

## 論文の内容の要旨

### 金属触媒を用いる環状エーテルのカルボニル化重合 (Metal-Catalyzed Carbonylative Polymerizations of Cyclic Ethers)

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#### Introduction

Aliphatic polyesters are among the most used biodegradable polymers in medical applications and have been extensively investigated. Ester linkages are frequently encountered in nature and hence it is expected that synthetic polymers containing such linkages and an appropriate structure would be environmentally degradable. One of the common synthetic methods towards aliphatic polyesters is a metal-catalyzed ring-opening polymerization (ROP) of lactones, such as  $\beta$ -lactones,  $\delta$ -lactones or  $\epsilon$ -lactones having a four-, six- or seven-membered ring. Nevertheless, this synthetic strategy is less attractive for an industrial application due to the multi-step and hence expensive syntheses of the lactones. Another shortcoming of such a process is its incompetence to produce polyesters by ROP of  $\gamma$ -lactones, five-membered ring cyclic esters, in practical reaction conditions: rapid back-biting immediately takes place to come back to the original  $\gamma$ -lactone due to the thermodynamic stability of its five-membered ring structure. Only a limited numbers of copolymerization with methyl methacrylate,  $\delta$ -valerolactone, and  $\epsilon$ -caprolactone has been reported for unsubstituted  $\gamma$ -lactones with low incorporation ratio of the  $\gamma$ -lactone (2-43%).

As another approach to polyester, carbonylative polymerization of oxirane, that is a three-membered cyclic ether, is known to provide an equivalent of poly( $\beta$ -lactone). Furukawa *et al.* reported the first example of copolymerization of oxirane with carbon monoxide (CO) using  $\text{AlEt}_3/\text{Co}(\text{acac})_3$  (acac = acetylacetonate) and  $\text{Al}^i\text{Bu}_3/\text{H}_2\text{O}/\text{Co}(\text{acac})_3$ . Recently, several other catalyst systems, such as  $\text{Co}_2(\text{CO})_8/\text{pyridines}$ ,  $\text{Na}[\text{Co}(\text{CO})_4]/\text{pyridines}$ , and acylcobalt complexes, have been reported as active catalysts in the alternating copolymerization of propylene oxide with CO.

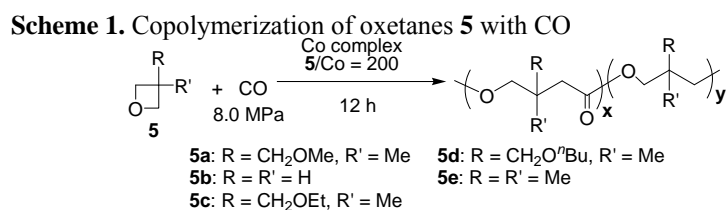
In this study, four acylcobalt complexes,  $\text{AcCo}(\text{CO})_3[\text{P}(p\text{-tolyl})_3]$  ( $p\text{-tolyl} = p\text{-Me-C}_6\text{H}_4\text{-}$ ) (1),  $\text{AcCo}(\text{CO})_3[\text{P}(\text{OPh})_3]$  (2),  $\text{AcCo}(\text{CO})_3[\text{P}(\text{NMe}_2)_3]$  (3), and  $\text{AcCo}(\text{CO})_2(\text{dppp})$  [dppp = 1,3-bis(diphenylphosphino)propane] (4) were synthesized, characterized, and examined as catalysts for the unprecedented carbonylative polymerization of oxetanes. Here, the first example of carbonylative polymerization of oxetanes, corresponding to the ring-opening unit of  $\gamma$ -lactone was successfully achieved to provide up to 63% of the incorporation of the 4-hydroxyalkanoate unit into the polymer.

## Syntheses of acetylcobalt complexes

Acetylcobalt complexes **1–4** were synthesized as potential catalysts for the oxetane/CO copolymerization. According to a literature, treatment of  $\text{Na}[\text{Co}(\text{CO})_4]$  with MeI and  $\text{P}(p\text{-tolyl})_3$  under CO atmosphere provided a phosphine complex **1**. Other acetylcobalt complexes, containing phosphite ligand **2**, phosphorous triamide ligand **3**, and bidentate phosphine ligand **4**, were also prepared in a process similar to that for **1**. All of complexes were characterized by  $^1\text{H}$ ,  $^{13}\text{C}$ , and  $^{31}\text{P}$  NMR as well as FT-IR, and elemental analyses. The X-ray single crystal analyses reveal that the complex adopts a trigonal bipyramidal conformation, with the acetyl and phosphorous ligands occupying the apical site, except for complex **4**, at which the dppp ligand occupies apical-equatorial site. The IR study indicates that electron density on cobalt center of the complexes is in the order of  $4 > 3 > 1 > 2$ .

## Reactions of oxetanes with CO

With complexes **1–4** in hand, the copolymerization of oxetanes **5** with CO was investigated (Scheme 1). Oxetane **5a** was readily prepared from commercially available



3-hydroxymethyl-3-methyloxetane. Copolymers containing both ester and ether units were obtained with complexes **1** and **2**, but no reaction proceeded with complexes **3** or **4**. The reaction of **5a** with CO using complex **1** ( $5\text{a}/\text{Co} = 200$ ) under 8.0 MPa of CO at 100 °C for 12 h gave copolymer with activity of  $300 \text{ g} \cdot (\text{mol of Co})^{-1} \cdot \text{h}^{-1}$ , ester/ether ratio of 27/73, and  $M_n$  of 4,900 g/mol (PDI = 1.5). The catalytic activity and the ester/ether ratio increased at higher temperature in the range of 100 °C to 140 °C, while the higher reaction temperature of 160 °C conversely reduced the ester unit formation. Thus, the copolymerization at 140 °C gave the highest incorporation of 4-hydroxyalkanoate unit (47%) into the polymer in this series. Molecular weights of the obtained copolymers decreased at higher reaction temperature in spite of an increase of the copolymer yields, most probably due to chain transfer. When compared at the same temperature, phosphite complex **2** exhibited the higher catalytic activity and produced the higher molecular weight copolymer than complex **1**, while it provided the copolymer with lower ester-unit content. Temperature dependency of catalytic activity, ester/ether ratio, and molecular weight observed with **2** was similar to that with **1**. The highest molecular weight of  $7,800 \text{ g} \cdot \text{mol}^{-1}$  was obtained with **2** at 80 °C. The reaction of unsubstituted oxetane **5b** with CO using **1** gave an oligomeric product with ester/ether ratio of 28/72. Copolymerization of ethyl ether **5c** with CO using the same catalyst provided a copolymer with ester

unit of 60%, higher than the copolymer derived from **5a** under the same reaction condition, and  $M_n$  of 2,900  $\text{g}\cdot\text{mol}^{-1}$ . Copolymerization with a longer alkyl chain at the alkoxy group, **5d**, initiated by the same catalyst, provided only an oligomeric product with unexpectedly lower ester unit. Copolymerization of dimethyl-substituted oxetane **5e** gave only trace amount of the copolymer. However, although **5c** derived-copolymer was higher in ester unit, the yield was considerably low (6%).

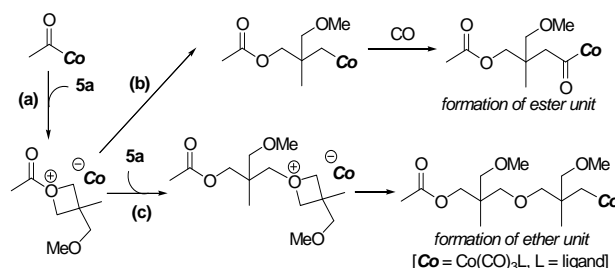
### Relation between electron density on Co and ester content in the copolymer

The difference in catalytic activity and the ester unit content are most likely due to the difference in electron density on cobalt center of the complexes. Scheme 2 describes a plausible mechanism of a desirable alternating incorporation of oxetane and CO to afford an ester unit (step a  $\rightarrow$  step b) and a competing ring-opening enchainment without carbonylation to give an ether unit (step a  $\rightarrow$  step c). The use of complexes with higher electron density on cobalt center would decelerate a cobaltate dissociation upon an attack of oxetane (step a), which accordingly would reduce the rate of the copolymerization. On the other hand, the higher electron density on the cobalt center is favorable for the nucleophilic attack of the dissociated cobaltate to the oxonium intermediate (step b), leading to the higher ester unit content.

In the discussion of the catalytic activity and the ester unit content based on the electron density of the cobalt center, it is necessary to

consider how the cobalt complex behaves upon CO pressure. Thus, the complexes were exposed under 7.0 MPa of CO at 100 °C and monitored by an *in situ* IR observation technique. Complex **1** was found to exist mostly as the phosphine adduct even after 3-hour exposure to CO. On the other hand, the CO exposure of complex **2** resulted immediately in the conversion to  $\text{AcCo}(\text{CO})_4$ . Accordingly, the higher electron density on the cobalt center of complex **1** should result in the lower catalytic activity and the higher ester unit content than  $\text{AcCo}(\text{CO})_4$  which is derived from complex **2** under the reaction condition.

Because a ligand dissociation seems critical under the polymerization reaction conditions, copolymerization of **5a**/CO in the presence of additional phosphorus ligands was examined. Addition of 1.0 equivalent either free  $\text{P}(p\text{-tolyl})_3$  or  $\text{P}(\text{OPh})_3$  ligand in the copolymerization of oxetane **5a** and CO initiated by phosphine complex **1** increased the ester unit up to 60%, yet it sacrificed the catalytic activity and molecular weight. While a large excess of the  $\text{P}(\text{OPh})_3$  up to 5.0 equivalent in the above copolymerization increased a slightly more ester unit, an equivalent excess of  $\text{P}(p\text{-tolyl})_3$  deactivated the reaction. Complex **2** provided a similar phenomenon only in the addition of free



**Scheme 2.**

P(OPh)<sub>3</sub> in 1 to 1 ratio to the catalyst. It gave lower ester unit when P(*p*-tolyl)<sub>3</sub> of 1.0 equivalent was added or gave only trace amount of the copolymer when the phosphite up to 5.0 equivalent was added. In the absence of any ligand, that is the reaction initiated by BnCOCo(CO)<sub>4</sub> (**6**), a copolymer with ester/ether ratio of 29/71, and *M<sub>n</sub>* of 3,900 g/mol (PDI = 1.9) was obtained in 37% yield. The above observations may be summarized as follows. The stronger electron donor P(*p*-tolyl)<sub>3</sub> increases the ester content when compared to the weaker donor (thus weaker binder) P(OPh)<sub>3</sub>. Addition of extra amount of a phosphorus ligand seems to increase the ester content. Large excess of a free phosphorus ligand retards the reaction. This was likely the result of an equilibrium shift from a tetracarbonylcobaltate species to a phosphorous-ligated cobaltate one. In other words, the more Lewis acidic ligand-free cobalt species tend to give higher ether content while the less acidic cobalt species, achieved by the coordination of a phosphorus ligand is less active for the homopolymerization of **5a**. As a result, copolymers with higher ester content were obtained in the presence of a proper amount of phosphorus ligands.

## Conclusion

The first example of copolymerization of oxetanes with CO initiated by acetylcobalt complexes was reported. The copolymerization afforded polymers containing ester and ether units. The phosphorous ligands ligated to cobalt center were observed to control the ratio of ester/ether units, catalytic activity and molecular weight of the copolymer. The reaction with a phosphite complex **2**, in which P(OPh)<sub>3</sub> was instantaneously substituted by CO under the copolymerization condition, provided a copolymer with higher molecular weight, while the reaction with a P(*p*-tolyl)<sub>3</sub> complex **1** gave a copolymer with higher ester unit content. In the presence of a free phosphorous ligand, a copolymer with 63% of ester content was achieved.