

## 論文の内容の要旨

論文題目 Study on Olefin Polymerization Reaction toward Utilization of Carbon Dioxide  
(二酸化炭素の利用に向けたオレフィン重合反応に関する研究)

氏名 中野 遼

### 1. Background and Objective

The development of efficient methods for the synthesis of bulk chemicals from renewable feedstocks is indispensable for the construction of a sustainable chemical economy in the future. Carbon dioxide (CO<sub>2</sub>) is one of the most attractive renewable C1 resources, because of its practical advantages such as abundance, economic efficiency and so on. Its favorable nature as a carbon source is, however, inextricably linked to its inherent inertness. Therefore, reactions of CO<sub>2</sub> must be combined with a high-energy reactant to gain a thermodynamic driving force. For large-scale utilization, chemical coupling of CO<sub>2</sub> with easily available chemical feedstocks is indispensable. Thus far, only a limited number of processes have succeeded in the use of CO<sub>2</sub>, examples being the industrial production of urea, salicylic acid, organic carbonates and polycarbonates.

In my predoctoral research, I aimed at the development of the copolymerization reaction of olefins and CO<sub>2</sub>. Olefins, one of the largest classes of chemicals produced today, should be suitable co-reagents due to the high potential energy of their C-C double bonds. Though extensive studies have focused on the catalytic coupling of olefins with CO<sub>2</sub> to form commodity and fine chemicals, methods to prepare olefin/CO<sub>2</sub> copolymers are still limited to the production of co-oligomers.

### 2. Thermodynamics and Kinetics of Ethylene/CO<sub>2</sub> Copolymerization

To start with this study, the thermodynamics and kinetics of ethylene/CO<sub>2</sub> copolymerization were investigated. From thermodynamic viewpoint, incorporation of CO<sub>2</sub> is highly endothermic by 21.9 kcal/mol, whereas incorporation of ethylene is exothermic by -12.5 kcal/mol (calculated by CBS-4M//B3LYP/6-31G\*). Then, the alternating copolymerization is thermodynamically infeasible at reasonable temperatures, and excess ethylene incorporation is required in order to compensate large thermodynamic stability of CO<sub>2</sub>. Although the obtained values suggest the thermodynamic feasibility of ethylene/CO<sub>2</sub> copolymerization, those kinetically means kinetic preference for ethylene homopolymerization. It is because the intermediates formed after CO<sub>2</sub> incorporation are thermodynamically uphill, reflecting thermodynamic stability of CO<sub>2</sub>. Since this qualitative speculation can be valid to any mechanism of polymerization, special kinetic design to circumvent the kinetic problem is essential to accomplish ethylene/CO<sub>2</sub> copolymerization.

### 3. Stepwise Approach using Meta-stable Intermediates

In order to circumvent the thermodynamic and kinetic barriers for olefin/CO<sub>2</sub> copolymerization, I first focused on the use of a meta-stable lactone intermediate, 3-ethylidene-6-vinyltetrahydro-2H-pyran-2-one (**1**), which is formed by the palladium-catalyzed condensation of CO<sub>2</sub> and 1,3-butadiene. Subsequent free radical polymerization of **1** may afford CO<sub>2</sub>/butadiene copolymer with a CO<sub>2</sub> content of 33 mol% (29 wt%). Although the polymerization of **1** was previously investigated by Dinjus *et al.*, they reported that the reaction did not proceed in the presence of radical, cationic, or anionic initiators.

After extensive screening for appropriate conditions, polymerization of lactone **1** was accomplished. The poly-**1** obtained in the presence of acetic acid only possessed bicyclic structure **α** (upper,  $M_n = 19,000$ ), whereas ZnCl<sub>2</sub>/ethylene carbonate conditions gave a polymer with units **α**, and monocyclic structures **β**, and **γ** (lower,  $M_n = 85,000$ ). The obtained polymers exhibited excellent thermal properties such as high glass-transition temperature (>170 °C) and decomposition temperature (>300 °C). Furthermore, the protocol was successfully applied to one-pot copolymerization of CO<sub>2</sub> and 1,3-butadiene, and one-pot terpolymerization of CO<sub>2</sub>, butadiene, and another 1,3-diene.

### 4. Direct Approach using Late Metal Catalysts

The direct copolymerization of olefins and CO<sub>2</sub> can be realized when all the reactions involved in thermodynamic compensation of CO<sub>2</sub> stability are at least competitive with olefin homopolymerization. Since such tuning of transition states is only possible with catalyst or enzyme, metal catalyzed coordination-insertion polymerization is the most promising candidate for the copolymerization with CO<sub>2</sub>, among possible mechanisms of polymerization reaction. Furthermore, considering feasibility of CO<sub>2</sub> related transition states, I focused on 5<sup>th</sup>-period late-transition-metal complexes using Pd, Rh, and so on. However the limited examples of olefin polymerization catalysts based on 5<sup>th</sup>-period late-transition metals, including Pd/ $\alpha$ -diimine, Pd/phosphine-sulfonate (PS), and Rh/1,4,7-triaza-cyclononane, could not afford ethylene/CO<sub>2</sub> copolymer but polyethylene even in the presence of large excess amount of CO<sub>2</sub>.

With Pd/ $\alpha$ -diimine and Pd/PS catalysts, the elementary reaction involved in CO<sub>2</sub> incorporation, namely CO<sub>2</sub> insertion into Pd-alkyl species and ethylene insertion into Pd-OCOR species, are further investigated. In the case of Pd/ $\alpha$ -diimine catalyst, it is reported that the 6-membered intermediate including  $\beta$ -acetate group is susceptible for thermal decomposition and therefore inactive for ethylene polymerization, which means olefin/CO<sub>2</sub> copolymerization may not proceed even if the Pd/ $\alpha$ -diimine catalyst can incorporate CO<sub>2</sub>. On the other hand, using Pd/PS complexes, Pd-OAc species can initiate ethylene polymerization. Nonetheless, the transformation between Pd-OAc and Pd-Me species could not be observed, which means the infeasibility of CO<sub>2</sub> insertion.

The observations abovementioned suggests that novel catalysts which can catalyze CO<sub>2</sub> incorporation faster than ethylene polymerization are necessary for the direct copolymerization with CO<sub>2</sub>. Based on the promising ability of Pd/PS to initiate ethylene polymerization from Pd-OAc species, I then carried out mechanistic study on ethylene polymerization reaction by Pd/PS catalysts, in order to elucidate the key role of the PS ligand to enable olefin polymerization reaction for rationale design of novel class of catalyst.

## 5. Mechanistic Study on Linear Polyethylene Formation Catalyzed by Palladium/Phosphine–Sulfonate Complexes

Since the seminal report by Drent and coworkers in 2002, the Pd/PS catalysts have attracted broad interest because of their unique ability to incorporate various polar monomers into linear polyethylene. Although a number of variants focusing on the substituent on the phosphorus atom have been developed aiming to improve the catalytic activity and the molecular weight of obtained homo/copolymers, the mechanistic rationale for the effect of the substituents on the phosphorous atom is still missing.

The mechanism of polyethylene formation by Pd/PS catalysts was studied, in order to reveal the key intermediates and transition states to determine the molecular weight and *linearity* of polyethylene, and also the effect of substituents on the key species. I started with dispersion-corrected DFT studies on whole mechanism of polyethylene formation starting from  $(R_2PC_6H_4SO_3)PdMe(2,6\text{-lutidine})$  ( $R = Me$  or  $t\text{-Bu}$ ), which enabled to extract the critical intermediates and transition states that determine the molecular weight and *linearity* of polyethylene (Scheme 1); ethylene insertion **TS(10'-11')** relative to ethylene dissociation **TS(10'-9')** and **9NA'** from the less stable alkylpalladium ethylene complex **10'** causes  $\beta$ -hydride elimination from a polymer chain.

Based on the key species suggested, the effects of various substituents on the phosphorus atom ( $R = t\text{-Bu}$ ,  $i\text{-Pr}$ , cyclohexyl (Cy), menthyl (Men), Ph, 2-MeOC<sub>6</sub>H<sub>4</sub> (*o*-Ani), and 2-[2',6'-(MeO)<sub>2</sub>C<sub>6</sub>H<sub>3</sub>]C<sub>6</sub>H<sub>4</sub> (biAr)) were investigated theoretically and experimentally. The obtained relative free energies of the key species **TS(10'-11')** (= rate-determining step for linear propagation) and **TS(10'-9')** (= rate-determining step for  $\beta$ -hydride elimination) are reasonably consistent with the experimentally observed trend of molecular weights of polyethylene formed by corresponding catalysts, namely, the larger energy difference resulted in the higher molecular weight. In addition to **TS(10'-9')**, catalysts bearing Men or biAr substituents on the phosphorus atom which produce high-molecular-weight polyethylene could retard 5<sup>th</sup> ligand associated ethylene dissociation steps leading to  $\beta$ -hydride elimination, and therefore the molecular weight of polyethylene was limited by spontaneous ethylene dissociation pathways via **9NA'**.

The obtained insight toward critical intermediates and transition states of palladium/phosphine–sulfonate system provided key rationale for how the phosphine–sulfonate ligands function to produce linear polyethylene: combination of a strong donor with steric bulk and a weak donor promotes linear polyethylene formation, suppressing ethylene dissociation from **10'** leading to  $\beta$ -hydride elimination.

## 6. Development of Palladium/Imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) Complexes

### 7. Study on Olefin/CO<sub>2</sub> Copolymerization Using Palladium/IzQO Complexes

### 8. Coordination–Insertion Copolymerization of Olefins and Polar Monomers Using Palladium/IzQO Catalysts

The insights obtained in 4.2 led me to develop a novel bidentate ligand imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO), in which the strongly donating and sterically bulky phosphine moiety in PS ligand was replaced by a N-heterocyclic carbene (NHC) moiety. The strong  $\sigma$ -donating ability of NHC can enhance the electronic asymmetry in the bidentate ligands, and

nucleophilic reactivity of metal-alkyl intermediate toward CO<sub>2</sub>. Moreover, the optimally oriented substituents on the nitrogen atom may provide a congested environment appropriate for improving molecular weight of polyolefins.

In literature, many group-10-metal complexes bearing NHC-based ligands were subjected to olefin polymerization, but most candidates showed poor activity for ethylene oligomerization. The widely accepted decomposition pathway of the catalysts is irreversible reductive elimination, forming imidazolium salts from metal hydride species, wherein the hydride attacks the vacant p-orbital of carbenes. The structural comparison among known group-10-metal complexes bearing tethered NHC ligands led me to postulate that the NHC-plane and metal plane should always be coplanar, so that overlap between the vacant p-orbitals of carbene and the cis-metal-hydride is minimized and thus catalyst decomposition via reductive elimination is retarded. This idea is reflected in the rigid skeleton of Pd/IzQO, in which the NHC-plane is fixed onto the palladium square plane.

Thus elaborated Pd/IzQO catalysts showed highly improved lifetime for ethylene homo/copolymerization at 80–120 °C, which underlines that the structural confinement of NHC-plane onto metal plane significantly retards catalyst decomposition of reductive elimination. Furthermore, propylene/polar monomer copolymerization was for the first time accomplished by Pd/IzQO catalysts. The steric environment provided by NHC enables regioselective insertion of  $\alpha$ -olefins and polar monomers, and thereby the Pd/IzQO catalyst successfully afforded regio-regulated polypropylene, propylene/allyl carboxylate copolymers, and propylene/methyl acrylate copolymer. This straightforward method for direct functionalization of polypropylene has been a longstanding challenge for polymer chemistry, as a potential substitute of the post-modification process industrialized at present.

Ethylene/CO<sub>2</sub> copolymerization using Pd/IzQO catalyst was studied theoretically and experimentally. DFT study revealed that Pd/IzQO can accelerate CO<sub>2</sub> insertion into Pd-alkyl species, yet it was still slower than ethylene insertion significantly. The experimental trials to copolymerize ethylene and CO<sub>2</sub> using Pd/IzQO catalysts with/without lithium salts resulted in the formation of polyethylene.

## 9. Conclusion and Perspective

In this thesis, I studied on olefin polymerization reaction toward utilization of CO<sub>2</sub>. Starting with theoretical consideration of ethylene/CO<sub>2</sub> copolymerization (Sec. 2), the two-step copolymerization of dienes and CO<sub>2</sub> was realized (Sec. 3). To accomplish direct olefin/CO<sub>2</sub> copolymerization, I examined late-transition-metal catalysts known to be active for olefin polymerization, and clarified that the incorporation of CO<sub>2</sub> is a bottleneck step for Pd/PS catalysts (Sec. 4.1). To devise a new class of late-transition-metal catalyst for olefin polymerization, I studied the mechanism of Pd/PS catalysis (Sec. 4.2). The obtained insight led to the design of IzQO ligand, with which palladium complex exhibited unprecedented ability for 1-alkene/polar monomers copolymerization (Sec. 4.3).

For the accomplishment of direct copolymerization reaction, further increment of electron density on metal center would facilitate the incorporation of CO<sub>2</sub> by increased nucleophilicity of alkyl chain-end. Efforts to this direction will simultaneously enhance the catalytic activity of olefin/polar monomers copolymerization, since the more electron-rich metal center should be less deactivated by the chelation of polar functional groups.