

博士論文

**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)

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1. Background and Objective¹

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 (CO₂) 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 CO₂ must be combined with a high-energy reactant to gain a thermodynamic driving force. For large-scale utilization, chemical coupling of CO₂ with easily available chemical feedstocks is indispensable. Thus far, only a limited number of processes have succeeded in the use of CO₂, examples being the industrial production of urea, salicylic acid, organic carbonates and polycarbonates.

In my predoctoral research, the objective was set to be the development of the copolymerization of olefins and CO₂. 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 CO₂ to form commodity and fine chemicals, methods to prepare olefin/CO₂ copolymers are still unexplored; all the known examples, which use dienes, vinyl ethers or acrylonitrile, produce only oligomers.²

2. Mechanistic Consideration: Intrinsic Difficulty for Olefin/CO₂ Copolymerization

To start with this study, the thermodynamics and kinetics of ethylene/CO₂ copolymerization were investigated. From thermodynamic view point, incorporation of CO₂ 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*).³ Then, the alternating copolymerization is thermodynamically infeasible at reasonable temperatures, and excess ethylene incorporation is required in order to compensate large thermodynamic stability of CO₂. The obtained thermodynamics was further considered from kinetic viewpoint in Figure 1. As successive incorporation of ethylene is indispensable to make the reaction exothermic, direct ethylene/CO₂ copolymerization (path ii, blue) has to compete with ethylene homopolymerization (path i, black). $\Delta\Delta G4^\ddagger$ would be comparable to $\Delta\Delta G1^\ddagger$ because both are the reaction of an alkyl chain-end with ethylene. Therefore, $\Delta G4^\ddagger$ should be much higher than $\Delta\Delta G1^\ddagger$, reflecting the thermodynamic stability of the intermediates **I** and **ICE**. This means, even if carbon dioxide uptake

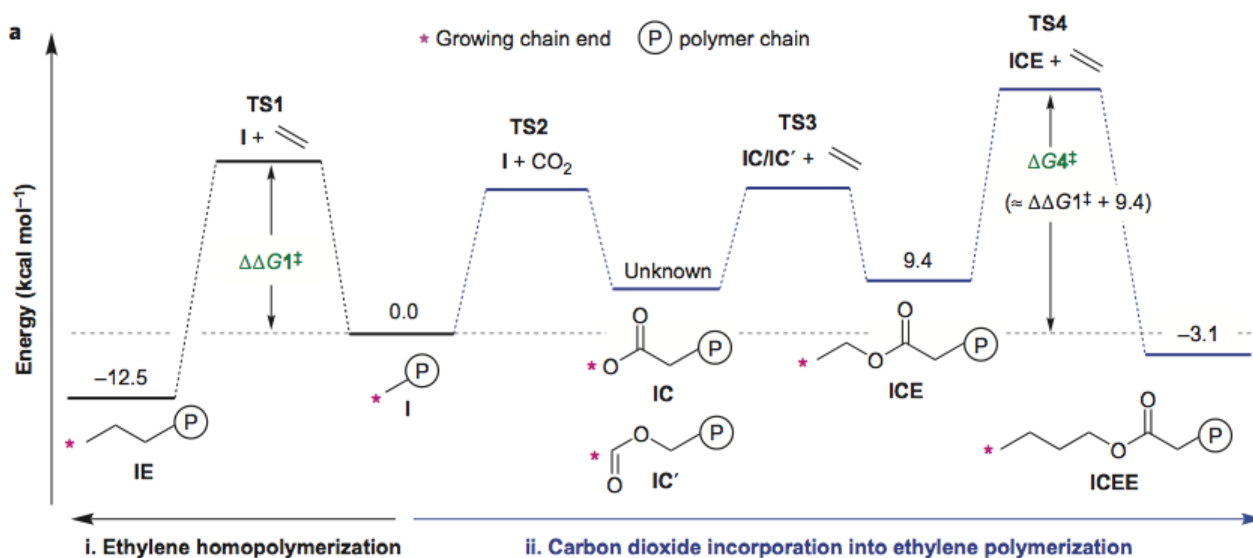


Figure 1. Tentative energy diagram of ethylene/CO₂ copolymerization. **I**, **C**, and **E** represent the initiation from primary alkyl species, CO₂, ethylene, respectively. For example, **IC** or **IC'** represents the isomeric reaction products from **I** and **C**. The growing chain end is shown simply with a purple asterisk because the discussion is applicable to any radical, cationic and anionic polymerization. Values ΔG (kcal mol⁻¹) are from the starting primary alkyl species **I**, approximated by the values calculated (CBS-4M//B3LYP/6-31G*). $\Delta\Delta G1^\ddagger$ is the assumed reaction barrier for the alkyl chain-end and ethylene.

(TS2) and carboxylation of ethylene (TS3) are accessible, ethylene/CO₂ copolymerization is kinetically unfavorable without any solution for TS4. Since this qualitative speculation can be valid to any mechanism of polymerization, this kinetic problem in TS4 may be a general bottleneck of olefin/CO₂ copolymerization.

3. Stepwise Approach: Copolymerization of Carbon Dioxide and Dienes via Lactone Intermediates

In order to circumvent the thermodynamic and kinetic barriers for olefin/CO₂ 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 CO₂ and 1,3-butadiene (Figure 2).⁴ Subsequent free radical polymerization of **1** may afford CO₂/butadiene copolymer with a CO₂ 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.⁵ The reported lack of reactivity of **1** may stem from its structural similarity to either a tiglic acid ester (Figure 2, red) or an α -substituted allyl ester (Figure 2, blue), both of which are substrates known to exhibit poor reactivity when subjected to common polymerization conditions.

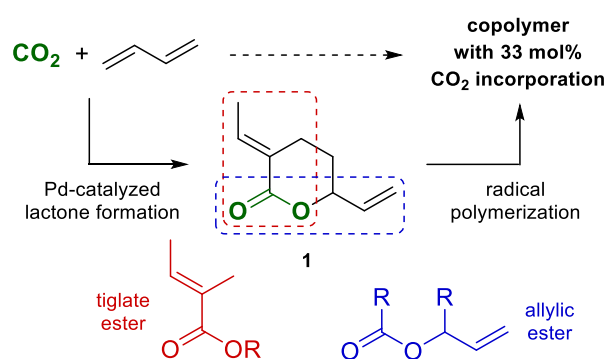


Figure 2. The concept: copolymerization of CO₂ and 1,3-butadiene via a lactone intermediate (**1**).

After extensive screening for appropriate conditions, polymerization of lactone **1** was accomplished (Figure 3). The poly-**1** obtained in the presence of acetic acid only possessed bicyclic structure α (upper, $M_n = 19,000$), whereas ZnCl₂/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 CO₂ and 1,3-butadiene, and one-pot terpolymerization of CO₂, butadiene, and another 1,3-diene.

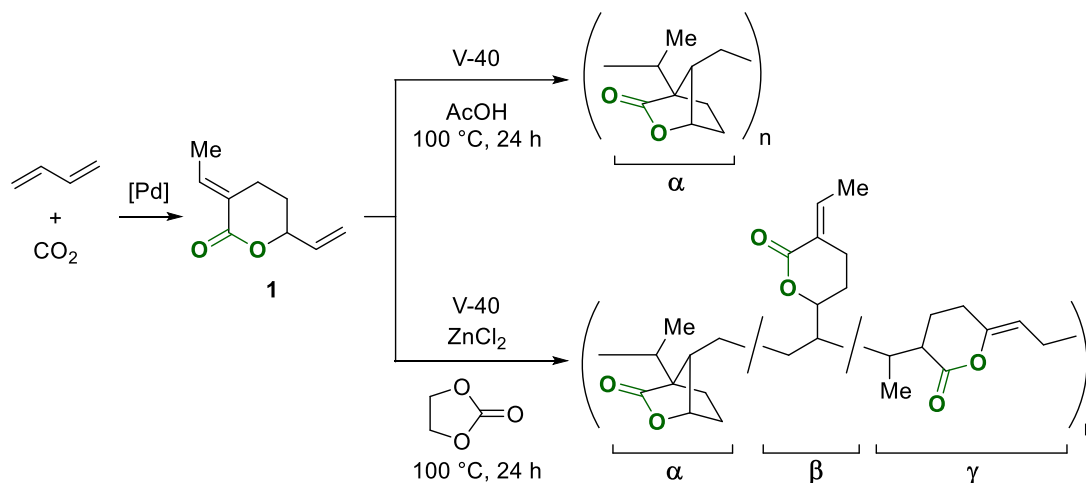


Figure 3. Copolymerization of butadiene and CO₂ via a lactone intermediate **1**.

4. Direct Approach: Incorporation of CO₂ into Olefin Polymerization

4.1. Trials using known Late-transition-metal Catalysts

The direct copolymerization of olefins and CO₂ can be realized when all the involved **TS2–4** are at least competitive with **TS1** (Figure 1). In order to facilitate **TS4** over **TS1**, an ester functional group recognition for enhancement of the reactivity of RCOOCH₂CH₂* chain-end over that of RCH₂CH₂CH₂CH₂* chain-end is indispensable. Since this kind of functional group recognition is recently demonstrated in supramolecular homogeneous catalysts,⁶ metal catalyzed coordination-insertion polymerization is the most promising candidate for the copolymerization with CO₂, among possible mechanisms of polymerization reaction.

Taking **TS2** and **TS3** into account, reactions corresponding to **TS2** and **TS3** are known to be catalyzed by 5th-period late-transition-metal complexes using Pd, Rh, and so on. In addition, the late-transition-metal catalysts should be active for repetitive olefin-insertion (**TS4**) to compensate the thermodynamic burden from CO₂ incorporation. However, limited number of olefin polymerization catalysts based on 5th-period late-transition metals are developed, examples including Pd/ α -diimine, Pd/phosphine–sulfonate (PS), and Rh/1,4,7-triaza-cyclononane (Figure 4).⁷ I observed that these complexes could not afford ethylene/CO₂ copolymer but polyethylene even in the presence of large excess amount of CO₂.

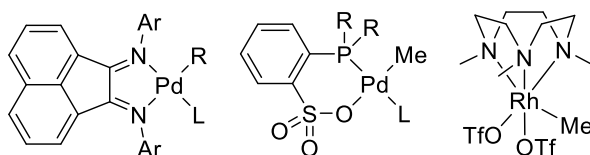


Figure 4. Known classes of polymerization catalysts based on 5th-period late transition metals.

The feasibility of **TS2** and **TS3** in Pd/ α -diimine and Pd/PS catalysts was further examined. In the case of Pd/ α -diimine catalyst, it is reported that the 6-membered intermediate including β -acetate group is susceptible for thermal decomposition and therefore inactive for ethylene polymerization (Figure 5),⁸ which means olefin/CO₂ copolymerization may not proceed even if the Pd/ α -diimine catalyst can incorporate CO₂. On the other hand, using Pd/PS complexes, I observed that **TS3** (addition of carboxylate to olefins) and **TS4** (following ethylene insertions) does proceed, as the initiation step for ethylene polymerization (Figure 6, top). Nonetheless, the transformation between Pd-OAc and Pd-Me species could not be observed, which means the infeasibility of **TS2** (Figure 6, bottom).

The observations abovementioned suggests that novel catalysts which can catalyze **TS2** and **TS3** faster than **TS1** are necessary for the direct copolymerization with CO₂. Based on the promising ability of Pd/PS to catalyze **TS3**, 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.

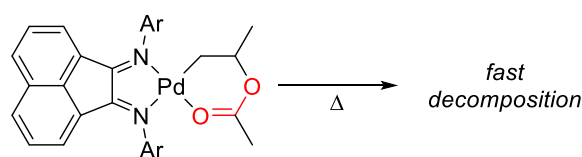


Figure 5. Thermal decomposition of 6-membered palladacycle including β -acetate group.

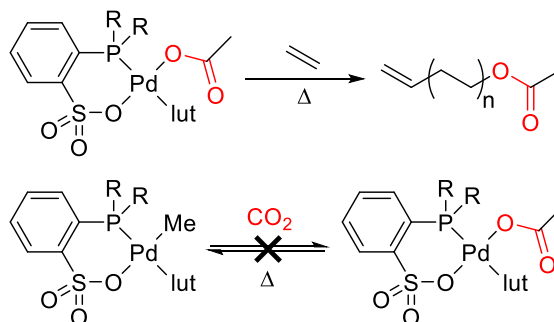
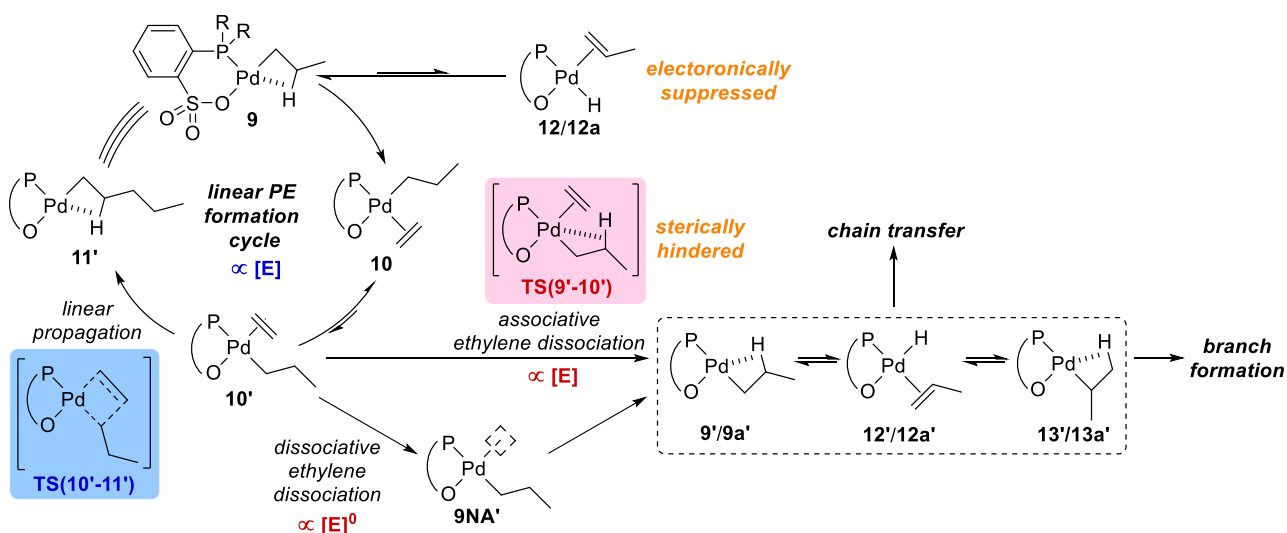


Figure 6. Observation of **TS3** and **TS4**, and infeasibility of **TS2** with Pd/PS catalysts.

4.2. Mechanistic Study on Pd/Phosphine–Sulfonate Catalysts

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.⁷ 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 (R₂PC₆H₄SO₃)PdMe(2,6-lutidine) (R = Me or *t*-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 β -hydride elimination from a polymer chain.



Scheme 1. Key steps for linear polyethylene formation and β -hydride eliminations leading to following chain transfer and methyl-branch formation during polymerization of ethylene by Pd/PS catalysts.

Based on the key species suggested, the effects of various substituents on the phosphorus atom (R = *t*-Bu, *i*-Pr, cyclohexyl (Cy), menthyl (Men), Ph, 2-MeOC₆H₄ (*o*-Ani), and 2-[2',6'-(MeO)₂C₆H₃]C₆H₄ (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 β -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 (Table 1). In addition to **TS(10'-9')**, catalysts bearing Men or biAr

Table 1. $\Delta\Delta G^\ddagger$ between **TS(10'-11')** and **TS(9'-10')**, and molecular weight of obtained polyethylene with various substituents on phosphorous atom.

R	$M_n/10^3$	$\Delta\Delta G^\ddagger$ (kcal/mol)
Me	---	1.4
<i>t</i> -Bu	6.2	2.6
<i>i</i> -Pr	6.7	4.2
Cy	11	4.2
Men	169	5.7
Ph	4.0	0.7
<i>o</i> -Ani	14	3.6
biAr*	227	6.0

Conditions for polymerization: cat. 0.10 mmol/L in toluene, ethylene 3.0 MPa, 80 °C, 60 min. Calculation: B3LYP-D3/6-31G*, Lanl2dz for Pd, single point PCM correction (SMD, toluene) *cat. 0.0050 mmol/L in toluene, ethylene 2.1 MPa, 85 °C, 60 min.

substituents on the phosphorus atom which produce high-molecular-weight polyethylene could retard 5th ligand associated ethylene dissociation steps leading to β -hydride elimination, and therefore the molecular weight of polyethylene was limited by spontaneous ethylene dissociation pathways via **9'NA**.

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 β -hydride elimination.

4.3. Development of Pd/ imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) catalyst

The insights obtained in 4.2 led me to develop a novel bidentate ligand imidazo[1,5-*a*]quinolin-9-olate-1-ylidene (IzQO) (Figure 7), in which the strongly donating and sterically bulky phosphine moiety in PS ligand was replaced by a N-heterocyclic carbene (NHC) moiety (Figure 7, green part). The strong σ -donating ability of NHC can enhance the electronic asymmetry in the bidentate ligands, and nucleophilic reactivity of metal-alkyl intermediate toward CO₂ (**TS2** in Figure 1).⁸ Moreover, the optimally oriented substituents on the nitrogen atom may provide a congested environment appropriate for improving molecular weight of polyolefins (Figure 7, red part).

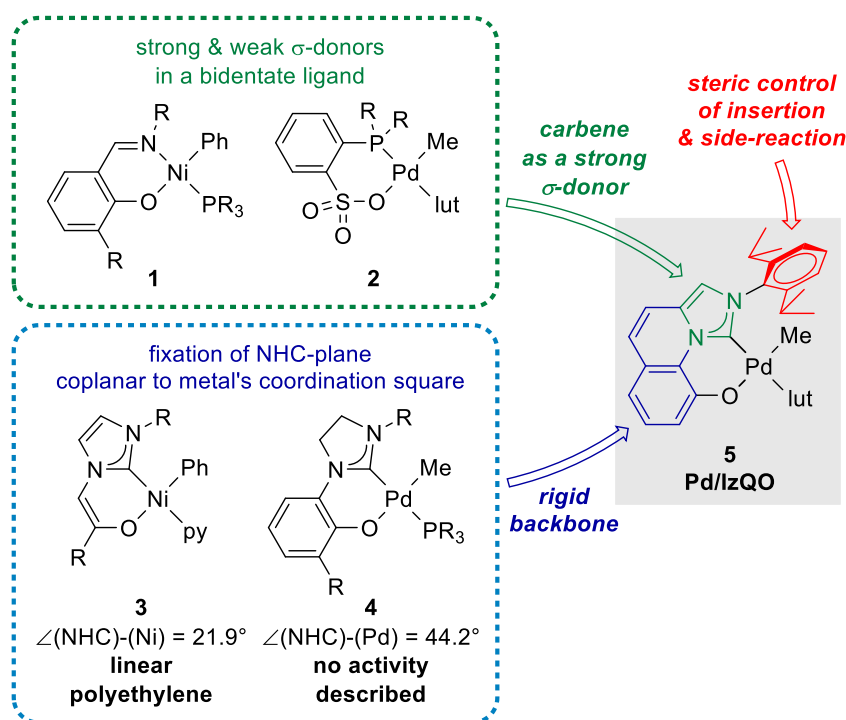


Figure 7. Design of imidazo[1,5-*a*]quinolin-9-olate-1-ylidene ligands **5**, based on complexes **1-4**.

Although many group-10-metal complexes bearing NHC-based ligands were subjected to olefin polymerization, 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 (Figure 8, left). A noteworthy exception in the literature is nickel/NHC-enolate **3** reported by Waymouth, which can form linear polyethylene and low-molecular-weight polypropylene with a short life-time.¹¹ To devise methods for further enhancing the catalyst durability, structural comparisons were made with complex **4** bearing the electronically similar NHC-phenolate ligand, which is inactive for polymerization (Figure 7, blue part).¹² While the NHC-moiety of **3** is nearly coplanar to the metal coordination square, with a mean dihedral angle of 21.9° , the NHC-moiety of **4** is twisted from the metal plane, with a mean dihedral angle of 44.2° . The differences in the catalytic activities and crystal structures between **3** and **4** 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 (Figure 8, right). This idea is reflected in the rigid skeleton of Pd/IzQO **5** (Figure 1, blue part), in which the NHC-plane is fixed onto the palladium square plane.

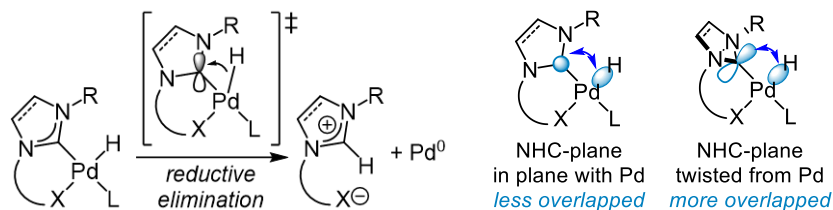


Figure 8. Decomposition pathway for NHC-based catalysts for polymerization (left), and effect of dihedral angle between NHC-plane and square plane of metal center for the transition structure (right).

Thus elaborated Pd/IzQO catalysts showed highly improved life-time 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 (Figure 9). The steric environment provided by NHC enables regioselective insertion of α -olefins and polar monomers, and thereby the catalyst **5** successfully afforded regio-regulated polypropylene, propylene/allyl carboxylate copolymers, and propylene/methyl acrylate copolymer. This straight-forward 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.

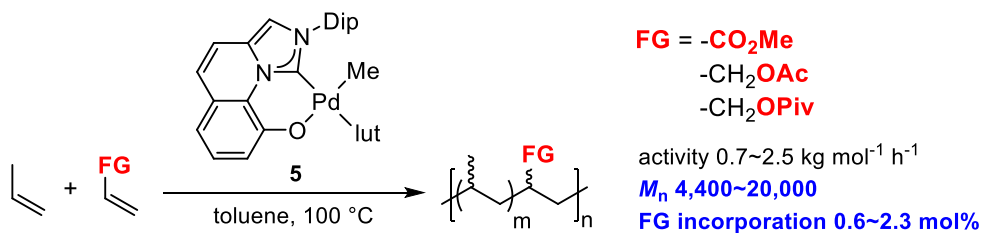


Figure 9. Copolymerization of propylene and polar monomer by Pd/IzQO complex **5**.

Ethylene/CO₂ copolymerization using Pd/IzQO catalyst was studied theoretically and experimentally. DFT study revealed that Pd/IzQO can accelerate **TS2** with enhancement by intramolecular chelation by lithium, but **TS2** was still slower than **TS1** by $\Delta\Delta G^\ddagger$ of 9.0 kcal/mol. The experimental trials to copolymerize ethylene and CO₂ using Pd/IzQO catalysts with/without lithium salts resulted in the formation of polyethylene, possibly due to the **TS2** problem.

5. Summary and Outlook

In this thesis, I studied on olefin polymerization reaction toward utilization of CO₂. Starting with theoretical consideration of ethylene/CO₂ copolymerization (Sec. 2), the two-step copolymerization of dienes and CO₂ was realized (Sec. 3). To accomplish direct olefin/CO₂ copolymerization, I examined late-transition-metal catalysts known to be active for olefin polymerization, and clarified **TS2** (= incorporation of CO₂) 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 CO₂ 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.

6. References

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7. Publications included in this thesis

1. "Copolymerization of Carbon Dioxide and Butadiene via a Lactone Intermediate"
Nakano, R.; Ito, S.; Nozaki, K. *Nature Chem.*, **2014**, *6*, 325–331.
2. "Copolymerization of Propylene and Polar Monomers Using Pd/IzQO Catalysts"
Nakano, R.; Nozaki, K. *J. Am. Chem. Soc.*, **2015**, *137*, 10934–10937.
3. "Elucidation of Key Role of Phosphine–Sulfonate Ligands in Palladium-Catalyzed Ethylene Polymerization: Effect of Ligand Structure on the Pivotal Species to Determine Molecular Weight and Linearity of Polyethylene"
Nakano, R.; Chung, L. W.; Watanabe, Y.; Okuno, Y.; Okumura, Y.; Ito, S.; Morokuma, K.; Nozaki, K.
to be submitted.