

# 博士論文（要約）

## Studies on Copolymerization of Ethylene by Period 4 Transition Metal Catalysts

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エチレンの共重合に関する研究）

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## [1. General Introduction]

Polyethylene (PE) is one of the most widely used plastic, with an annual production over 100 million tons. Its inherent nonpolar nature is advantageous for high chemical resistance and low gas permeability, but often limits its adhesiveness, printability and miscibility. For the introduction of polar functional group onto a surface of high-density PE, copolymerization of ethylene with polar monomer using a Pd catalyst in place of the early transition metal catalysts, has been mainly studied due to its high tolerance against polar functional groups.[1] The use of noble period 5 Pd, however, would be potentially problematic on its industrial application.

For this reason, catalysts using period 4 late transition metals such as Fe, Co, and Ni, have attracted intensive attention due to their inexpensive cost, high natural abundance, lower oxophilicity than early transition metals,[2] and high performance on the ethylene homopolymerization. Nevertheless, application of those catalysts to the copolymerization with polar monomers has not been well-established yet when compared to Pd catalysts, probably due to their lower tolerance against polar functional groups. For example, it was reported that Fe–bis(imino)pyridine catalysts produced homo-PE or homo-PP exclusively in the presence of the polar monomers, and the fast  $\beta$ -FG elimination after the polar monomer insertion was proposed as one of the reason.[3] In this thesis, I focused on Co and Ni catalysts for the copolymerization of ethylene and polar monomers, with following two topics: “Statistical and block copolymerization using Co–cyclopentadienyl catalyst” and “Copolymerization using Ni catalyst bearing methylene-bridged bidentate ligand”.

## [2. Statistical and block copolymerization using Co–cyclopentadienyl catalyst]

For the coordination polymerization of ethylene, two types of Co catalyst have been investigated so far. First, a Co(II) halide complex bearing a tridentate nitrogen ligand has been intensively studied, by mixing with an alkylaluminum cocatalyst such as methylaluminumoxane.[4] Although this catalyst has showed a high performance on the ethylene homopolymerization and showed an activity even for the homopolymerization of (meth)acrylates,[5] there has been no example reported on the copolymerization with polar monomer using this catalyst yet. A notable feature of this catalyst is its activation step; it is known that before generating alkylCo(I) active species, the halide–Co(II) bond in this catalyst undergoes homolytic cleavage assisted by the alkylaluminum cocatalyst.[6]

The second type is a cationic Co(III) complex with cyclopentadienyl ligand. The mechanism of coordination polymerization from the alkyl–Co(III) bond has been carefully studied by M. Brookhart and co-workers.[7] In spite of no example on the copolymerization with polar monomer either, I expected that this catalyst would be a promising candidate for the copolymerization catalyst because (i) the ethylene homopolymerization in the presence of polar MeCN additive[8] and the syntheses of PE end-capped with polar functional groups[9] were reported, suggesting a high tolerance against polar functional groups, and (ii) the migratory insertion of methyl acrylate (MA) into a H–Co(III) bond was reported,[10] which can be extendable to the insertion into C–Co(III) bond.

As noted above, the cationic species including alkyl–Co(III) bond is considered as the active species of the coordination polymerization by Co–cyclopentadienyl catalyst. In many cases, such a C–Co(III) bond in the Co(III) complex is known to undergo homolytic cleavage owing to its low bond dissociation enthalpy (BDE), and this reaction is well-known as the key step in organometallic-mediated radical polymerization (OMRP).[11] Despite no example on the OMRP using a Co–cyclopentadienyl complex, I expected that if the C–Co(III) bond dissociates homolytically during the coordination polymerization by Co–cyclopentadienyl catalyst, *in-situ* generated PE radical species can initiate the sequential radical polymerization, resulting in the formation of PE-based block copolymer. In this work, copolymerization of ethylene and MA was investigated using Co–cyclopentadienyl catalysts.

**Table 1.** Copolymerization of ethylene and MA

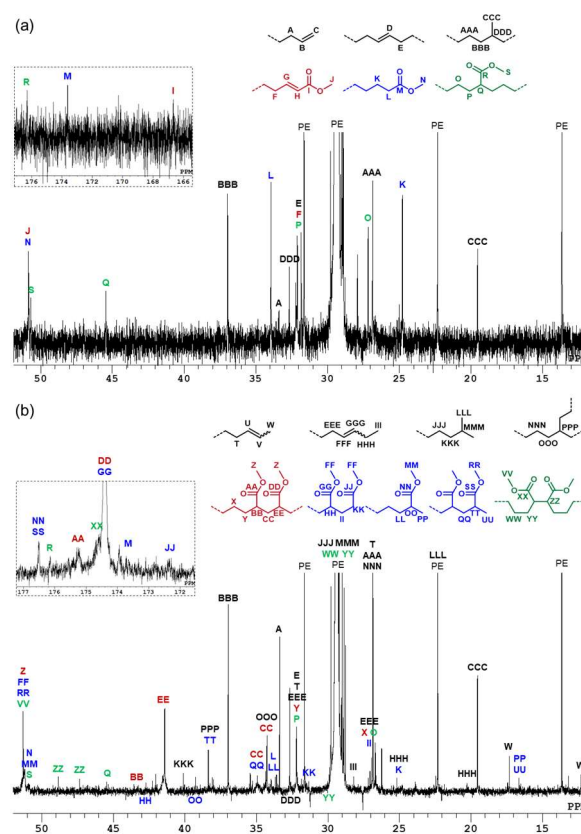
$\text{Ar}^F = 3,5\text{-(CF}_3\text{)}_2\text{C}_6\text{H}_3$

entry	catalyst/ cocatalyst	MA (mL)	time (h)	yield (g)	activity (g/mmol·h)	$M_n$ (g/mol) <sup>a</sup>	$M_w/M_n$ <sup>a</sup>	i.r. (mol%) <sup>b</sup>
1	<b>1</b>	0.2	18	0.021	0.04	1,400	2.6	1.6
2	<b>1</b> /Al(O <sup>i</sup> Pr) <sub>3</sub>	0.2	18	0.021	0.04	1,100	3.2	1.3
3	<b>1</b> /MMAO	0.2	18	0.006	0.01	1,100	5.5	3.3
4	<b>2</b> /MMAO	0.1	18	0.810	4.57	5,400	3.0	0.1
5	<b>2</b> /MMAO	0.2	18	0.204	1.15	1,600	4.1	1.3
6	<b>2</b> /MMAO	0.3	18	0.117	0.66	1,100	2.6	6.6
7	<b>2</b> /MMAO	0.4	18	0.115	0.65	1,100	2.8	7.1

Conditions: In entries 1–3, a mixture of **1** (0.029 mmol) and the selected cocatalyst (1.0 eq. of MA) was used, while an admixture of **2** (0.0098 mmol) and MMAO (Al/Co = 340) was used in entries 4–7. The selected catalyst and cocatalyst was mixed with MA in toluene (total volume 20 mL), and the mixture was stirred under an atmosphere of ethylene (2.5 MPa) at 30 °C in a 50-mL autoclave. MMAO = isobutyl-modified methylaluminoxane in *n*-hexane. <sup>a</sup> Determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration. <sup>b</sup> Ester incorporation ratio, determined by <sup>1</sup>H NMR analysis.

After polymerization in toluene at 30 °C for 18 h, a polymeric product was provided by precipitation from MeOH. Copolymerization results are summarized in Table 1 and <sup>13</sup>C NMR spectra is shown in Figure 1. First, cationic complex **1** was selected for the catalyst due to its high tolerance against polar MeCN additive as noted above (entry 1).[8] Based on the structural analysis, the obtained polymer was determined to be a statistical copolymer. In Figure 1a, characteristic peaks of terminal alkene (A), internal alkene (E), methyl-branch (AAA–DDD), terminal α,β-unsaturated ester (F–J), terminal saturated ester (K–N), and most notably, internal ester (O–S) were observed. These structures can be explained to be formed by coordination polymerization mechanism consisting of: (i) insertion of both ethylene and MA into C–Co(III) bond, (ii) chain termination through β-H elimination, (iii) occasional isomerization of a terminal alkene to an internal alkene, and (iv) protonation during quenching by MeOH after MA insertion. Interestingly, no branched terminal ester was observed, suggesting the preferential 2,1-insertion of MA into the PE–metal bond,[12] similar to the insertion into H–Co(III) bond.[10] To the best of my knowledge, this would be the first example of the coordination copolymerization with a polar monomer by a Co catalyst.

Subsequently, two aluminum-based additives were employed, expecting that their Lewis acidities would lessen the catalyst poisoning of polar carbonyl group. The addition of both Al(O<sup>i</sup>Pr)<sub>3</sub> and isobutyl-modified methylaluminoxane (MMAO) afforded small amount of polymers (entries 2 and 3), but they were found to have different structures; the polymer from entry 2 showed an essentially identical <sup>1</sup>H NMR spectrum to that from entry 1, while a consecutive ester structure (oligoMA) was observed in a <sup>1</sup>H NMR spectrum of the polymer from entry 3.



**Figure 1.** <sup>13</sup>C NMR spectra of copolymers from entries 1 (a) and 5 (b) of Table 1. The inset in (b) is the part of quantitative <sup>13</sup>C NMR spectrum of copolymer from entry 6.

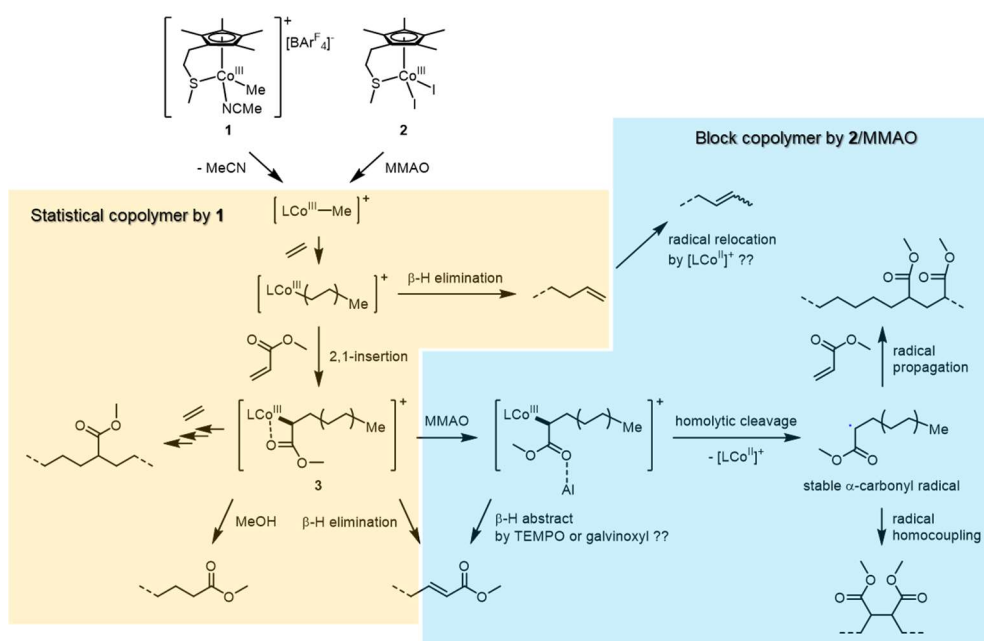
Since MMAO is known to generate a cationic methylCo(III) species from neutral Co diiodide **2**,<sup>[8]</sup> an admixture of **2**/MMAO was then applied, and the copolymer was obtained as expected. The more amount of MA resulted in a higher MA content at the expense of activity and  $M_n$  (entries 4–7). Nevertheless, all polymers from entries 3–7 showed essentially identical  $^1\text{H}$  NMR spectra.

In the  $^{13}\text{C}$  NMR spectrum (Figure 1b), characteristic peaks of the oligoMA (Z–EE) was mainly observed while those of terminal  $\alpha,\beta$ -unsaturated ester (F–J) disappeared, different to Figure 1a. In addition, characteristic peaks of terminal 2-alkene (T, W) and 1,2-dicarbomethoxy (VV–ZZ) moieties were observed. The existence of oligoMA did not only indicated the formation of block copolymer, but also the possibility of two independent homopolymerizations, resulting in the formation of homo-PE and homo-PMA blend. In this work, the latter case was excluded because the characteristic peak of junction position between ethylene-rich unit and oligoMA (X–BB) was determined by NMR analysis. The formation of block copolymer was further supported by fractionation and diffusion ordered spectroscopy (DOSY) NMR analysis. From the result of the differential scanning calorimetry (DSC) analysis, the block copolymer showed more bimodal-like peaks than the statistical copolymer.

As the mechanism of oligoMA formation, a radical pathway seemed to be involved because (i) the oligoMA showed atactic structure known to be produced by free-radical polymerization,<sup>[13]</sup> (ii) the 1,2-dicarbomethoxy structure was found as noted above, which was reported to be made by redox coupling<sup>[14]</sup> or combination of polyacrylate-end radicals,<sup>[15]</sup> and (iii) additions of a stable radical compound such as galvinoxyl or TEMPO afforded copolymers including the terminal  $\alpha,\beta$ -unsaturated ester, originally not detected from the block copolymer.

A proposed mechanism is described in Scheme 1. First, the coordination polymerization of ethylene takes place from the cationic methylCo(III) species followed by the MA insertion into PE–Co(III) bond. In this case, 2,1-insertion is expected to be preferential as discussed above, giving an  $\alpha$ -carbonylCo(III) species **3**. When complex **1** is used as a catalyst, the species **3** can undergo the re-insertion of ethylene to form the internal ester, or be quenched by MeOH to afford the terminal saturated ester, or undergo the  $\beta$ -H elimination to give the terminal  $\alpha,\beta$ -unsaturated ester. On the other hand, when an admixture of **2**/MMAO is employed, a facile homolytic cleavage of  $\alpha$ -carbonyl–Co(III) bond in the species **3** is expected to occur because it will generate a stabilized  $\alpha$ -carbon radical species; it was reported that the BDE of  $\alpha$ -carbonyl–Co(acac)<sub>2</sub> bond was estimated to be significantly lower ( $-1.50\text{ kcal}\cdot\text{mol}^{-1}$ ) than that of methyl–Co(acac)<sub>2</sub> bond ( $14.55\text{ kcal}\cdot\text{mol}^{-1}$ ).<sup>[16]</sup> The generated  $\alpha$ -carbon radical species can initiate the sequential propagation of MA, or undergo homocoupling to give the 1,2-dicarbomethoxy structure.

**Scheme 2.** Proposed mechanism for Co-catalyzed copolymerization



In this case, MMAO was expected to facilitate the homolytic cleavage by its Lewis acidity. Since the 2,1-insertion of MA into a H–Co(III) bond is reported to form an  $\alpha$ -carbonylCo(III) intermediate with an intramolecular chelation of carbonyl group,[10] the species **3** was assumed to have a similar intramolecular chelation. Such an intramolecular chelation is known to stabilize the complex and to allow a higher BDE of the C–Co(III) bond; it was reported that the intramolecular chelation in a HVAc–Co(acac)<sub>2</sub> complex was estimated to increase BDE more than 2.3 kcal·mol<sup>-1</sup>.[17] During the copolymerization, there would be Lewis acidic sites located close to a non-coordinating anionic –[AlO<sub>2</sub>]<sup>-</sup> moiety due to the polymeric structure of MMAO, which could inhibit the intramolecular chelation in species **3**, resulting in the more facile homolytic cleavage.

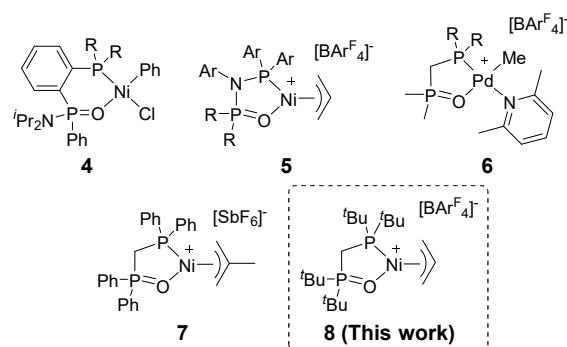
Based on the proposed mechanism, the re-formation of terminal  $\alpha,\beta$ -unsaturated ester induced by 2/MMAO/[stable radical compound] can be attributed to the reaction of species **3** with stable radical compound. Indeed, similar  $\beta$ -H abstract reactions by TEMPO were suggested in the Cu-catalyzed dehydrogenations.[18] Meanwhile, the quantitative <sup>13</sup>C NMR analysis revealed that a terminal 2-alkene was the most abundant terminal structure in the block copolymer. Since it was not observed in the statistical copolymer by catalyst **1**, formation of this structure through conventional “chain walking”[19] was hardly expected. Instead, a radical relocation by *in-situ* generated open-shell Co(II) species might occur to convert the terminal 1-alkene into 2-alkene. Indeed, a similar isomerization of terminal 1-alkene toward 2-alkene by an open-shell Ni(I) species, was recently reported.[20]

The proposed mechanism was further supported by the copolymerization results with other comonomers using 2/MMAO; when methyl methacrylate or styrene was examined, copolymers with consecutive functional group incorporation were produced, while when vinyl acetate or allyl acetate was employed, only a homo-PE was afforded as a product. The latter acetates are known as “less activated monomer” due to their low reactivity toward OMRP.[11] Similarly, a homo-PE was obtained from the copolymerization with ethyl 2-hexenoate, also considered to be less active toward radical polymerization.[21] Although a further mechanistic investigation is required, this would be the first example of radical polymerization from Co-cyclopentadienyl complex, and the first synthesis of PE-based block copolymer without any external stimulus or sequential addition of polar monomers.

### [3. Copolymerization using Ni catalyst bearing methylene-bridged bidentate ligand]

Ni catalyst is a promising candidate for the replacement of Pd catalyst; in the ethylene homopolymerization by  $\alpha$ -diimine-type catalysts, Ni catalysts are known to produce PE with higher activity and molecular weight than Pd catalysts.[22] Nevertheless, application of Ni catalysts to the copolymerization with polar monomer has been less-established. In many cases, they suffer from poor thermal stability which makes it difficult to control exothermic olefin polymerization reactions. Furthermore, intrinsically higher oxophilicity of Ni than Pd often forces the use of polar monomers possessing functional groups at a remote position, while application of fundamental polar monomer is highly limited; there have been only a few reports on the copolymerization with allyl acetate (AAc) using Ni catalysts,[23] in which the molecular weights of copolymers were less than 10,000 and the incorporation ratios of AAc were also lower than 1.0 mol%.

Ni catalysts for the copolymerization with polar monomer have usually employed unsymmetrical bidentate ligands such as phosphine–sulfonate,[23a, 24] imidazo[1,5-a]quinoline-9-olate-1-ylidene (IzQO),[23b] and bisphosphine monoxide (BPMO). Among those ligands, BPMO including strong  $\sigma$ -donor (phosphine) and weak  $\sigma$ -donor (phosphine oxide), has been used as a ligand of Pd catalyst for copolymerization.[1b,12] Pd–BPMO catalysts are thermally robust and afford a highly linear copolymer. Due to these fascinating features, two BPMO ligands have



**Figure 2.** Polymerization catalysts bearing BPMO ligands

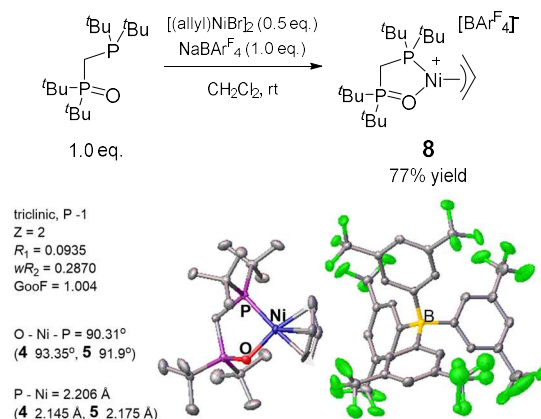
been applied to Ni catalysts for copolymerization (Scheme 2). First, neutral Ni catalysts **4** with phosphine phosphonic amide ligands were examined to the copolymerization with monomers containing remote polar functional groups, by mixing with NaBARF<sub>4</sub>.<sup>[25]</sup> It was mentioned, however, that fundamental polar monomer such as methyl acrylate or vinyl acetate completely stopped the ethylene polymerization. Second, cationic allylNi complexes **5** with diphosphazene monoxide ligands were studied for the copolymerization with acrylates.<sup>[26]</sup> The complexes with bulky biarylphosphine ligands showed a comparable copolymerization performance to Pd counterparts.

As well as substituents on the phosphine and phosphine oxide, a backbone structure also changes the steric and electronic environment of the BPMO ligand, which affects the polymerization performance of catalyst. Recently, it was reported that Pd catalysts **6** with methylene-bridged BPMO ligands for the copolymerization with various fundamental polar monomers such as AAc, vinyl acetate, butyl vinyl ether, acrylonitrile, and methyl (meth)acrylate.<sup>[27]</sup> Introduction of methylene backbone allowed much narrower bite angles and longer O–Pd(II) bond distance than those in the Pd catalyst with phenylene-bridged BPMO ligand. Although a similar methylene-bridged BPMO ligand consisting of diphenylphosphine and diphenylphosphine oxide was previously applied to the cationic methallylNi(II) complex **7**,<sup>[28]</sup> only an ethylene oligomerization was examined with that complex.<sup>[29]</sup> Since it was reported that the replacement of diarylphosphine in the Pd–BPMO catalyst with bulky dialkylphosphine changed the major product from oligoethylene to PE,<sup>[27]</sup> I expected that a Ni complex bearing methylene-bridged BPMO ligand with bulky di-*t*-butylphosphine would be a promising candidate for the copolymerization catalyst. In this work, copolymerization with AAc was studied using an allylNi(II) complex **8** with methylene-bridged BPMO ligand.

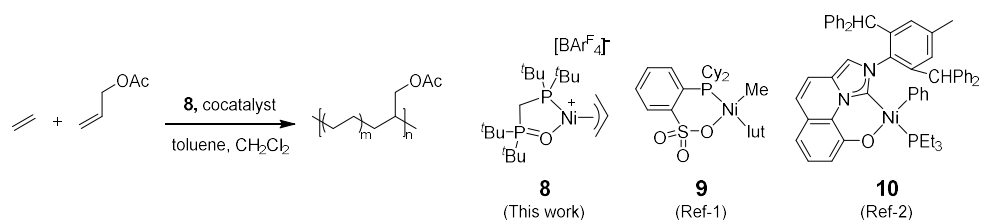
Cationic allylNi(II) complex **8** was prepared from the ligand synthesized according to the literature,<sup>[30]</sup> NaBARF<sub>4</sub>, and [(allyl)NiBr]<sub>2</sub> precursor, and characterized by X-ray crystallographic analysis (Figure 3). Compared to other reported Ni–BPMO complexes **4** and **5**,<sup>[25,26]</sup> complex **8** exhibited narrower bite angle (90.31°) and longer P–Ni bond distance (2.206 Å).

Complex **8** was then employed to the copolymerization with AAc, and copolymerization results are listed in Table 2. After polymerization at 80 °C for 47 h, a copolymer was afforded by precipitation from MeOH. First, complex **8** showed almost no activity when used solely (entry 1). Subsequently, some Lewis acidic cocatalysts were used in entries 3–7, expecting the dissociation of strong coordinating allyl moiety.<sup>[26,31]</sup> MMAO significantly increased activity (entry 4), while B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub> or ZnEt<sub>2</sub> showed only slight increase (entries 2 and 3). The use of MMAO, however, resulted in the slightly lower *M<sub>n</sub>* and much higher *M<sub>w</sub>*/*M<sub>n</sub>* than the cases of other cocatalysts.

As noted above, there have been the limited number of examples on the copolymerization with AAc using Ni catalysts. For comparison to those examples, complex **8** was examined to the copolymerization with selected conditions used for those catalysts in literatures. It showed much higher activity and *M<sub>n</sub>* than previously reported Ni phosphine–sulfonate catalyst **9**<sup>[23a]</sup> whereas lower incorporation ratio was also observed (entry 5 vs ref-1). On the other hand, when compared to the Ni–IzQO catalyst **10**<sup>[23b]</sup>, largely increased activity but diminished *M<sub>n</sub>* and incorporation ratio were obtained (entry 6 vs ref-2). Although complex **8** required a MMAO cocatalyst, these copolymerization results suggest the potential of methylene-bridged BPMO ligand for the Ni catalyst. Synthesis of new complexes with avoiding the strong coordinating allyl ligand, or modification of substituents on both phosphine and phosphine oxide is considered to be necessary for the catalyst with higher copolymerization performance.



**Figure 3.** Synthesis and molecular structure of **8**

**Table 2.** Copolymerization of ethylene and AAc

entry	catalyst	cocatalyst (equiv.)	ethylene (MPa)	AAc (mL)	temp. (°C)	time (h)	yield (g)	activity (g/mmol·h)	<i>M<sub>n</sub></i> (g/mol) <sup>a</sup>	<i>M<sub>w</sub></i> / <i>M<sub>n</sub></i> <sup>a</sup>	i.r. (mol%) <sup>b</sup>
1	<b>8</b>	-	2.0	1.0	80	47	0.002	0.001	-	-	-
2	<b>8</b>	B(C <sub>6</sub> F <sub>5</sub> ) <sub>3</sub> ( <b>10</b> )	2.0	1.0	80	47	0.029	0.02	5,900	2.6	0.21
3	<b>8</b>	ZnEt <sub>2</sub> ( <b>10</b> )	2.0	1.0	80	47	0.034	0.02	7,600	2.7	0.10
4	<b>8</b>	MMAO (100)	2.0	1.0	80	47	1.138	0.78	4,200	5.0	0.20
5 <sup>c</sup>	<b>8</b>	MMAO (100)	3.0	3.0	30	3	0.108	1.8	9,400	6.5	0.04
ref-1 [23a]	<b>9</b>	-	3.0	3.0	30	3	0.072	1.2	900	1.9	0.24
6 <sup>d</sup>	<b>8</b>	MMAO (100)	3.0	2.0	60	15	0.137	0.91	900	10.8	0.09
ref-2 [23b]	<b>10</b>	Ni(cod) <sub>2</sub> ( <b>2</b> )	3.0	2.0	60	15		0.13	4500	2.5	0.72

Conditions: In entries 1–4, a solution of **8** (31.2 μmol) and AAc in 3.0 mL of dichloromethane was mixed with selected cocatalyst in toluene (total volume 15 mL), and the mixture was stirred under an atmosphere of ethylene (2.0 MPa) at 80 °C for 47 hours in a 50-mL autoclave. AAc = allyl acetate, Ar<sup>F</sup> = 3,5-bis(trifluoromethyl)-C<sub>6</sub>H<sub>3</sub>, lut = 2,6-lutidine, MMAO = isobutyl-modified methylaluminoxane in *n*-hexane, cod = cyclooctadiene. <sup>a</sup> Determined by size-exclusion chromatography using polystyrene standards and corrected by universal calibration. <sup>b</sup> Ester incorporation ratio, determined by <sup>1</sup>H NMR analysis. <sup>c</sup> A solution of **8** (20 μmol), MMAO (Al/Co = 100), and AAc (3.0 mL) in 12.0 mL of dichloromethane was stirred under an atmosphere of ethylene (3.0 MPa) at 30 °C for 3 hours. This is the same condition with entry ref-1. <sup>d</sup> A solution of **8** (10 μmol) and AAc (2.0 mL) in 1.0 mL of dichloromethane was mixed with MMAO (Al/Co = 100) in toluene (total volume 10 mL), and the mixture was stirred under an atmosphere of ethylene (3.0 MPa) at 60 °C for 15 hours. This is the slightly modified condition from entry ref-2.

## [4. References]

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