

博士論文(要約)

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)

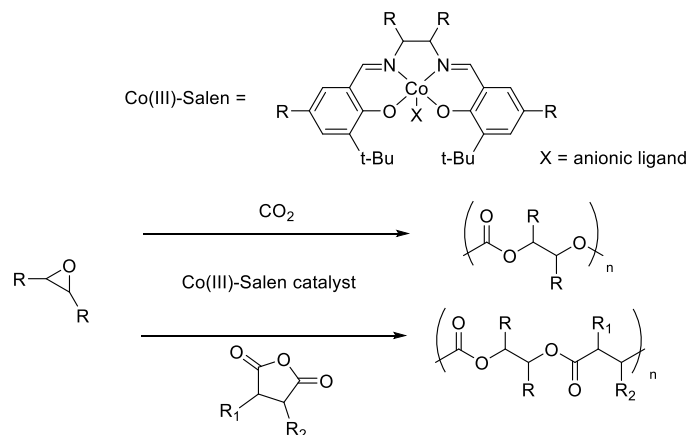
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## [Introduction and Background]

In the last half century, ring-opening copolymerization of an epoxide with CO<sub>2</sub> or a diacid anhydride compound mediated by Lewis acidic metal species have been investigated eagerly.<sup>12</sup> Recently, Salen type complexes of trivalent cobalt (Co(III)-Salen) were reported to be active catalysts for both epoxide/CO<sub>2</sub> and epoxide/diacid anhydride copolymerization reactions (Scheme 1). In spite of the continuous efforts devoted for the catalyst development, general method for improvement of the catalytic activity is still under investigation. In this thesis, I investigated the strategy to improve the activity of this Co-Salen type complexes focusing on the structure and electronic state of the catalysts.

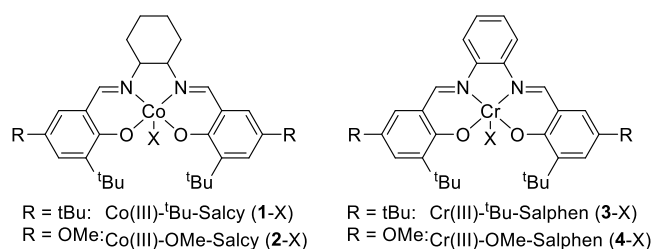


**Scheme 1:** Co(III)-Salen type complex and general scheme of target reaction

## 1. Co(III)-Salcy for the copolymerization of propylene oxide(PO) with CO<sub>2</sub>

### 1-1. Background of this section

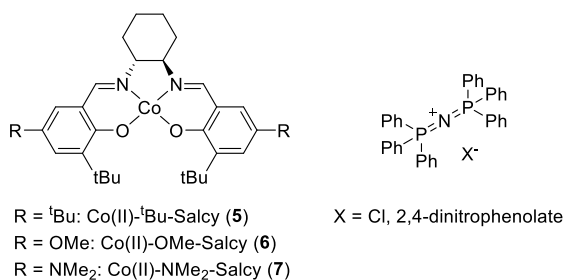
In the last decades, Co(III)-Salcy and Cr(III)-salphen complexes such as Co(III)-<sup>t</sup>Bu-Salcy (**1**) and Cr(III)-<sup>t</sup>Bu-salphen (**3**) in Figure 1 have been well studied owing to their high catalytic activities for the copolymerization of epoxide with CO<sub>2</sub>.<sup>3</sup> Introduction of substituents at the *para*-positions of phenolic oxygens in the salen complexes is common approaches to tune the electronic nature of the metal center. For example, it is reported that Cr(III)-OMe-salphen (**4**) enhanced the activity for the copolymerization of cyclohexene oxide (CHO) with CO<sub>2</sub> when compared to the <sup>t</sup>Bu-substituted complex **3** (Figure 1).<sup>4</sup>



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

On the other hand, the activity of electron donating group substituted Co(III)-Salcy complex (Co(III)-MeO-Salcy (**2**)) have not been investigated, possibly because the synthetic difficulty of that complex. Here I report the copolymerization of PO/CO<sub>2</sub> by using *in situ* generated Co(III)-Salcy complexes. The copolymerization reaction catalyzed by the simple admixture of Co(II)-MeO-Salcy

complex (6) with  $[\text{Cp}_2\text{Fe(III)}]\text{PF}_6$  and bis(triphenylphosphoranylidene)ammonium 2,4-dinitrophenolate (PPNDNP) resulted in the higher activity than that of Co(II)-*t*Bu-Salcy (5) (Figure 2).



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

## 1-2. Result and discussion

Copolymerization of PO and CO<sub>2</sub> with *in situ* generated catalysts was examined in the procedure described in Table 1. Three Co(II)-Salcy complexes were examined for the reaction, namely, the ones having *tert*-Bu, MeO and NMe<sub>2</sub> groups (5, 6 and 7). The results are summarized in Table 1.

In entries 1 and 2, copolymerization reaction was carried out using complexes generated by *in situ* oxidation of 5 and 6 with FcPF<sub>6</sub> in the presence of PPNDNP co-catalyst. TON for PPC of 802 for 5 and 976 for 6 (entries 1 and 2).

**Table 1.** Copolymerization result by using *in situ* method<sup>a</sup>

1) milled the mixture  
 2) one portion (20 wt%) was placed in an autoclave  
 3) 1 mL of THF was added  
 4) stirred for 30 min at 22 °C  
 5) dried in vacuo

entry	Complex	TON for			
		PPC <sup>bc</sup>	CPC <sup>bc</sup>	MW(kg/mol) <sup>c</sup>	Mw/Mn <sup>d</sup>
1	5	802±26	0	32.4±2.8	1.2
2	6	976±18	0	32.1±1.4	1.2
3	7	2±1	1±0	-	-

<sup>a</sup> The average data are described here. <sup>b</sup> TON determined by <sup>1</sup>H NMR analysis. <sup>c</sup> We calculated average value and standard deviation for each entry's 3 or 5 runs and the described standard deviation as "+/-". <sup>d</sup> Determined by size-exclusion chromatography (SEC) analysis using THF as an eluent and polystyrene as a standard.

this copolymerization reaction needs appropriate electron donating groups. The equilibrium between Co(III)/L and Co(II)/L<sup>+</sup> could be involved in the reactions with 6 and 7. Fujii *et al.* reported that methoxy group attached Co-Salcy complex **2-OTf** have the equilibrium between Co(III)-Salcy and Co(II)-Salcy<sup>+</sup>.<sup>5</sup> The stronger electron donating nature of the dimethylamino groups could have increased the contribution of radical cationic species Co(II)-Salcy<sup>+</sup>. Since divalent Co metal have no activity for PPC synthesis, this could be the reason for the low reactivity of Co(II)-NMe<sub>2</sub>-Salcy 7. To support the equilibrium between Co(III)-NMe<sub>2</sub>-Salcy and Co(II)-NMe<sub>2</sub>-Salcy<sup>+</sup>, I carried out EPR

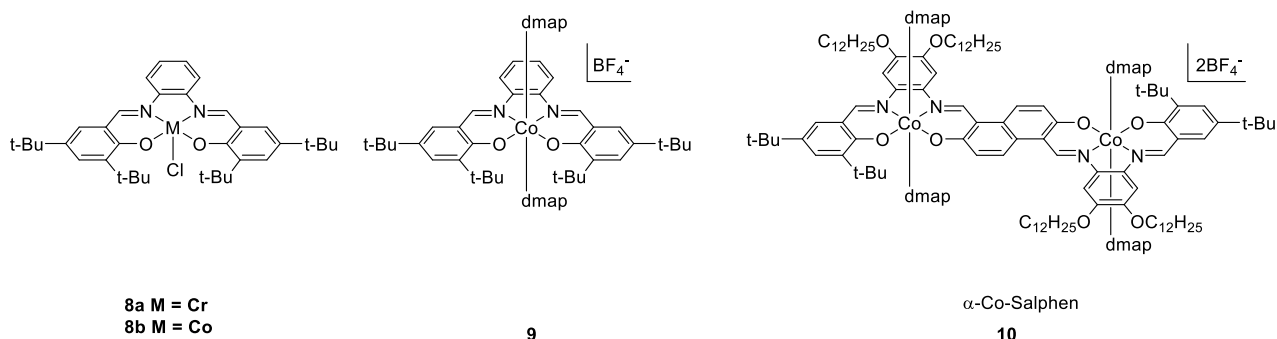
measurement of Co(III)-NMe<sub>2</sub>-Salcy. As a result, I could observe a EPR signal in the Co(III)-NMe<sub>2</sub>-Salcy solution.



**Figure 3:** LMCT equilibrium in Co(III)-Salcy

## 2. Co(III)-Salphen-DMAP<sub>2</sub> for the copolymerization of epoxide with phthalic anhyde

### 2-1. Background of this section

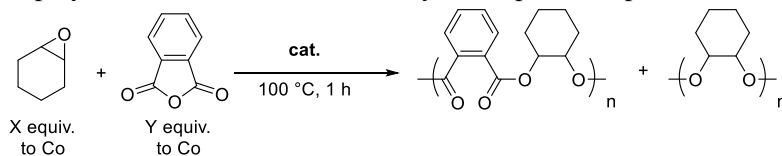


**Figure 4:** Co-Salphen type complexes

Since its discovery in 1960,<sup>6</sup> copolymerization of epoxide with diacid anhydride have been investigated. It is one of the direct methods to access for polyester compounds.<sup>1</sup> Catalysts effective for the copolymerization of epoxide with CO<sub>2</sub> were often utilized for this type of copolymerization. In literature, Cr(III)-Salphen-Cl(**8a**) was reported to show high activity for Phthalic anhydride(PA)/CHO copolymerization and has been referred as the benchmark catalyst for this copolymerization. It is notable that Co(III)-Salphen-Cl (**8b**) with 4-dimethylaminopyridine (DMAP) co-catalyst (**8b/DMAP**) showed almost the same activity as the Cr(III) complex, **8a/DMAP**.<sup>7</sup> In spite of its high activity, further studies on the Co-Salphen type catalyst has been rather unexplored so far. Here, I found that 2 DMAP coordinated cationic Co-Salphen complex(**16**) have highest activity for the copolymerization of CHO/PA as the monometallic metal salen catalyst. I synthesized and used **9** and its related bimetallic complex **10**<sup>8</sup> for the copolymerization of CHO with PA .

### 2-2. Result and future works

I applied catalysts to the copolymerization of epoxide with phthalic anhydride (PA) (Table 2).

**Table 2:** Copolymerization of CHO with PA by Co-salphen complexes

entry	Complex	X=	Y=	TON for polyester	MW(kg/mol)	Mw/Mn
1	<b>9</b>	500	500	282	15.1	1.1
2	<b>8b</b>	500	500	194	7.3	1.2
3	<b>9</b>	4000	500	240	5.9	1.1
4	<b>10</b>	4000	500	305	5.0	1.1

As a result, the Co complexes **9** and **10** showed higher activity than the Co complex **8b**(entry 2). To check the initiator of these reaction, I analyzed resulting polymer in entry 1 by using the MALDI-TOF-MS. Only DMAP initiated polymer was observed in MALDI-TOF-MS spectrum of resulting polymers. From these results, I can say that DMAP is better initiator than Cl<sup>-</sup> for the Co(III)-salphen system. The TON value 282 for polyester from CHO/PA, accomplished with Salphen/Co complex **9** is the highest value for the single metal salen type catalyst system thus far reported.

### 3. Reference

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