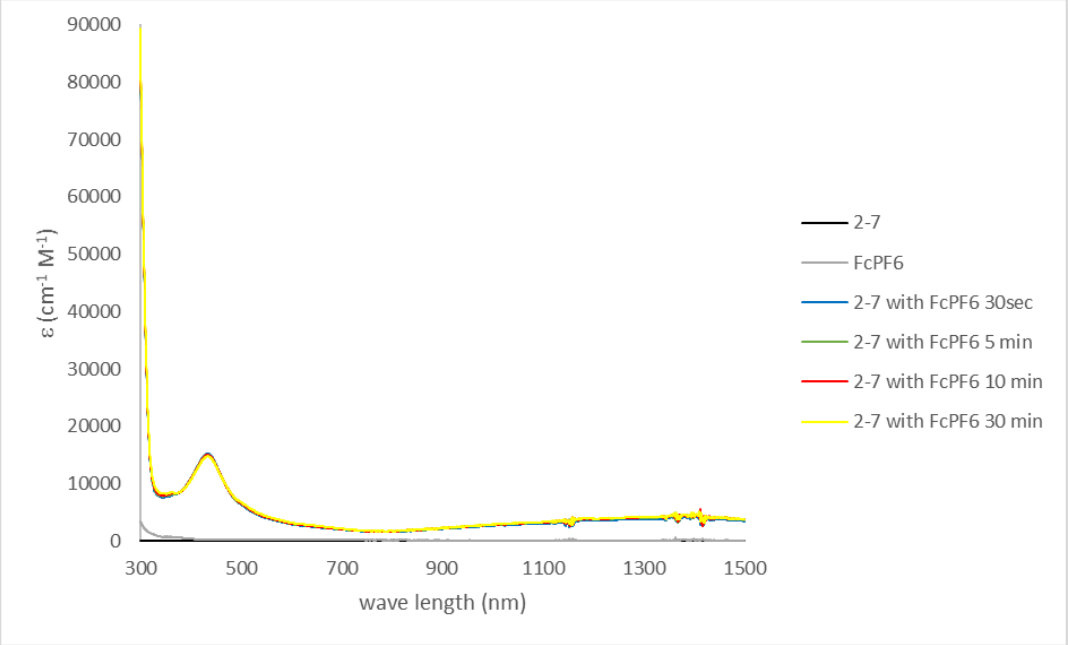


Figure 2-14: UV-Vis-NIR spectrum of Co(II)-NMe$_2$-Salcy (2-7, 5.0×10^{-5} mol/L in CH_2Cl_2), $FcPF_6$ (5.0×10^{-5} mol/L in CH_2Cl_2) and 30sec, 5min, 10 min and 30 min spectra after mixing 2-7 and $FcPF_6$ (2.5×10^{-5} mol/L).

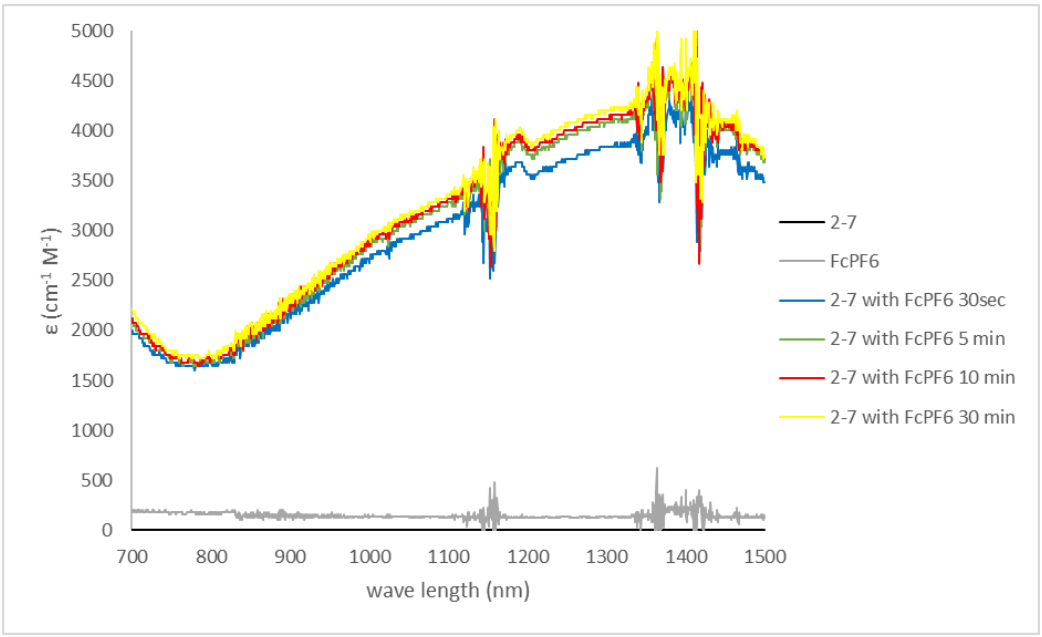


Figure 2-15: NIR region enlarged view of Figure 2-13.

2.10 Reference

(1) Inoue, S.; Koinuma, H.; Tsuruta, T.; Vol, P. L.; Carbon, C. D. *J. Polym. Sci. Part B Polym. Lett.* **1969**, *7*, 287–292.

(2) Darensbourg, D. J.; Holtcamp, M. W. *Macromolecules* **1995**, *28* (eq 2), 7577–7579.

(3) Cui, D.; Nishiura, M.; Tardif, O.; Hou, Z. *Organometallics* **2008**, *27* (11), 2428–2435.

(4) Darensbourg, D. J. *Chem. Rev.* **2007**, *107* (6), 2388–2410.

(5) LI, B.; WU, G.-P.; REN, W.-M.; WANG, Y.-M.; RAO, D.-Y.; LU, X.-B. *J. Polym. Sci. Part a-Polymer Chem.* **2008**, *46* (3), 6102–6113.

(6) Nakano, K.; Nakamura, M.; Nozaki, K. *Macromolecules* **2009**, *42* (18), 6972–6980.

(7) Cohen, C. T.; Chu, T.; Coates, G. W.; Cohen, C. T.; Chu, T.; Chu, T.; Coates, G. W.; Coates, G. W.; Cohen, C. T.; Chu, T.; Chu, T.; Coates, G. W.; Coates, G. W. *J. Am. Chem. Soc.* **2005**, *127* (31), 10869–10878.

(8) Lu, X. B.; Ren, W. M.; Wu, G. P. *Acc. Chem. Res.* **2012**, *45* (10), 1721–1735.

(9) Kielland, N.; Whiteoak, C. J.; Kleij, A. W. *Adv. Synth. Catal.* **2013**, *355* (11–12), 2115–2138.

(10) (1997) 26 - Cobalt, Rhodium and Iridium, in *Chemistry of the Elements (Second Edition)*, Butterworth-Heinemann, Oxford, pp. 1113–1143.

(11) Tokunaga, M.; Larrow, J. F.; Kakiuchi, F.; Jacobsen, E. N. *Science* **1997**, *277* (5328), 936–938.

(12) Venkatasubbaiah, K.; Feng, Y.; Arrowood, T.; Nickias, P.; Jones, C. W. *ChemCatChem* **2013**, *5* (1), 201–209.

(13) Kochem, A.; Kanso, H.; Baptiste, B.; Arora, H.; Philouze, C.; Jarjayes, O.; Vezin, H.; Luneau, D.; Orio, M.; Thomas, F. *Inorg. Chem.* **2012**, *51* (20), 10557–10571.

(14) Dzygiel, P.; Reeve, T. B.; Piarulli, U.; Krupicka, M.; Tvaroska, I.; Gennari, C. *European J. Org. Chem.* **2008**, No. 7, 1253–1264.

(15) Estévez, R. E.; Oller-López, J. L.; Robles, R.; Melgarejo, C. R.; Gansäuer, A.; Cuerva, J. M.; Oltra, J. E. *Org. Lett.* **2006**, *8* (24), 5433–5436.

(16) Darensbourg, D. J.; Ganguly, P.; Choi, W. *Inorg. Chem.* **2006**, *45* (10), 3831–3833.

(17) Ohkawara, T.; Suzuki, K.; Nakano, K.; Mori, S.; Nozaki, K. *J. Am. Chem. Soc.* **2014**, *136* (30), 10728–10735.

(18) Kurahashi, T.; Kikuchi, A.; Tosha, T.; Shiro, Y.; Kitagawa, T.; Fujii, H. *Inorg. Chem.* **2008**, *47* (5), 1674–1686.

(19) Kurahashi, T.; Fujii, H. *J. Am. Chem. Soc.* **2011**, *133* (21), 8307–8316.

(20) Kurahashi, T.; Fujii, H. *Inorg. Chem.* **2013**, *52* (7), 3908–3919.

(21) The lower activity in entries 3 and 4 might be attributed to the trace amount of silver salt.

(22) Paul, S.; Romain, C.; Shaw, J.; Williams, C. K. *Macromolecules* **2015**, *48* (17), 150819141045005.

(23) Coates, G. W.; Moore, D. R. *Angew. Chemie - Int. Ed.* **2004**, *43* (48), 6618–6639.

(24) Time dependent UV measurement was carried out to observe the oxidation process of **2-7** upon exposure to $FcPF_6$. However, the result indicated that Co(III)-NMe_2-Salcy and Co(II)-NMe_2-Salcy radical cationic species reached equilibrium within 30 sec.

(25) Xia, W.; Salmeia, K. A.; Vagin, S. I.; Rieger, B. *Chem. - A Eur. J.* **2015**, *21* (11), 4384–4390.

(26) Chiang, L.; Allan, L. E. N.; Alcantara, J.; Wang, M. C. P.; Storr, T.; Shaver, M. P. *Dalt. Trans.* **2014**, *43* (11), 4295–4304.

(27) Leung, W.-H. H.; Chan, E. Y. Y.; Chow, E. K. F.; Williams, I. D.; Peng, S.-M. M. *J. Chem. Soc. Dalt. Trans.* **1996**, No. 7, 1229–1236.

(28) Le Bras, J.; Jiao, H.; Meyer, W. E.; Hampel, F.; Gladysz, J. . *J. Organomet. Chem.* **2000**, *616* (1), 54–66.

2.11 Authorization

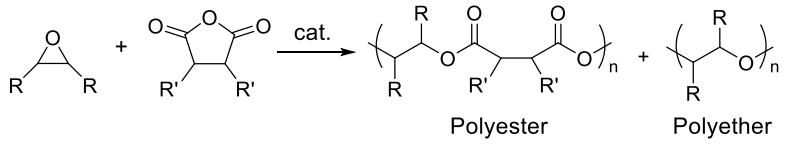
A part of this chapter is reprinted from *Chem. - A Eur. J.* **2016**, *22* (38), 13677–13681. with permission from John Wiley & Sons, Inc.

Chapter 3

Investigation of Axial Ligands Effect on the Catalytic Activity of Co-Salphen Complex for the Copolymerization of Cyclohexene Oxide with Phthalic Anhydride

3.1 Introduction

Aromatic polyesters (polyarylates) and semi-aromatic polyesters (poly(alkylene terephthalates)) are widely used as common materials such as thermoplastics or biodegradable materials.[1] Recently, aliphatic polyesters have also been attracting much attention due to their biodegradability and flexibility.[2,3] To access polyesters, two representative methods often used are, the polycondensation reaction of diacids with diols, and ring-opening polymerization of cyclic esters.[3] Polycondensation reaction have required finely controlled and dehydrated reaction condition to obtain the high molecular weight and low polydispersity polyester. On the other hand, the number of accessible polyesters given by the ring-opening polymerization have been rather limited due to the lower variation of cyclic monomers. As an alternative way to access polyesters, we can use ring-opening copolymerization (ROCOP) of epoxides with cyclic diacid anhydrides by using Lewis acidic metal catalysts (Scheme 3-1).[4]



Scheme 3-1: General scheme of ROCOP of epoxide with diacid anhydride.

Since its discovery in 1960,[5] many kinds of Lewis acidic metal mediated copolymerization of epoxide with diacid anhydride were reported so far. For this kind of copolymerization, metal(III)-Salen type complexes have been known as easily prepared and highly active catalyst system.[4] In particular, Cr(III)-Salphen-Cl (Figure 3-1, **3-1**) complex in combination with 1 equivalent of 4-dimethylaminopyridine (DMAP) has been known as the benchmark catalyst system: The TON of **1** with DMAP for copolymerization of cyclohexene oxide (CHO) with phthalic anhydride (PA) was 243 at 135 °C in 1 hour. Duchateau and co-workers have extensively investigated the reaction mechanism of the metal-salphen complexes aiming at improvement of the catalytic activity.[6-9]

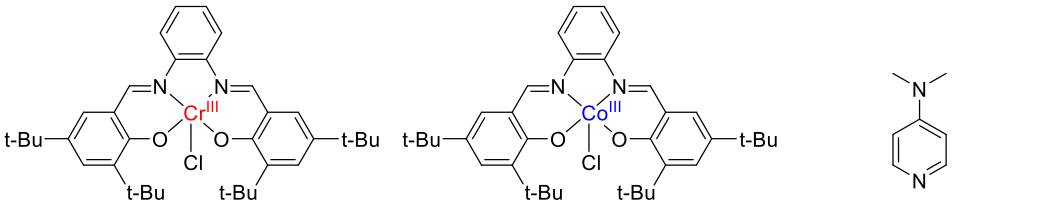
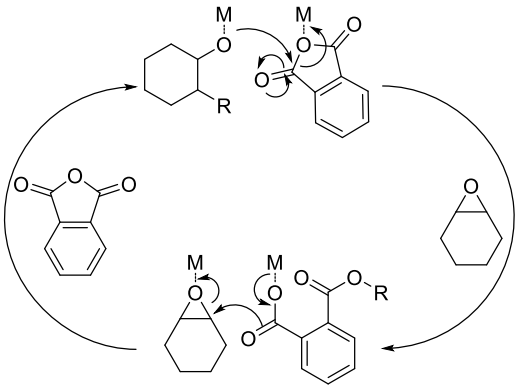


Figure 3-1: Reported metal-Salphen complexes.

In contrast to the well-studied Cr-Salphen type catalyst, much less attention have been paid to Co-Salphen type complexes because Co-salphen type complex have generally shown lower activity than Cr-salphen complex for copolymerization of epoxide with diacid anhydride.[7] In 2012, Duchateau and co-workers reported that Co-Salphen-Cl (**3-2**) with 1 equivalent DMAP co-catalyst showed TOF of 243 h^{-1} at 135 °C for the bulk copolymerization of CHO with PA. This activity was comparative with Cr-Salphen complex **3-1** in the presence of 1 equivalent of DMAP co-catalyst.

Recently, bimetallic catalysts have been intensively studied for the copolymerization reaction. In 2013, Xiao-Bing Lu and co-workers reported that bimetallic Cr-salan catalyst showed 4 times higher activity than the corresponding monometallic Cr-salan catalyst for the copolymerization of epichlorohydrin with maleic anhydride.[10] Subsequently, they have reported highly active bimetallic Al, Co, and Cr-salen catalyst for the copolymerization of CHO with PA.[11] In this study, they have proposed a concerted mechanism of the two metal-species, that is the ring opening reactions of an epoxide and an acid anhydride were both mediated by the two metal centers (Scheme 3-2). A similar bimetallic mechanism has also been proposed for the copolymerization of epoxide with CO_2 by using bimetallic complexes (see chapter 1-3-3).[4,12] For both copolymerization, drastic activity improvement have been exhibited when two metal species are at the proper distance.[11,13]



Scheme 3-2: Proposed bimetallic mechanism for copolymerization of CHO with PA.

Previously, Duchateau and co-workers have considered the role of DMAP in the copolymerization of CHO with PA. Polyester produced by adding 1 equivalent of DMAP to **3-1** catalyst have been analyzed by MALDI-TOF-MS. They have found that the detected polymers were only initiated by DMAP but not Cl.[6] From this result, they have speculated that DMAP was the key for the high catalytic activity possibly due to the efficient initiation. Encouraged by the positive effect of DMAP in the Cr(III) catalyst system, I focused my interest on the use of DMAP as the axis ligand instead of Cl in Co(III) catalysts.

Here, I found that cationic Co(III)-Salphen type catalysts bearing two DMAP molecules (Figure 3-2, **3-3**) showed very high activity, TOF of 282 h^{-1} for copolymerization of CHO with PA at 100 °C. This value is the highest activity within the monometallic catalyst ever reported. In addition, I also found that the activity of bimetallic complex **3-5** is much higher than monometallic complex **3-4**. These cationic complexes also served as a catalyst for the copolymerization of epoxide with CO_2 to selectively produce the polycarbonate.

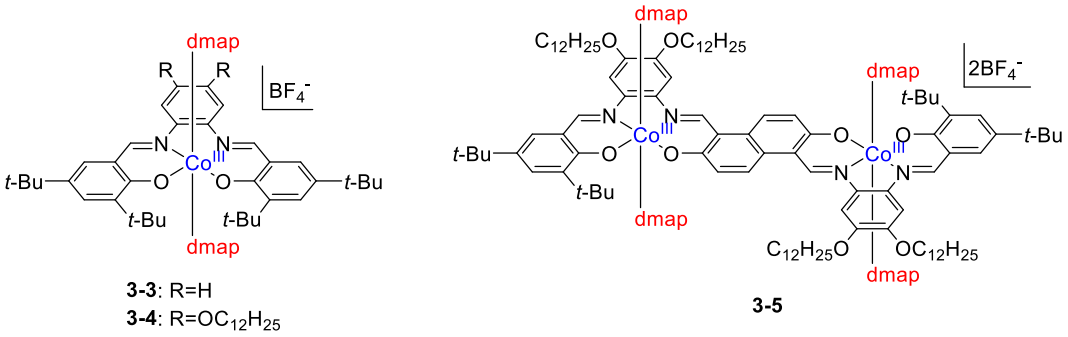
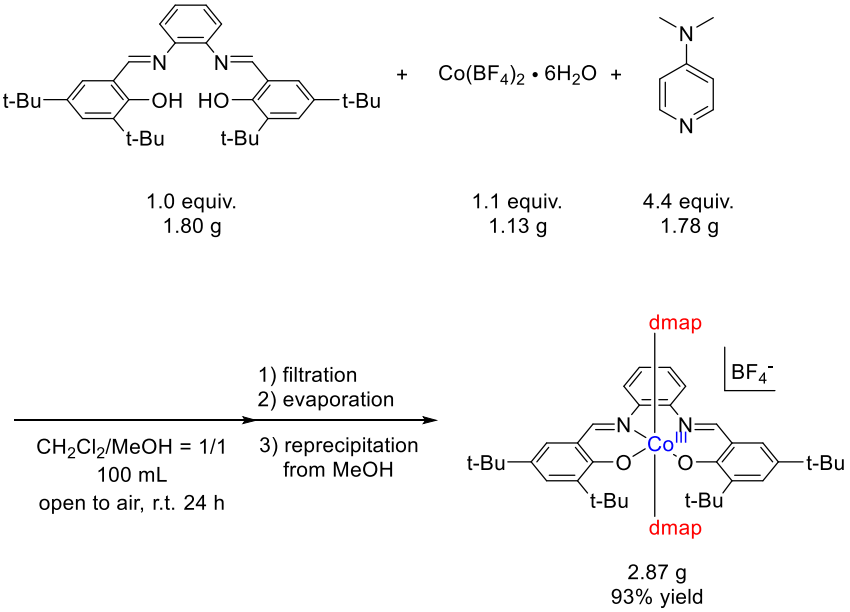


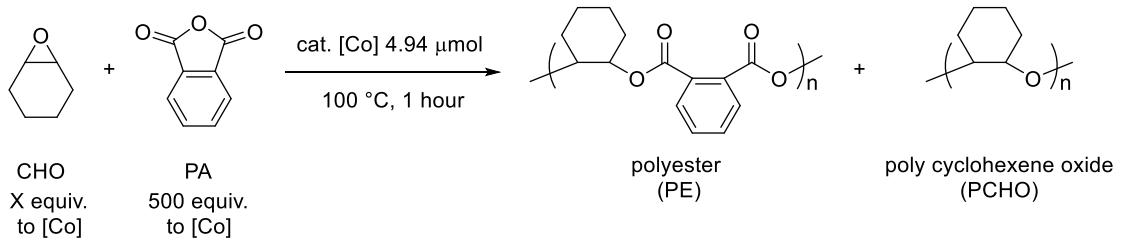
Figure 3-2: Cationic Co-Salphen complexes synthesized in this work.

3.2 Result and Discussion

First, I carried out the synthesis of new complex **3-3**. Simple mixing of salphen ligand, $Co(BF_4)_2 \cdot 6H_2O$, and DMAP gave the complex **3-3** in a 93% yield (Scheme 3-3).



Scheme 3-3: Reaction scheme to synthesize the complex **3-3**.



Scheme 3-4: The copolymerization of CHO with PA.

Table 3-1: The results of copolymerization of CHO with PA catalyzed by Cr(III) or Co(III)-Salphen catalysts. [a]

Entry	catalyst	CHO equiv. X =	TON[b] for		Polyester Ratio (%)	M_n[c] (kg/mol)	M_w/M_n[c]
			PE	PCHO			
1[d]	**3-3**	500	282	12	96	15.1	1.1
2	**3-4**	500	266	14	95	19.1	1.1
3[e]	**3-1**	500	268	27	91	7.9	1.2
4[e]	**3-2**	500	194	48	80	7.3	1.2
5	**3-3**	4000	240	12	95	5.9	1.1
6	**3-4**	4000	229	16	93	7.2	1.1
7	**3-5**	4000	305	32	91	5.0	1.1

a All copolymerization was performed at 100 °C, for 2 hours. b TON determined by ^{1}H NMR analysis. c Determined by size-exclusion chromatography (SEC) analysis using THF as an eluent and polystyrene as a standard. d Stir bar was stopped during the reaction e 1 equiv. of DMAP to catalyst was added as the co-catalyst

Copolymerization of CHO and PA with metal-salphen type catalysts was examined in the procedure described in Scheme 3-4 and the results were summarized in Table 3-1. First, cationic Co(III)(dmap)$_2$ catalysts **3-3** and **3-4** were successfully applied to this copolymerization reaction (entries 1 and 2). The catalyst **3-3** showed TON of 282, that is the highest value ever reported for this copolymerization reaction by monometallic catalyst. Complex **3-4**, an analog of **3-3** with two long alkyl ether chains also showed high activity (TON 266), but the value being slightly lower than that with **3-3**. From this result, I found that introduction of electron donating groups on the ligand lowered the activity of complexes for this copolymerization reaction. This could be explained that, the strong Lewis acidity play an important role for this copolymerization reaction. Both **3-3** and **3-4** produced very small

amount of ether linkage (~95% polyester selectivity). To compare these complexes, I also carried out the same copolymerization reaction by using the known benchmark complex Cr(III)Cl complex **3-1** and Co(III)Cl complex **3-2** under the same reaction conditions (entries 3 and 4). The TON of **3-1** was 268, the value being almost the same as that with catalyst **3-4**, but the polyester selectivity was lower (~90% polyester selectivity) than that with **3-4**. The activity of **3-2** for this copolymerization was much lower than other complexes. The TON of 194 and 80% polyester selectivity were observed in this condition.

In entries 1 and 2, the magnetic stirring was not sufficient at higher conversion of the monomers because of the high viscosity of the product solution. Accordingly, the copolymerization was also examined in the presence of excess amount of CHO. Even in this condition, high activity was observed for complexes **3-3** and **3-4** (entries 5 and 6), that is, TON values were 240 and 229, respectively. It is notable that complex **3-5,** a bimetallic analog of **3-4**, showed even higher activity (TON of 305, entry 7). In literature, several examples were reported for the improvement of catalytic activity with a bimetallic species when compared to its counterpart monometallic species. For example, Xiao-Bing Lu and co-workers reported highly active bimetallic Al-salen complexes. They reported that Al-Al distance of these complexes were ca. 7.7-7.9 Å in their X-ray single crystal analyses.[11] Williams also reported highly active Zn bimetallic system with Zn-Zn distance of 3.1 Å.[14] Compared with these metal-metal distances of the bimetallic complexes, the Co-Co distance of complex **3-5**, estimated to be 10.3 Å based on DFT calculation of its Ni analog[15], is rather too long. This result indicated that the observed "bimetallic effect" for catalyst **3-5** could be different from the simple fixation of the two metal centers in the reaction mechanism depicted in Scheme 3-2.

The MALDI-TOF-MS measurement of the polyesters obtained by complexes **3-1** and **3-3** revealed that the copolymerization was initiated by DMAP (Figure 3-3). Detected series were, (i) DMAP with polyester unit signals (indicated by ♣), (ii) DMAP with polyester unit signals and one additional cyclohexene oxide unit (indicated by ♥), and (iii) One H_2O molecule eliminated from (ii) (indicated by ♦). Probably, polymers of series (ii) were terminated by cyclohexene oxide ring opening because it could cause the dehydration while anhydride moiety terminated polymer

does not undergo the dehydration. On the other hand, two structures are possible for series (i), namely, the polymerization was initiated by the nucleophilic ring opening by DMAP first occurred at either CHO or PA. From this observation, it is suggested that DMAP was the sole initiator of this copolymerization reaction. Only DMAP initiated fragment was also observed for polyester obtained by complex **3-2**. This is the same result as observed by Duchateau and co-workers for the copolymerization of CHO with PA by tetraphenylporphyrin-Cr-Cl complex with DMAP co-catalyst.[6]

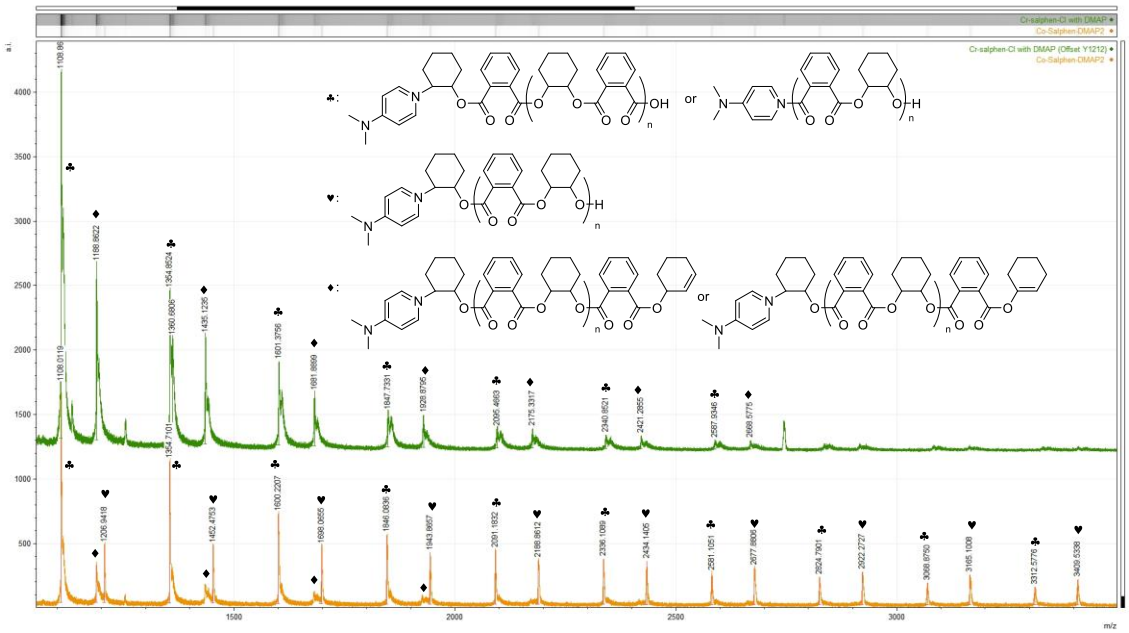


Figure 3-3: MALDI-TOF-MS spectrum of the polyester obtained with **3-1** (upper) and **3-3** (bottom).

The higher activity of catalyst **3-3** than catalyst **3-2** could be explained as follows. From the result of MALDI-TOF-MS measurement, DMAP mainly worked as the initiator. Therefore, during the propagation step, **3-2** and **3-3** probably have the structure shown in Figure 3-4.

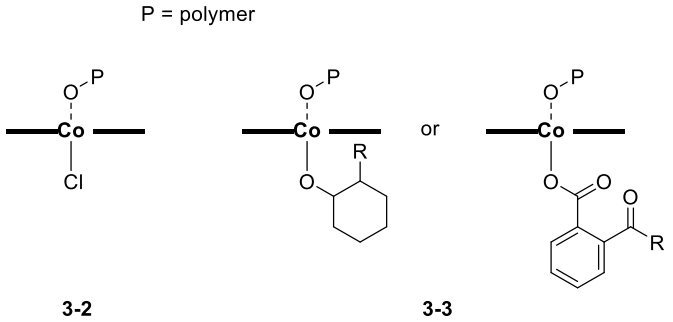
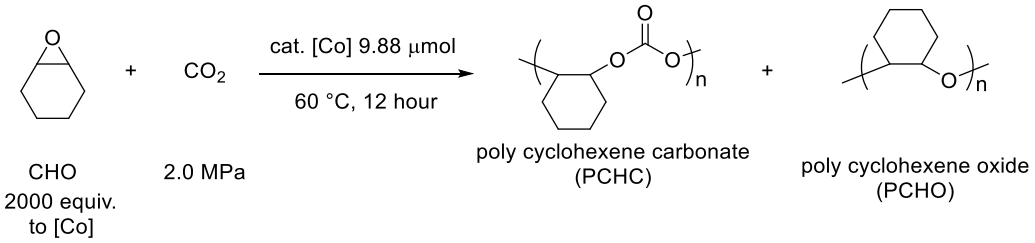


Figure 3-4: Proposed structure of **3-2** and **3-3** during the propagation.

During the polymer propagation step, Cl was always coordinated as the trans ligand in **3-2**. On the other hand, complex **3-3** had the alkoxide or carboxylate as the trans axial ligand. Compared with Cl ligand, alkoxide or carboxylate is a more electron donating ligand. This electron donation would decrease the activation energy of epoxide ring-opening reaction and diacid anhydride ring-opening reaction by the same way as was discussed in chapter 2 (Figure 2-3).

The catalysts **3-1**~**3-5** here newly developed were also applicable to the copolymerization of epoxide with CO_2. Reaction procedures were summarized in Scheme 3-5 and results of copolymerization reaction were summarized in Table 3-2.



Scheme 3-5: Procedure for the copolymerization of CHO with CO_2.

Table 3-2: The results of copolymerization of CHO with CO_2.[a]

Entry	catalyst	TON[b] for		**PCHC ratio (%)**	M_n[c] (kg/mol)	M_w/M_n[c]
		PCHC	PCHO			
1	**3-3**	202	4	98	6.0	1.1
2	**3-4**	285	21	93	13.7	1.1
3	**3-5**	347	9	97	9.9	1.1
4[d]	**3-1**	411	15	96	6.5	1.2
5[d]	**3-2**	66	12	85	2.0	1.2

a All copolymerization was performed at 60 °C under 2.0 MPa of CO_2 pressure for 12 hours. b TON determined by ^{1}H NMR analysis. Cyclic carbonate was not observed in this case c Determined by size-exclusion chromatography (SEC) analysis using THF as an eluent and polystyrene as a standard. d 1 equiv. of DMAP to catalyst was added as the co-catalyst

After the copolymerization reaction, cyclic carbonate was not observed at all in any entries. Complex **3-3** showed moderate reactivity for the copolymerization of CHO with CO_2 (TON of 202) with high PCHC selectivity of 98% The complex **3-4** which is the long alkyl ethers attached analog of **3-3** showed higher activity for this copolymerization reaction (TON of 285) and high selectivity (93%). Probably, this activity improvement is derived from the "electron-donating group effect" as was discussed in the previous chapter of this thesis.[16] Bimetallic complex **3-5** showed further improved activity for this copolymerization with TON of 347, higher than that with its monometallic analog **3-4**. As for the bimetallic effect in the copolymerization of epoxide with CO_2, Rieger and co-workers predicted that 4.3-5.0 Å was the ideal distance for the copolymerization of ethylene oxide with CO_2 by using Zn bimetallic complexes.[17] Williams and co-workers reported highly active Co(II)-Co(III) bimetallic complexes for copolymerization of CHO with CO_2 have ca. 2.95 Å Co-Co distance.[18] Xiao-Bing Lu reported the highly active bimetallic complex that have 7.7~7.9 Å metal-metal distance.[19] Compared with these complexes, the Co-Co distance of 10.3 Å for **3-5** estimated above is exceptionally long.

To compare the activity of these cationic complexes, complex **3-1**, known as a good catalyst for the copolymerization of epoxide with CO_2,[1] showed the highest activity (TON of 411) in the complexes examined in this study. In sharp contrast, complex **3-2** showed the lowest activity

(TON of 66) and polycarbonate selectivity (85%). In both epoxide/AH and epoxide/CO_2 copolymerization reactions, cationic Co-salphen-$DMAP_2$ type catalyst showed higher activity than neutral Co-salphen-Cl complex **3-2**. This could be explained by the electron donating ability of the axial ligand, that is oxygen anion is more electron-donating than Cl, during the propagation as was discussed for the copolymerization of CHO with PA (Figure 3-4).

3.3 Conclusion

In conclusion, I found the highly active cationic Co-Salphen-$DMAP_2$ type catalysts **3-3**, **3-4**, and **3-5** for the copolymerization of cyclohexene oxide with phthalic anhydride. Compared with the benchmark Cr catalyst **3-1** and Co-Salphen-Cl complex **3-2** with DMAP co-catalyst, these complexes showed a higher activity for the copolymerization of CHO with PA. From the result of MALDI-TOF-MS measurement of the resulting polyesters, it was suggested that DMAP served as the sole initiator.

I also found that complex **3-5** showed the higher activity than monometallic analog **3-4**. The the Co-Co distance of 10.3 Å for **3-5** is rather too long compared to the ideal distance in the reported examples for the “bimetallic effect” and details of its origin is still unclear so far.

These complexes **3-3~3-5** also showed improved but yet moderate activity for the copolymerization of cyclohexene oxide with CO_2, compared to **3-2**. Here again, complex **3-5** showed “bimetallic effect” in this copolymerization reaction.

3.4 Experimental Section

Generals are common to chapter 2.

Complexes [*N*,*N*’-Bis(3,5-di-*tert*-butyl-salicylidene)-1,2-phenylenediaminato] cobalt(III) chloride,[21] [*N*,*N*’-Bis(3,5-di-*tert*-butyl-salicylidene)-1,2-phenylenediaminato] chromium(III) chloride[22], [*N*,*N*’-Bis(3,5-di-*tert*-butyl-salicylidene)-4,5-bis(dodecyloxy)-1,2-phenylenediaminato]cobalt(III) bis(4-

dimethylaminopyridine) tetrafluoroborate[23], and bimetallic Co-salphen-DMAP$_2$[23] complex, were synthesized according to the literatures. Cyclohexene oxide was distilled under nitrogen after drying over calcium hydride. Phthalic anhydride was recrystallized from dichloromethane/hexane and further purified by sublimation.

Synthesis of [*N*,*N*'-Bis(3,5-di-*tert*-butyl-salicylidene)-1,2-phenylenediaminato] bis(4-dimethylaminopyridine) cobalt(III) tetrafluoroborate

A mixture of *N*,*N*'-Bis(3,5-di-tert-butyl-salicylidene)-1,2-phenylenediamine(1.80 g, 3.33 mmol), Co(II) tetrafluoroborate hexahydrate (1.13 g, 3.31 mmol), and DMAP (1.78 g, 14.6 mmol) was placed in a 200 mL round-bottom flask equipped with a Teflon coated stir bar and dissolved with 50 mL of dichloromethane and 50 mL of methanol. After stirring for 12 hours under air at ambient temperature, the reaction mixture was concentrated by evaporation and water was added to the reaction mixture to reprecipitate the desired product. After filtration, the obtained brown solid was dissolved in dichloromethane and hexane was layered on the product solution to recrystallize the product. After the recrystallization, 2.87 g of product was obtained in 93% yield. ^{1}H-NMR (CD_2Cl_2, 500 MHz) δ: 8.47 (2H, s), 8.04 (2H, dd, J = 6.3, 3.4 Hz), 7.53 (2H, d, J = 2.4 Hz), 7.47 (2H, dd, J = 6.2, 3.3 Hz), 7.25 (4H, d, J = 7.6 Hz), 7.15 (2H, d, J = 2.6 Hz), 6.19 (4H, d, J = 7.6 Hz), 2.86 (12H, s), 1.54 (18H, s), 1.31 (18H, s). ^{13}C-NMR (CD_2Cl_2, 126 MHz) δ: 165.7, 158.9, 155.3, 149.8, 144.0, 143.8, 137.9, 133.4, 129.5, 128.9, 117.2, 116.9, 107.7, 39.3, 36.3, 34.3, 31.2, 30.2. Elemental analysis: Calcd. for $C_{50}H_{66}N_6O_2CoBF_4$: C, 64.65; H, 7.16; N, 9.05. Found: C, 64.42; H, 7.08; N, 9.33.

CHO/PA copolymerization reaction

A mixture of Co or Cr complex (4.94 μmol of Co or Cr) and phthalic anhydride (367.4 mg, 2.47 mmol) was placed in a dried 20 mL Schlenk flask equipped with a Teflon coated stir bar. The air in the flask was replaced by nitrogen and cyclohexene oxide was added the flask via syringe.

After addition of cyclohexene oxide, flask was sealed with glass stopper and soaked in the pre-heated oil bath. After the 1 hour, remained cyclohexene oxide was removed *in vacuo* and phenanthrene (ca. 0.15 mmol) was added as an internal standard for ^{1}H NMR measurement.

CHO/CO_2 copolymerization reaction

A Co(III)-complex (9.88 μmol) was placed in a 50 mL autoclave (pre-heated at 150 °C for 2 h and cooled down *in vacuo*) equipped with a Teflon stir bar. To this, was added cyclohexene oxide (2.0 mL, 19.8 mmol) under Ar atmosphere. The autoclave was then pressurized with 2.0 MPa of CO_2 and was left to stir at 60 °C for 12 h. The reactor was vented at ambient temperature. After the reaction, the resulting polymeric mixture was vacuumed to remove the residual cyclohexene oxide. The remaining mixture was then dissolved in methylene chloride (10 mL) and quenched with 1M HCl solution (0.2 mL). To this, was added phenanthrene (ca. 0.15 mmol) as an internal standard for ^{1}H NMR measurement. An aliquot, ca. 1 mL of the solution was sampled for the ^{1}H NMR and SEC analysis.

3.5 Reference

(1) Köpnick, H.; Schmidt, M.; Brügging, W.; Rüter, J.; Kaminsky, W. In *Ullmann's Encyclopedia of Industrial Chemistry*; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, Germany, 2000.

(2) Stevens, E. . *Green plastics : an introduction to the new science of biodegradable plastics*; Princeton, N.J. ; Oxford : Princeton University Press, 2002.

(3) *Handbook of Thermoplastic Polyesters*; Fakirov, S., Ed.; Wiley-VCH Verlag GmbH & Co. KGaA: Weinheim, FRG, 2002.

(4) Paul, S.; Zhu, Y.; Romain, C.; Brooks, R.; Saini, P. K.; Williams, C. K. *Chem. Commun.* **2015**, *51*, 6459–6479.

(5) Fischer, R. F. *J. Polym. Sci.* **1960**, *44* (143), 155–172.

(6) Huijser, S.; Hosseininejad, E.; Sablong, R.; Jong, C. De; Koning, C. E.; Duchateau, R. *Macromolecules* **2011**, *44* (5), 1132–1139.

(7) Hosseini Nejad, E.; Van Melis, C. G. W.; Vermeer, T. J.; Koning, C. E.; Duchateau, R. *Macromolecules* **2012**, *45* (4), 1770–1776.

(8) Hosseini Nejad, E.; Paoniasari, A.; Koning, C. E.; Duchateau, R. *Polym. Chem.* **2012**, *3* (5), 1308.

(9) Nejad, E. H.; Paoniasari, A.; Van Melis, C. G. W.; Koning, C. E.; Duchateau, R. *Macromolecules* **2013**, *46* (3), 631–637.

(10) Liu, J.; Bao, Y.-Y.; Liu, Y.; Ren, W.-M.; Lu, X.-B. *Polym. Chem.* **2013**, *4* (5), 1439–1444.

(11) Li, J.; Liu, Y.; Ren, W.-M.; Lu, X.-B. *J. Am. Chem. Soc.* **2016**, jacs.6b07520.

(12) Buchard, A.; Jutz, F.; Kember, M. R.; White, A. J. P.; Rzepa, H. S.; Williams, C. K. *Macromolecules* **2012**, *45* (17), 6781–6795.

(13) Liu, Y.; Ren, W.-M.; He, K.-K.; Lu, X.-B. *Nat. Commun.* **2014**, *5*, 5687.

(14) Saini, P. K.; Romain, C.; Zhu, Y.; Williams, C. K. *Polym. Chem.* **2014**, *5* (20), 6068–6075.

(15) Houjou, H.; Yagi, K.; Yoshikawa, I.; Mutai, T.; Araki, K. *J. Phys. Org. Chem.* **2016**.

(16) Hatazawa, M.; Nakabayashi, K.; Ohkoshi, S.; Nozaki, K. *Chem. - A Eur. J.* **2016**, *22* (38), 13677–13681.

(17) Klaus, S.; Lehenmeier, M. W.; Herdtweck, E.; Deglmann, P.; Ott, A. K.; Rieger, B. *J. Am. Chem. Soc.* **2011**, *133* (33), 13151–13161.

(18) Kember, M. R.; Jutz, F.; Buchard, A.; White, A. J. P.; Williams, C. K. *Chem. Sci.* **2012**, *3* (4), 1245.

(19) Liu, Y.; Ren, W. M.; Liu, J.; Lu, X. B. *Angew. Chemie - Int. Ed.* **2013**, *52* (44), 11594–11598.

(20) Darensbourg, D. J. *Chem. Rev.* **2007**, *107* (6), 2388–2410.

(21) Jiang, C. W.; Zhao, C. C.; Zhou, K. Y. *Adv. Mater. Res.* **2013**, *734–737*, 2159–2162.

(22) Darensbourg, D. J.; Mackiewicz, R. M.; Rodgers, J. L.; Phelps, A. L. *Inorg. Chem.* **2004**, *43* (6), 1831–1833.

(23) R. Takahashi, Y. Nagano, I. Yoshikawa, H. Houjou, to be submitted

Chapter 4
Conclusion and Perspective

4.1 Conclusion

In my doctoral thesis, I investigated the relationship between the electronic state of Co(III)-salen complexes and their activity for the copolymerization of epoxide with CO_2 or diacid anhydride. Throughout the studies, for both copolymerization reactions, it was suggested that appropriate electron donation from the ligand to a metal center, in other words, appropriate Lewis acidity of metal center, is required for the improvement of the catalytic activity.

In chapter 2, the electron donating group effect on the Co(III)-Salcy complexes for the copolymerization of PO with CO_2 was studied by using *in situ* generation of active Co(III)-Salcy species from Co(II)-Salcy complex. It was found that appropriate strength of electron donating group is effective for copolymerization of PO with CO_2 when PPNDNP was used as a co-catalyst. When the electron density of the ligand was even higher, LMCT of Co(III)-Salcy complex was suggested to suppress the activity for the copolymerization reaction.

In chapter 3, I investigated the axial ligand effect on the Co(III)-Salphen complexes for the copolymerization of CHO with PA. Co(III)-Salphen-$DMAP_2$ catalyst showed higher activity than Co(III)-Salphen-Cl or Cr(III)-Salphen-Cl catalyst when accompanied with 1 equiv. of DMAP co-catalyst. This high activity could probably be attributed to the difference of electron donation from the axial ligand during the propagation steps (see chapter 3-3). In addition, rather unusual bimetallic effect was detected using the Co-Salphen type catalyst which has ca. 10.3 Å fixed Co-Co distance (complex **3-5**); this bimetallic catalyst showed higher activity for both CHO/PA and CHO/CO_2 copolymerization reactions when compared to its monometallic counterpart (complex **3-4**). The metal-metal distance is much longer than the values which is said to be appropriate for such class of copolymerizations by the DFT calculation (4.3-5.0 Å). It is less likely that the activity improvement was derived from the concerted mechanism of two metal species and thus further consideration on another mechanism is a future work.

4-2 Perspective of this research: Further catalyst design

In this section, I would like to propose a perspective of this research field based on this research. For dramatic improvement of catalytic activities, the use of multimetallic complex seems to be a possible candidate. When cobalt was used as the metal center of bimetallic complex, Williams have reported that Co(II)-Co(III) bimetallic complex showed higher activity than Co(III)-Co(III) or Co(II)-Co(II) bimetallic system.[1] From this result, one can estimate that fine tuning of oxidation state is a powerful tool for the high activity of multimetallic complexes. However, isolation of each multi-metallic complex varied in the oxidation state of the metal centers should be of much difficulty. For that case, the *in-situ* oxidation method here I developed would be effectively utilized for the generation of desired species.

Since multi-metallic complex with flexible backbone have been known as the good catalyst for both copolymerization,[2,3] here I propose the complex shown in below figure as a possible candidate (Figure 4-1 , (a)). This structure is designed based on the complex (Figure 4-1 (b)) synthesized by Nabeshima and co-workers.[4]

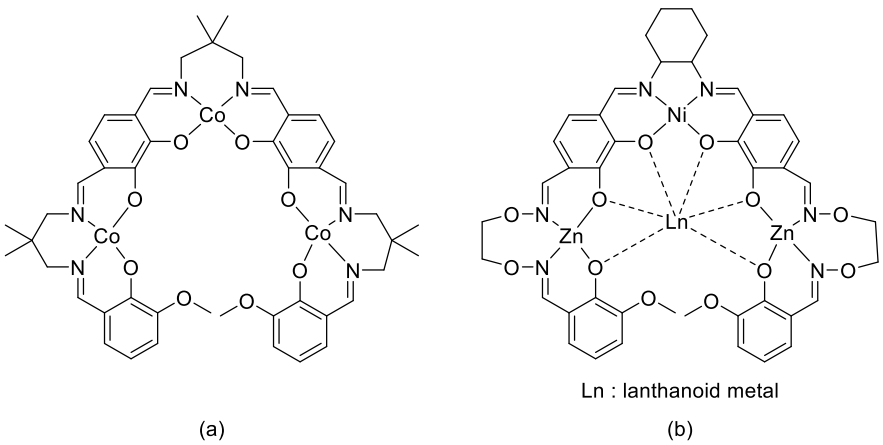
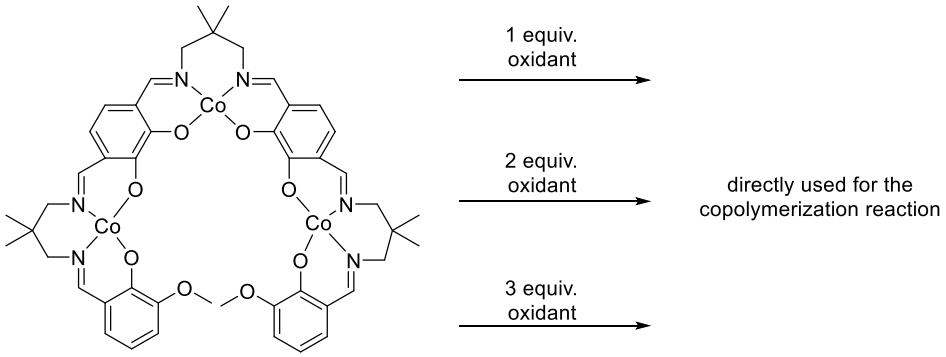


Figure 4-1: Proposed structure of new complex(a) and Nabeshima reported complex(b).

For this complex (a) in Figure 4-1, the *in-situ* oxidation method would generate Co(II)-Co(II)-Co(III), Co(II)-Co(III)-Co(III), and Co(III)-Co(III)-Co(III) complexes depending on the amount of added oxidant (Scheme 4-1).



Scheme 4-1: *In-situ* oxidation strategy for the catalyst screening.

This structure has a very flexible structure and multi coordination sites. Recently, Williams and co-workers have reported that a hetero bimetallic complex (See Figure 1-15) showed higher activity than homo bimetallic complex for the copolymerization of CHO with CO_2. This activity improvement is attributed to the difference of appropriate Lewis acidity for each ring-opening and CO_2 insertion reaction. When hetero bimetallic complex is used for the reaction, each reaction can be carried out on the different Lewis acidic metal center.

The complex in Figure 4-1 can also be coordinated by Lewis acidic metals such as alkali metal cations, lanthanoids metal cations, and so on (Figure 4-2 (a)).

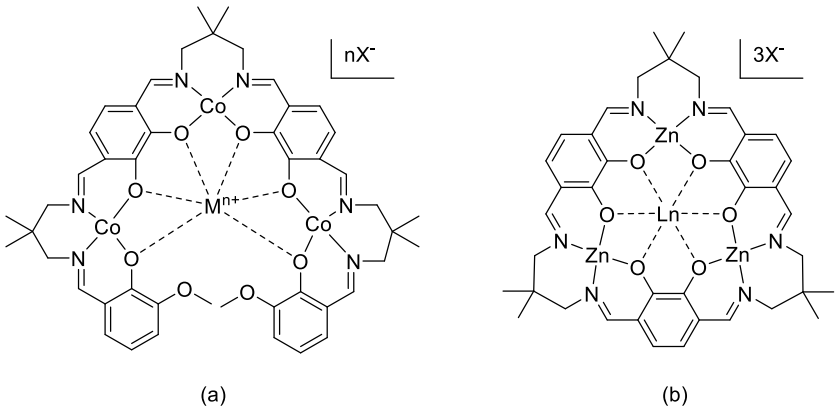


Figure 4-2: Lanthanoid metal coordinated macrocyclic type complexes.

Although highly active Zn-Lanthanoid hetero multimetallic complex (Figure 4-2 (b)) was reported by Mashima and Okuda[5], this Co-Lanthanoid or Co-alkali metal hetero multimetallic complex is a new class of combination and it is expected to have activity for the copolymerization of epoxide with CO_2 or diacid anhydride because of this flexible backbone. Nabeshima and co-workers also reported Zn-Ni-Lanthanoid hetero tetranuclear system by using same types of ligand.[4] This types of multimetallic complex synthesis would give a hint for the highly active catalyst.

4.3 Perspective for the research field of copolymer synthesis using epoxide as a comonomer

In the copolymerization of epoxide with CO_2 field, recently many researchers have extensively investigated new polymer architecture such as a cyclic polymer[6], stereocomplex[7], and post functionalization[8,9] for the thermal property improvement or biological application. In the copolymerization of epoxide with diacid anhydride field, new combination of epoxide and diacid anhydride have been extensively investigated for the control of thermal property and biodegradable polyester synthesis.[10] However, the low activity and stability of the polymerization catalyst remain unsolved. I think one should further develop new catalyst structures that can control the coordination sphere flexibly. Because of this flexibility, metals would be able to change the distance of its metal-metal distance to appropriate distance for each reaction step. The metallopolymer type complex and supramolecular type complex could be promising candidates for this purpose.[11,12] I hope this types of complexes open a new era of copolymerization catalyst.

4.4 Reference

(1) Kember, M. R.; Jutz, F.; Buchard, A.; White, A. J. P.; Williams, C. K. *Chem. Sci.* **2012**, *3* (4), 1245.

(2) Li, J.; Liu, Y.; Ren, W.-M.; Lu, X.-B. *J. Am. Chem. Soc.* **2016**, jacs.6b07520.

(3) Kissling, S.; Lehenmeier, M. W.; Altenbuchner, P. T.; Kronast, a.; Reiter, M.; Deglmann, P.; Seemann, U. B.; Rieger, B. *Chem. Commun.* **2015**, *51* (22), 4579–4582.

(4) Akine, S.; Matsumoto, T.; Nabeshima, T. *Angew. Chemie - Int. Ed.* **2016**, *55* (3), 960–964.

(5) 田川莉紗; KLEEMANN, J.; 喜多祐介; 奥田純; 真島和志. 日本化学会第95春季年会; 2015; 3E6-04.

(6) Honda, S.; Sugimoto, H. *J. Polym. Sci. Part A Polym. Chem.* **2016**, *54* (20), 3336–3342.

(7) Liu, Y.; Ren, W.-M.; Zhang, W.-P.; Zhao, R.-R.; Lu, X.-B. *Nat. Commun.* **2015**, *6*, 8594.

(8) Honda, S.; Sugimoto, H. *Macromolecules* **2016**, *49* (18), 6810–6816.

(9) Tsai, F. Te; Wang, Y.; Darensbourg, D. J. *J. Am. Chem. Soc.* **2016**, *138* (13), 4626–4633.

(10) Longo, J. M.; Sanford, M. J.; Coates, G. W. *Chem. Rev.* **2016**, acs.chemrev.6b00553.

(11) Akine, S.; Utsuno, F.; Piao, S.; Orita, H.; Tsuzuki, S.; Nabeshima, T. *Inorg. Chem.* **2016**, *55* (2), 810–821.

(12) Houjou, H.; Yagi, K.; Yoshikawa, I.; Mutai, T.; Araki, K. *J. Phys. Org. Chem.* **2016**.

Acknowledgement

The study presented in this thesis has been carried out under the supervision of Professor Kyoko Nozaki at the University of Tokyo from 2014 to 2017. I would like to express my deepest appreciation to Professor Kyoko Nozaki for her constant guidance, valuable suggestions, warm encouragement and enthusiasm. I have learned a lot of things from her wide perspective in science.

I am deeply grateful to the committee members, Professor Hiroshi Sugimioto, Professor Naoko Yoshie, Associate Professor Hirohiko Hojo, Lecturer Hiroshi Sato for improving my Ph. D. thesis.

I would like to express my deep gratitude to my previous supervisor, Associate Professor Hidetake Seino who taught me various chemical technique, importance of persistent thinking in the research and passion to chemistry.

I would like to express my deep gratitude to Toyama Chemical Society members, Associate Professor Masafumi Yano, Assistant Professor Masaya Miyagawa, Dr. Takanori Kajioka, Dr. Hideto Kempe, Mr. Fumiya Miyamoto, Ms. Yukino Fukahori, Ms. Akiko Hashimoto, Ms. Sayaka Katayama and Mr. Jun-nosuke Okino for supporting my daily life and fruitful discussion with them.

Thank are extended to the excellent supervisors in the Nozaki laboratory, Associate Professor Ryo Shintani, Assistant Professor Koji Nakano, Assistant Professor Brad P. Carrow, Assistant Professor Shingo Ito and Assistant Professor Shuhei Kusumoto for their helpful and valuable discussion throughout the course of this work.

I appreciate the research coworkers, Professor Shin-ichi Ohkoshi, Assistant Professor, Koji Nakabayashi and Mr. Rei Takahashi for their support.

I would like to thank the past and present members of Nozaki laboratory, especially Ms. Midori Akiyama, Mr. Keisuke Takahashi, Mr. Yusuke Mitsushige worked with me as the same grade students. And Mr. Tadashi Omoto, Mr. Jing Yuan Deng and Ms. Yuko Hirooka worked with me on the same polymer research projects.

I would like to thank Ms. Ritsuko Inoue for kind assistance of daily laboratory life.

I also wish to express my gratitude to Professor Brent Sumerlin and his laboratory members for their kindness and many helps during the stay. The research and the experience in the Sumerlin lab extended my field of view.

I would like to thank the Japan Society for the Promotion of Science for their Program for Leading Graduate Schools (MERIT).

Finally, I would like to express my sincere acknowledgement to my family, Koitsu, Sueko and Hirokazu for their constant assistance and encouragement.

March, 2017

Masahiro Hatazawa

List of publications

Parts of the thesis have been published in the following journals or to be submitted

[1] Hatazawa, M.; Nakabayashi, K.; Ohkoshi, S.; Nozaki, K.

“In Situ Generation of Salen/Co(III) Complexes for Copolymerization of Propylene Oxide and CO_2”

Chem. Eur. J. **2016**, *22*, 13677-13681.

[2] Hatazawa, M.; Takahashi, R.; Houjou, H.; Nozaki, K.

“Development of Highly Active Cationic Co-Salphen Type Complexes for the Copolymerization of Cyclohexene Oxide with Phthalic Anhydride”

To be submitted.

Following paper are not included in this thesis

[3] Hatazawa, M.; Seino, H.; Yoshie, N.

“Reversible Reduction of *N*,*N*′-Diarylimidazolinium Cations with Hydrogen Catalyzed by Transition Metal Complexes as a Functional Model of [Fe]-Hydrogenase”

To be submitted.