Design and Synthesis of New Transition Metal Complex Catalysts for Synthesis of New Polyolefins

(新規オレフィン系ポリマーの創製を可能とする高性能分子触媒の設計・創製)

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Content

Part I. Precise synthesis of new ethylene copolymers by using nonbridged half-titanocene catalysts

Part II. Design and synthesis of new transition metal complex catalysts for olefin coordination polymerization

Chapter 1

General Introduction

Polyolefins are the largest volume polymers in the plastics industry today. The market demand is growing even in the conventional polyolefins such as polyethylene (PE) and polypropylene (PP), because they have excellent physical and chemical properties with low cost, low density, good processability and etc.[1] Most of them have been produced by transition metal catalyzed coordination polymerization using heterogeneous multi-site catalysts such as Ziegler-Natta catalyst and Phillips catalyst. Following the discovery of homogeneous metallocene catalyst, research of homogeneous single-site complex catalysts based on well-defined organometallic complexes has been developed during the last three decades.[2-5] A significant advantage of the single site catalysts compared to the heterogeneous mult-site catalysts is that they can control the primary structure of the resultant polymers such as molecular weight, molecular weight distribution, comonomer content, both regio- and stereo-regularity by optimization of the active site through catalyst design.[3b] Recently, considerable attention has been paid to produce new polyolefins with specified properties such as high transparency for optical material and higher heat tolerance compared to PE and PP, by using newly designed complex catalysts. Therefore, studies concerning design and synthesis of efficient transition metal complex catalysts have been investigated in this field.[1-5]

This introductory chapter describes overview of the olefin coordination polymerization.

Heterogeneous multi-site catalyst

Before the invention of the coordination polymerization, polyethylene was produced by free radical polymerization under high pressure (100-350 MPa) and high temperature (150-350 ^{o}C).[1] The polyethylene is highly branched owing to the radical backbiting processes, and is called low density polyethylene (LDPE).

The coordination polymerization was started in the 1950s. In the 1953, Ziegler found catalyst prepared from $TiCl_4$ and $AlEt_3$ can polymerize ethylene under lower pressure and lower temperature than the free radical process, and afford linear polyethylene classified as high density polyethylene (HDPE).[6] In the 1954, Natta found that $TiCl_3/Et_2AlCl$ catalyst is able to polymerize propylene stereoselectively and yield predominantly *isotactic* polypropylene.[7] In the same 1950s, Cr based catalyst and Mo based catalyst that can afford HDPE were also found by Phillips Petroleum[8] and Standard Oil[9] respectively. Additionally, the Ziegler catalyst could copolymerize ethylene with α-olefins and afford copolymer, so-called linear low density polyethylene (LLDPE), that has similar density and crystallinity with LDPE, but has linear backbone unlike LDPE (Figure 1) .[1]

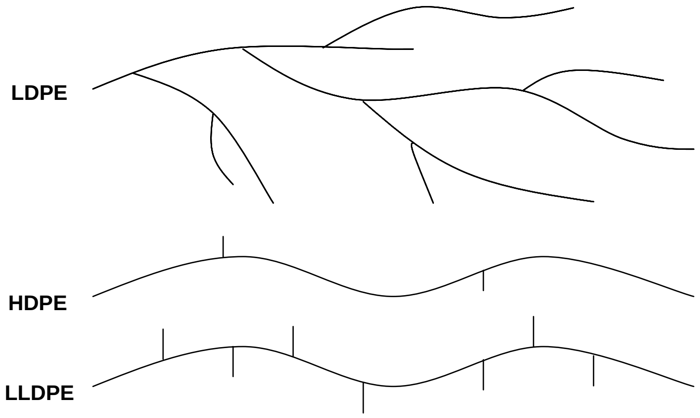


Figure 1. Structures of low density polyethylene (LDPE), high density polyethylene (HDPE) and linear low density polyethylene (LLDPE).

The above heterogeneous catalysts have been major catalysts for the industrial production of PE and PP,[1] however, they have significant disadvantages for precise polymerization owing to the multiple active sites. These catalysts usually afford nonuniform polymers containing different primary structures because each of the active sites has its own rate constants for monomer enchainment, commoner enchainment, stereo- and region-selectivity, chain transfer, and deactivation.[3c]

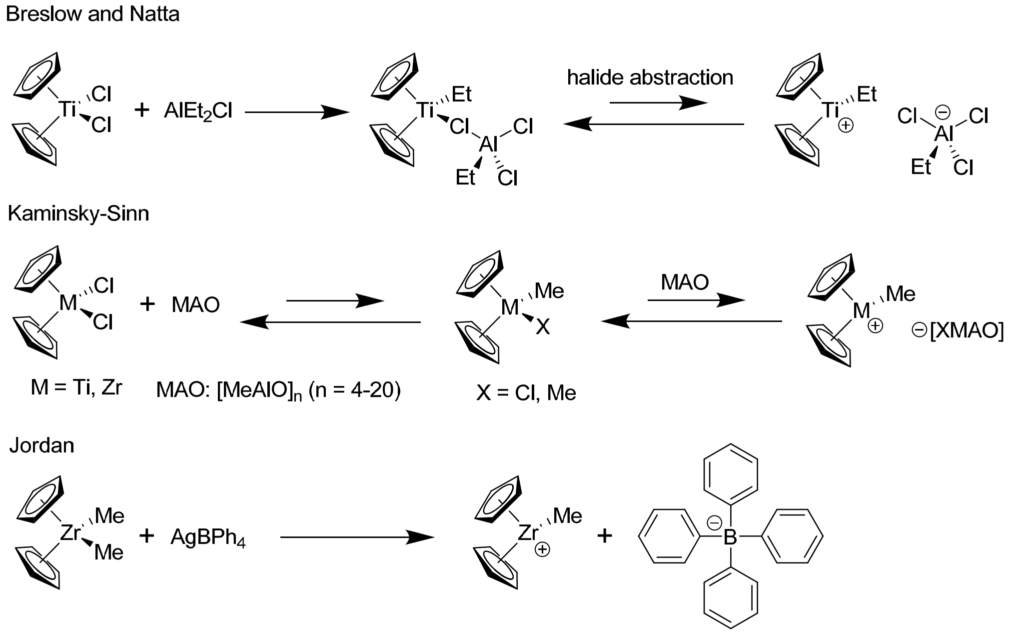
Homogenious single-site complex catalyst

Homogeneous complex catalysts have been focused on controlled coordination polymerization because they have possibility to be single-site catalysts. The significant advantages of the single-site catalysts enable not only to afford polymers with unimodal molecular weight and composition, but also to tune the reactivity of the active site through catalyst design.

The first example of homogeneous complex catalyst was reported by Breslow[10] and Natta[11] independently in the 1957. Cp_2TiCl_2 complex polymerized ethylene in the presence of $AlEt_3$ or $AlClEt_2$ although the catalytic activity was lower than that of the Ziegler catalyst. Importantly, the catalytically active species in the system was suggested as $Cp_2Ti(IV)^+$-R species formed through alkylation and halide abstraction by the organoaluminum compounds (Scheme 1).[12]

The highly active homogeneous polymerization catalysts consisting of titanocenes (Cp_2TiX_2) and zirconocenes (Cp_2ZrX_2) [X = Cl, or Me] with methylaluminoxane (MAO) cocatalysts were firstly reported by Kaminsky and Shinn in the 1980s.[13] The zirconocenes/MAO catalysts showed 10 to 100 times higher catalytic activity than the Ziegler catalyst, and the molecular weight distribution of the resultant polyethylene (M_w/M_n ca. 2) was in agreement with the theoretical value of single-site nature.[13c] A key of the high catalytic activity with single-site manner is MAO cocatalyst comprised from $(MeAlO)_n$ ($n \approx 5$-20), which plays many significant roles for the polymerization.[2b,3d] One function is generation of catalytically active species such as $[Cp_2Zr^+(IV)R][XMAO^-]$ (X = Cl, Me), through alkylation and following halogen or methyl abstraction of the precatalysts (Scheme 1). Other important role is formation of weak ion pair as counter anion with the cationic active species by delocalization of the negative charge on the big $[XMAO^-]$ molecule.

Scheme 1



Despite the success of MAO cocatalyst in promoting high-active single-site complex catalyst systems, the cocatalyst also exhibits disadvantaged features. Large Al/metal molar ratio on the order of 10^2 to 10^5 is required to show reasonable activity and stable kinetic profiles,[3d,14] and the ratio increases furthermore under low catalyst concentration.[13b] The reason is explained that MAO is necessary not only to scavenge impurities in the polymerization system, but also to overcome large equilibrium constant between the active cationic species and the dormant dialkyl or alkyl halide species, and to reactivate deactivated species.[2i]

The possibility of MAO free catalyst system was firstly opened by Jordan in the 1986.[15] He reported cationic alkyl metallocene complex of the type $[Cp_2Zr^+Me(THF)][B^-Ph_4]$ that prepared by reaction of Cp_2ZrMe_2 with 1 equivalent of $AgBPh_4$ polymerized ethylene in the absence of Al cocatalysts (Scheme 1).[15] Following the discovery, highly effective borate cocatalysts such as $[C_6H_5N(H)Me_2][B(C_6F_5)_4]$, $[Ph_3C][B(C_6F_5)_4]$ were developed.[3d]

Mechanistic aspects for olefin coordination polymerization

The proposed mechanism of the olefin coordination-insertion polymerization consists of (1) generation of active species, (2) propagation of polymer chain, and (3) chain transfer of polymer chain (Scheme 2).

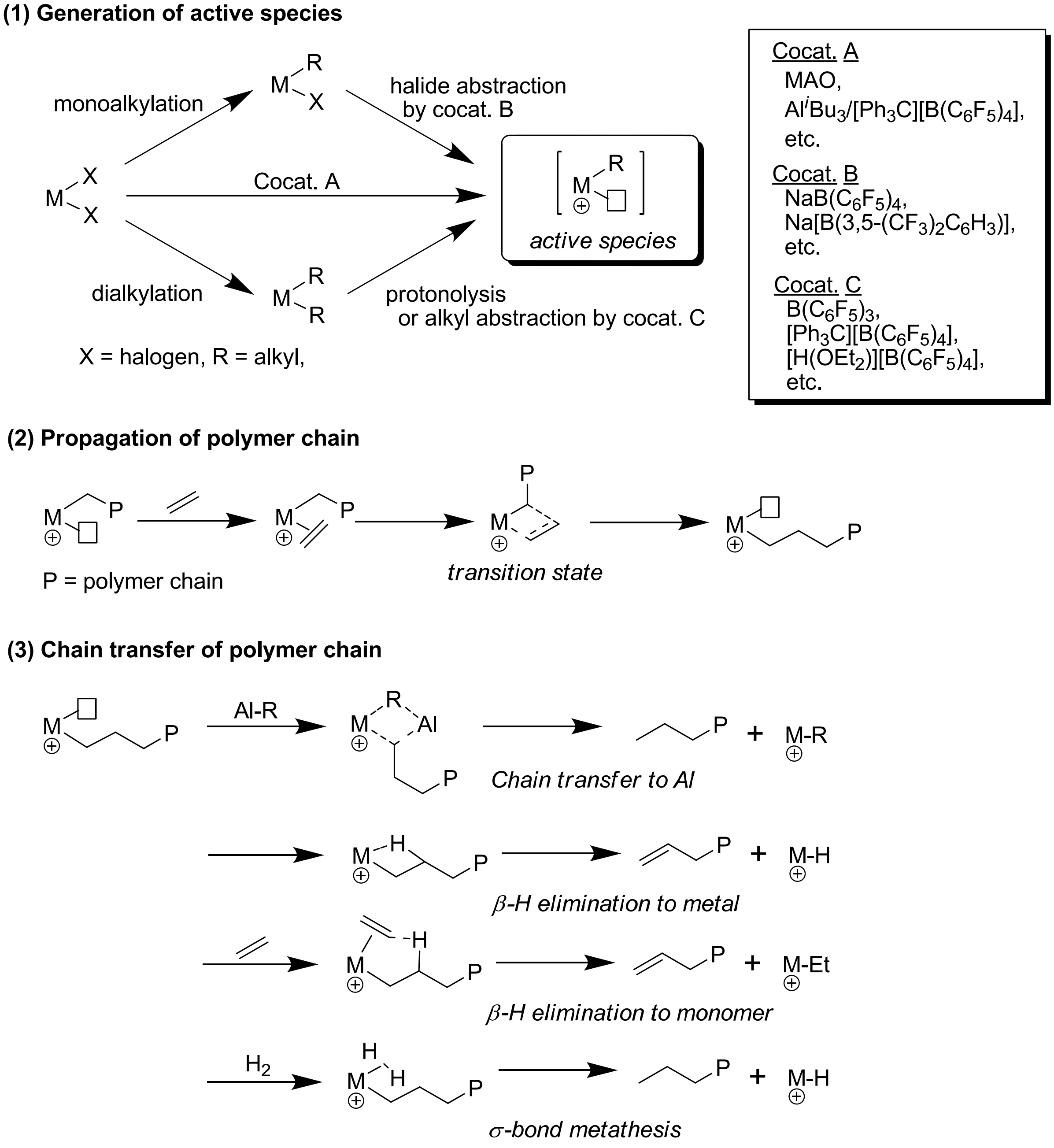
The first step is the generation of catalytically active species, generally cationic alkyl species, by reaction of inactive precatalysts with cocatalysts. Although several types of combinations of the precatalysts and cocatalysts are well-known as shown in scheme 2, the similar active species is believed to be generated.

Cossee-Arlman mechanism has been generally accepted as the propagation mechanism,[16] although various modifications to this mechanism have been also reported.[17] In the mechanism, monomer molecule coordinates to the vacant site of the active metal center and subsequently inserts into the metal-alkyl bond, and then similar active species is regenerated.

Three types of the chain transfer mechanisms are well known: polymer chain transfer to alkyl aluminum compounds of the cocatalysts or scavenger, β-H elimination to the active metal center or to the monomer, and σ-bond metathesis by H_2.[18] In case of propylene and 1-butene polymerization, β-alkyl elimination is also reported.[19] The rate ratio between the propagation and the chain transfer restricts the molecular weight of the resultant polymer.

A significant mechanistic feature of the coordination polymerization compared to radical, cationic, and anionic polymerizations, is that the active catalyst molecule exists on the chain end of the propagating polymer. Thus, the catalysts in the coordination polymerization are able to control primary structure of the resultant polymers precisely such as the molecular weight, comonomer content, regio- and stero-regularity by optimization of the active site through catalyst design.

Scheme 2


(1) Generation of active species
monoalkylation
halide abstraction by cocat. B
Cocat. A
dialkylation
protonolysis or alkyl abstraction by cocat. C
active species
X = halogen, R = alkyl,
Cocat. A
MAO,
Al^{i}Bu$_3$/[Ph$_3$C][B(C$_6$F$_5$)$_4$],
etc.
Cocat. B
NaB(C$_6$F$_5$)$_4$,
Na[B(3,5-(CF$_3$)$_2$C$_6$H$_3$)],
etc.
Cocat. C
B(C$_6$F$_5$)$_3$,
[Ph$_3$C][B(C$_6$F$_5$)$_4$],
[H(OEt$_2$)][B(C$_6$F$_5$)$_4$],
etc.
(2) Propagation of polymer chain
P = polymer chain
transition state
(3) Chain transfer of polymer chain
Al-R
Chain transfer to Al
β-H elimination to metal
β-H elimination to monomer
H$_2$
σ-bond metathesis
M-R
M-H
M-Et

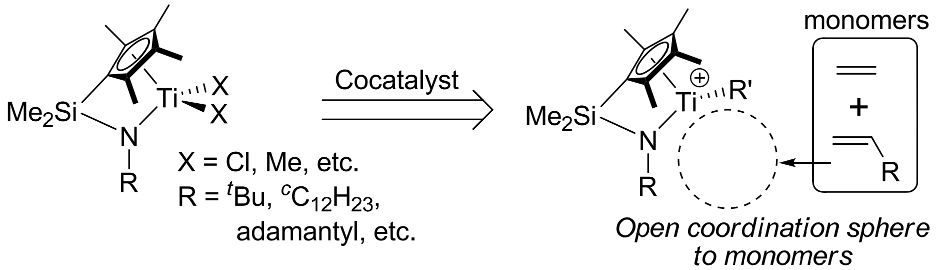
Precise synthesis of ethylene copolymer by single-site catalyst

Ethylene based copolymers, such as LLDPE, ethylene-propylene (EP) rubber and ethylene-propylene-diene-methylene linkage (EPDM) rubber, are of great practical interest as promising targets for the application of the single-site catalysts, because these copolymers prepared by the catalysts exhibit good physical properties such as impact resistance, sealing and elasticity, owing to the unimodal comonomer and molecular weight distribution.[1] And the properties are precisely tunable by adjustment of the ratio of individual component in the copolymers as well as by precise control of the monomer distribution through the employed catalysts.[2a]

Bridged Cp-amide titanium complexes of the type $Me_2Si(C_5Me_4)(NR)]TiX_2$ [R = alkyl, X = halogen, alkyl], so called constrained geometry catalysts (CGC), are one of few commercially exploited single-site catalysts for ethylene copolymerization.[1,2e,20] The catalysts exhibit both high catalytic activities and more efficient incorporations of sterically hindered comonomers such as higher α-olefins, styrene, and norbornene in the ethylene copolymerizations than the heterogeneous catalysts and the metallocene catalysts.[2e,20] The efficiency has been explained that the formation of large coordination space allows better accessibility for the bulky monomers (Scheme 4).[2e]

Scheme 4

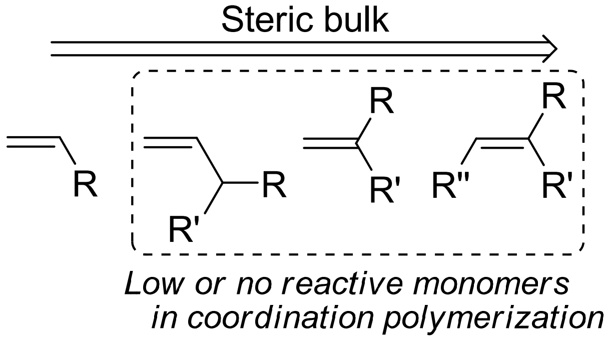
Constrained Geometry Catalysts (CGC) [2e,20]



Features in ethylene copolymerization
- High catalytic activity
- High thermal stability (even at 160 °C)
- Efficient comonomer incorporation such as higher α-olefin, norbornene, styrene

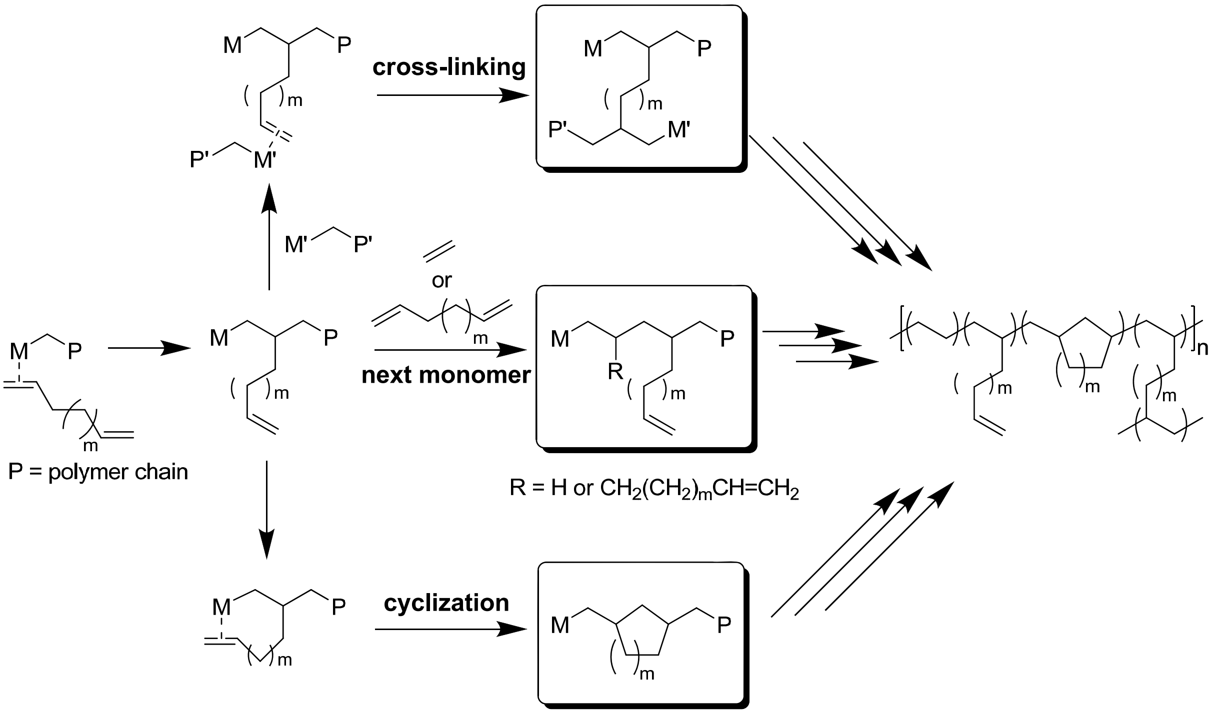
Despite the success of CGC, available comonomers for the coordination polymerization have been limited to sterically less hindered olefins. Especially, examples concerning ethylene copolymerizations with more sterically hindered monomers such as γ-branch-α-olefins,[21,22] di-[23,24] and tri-substituted-α-olefins are rare (Scheme 5). Moreover, there are no reports concerning the copolymerizations with both high catalytic activity and efficient comonomer incorporation. Thus, the ethylene copolymers incorporating these hindered olefins are highly expected to show unique properties owing to the new structures.

Scheme 5



More recently, considerable attention has been also paid to precise controlled synthesis of ethylene copolymers containing olefinic side chains through copolymerization of ethylene with nonconjugated dienes using the single-site catalysts. This is because these copolymers are expected to show good elastomeric properties as seen in the EPDM rubbers, and introduction of polar functional groups to the side chains by chemical reaction enables to afford polar functionalized ethylene copolymers[25] that have been difficult to prepare by direct copolymerization of ethylene with polar olefins owing to the poisoning and interaction of the metal center with the polar functional groups.[2a,2e,26,27] However, undesired side reactions of the unsaturated side chains with the active species, cyclization and cross-linking, often prevent the precise synthesis of unsaturated polyethylenes in the copolymerization of ethylene with nonconjugated dienes (Scheme 6).[25g,k,28] Thus, available nonconjugated dienes have been also limited so far.

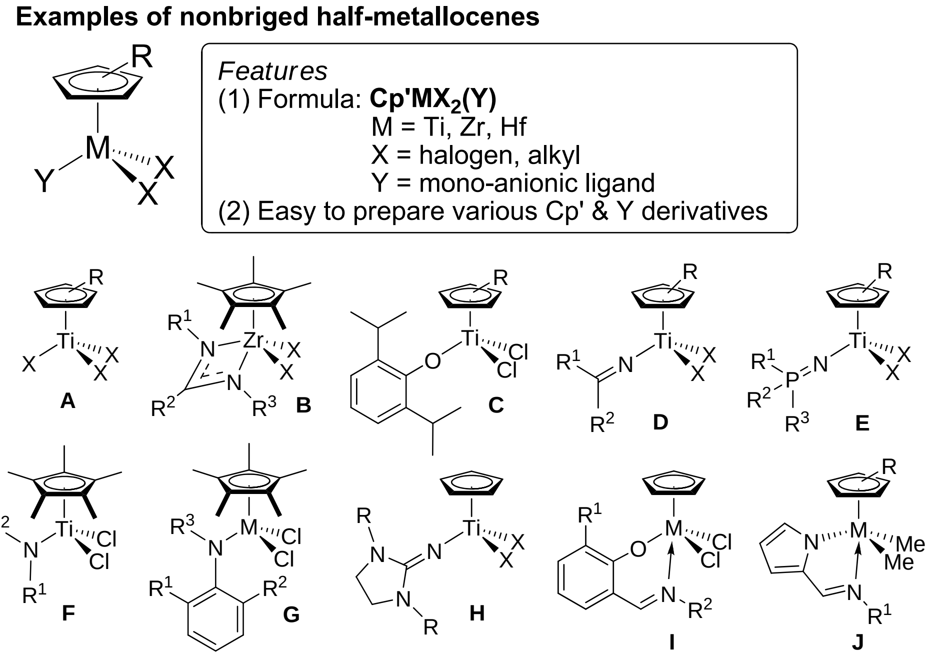
Scheme 6



Nonbridged half-metallocene catalysts

Recently, group 4 nonbridged half-metallocene complexes of the type Cp'MX$_2$(Y) (Cp' = cyclopentadienyl group; M = Ti, Zr, Hf; X = halogen, alkyl; Y = anionic ligands such as OAr, NR$_2$, N=CR$_2$, N=PR$_3$, etc.), have been considered as one of the promising candidates for new efficient catalysts, because these catalysts exhibit unique characteristics for the production of new polymers that are not prepared by the heterogeneous catalysts as well as by the ordinary metallocenes and CGC (Scheme 7).[4b,5,29-31] Moreover, their syntheses are generally simplified (one or two steps in high yields), and thus ligand modification should be much easier compared to CGC. For example, Cp'TiX$_3$ (**A**) can afford *syndiotactic* polystyrene with high catalytic activity although Ti(III) species is suggested as the active species.[30] The zirconium amidinate complexes, Cp*ZrX$_2$[N(R^1)C(Me)N(R^2)] (**B**), not only proceed isospecific living polymerizations of 1-hexene and vinylcyclohexane, but also are able to afford stereogradient PP and stereoblock poly(α-olefins)s with living manner.[31]

Scheme 7



Features
(1) Formula: **Cp'MX$_2$(Y)**
M = Ti, Zr, Hf
X = halogen, alkyl
Y = mono-anionic ligand
(2) Easy to prepare various Cp' & Y derivatives

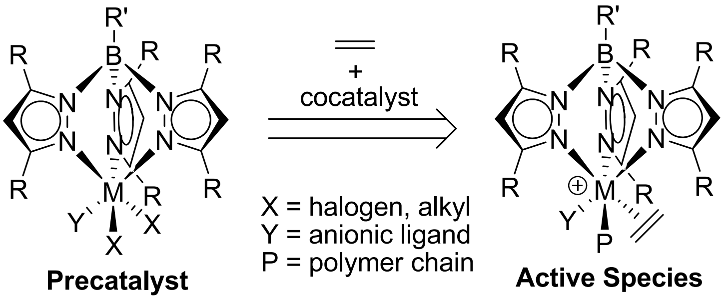
Nomura demonstrated that nonbridged half-titanocenes containing an aryloxo ligand of the type Cp'TiCl$_2$(OAr) (**C**), not only exhibit notable catalytic activity for olefin polymerization,[32-38] but also display unique characteristics in ethylene copolymerizations with α-olefin,[34] styrene[35] and norbornene[36] (Scheme 6). These catalysts had achieved efficient incorporation of cyclohexene, disubstituted olefin, in the ethylene copolymerization as the first example.[37] It was also revealed that a simple replacement of substituent on both the cyclopentadienyl fragment and the aryloxo ligand can modify to an efficient catalyst for desired copolymerization.

Moreover, it is reported that these catalysts polymerize nonconjugated dienes such as 1,5-hexadiene and 1,7-octadiene, with more favored repeated monomer insertion than the side reactions unlike the conventional catalysts, and the resultant polymers contain olefinic side chains with uniform distributions.[38] The catalysts also exhibit notable catalytic activity in ethylene/1-octene/1,7-octadiene terpolymerization and afford unsaturated ethylene copolymer without the side reactions.[38a]

Tris(pyrazolyl)borate group 4 metal complex catalyst

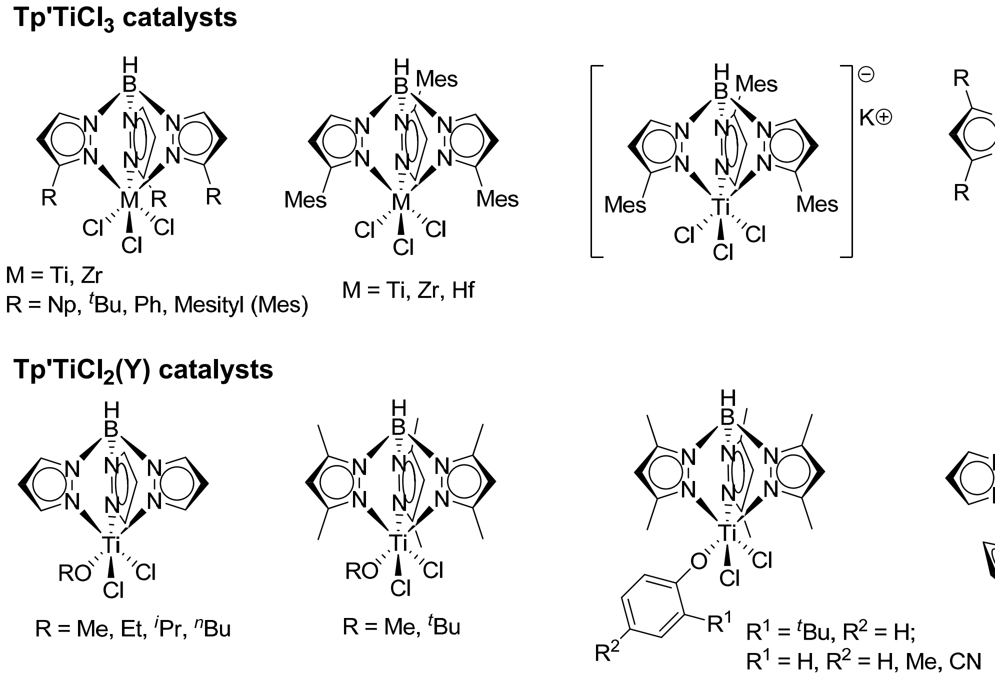
Tris(pyrazolyl)borate (Tp’) ligands have been considered as one of the most promising alternatives of Cp’ ligands because they are same mono-anionic 5-electron donors with Cp’, and their electronic and steric properties are tunable by introduction of substituents on the pyrazolyl rings.[39,40] Additionally, the strong σ-electron donor property of Tp’ is expected to stabilize the catalytically active species and Tp’ complexes would fold octahedral geometry that may form a more suited steric environment especially for insertion than tetrahedral geometry like Cp’ complexes.[39,40] Therefore, group 4 Tp’ complexes containing an anionic ligand of the type Tp’MX$_2$(Y) (M = Ti, Zr, Hf; Y = anionic donor ligand) can be expected as efficient catalysts for olefin polymerization like the nonbridged half-metallocenes Cp’MX$_2$(Y) (Scheme 8). However, although it is well known that Tp’MCl$_3$ complexes exhibit from moderate to high catalytic activities for ethylene polymerization in the presence of MAO,[41,42] only few examples for coodination polymerization using Tp’MX$_2$(Y) were known and the studies including the structural analysis and the effect of ligand on the activity in olefin polymerization have not been reported so far (Chart 1).[41b-c,42c,43]

Scheme 8



Expected features of Tp'MX$_2$(Y) catalysts
- High stability and activity by strong σ-donation of Tp'
- Simple preparation of various Tp' & Y derivatives
- Favorable environment for insertion by octahedral geometry

Chart 1



Aim of this thesis

As described above, design and synthesis of new transition metal complex catalysts for precise synthesis of new polyolefins have been one of the most attractive subjects in this field, because the new polymers can be expected to show unique properties owing to the new structures.[2-5] Especially, precise and efficient synthesis of the ethylene copolymers incorporating the sterically hindered comonomers and containing the unsaturated or polar side chains that have been difficult to prepare by the heterogeneous catalysts as well as the ordinary metallocene catalysts and CGC, has been important target in both academic and industrial interests.

The nonbridged half-titanocenes, Cp’TiX_2(OAr), are promising candidates for the subjects because these catalysts exhibit better comonomer incorporation in ethylene copolymerization than the conventional catalysts.[32-37] Moreover, these catalysts favor insertion of next monomer in the polymerization of nonconjugated diene than the side reactions compared to the conventional catalysts.[38]

One of the aims of this thesis is to explore the possibilities of the nonbridged half-titanocene catalysts for precise synthesis of the ethylene copolymers incorporating the sterically hindered comonomers or containing the unsaturated side chains. In case of the latter polymers, introduction of polar functionalities to the side chains is also explored for precise synthesis of the polar functionalized polyethylene. Another aim of this thesis is design and synthesis of new transition metal catalysts based on the obtained knowledge in the first aim. In particular, group 4 metal nonbridged half-metallocenes containing an aryloxo ligand Cp'MCl_2(OAr) [M = Ti, Zr, Hf] are focused to explore the effect of the centered metal. Moreover, hydrotris(pyrazolyl)borate titanium complexes containing an aryloxo ligand of the type Tp'TiX_2(OAr) are also focused because Tp' ligands are highly expected as promising alternative of Cp' ligands.[39-40]

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Part I

Precise synthesis of new ethylene copolymers by using nonbridged half-titanocene catalysts

Chapter 2

Precise synthesis of ethylene/vinylcyclohexane and ethylene/2-methyl-1-pentene copolymers by using nonbridged half-titanocene catalysts

Introduction

Precise synthesis of new polyolefins that have never been prepared by conventional catalysts is one of the most attractive subjects in the field of transition metal catalyzed coordination polymerization, because unique properties due to the new structures can be highly expected.[1-3] And copolymerization is an important process that usually allows the alteration of the properties of materials through adjustment of the ratio of individual component in copolymers. Although copolymers prepared by copolymerizations with ethylene with linear α-olefins such as propylene, 1-butene and 1-hexene are well known and were widely used as linear low density polyethylene (LLDPE), examples for copolymerizations with sterically hindered olefins such as γ-branch-α-olefins[4-7] and 2,2-disubstituted-α-olefins[8-14] have been limited so far.

Vinylcyclohexane (VCH) has been investigated in the γ-branch-α-olefins for ethylene copolymerization because *isotactic* poly(VCH) exhibits such valuable properties as high thermostability and excellent dielectric properties.[7] However, there are no examples of precise synthesis for ethylene copolymers with both high VCH content and high molecular weight. For example, the VCH contents in the ethylene/VCH copolymers using Cp_2ZrCl_2, Cp_2ZrMe_2/methylaluminoxane (MAO) catalyst at 25 or 70 °C under excess VCH molar ratios were low (0.6-1.7 mol%), and the resultant copolymers possessed low M_n values ($(5.0\text{-}6.1) \times 10^3$).[4] Moreover, the VCH contents in the ethylene/propylene/VCH terpolymers prepared by *rac*-Me_2Si[2-MeBenz[e]-Ind]$ZrCl_2$-MAO catalyst were also low (0.6-0.9 mol %), although these copolymerizations were performed under relatively high VCH concentrations compared to ethylene and propylene.[5] In addition, an efficient VCH dimerization took place with exclusive selectivity in the presence of Cp_2TiCl_2, Cp_2HfCl_2, Cp_2ZrCl_2, and $[Me_2Si\text{-}(Cp)_2]ZrCl_2$-MAO catalysts.[6]

Moreover, 2,2-disubstituted-α-olefins have been also investigated for ethylene copolymerization because LLDPE from 2,2-disubstituted-α-olefins would exhibit better properties about weather resistance and chemical resistance compared to that from linear α-olefins. Examples of the ethylene/2,2-disubstituted-α-olefins copolymerization are limited. For example, ethylene/isobutene (IB) copolymerization by linked half-titanocenes[8-10] and $[Et(indenyl)_2]ZrCl_2$-cocatalyst systems were reported recently,[11] and cyclopolymerization of 2-methyl-1,5-hexadiene was also known as a related example.[12] Moreover, ring-opening (or addition) (co)polymerization of strained methylenecycloalkanes such as methylenecyclobutane, methylenecyclopropane, and the derivatives (with ethylene) were also known.[13-14]

The ethylene/IB copolymerization by the $[Et(indenyl)_2]ZrCl_2$-MAO catalyst afforded the copolymer with low IB content (2.8 mol%) even under large IB/ethylene feed molar ratio (4000). The binuclear linked half-titanocene $(\mu\text{-}CH_2CH_2\text{-}3,3')\{(\eta^5\text{-indenyl})[1\text{-}Me_2Si(N^tBu)]TiMe_2\}_2/1,4\text{-}(C_6F_5)_2BC_6F_4B(C_6F_5)_2$ catalyst afforded the ethylene copolymer with 15.2 mol% IB content, but the molecular weight distribution was somewhat broad (M_w/M_n = 3.52).[10] Although the linked half-titanocenes $[Me_2Si(C_5Me_4)(N\text{-cyclododecyl})]TiMe_2/[PhNMe(H)][B(C_6F_5)_4]$ afforded the ethylene copolymer with 33 mol% IB content under a certain condition (ethylene 4.4 bar, M_n = 10,300, M_w/M_n = 2.5), the resultant polymer in the copolymerization of ethylene with 2-methyl-1-pentene (2M1P) by the catalyst possessed broad molecular weight distribution with rather low M_n value (M_n = 10,780, M_w/M_n = 5.9, 2M1P content = 9.0 mol%).[8]

Nonbriged half-titanocenes containing an aryloxo ligand of the type $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp' = cyclopentadienyl group] are promising candidates for the ethylene/VCH and ethylene/2M1P copolymerizations.[3a,15-18] This is because the catalysts exhibit not only notable catalytic activities but also efficient comonomer incorporations in copolymerizations of ethylene with α-olefin,[16] styrene,[17] norbornene[18] and cyclohexene.[19]

This chapter deals with the exploration of (1) the possibilities for the ethylene/VCH and ethylene/2M1P copolymerizations using the nonbridged half-titanocene catalysts and (2) the effect of subsituent of both the Cp' and mono-anionic ligands in the catalysts on the catalytic activity and the comonomer incorporation as well as the molecular weight and molecular weight distribution, comonomer distribution of the copolymers. Moreover, polymerization mechanism of the ethylene/2M1P copolymerization is also dealt in this chapter.

Results and Discussion

1. Copolymerization of ethylene with vinylcyclohexane

Two complexes, $Cp'TiCl_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ [Cp' = Me_5C_5 = Cp* (**1**), ${}^{t}BuC_5H_4$ (**2**)], were chosen as the catalyst precursors for copolymerization of ethylene with vinylcyclohexane (VCH) because these catalysts are highly effective for ethylene copolymerizations as described above.[16-19] The Cp*-ketimide analogue, $Cp^*TiCl_2(N{=}C{}^{t}Bu_2)$ (**3**), was also chosen for exploring the effect of the anionic ancillary ligand, and the Cp-ketimide analogue, $CpTiCl_2(N{=}C{}^{t}Bu_2)$ (**4**), was chosen because the **4**-MAO catalyst not only exhibited notable catalytic activity for ethylene/α-olefin copolymerizaion[20] but also showed better comonomer incorporation than **1-2** in ethylene/norbornene copolymerization.[19] The linked half-titanocenes $[Me_2Si(C_5Me_4)(N{}^{t}Bu)]TiCl_2$ (**5**) was chosen as comparison. MAO prepared as a white solid by removing toluene and $AlMe_3$ from commercially available MAO solution was chosen as the cocatalyst, because it is highly effective cocatalyst for the catalyst precursors **1-5** in ethylene/α-olefin copolymerization to prepare high molecular weight copolymers with unimodal molecular weight distributions in high reproducibility.[16,20] The results for copolymerization of ethylene with VCH using the **1-5**/MAO catalysts at 25 °C are summarized in Table 1 (Scheme 1). The VCH contents in the obtained polymers were determined by ^{13}C NMR spectra.

Scheme 1

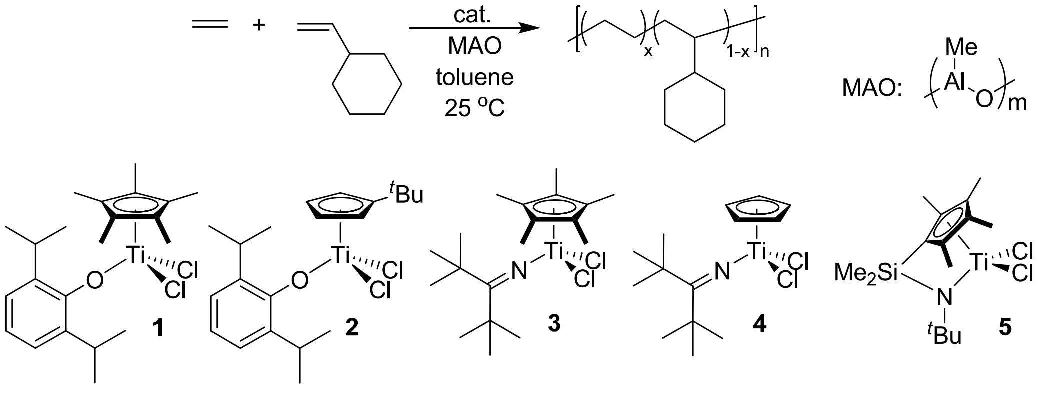


Table 1. Copolymerization of ethylene with vinylcyclohexane (VCH) by various half-titanocenes, Cp'TiCl$_2$(Y) [Y = O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**); Y = N=C^{t}Bu$_2$, Cp' = Cp* (**3**), Cp (**4**)] and [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**5**)-MAO catalyst systems.[a]

run	cat. [(μmol)]	MAO [mmol] (Al/Ti × 10^{-3})[b]	ethylene [atm]	VCH [M]	time [min]	yield [mg]	activity[c]	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	VCH[e] [mol%]
1	**1** (0.1)	3.0 (30)	4	0	10	202	12,100	40	3.7	
2	**1** (0.2)	1.5 (7.5)	6	1.22	10	647	19,400	15	2.3	
3	**1** (0.2)	3.0 (15)	6	1.22	10	692	20,800	13	2.4	21.9
4	**1** (0.2)	4.5 (22.5)	6	1.22	10	590	17,700	15	2.3	
5	**1** (0.2)	3.0 (15)	8	1.22	6	438	21,900	23	2.1	17.6
6	**1** (0.2)	3.0 (15)	6	1.22	6	334	16,700	19	2.0	21.8
7	**1** (0.2)	3.0 (15)	6	2.43	6	282	14,100	10	2.3	31.2
8[f]	**1** (0.2)	3.0 (15)	6	2.43	6	338	16,900	14	1.8	32.7
9	**1** (0.2)	3.0 (15)	4	1.22	6	128	6,400	13	2.0	29.0
10	**1** (0.2)	3.0 (15)	4	2.43	6	113	5,650	11	1.8	37.4
11	**2** (0.2)	3.0 (15)	6	2.43	6	192	9,600	0.83	2.7	40.7
12	**3** (0.1)	3.0 (30)	6	2.43	6	52	5,200	32	3.1	11.1
13	**4** (0.2)	3.0 (15)	6	2.43	6	143	7,150	28	2.9	24.8
14	**5** (0.2)	3.0 (15)	6	2.43	6	342	17,100	11	2.0	11.8

[a] Conditions: VCH + toluene total 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] VCH content in copolymer (mol %) estimated by ^{13}C NMR spectra. [f] 40 °C.

It was revealed that the copolymerization by the **1**-MAO catalyst took place, and the resultant copolymers possessed high molecular weights with unimodal molecular weight distributions (M_n = 10-23 × 10^4, M_w/M_n = 1.8-2.3) as well as single glass transition temperatures (T_g) (runs 2-10, Figure 1). The catalytic activities of the copolymerization were lower than that of the ethylene homopolymerization, and the activities decreased with increasing the VCH concentrations (runs 1, 9-10). The Al/Ti molar ratios affected to the catalytic activities, but didn't affect to both the VCH contents and the M_n values of the obtained copolymers (runs 2-4). The VCH contents in the copolymers increased with increasing the VCH/ethylene feed molar ratios and the T_g values increasing with increasing VCH contents in the copolymers (runs 5-7, 9-10 and Figure 1). A linear relationship between the T_g values and the VCH contents of the copolymers was observed (Figure 2). These results indicate that the copolymerization by **1** took place with a single catalytically active species.

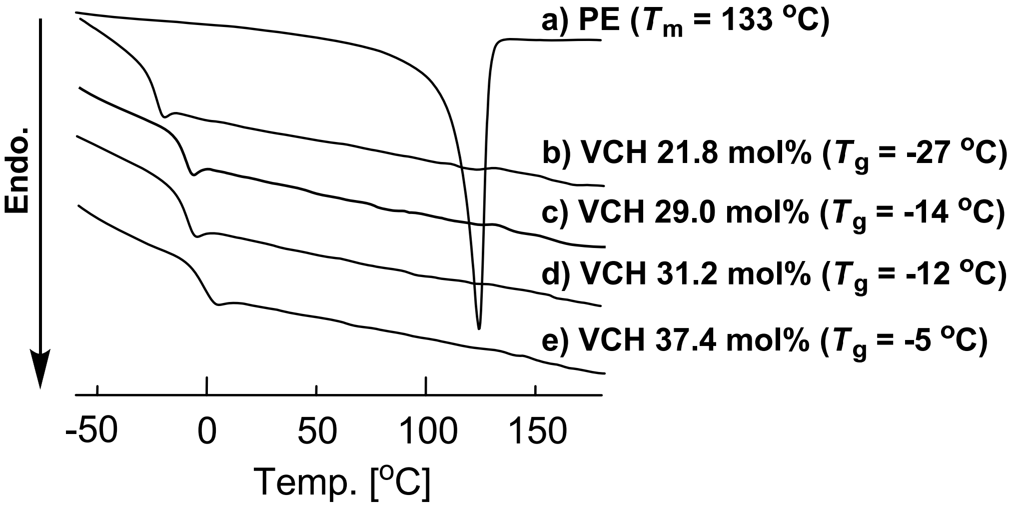


Figure 1. DSC thermograms of polyethylene and ethylene/VCH copolymers prepared by **1**-MAO catalyst [(a) poly(ethylene) (PE), (b) run 6, (c) run 9, (d) run 7, and (e) run 10]

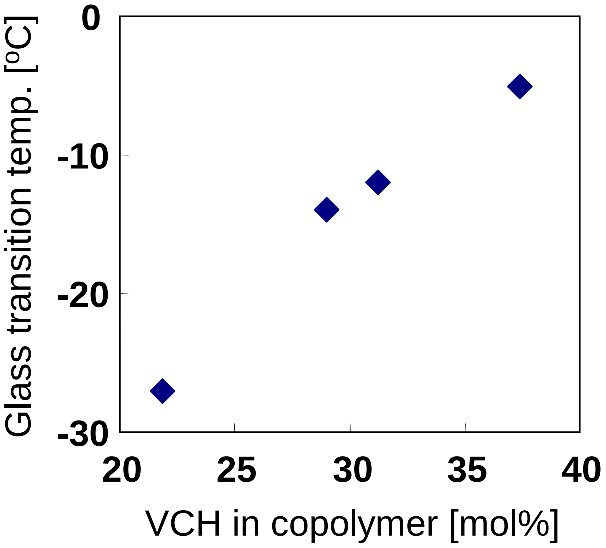


Figure 2. Plots of T_g vs VCH contents of ethylene/VCH copolymers prepared by **1**-MAO catalyst.

The *tert*-BuC_5H_4 analogue (**2**) showed better VCH incorporation than **1** under the same condition (runs 7, 11) as seen in the copolymerization of ethylene with 1-hexene,[16b] but the M_n value was low (M_n = 8,300). The Cp-ketimide analogue (**4**) showed relatively efficient VCH incorporation under the same condition, and afforded high molecular weight copolymer with unimodal molecular weight distribution (run 13). The Cp*-ketimide analogue (**3**) also incorporated VCH, but the VCH content in the copolymer was lower than that by **4** (runs 12-13) although no significant differences in ethylene/1-hexene copolymerization between **3** and **4** were not observed.[20] The fact suggests that the substituents on the Cp' play a key role of VCH incorporation.

Although $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**) also incorporated VCH and afforded high molecular weight copolymer with unmodal molecular weight distribution (run 14), the VCH content was lower than these by **1-2, 4** (runs 7, 11, 13).

Figure 3 shows a typical ^{13}C NMR spectrum of poly(ethylene-*co*-VCH) in C_6D_6/1,2,4-trichlorobenzene at 110 °C, and all resonances were identified by the DEPT analysis and by comparison with the poly(VCH) reported previously.[21] The resonances of not only the isolated VCH inserted sequence among the repeated ethylene insertion ($\alpha\delta$, $\beta\delta$, $\gamma\delta^+$), but also the alternating VCH sequence ($\alpha\gamma$, $\beta\beta$) were also observed. The resonance ascribed to the repreated VCH insertion ($\alpha\alpha$) was also detected although the intensity was extremely low. The fact clearly explains the reason that the low activities were observed in homopolymerization of VCH by the **1-4**/MAO catalysts as described below.

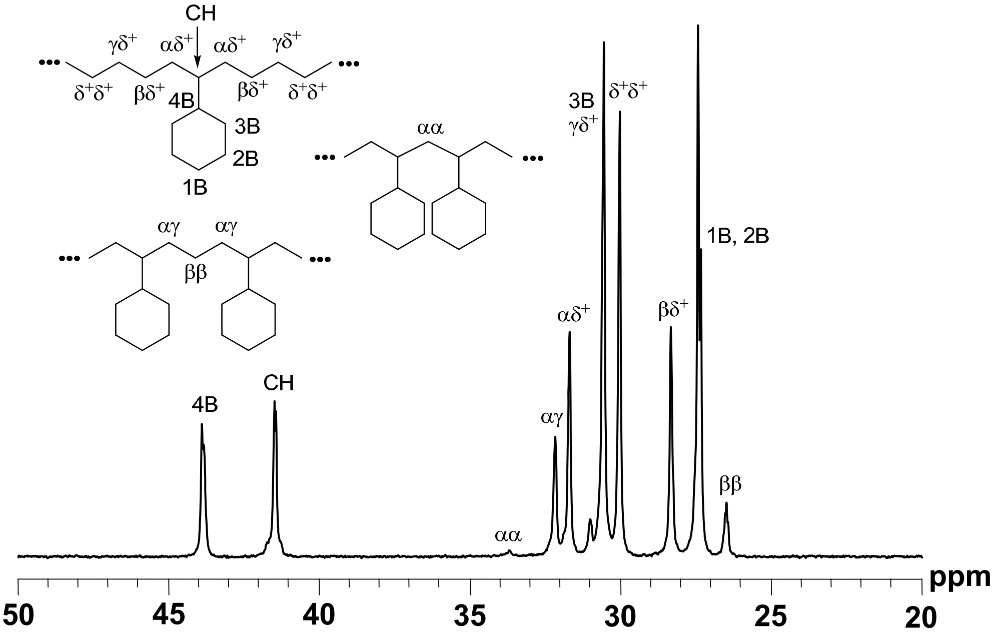


Figure 3. ^{13}C NMR spectrum of poly(ethylene-*co*-VCH) prepared by **1**-MAO in C_6D_6/1,2,4-trichlorobenzene at 110 °C (run 9, VCH content 29.0 mol%).

Homopolymerization of VCH by **1-4** was also conducted at 25 °C in the presence of MAO (Scheme 2) and the results are summarized in Table 2. It was revealed that the homopolymerization by the **1**, **3-4**/MAO took place with low activities, and the resultant polymers had unimodal molecular weight distributions (runs 15, 17-18). In contrast, the **2**-MAO catalyst afforded only colorless liquid (run 16). Figure 4 shows the ^{13}C NMR spectra of the products by **1-4** (in $CDCl_3$ at r.t.), and the resonances were identified by comparison with the previous reports.[21] The sharp resonances of carbons 5 and 6 that identified as *isotactic* poly(VCH) were observed in the spectra of the polymers by **1, 3-4**. The sharpness of the resonance ascribed to the carbon 4 of the product by **1** indicates that this is more stereoregular than these by **3-4**. On the other hand, the complexity of the spectrum by **2** indicated that the product by **2** is highly stereo- or regio-irregular. These results indicate that the **1**, **3-4**/MAO catalysts could afford ethylene copolymers with 0-100 mol% VCH content as well as with low stereo- or regio-irregularity.

Scheme 2

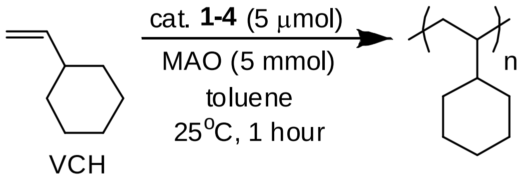


Table 2. Homopolymerization of vinylcyclohexane (VCH) by various half-titanocenes, Cp'TiCl$_2$(Y) [Y = O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp' = Cp* (**1**), ^{t}BuC$_5$H$_4$ (**2**); Y = N=C^{t}Bu$_2$, Cp' = Cp* (**3**), Cp (**4**)]-MAO catalyst systems.[a]

run	cat. ([μmol])	yield [mg]	TON	M_n[b]	M_w/M_n[b]
15	**1** (5.0)	111	201	16,100	1.71
16	**2** (5.0)	17	31		
17	**3** (5.0)	82	150	7,100	1.70
18	**4** (5.0)	61	110	7,900	1.41

[a] Conditions: VCH 5 mL + catalyst toluene solution 0.5 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO) 5 mmol, 25 °C, 1 hour. [b] GPC data in THF vs polystyrene standards.

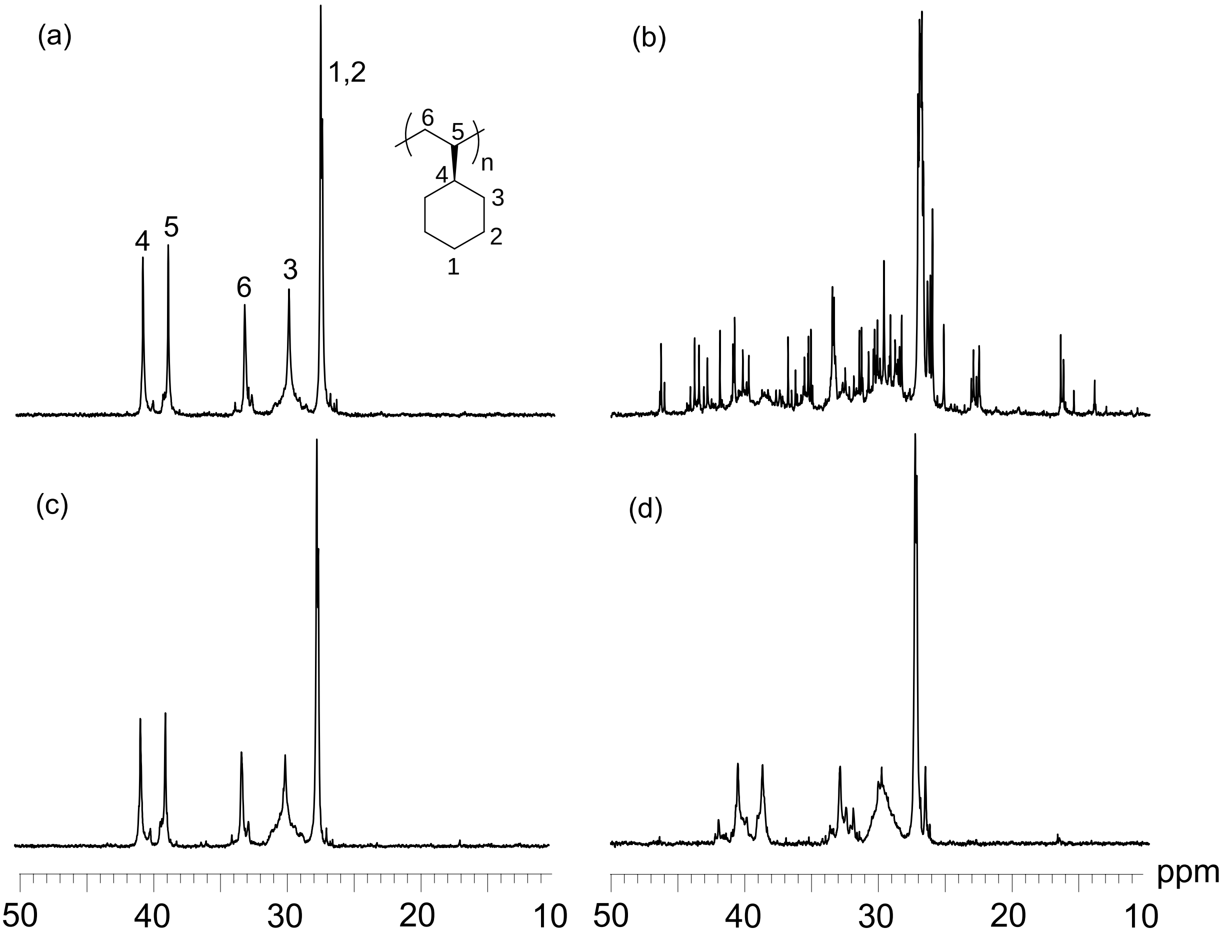


Figure 4. ^{13}C NMR spectra for poly(VCH)s prepared by (a) **1**, (b) **2**, (c) **3,** and (d) **4**-MAO catalyst systems.

2. Copolymerization of ethylene with 2-methyl-1-pentene

Copolymerization of ethylene with 2-methyl-1-pentene (2M1P) using **1-5** was conducted at 25 °C in toluene in the presence of MAO cocatalyst (Scheme 3). And the half-titanocene Cp*$TiCl_3$ (**6**) and the ordinary metallocene Cp_2ZrCl_2 (**7**) were also chosen as the catalysts for comparison. MAO prepared as a white solid was chosen as the cocatalyst due to the same reason with the ethylene/VCH copolymerization. The results of the copolymerization by the **1-7**/MAO catalysts under various conditions are summarized in Table 3, and the 2M1P contents in the obtained polymers were determined by ^{13}C NMR spectra.

Scheme 3

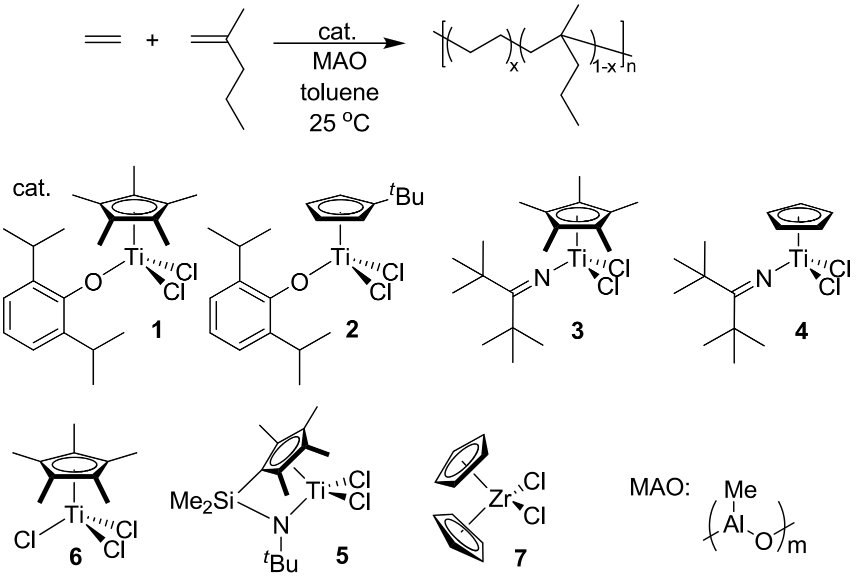


Table 3. Copolymerization of ethylene (E) with 2-methyl-1-pentene (2M1P) by various half-titanocenes, Cp'$TiCl_2$(Y) [Y = O-2,6-^{i}$Pr_2C_6H_3$, Cp' = Cp* (**1**), ^{t}BuC_5H_4 (**2**); Y = N=C^tBu_2, Cp' = Cp* (**3**), Cp (**4**); Y = Cl, Cp' = Cp* (**6**)], [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**), and Cp_2ZrCl_2 (**7**)-MAO catalyst systems.[a]

run	cat. [(μmol)]	MAO [mmol] (Al/Ti)[b]	ethylene [atm]	2M1P [M]	time [min]	yield [mg]	activity[c]	M_n[d] $\times10^{-4}$	M_w/M_n[d]	2M1P[e] [mol%]
19	**1** (0.1)	3.0 (30000)	4	-	10	202	12100	40	3.7	
20	**1** (0.5)	1.5 (3000)	6	1.35	10	412	4940	11	1.7	
21	**1** (0.5)	3.0 (6000)	6	1.35	10	582	6980	13	1.7	
22	**1** (0.5)	4.5 (9000)	6	1.35	10	672	8060	13	1.7	3.2
23	**1** (0.5)	6.0 (12000)	6	1.35	10	656	7870	13	1.8	
24	**1** (0.5)	4.5 (9000)	6	1.35	10	705	8460	12	2.1	3.3
25	**1** (0.5)	4.5 (9000)	6	2.70	10	480	5760	10	1.8	5.7
26	**1** (0.5)	4.5 (9000)	4	1.35	10	353	4240	6.5	2.0	5.0
27	**1** (0.5)	4.5 (9000)	4	2.70	10	223	2680	4.9	1.6	9.4
28	**2** (2.0)	2.0 (1000)	6	1.35	10	111	333	5.0	2.6	
29	**2** (2.0)	3.0 (1500)	6	1.35	10	191	573	5.8	2.0	
30	**2** (2.0)	4.0 (2000)	6	1.35	10	270	810	5.5	1.9	2.3
31	**2** (2.0)	5.0 (10000)	6	1.35	10	264	792	6.3	1.8	
32	**2** (2.0)	4.0 (2000)	6	2.70	10	226	678	4.3	2.0	3.2
33	**2** (2.0)	4.0 (2000)	4	1.35	10	156	468	3.1	2.1	3.2
34	**2** (2.0)	4.0 (2000)	4	2.70	10	108	324	1.8	2.3	5.1
35	**3** (0.2)	3.0 (60000)	6	1.35	10	393	11800	68	2.0	
36	**3** (0.2)	3.0 (60000)	6	2.70	10	259	7770	63	1.9	0.3
37	**4** (0.2)	3.0 (60000)	6	-	10	636	19100	53	2.1	
38	**4** (0.2)	3.0 (60000)	6	1.35	10	336	10100	43	2.0	
39	**4** (0.2)	3.0 (60000)	6	2.70	10	232	6960	34	1.8	0.3
40	**5** (1.0)	3.0 (3000)	6	1.35	6	200	2000	13	2.4	
41	**5** (1.0)	3.0 (3000)	6	2.70	6	184	1840	12	2.4	0.3
42	**5** (1.0)	3.0 (3000)	4	1.35	6	142	1420	9.7	2.5	
43	**5** (1.0)	3.0 (3000)	4	2.70	6	132	1320	7.4	2.4	0.4
44	**6** (1.0)	3.0 (3000)	6	1.35	6	458	4580	bimodal		
45	**6** (1.0)	3.0 (3000)	6	2.70	6	415	4150	bimodal		trace
46	**7** (0.2)	3.0 (60000)	6	2.70	10	153	4590	148	2.7	trace

[a] Conditions: 2M1P + toluene total 30 mL, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] 2M1P content in copolymer (mol %) estimated by ^{13}C NMR spectra.

It was revealed that the copolymerization by the **1**-MAO catalyst took place, and the obtained copolymers possessed relatively high molecular weights with unimiodal molecular weight distributions (M_n = 4.9-13, M_w/M_n = 1.6-2.1) (runs 20-27). The catalytic activities of the copolymerization were lower than that of the ethylene homopolymerization, and the activities decreased with increasing the 2M1P concentrations (runs 19, 26-27). The Al/Ti molar ratios affected to the catalytic activities, but didn't affect to both the 2M1P contents and the M_n values of the obtained copolymers (runs 20-23). The 2M1P contents in the copolymers increased with increasing the 2M1P/ethylene feed molar ratios and the melting points (T_m) decreased with increasing the 2M1P contents in the copolymers (runs 24-26, Figure 5). A linear relationship between the T_m values and the 2M1P contents of the copolymers was observed (Figure 6). These results indicate that the copolymerization by **1** took place with a single catalytically active species.

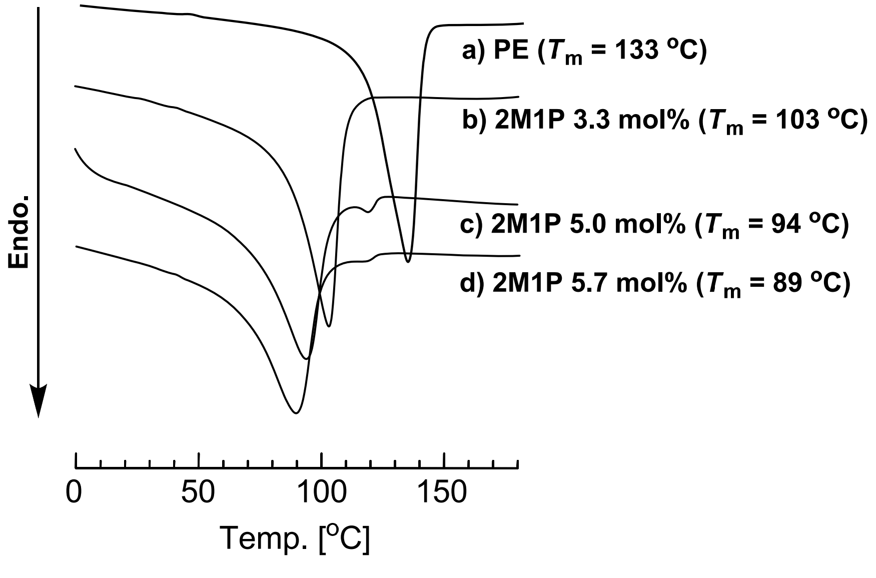


Figure 5. DSC thermograms of polyethylene and ethylene/2M1P copolymers prepared by **1**-MAO [(a) poly(ethylene) (PE), copolymers of (b) run 24, (c) run 26, (d) run 25]

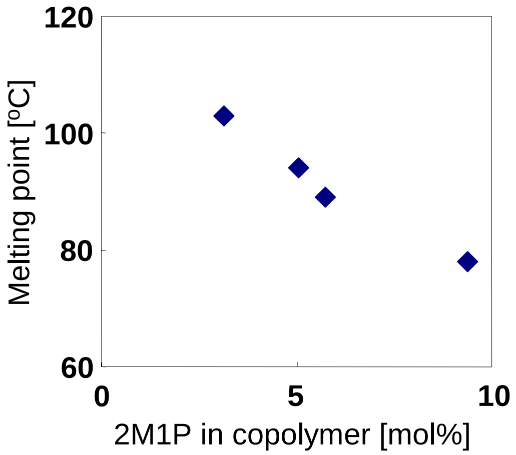


Figure 6. Plots of T_m vs 2M1P contents of ethylene/2M1P copolymers prepared by **1**-MAO catalyst (run 24-27).

In contrast, the 2M1P contents in the copolymers prepared by the *tert*-BuC_5H_4 analogue (**2**) were lower than those by **1** under the same conditions (runs 24-27, 30, 32-34) although **2** incorporates 1-hexene and vinylcyclohexane (VCH) more efficiently than **1** in the ethylene/1-hexene[16b] and ethylene/VCH copolymerizations.[22] This may be due to the steric hindrance of the *tert*-Bu group on the Cp' ligand against the Me group in coordinated 2M1P.

The 2M1P contents in the resultant polymers prepared by the Cp'-ketimide analogue (**3-4**) and Cp*$TiCl_3$ (**6**) under the same condition were negligible (runs 36 39, 45). This result clearly indicates that the anionic ancillary donor ligand (Y) in Cp'$TiCl_2$(Y) plays an essential role for 2M1P incorporation in the copolymerization.

The linked half-titanocene [$Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**) also showed negligible 2M1P incorporation although the activities and the M_n values of the resultant polymers decreased with increasing the 2M1P concentrations (runs 40-43). The ordinary metallocene catalyst Cp_2ZrCl_2 (**7**) also afforded polymer with negligible 2M1P incorporation (run 46).

Figure 7 shows a typical ^{13}C NMR spectrum for the poly(ethylene-*co*-2M1P) prepared by **1** (run 27 in *o*-dichlorobenzene-d_4 at 110 ^{o}C), and all resonances were identified by the DEPT analysis as well as by comparison with the poly(ethylene-*co*-isobutene) reported previously.[8,10]

The resonances of not only the isolated 2M1P sequences among the repeated ethylene insertion ($\alpha\delta$, $\beta\delta$, $\gamma\delta^+$), but also the alternating 2M1P sequences ($\alpha\gamma$, $\beta\beta$) were also observed, although the ratio of the alternating sequences were low. No resonances ascribed to the repeated 2M1P incorporation were observed. This fact would explain the reason that no catalytic activity was observed in an attempted 2M1P homopolymerization by the **1**-MAO catalyst system. It means that it would be difficult to prepare ethylene/2M1P copolymers with more than 50 mol% 2M1P content by the **1**-MAO catalyst unlike ethylene/1-hexene and ethylene/VCH copolymerizations.

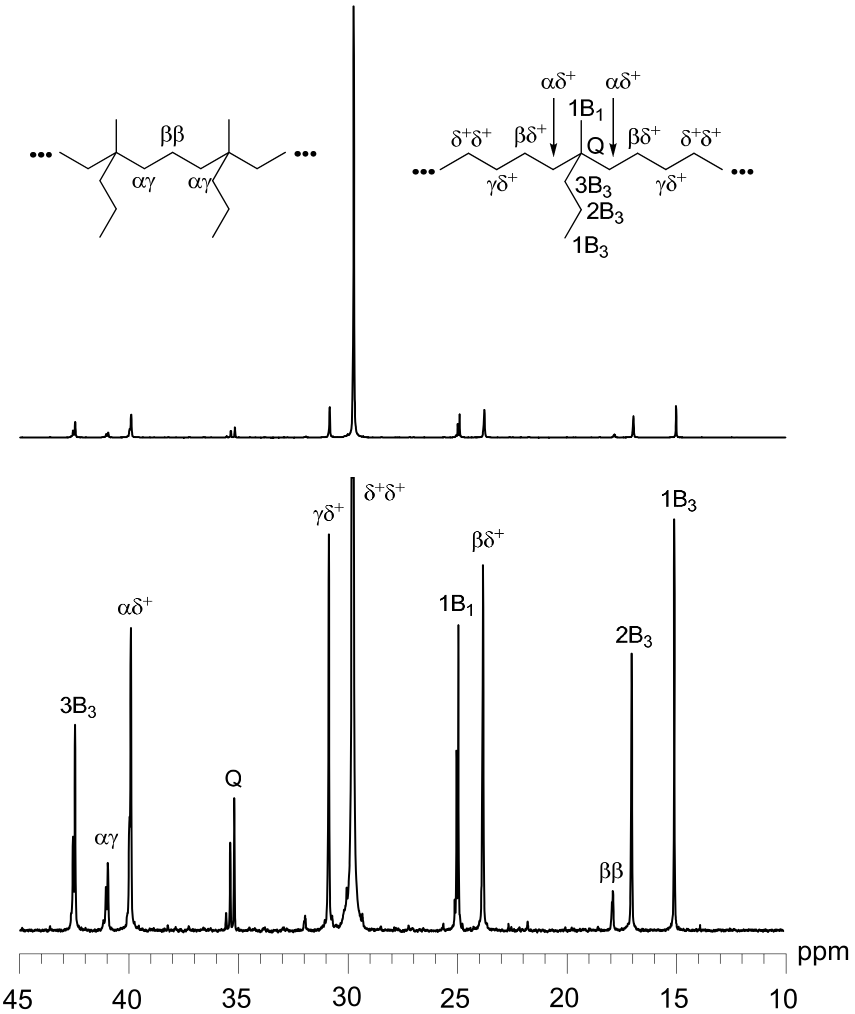


Figure 7. ^{13}C NMR spectra for poly(ethylene-*co*-2M1P) (run 27) in *o*-dichlorobenzene-d_4 at 110 °C [full spectrum (top), expanded spectrum (bottom)].

Effect of cyclopentadienyl fragment on 2M1P incorporation in the copolymerization

It has been known that the structural features of catalysts, in particular the steric bulk of ligand, bite angle, configuration and conformation, strongly affect to the coordination and insertion of olefin monomers in the transition-metal catalyzed coordination polymerization.[24] It was reported previously that the substituents on the cyclopentadienyl ligand in Cp'$TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ directly affected the comonomer incorporation in copolymerizations of ethylene with α-olefin,[16b,23] styrene,[17] norbornene,[18] and cyclohexene.[19] Since significant difference in the 2M1P incorporation between the Cp* (**1**) and the $^tBuC_5H_4$ (**2**) analogues was observed, copolymerization of ethylene with 2M1P using additional 6 complexes, Cp'$TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp' = 1,2,3,4-Me_4C_5H (**8**), 1,2,4-$Me_3C_5H_2$ (**9**), 1,3-$Me_2C_5H_3$ (**10**), 1,3-$^tBu_2C_5H_3$ (**11**), indenyl (**12**), Cp (**13**)] was conducted to explore the effect of substituents of the Cp' fragment on the copolymerization (Chart 1). The results of the copolymerization under various conditions by the **1-2, 8-13**/MAO catalyst systems are summarized in Table 4.

Chart 1

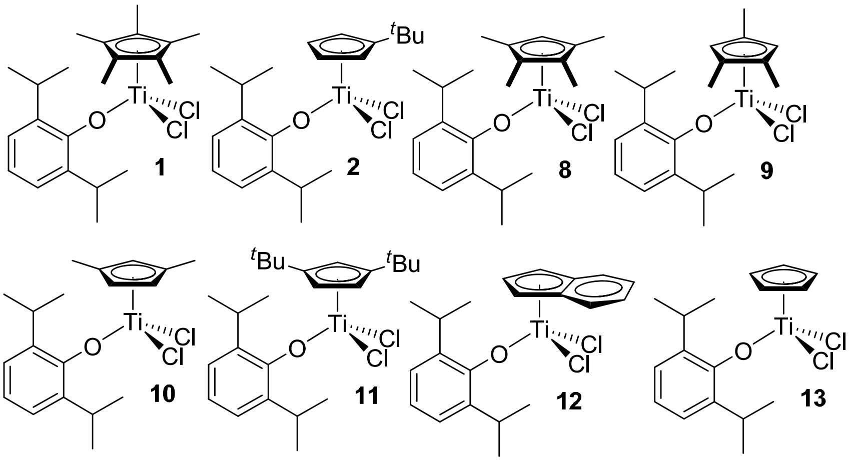


Table 4. Effect of cyclopentadienyl fragment in copolymerization of ethylene with 2-methyl-1-pentene (2M1P) by Cp'$TiCl_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ [Cp' = Cp* (**1**), ${}^{t}BuC_5H_4$ (**2**), 1,2,3,4-Me_4C_5H (**8**), 1,2,4-$Me_3C_5H_2$ (**9**), 1,3-$Me_2C_5H_3$ (**10**), 1,3-${}^{t}Bu_2C_5H_3$ (**11**), indenyl (**12**), Cp (**13**)]-MAO catalyst systems.[a]

run	cat. [(μmol)]	MAO [mmol] (Al/Ti)[b]	ethylene [atm]	2M1P [M]	time [min]	yield [mg]	activity[c]	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	2M1P[e] [mol%]
24	**1** (0.5)	4.5 (9000)	6	1.35	10	705	8460	12	2.1	3.3
25	**1** (0.5)	4.5 (9000)	6	2.70	10	480	5760	10	1.8	5.7
26	**1** (0.5)	4.5 (9000)	4	1.35	10	353	4240	6.5	2.0	5.0
27	**1** (0.5)	4.5 (9000)	4	2.70	10	223	2680	4.9	1.6	9.4
47	**8** (1.0)	3.0 (3000)	6	1.35	6	255	2550	7.7	2.7	3.0
48	**8** (1.0)	3.0 (3000)	6	2.70	6	183	1830	5.6	3.0	5.1
49	**8** (1.0)	3.0 (3000)	4	1.35	6	137	1370	4.1	2.9	4.6
50	**8** (1.0)	3.0 (3000)	4	2.70	6	101	1010	3.0	2.6	8.0
51	**9** (1.0)	3.0 (3000)	6	1.35	6	208	2080	6.6	2.6	3.8
52	**9** (1.0)	3.0 (3000)	6	2.70	6	192	1920	5.8	2.3	6.1
53	**9** (1.0)	3.0 (3000)	4	1.35	6	139	1390	4.4	2.6	5.5
54	**9** (1.0)	3.0 (3000)	4	2.70	6	92	920	2.5	2.6	9.5
55	**10** (2.0)	3.0 (1500)	6	1.35	6	193	970	2.4	4.3[f]	
56	**10** (2.0)	3.0 (1500)	6	2.70	6	188	940	1.9	4.1	5.6
57	**10** (2.0)	3.0 (1500)	4	1.35	6	109	550	1.7	3.8	
58	**10** (2.0)	3.0 (1500)	4	2.70	6	81	410	1.2	3.4	
59	**11** (0.5)	3.0 (6000)	6	1.35	6	260	5200	25	2.6	0.7
60	**11** (0.5)	3.0 (6000)	6	2.70	6	166	3320	17	2.4	1.3
30	**2** (2.0)	4.0 (2000)	6	1.35	10	270	810	5.5	1.9	2.3
32	**2** (2.0)	4.0 (2000)	6	2.70	10	226	678	4.3	2.0	3.2
61	**12** (1.0)	3.0 (3000)	6	1.35	6	242	2420	5.3	5.2	
62	**12** (1.0)	3.0 (3000)	6	2.70	6	176	1760	3.7	5.6	3.2
63	**12** (1.0)	3.0 (3000)	4	1.35	6	137	1370	3.8	5.3	
64	**12** (1.0)	3.0 (3000)	4	2.70	6	101	1010	2.2	6.2	
65	**13** (1.0)	3.0 (3000)	6	1.35	6	191	1910			
66	**13** (1.0)	3.0 (3000)	6	2.70	6	191	1910			0.33

[a] Conditions: 2M1P + toluene total 30 mL, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in o-dichlorobenzene vs polystyrene standards. [e] 2M1P content in copolymer (mol %) estimated by ^{13}C NMR spectra. [f] Observed low molecular weight shoulder.

It was revealed that **8-12** also incorporated 2M1P and afforded copolymers with relatively high molecular weights (M_n = 1.2-7.7 × 10^4, runs 47-64). Although the reduction of the steric bulk on the Cp' ligand was expected to improve the 2M1P incorporation, no significant differences in the 2M1P contents were observed in the polymers prepared by **1**, **8-10** (runs 24-27, 47-58). In contrast, the Cp analogue (**13**) showed negligible 2M1P incorporations (runs 65-66). The 2M1P contents were decreased when the 1,3-^{t}Bu$_2$C$_5$H$_3$ analogue (**11**) was employed instead of the ^{t}BuC$_5$H$_4$ analogue (**2**) (runs 30, 32, 59-60). The 2M1P incorporation by the indenyl analogue (**12**) was not so efficient as that by the Cp* analogue (runs 24-27, 61-64), although **12** exhibits better norbornene incorporation than **1** in the ethylene/norbornene copolymerization.[18]

Figure 8 shows the DSC thermograms of the copolymers prepared by **1-2, 8-13** under the same condition (ethylene 6 atm, 2M1P 2.70 M). It was revealed that the copolymers prepared by **2, 8-10, 12** possessed several melting points. This finding and the somewhat broad M_w/M_n values of the polymers by **8-10, 12** suggest that the copolymerizations by the **2**, **8-10, 12**-MAO catalysts proceeded with multi-catalytically active species. In contrast, the 1,3-^{t}Bu$_2$C$_5$H$_3$ analogue (**11**) afforded copolymers with uniform 2M1P components, but the 2M1P contents were low. These results indicate that Cp* and 1,3-^{t}Bu$_2$C$_5$H$_3$ ligands would highly stabilize the active species and the Cp* analogue **1** is the most suited as the catalyst precursor for the copolymerization in terms of both the activity and the 2M1P incorporation with a single catalytically active species.

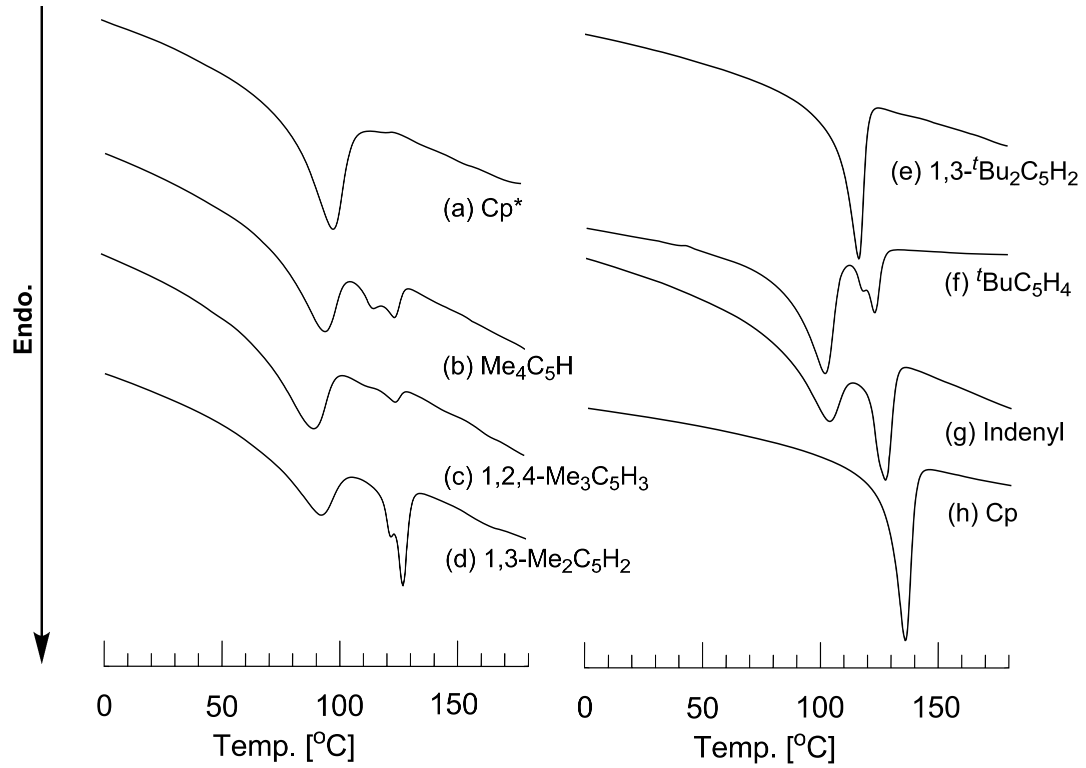
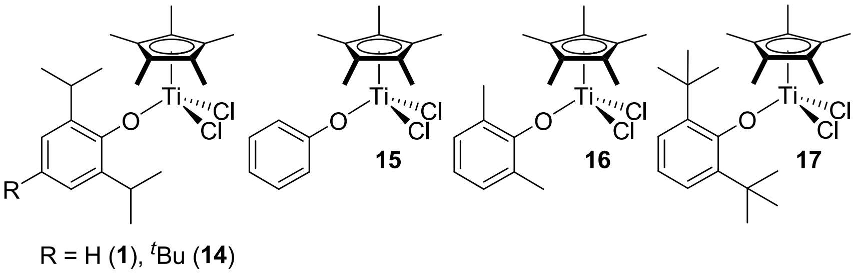


Figure 8. DSC thermograms of ethylene/2M1P copolymers prepared by Cp'$TiCl_2$(O-2,6-${}^iPr_2C_6H_3$)-MAO [Cp' = (a) Cp* (**1**), run 25; (b) MeC_5H (**8**), run 48; (c) 1,2,4-$Me_3C_5H_2$ (**9**), run 52; (d) 1,3-$Me_2C_5H_3$ (**10**), run 56; (e) 1,3-${}^tBu_2C_5H_3$ (**11**), run 60; (f) ${}^tBuC_5H_4$ (**2**), run 32; (g) indenyl (**12**), run 62; (h) Cp (**13**), run 66].

Effect of aryloxo ligand on 2M1P incorporation in the copolymerization

Copolymerization of ethylene with 2M1P using Cp*$TiCl_2$(O-2,6-${}^iPr_2$-4-${}^tBuC_6H_2$) (**14**) and Cp*$TiCl_2$(O-2,6-$R_2C_6H_3$) [R = H (**15**), Me (**16**), ^{i}Pr (**1**), ^{t}Bu (**17**)] (Chart 2) was conducted to explore the effect of substituent in the aryloxide ligand on the copolymerization. This is because that the substituent of the aryloxide ligand affects to not only the catalytic activities but also the molecular weights of the resultant polymers in ethylene/1-hexene copolymerization and 1-hexene polymerization.[23,24] The results of the copolymerization under various conditions by the **1, 14-17**/MAO catalyst systems are summarized in Table 5.

Chart 2



It was revealed that the copolymerization by the 2,6-diisopropylphenoxy analogue (**14**) proceeded with similar catalytic activity with **1** and the resultant copolymers possessed the similar molecular weights and molecular weight distributions, and 2M1P contents compared to these by **1** under the same conditions (runs 24-27, 67-70). In contrast, the 2M1P contents of the copolymers by the other phenoxy analogues (**15-17**) were lower than these by **1, 14** and the molecular weight distributions were broad (M_w/M_n = 8.1-53) (runs 71-76). These results indicate that the copolymerization by the **15-17**/MAO catalysts proceeded with multi-catalytically active species. it is thus clear that the use of both Cp* and 2,6-diisopropylphenoxide ligands is essential to obtain ethylene/2M1P copolymers with high catalytic activity as well as efficient and uniform 2M1P incorporation.

Table 5. Effect of aryloxide ligand in copolymerization of ethylene with 2-methyl-1-pentene (2M1P) by Cp*TiCl$_2$(OAr) [Ar = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), 2,6-^{i}Pr$_2$-4-^{t}Bu-C$_6$H$_2$ (**14**), C$_6$H$_5$ (**15**), 2,6-Me$_2$C$_6$H$_3$ (**16**), 2,6-^{t}Bu$_2$C$_6$H$_3$ (**17**)]-MAO catalyst systems[a].

run	cat. [(μmol)]	MAO [mmol] (Al/Ti)[b]	ethylene [atm]	2M1P [M]	time [min]	yield [mg]	activity[c]	M_n[d] ×10^{-4}	M_w/M_n[d]	2M1P[e] [mol%]
24	**1** (0.5)	4.5 (9000)	6	1.35	10	705	8460	12	2.1	3.3
25	**1** (0.5)	4.5 (9000)	6	2.70	10	480	5760	10	1.8	5.7
26	**1** (0.5)	4.5 (9000)	4	1.35	10	353	4240	6.5	2.0	5.0
27	**1** (0.5)	4.5 (9000)	4	2.70	10	223	2680	4.9	1.6	9.4
67	**14** (0.2)	3.0 (15000)	6	1.35	6	188	9400	13	2.5	2.8
68	**14** (0.2)	3.0 (15000)	6	2.70	6	132	6600	10	2.4	5.3
69	**14** (0.5)	3.0 (6000)	4	1.35	6	220	4400	5.5	2.3	5.0
70	**14** (0.5)	3.0 (6000)	4	2.70	6	161	3220	3.9	2.2	8.4
71	**15** (0.5)	3.0 (6000)	6	1.35	6	280	5600	1.1	8.1[f]	
72	**15** (0.5)	3.0 (6000)	6	2.70	6	200	4000	1.3	12.5[f]	trace
73	**16** (1.0)	3.0 (3000)	6	1.35	6	347	3470	1.8	8.4	
74	**16** (1.0)	3.0 (3000)	6	2.70	6	246	2460	1.6	12.1	1.3
75	**17** (5.0)	3.0 (600)	6	1.35	6	49	100	0.34	53.0	
76	**17** (5.0)	3.0 (600)	6	2.70	6	51	100	0.34	28.6	

[a] Conditions: 2M1P + toluene total 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] 2M1P content in copolymer (mol %) estimated by ^{13}C NMR spectra.

Effect of cocatalyst in the ethylene/2M1P copolymerization

Copolymerization of ethylene with 2M1P using two complexes, Cp*TiX$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [X = Cl (**1**), Me (**18**)], was conducted at 25 °C in the presence of various cocatalysts to explore the effect of cocatalyst (Scheme 4). This is because it has been known that the cocatalysts sometimes affect strongly to not only the comonomer incorporation and catalytic activity but also the molecular weight and molecular weight distribution of the resultant polymers.[10,26] Three types of modified MAO (MMAO), {[(MeAlO)$_x$(^{i}BuAlO)$_y$]$_n$, MMAO-3BH, x/y = 3.54; MMAO-3AH, x/y = 2.67, MMAO-3AT, x/y = 2.33}, prepared as white solids by removing toluene or *n*-hexane, AlMe$_3$, and Al^{i}Bu$_3$ from MMAO, and two borate compounds, [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (B1) and [Ph$_3$C][B(C$_6$F$_5$)$_4$] (B2), were chosen as the cocatalysts for this study and the results are summarized in Table 6.

Scheme 4

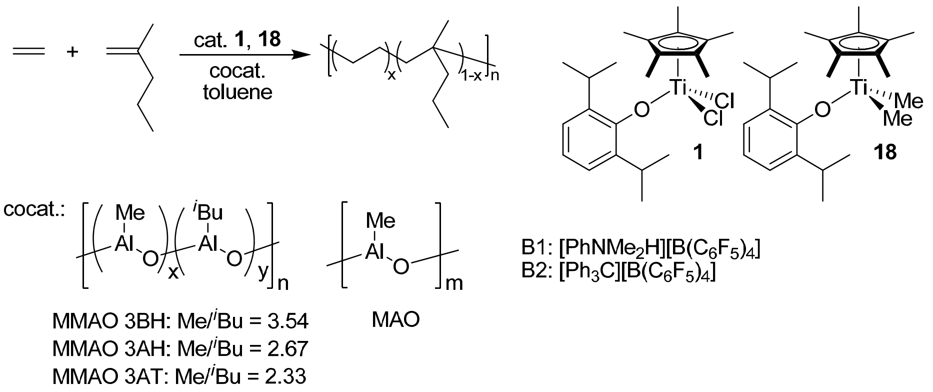


Table 6. Copolymerization of ethylene with 2-methyl-1-pentene (2M1P) by Cp*TiX$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [X = Cl (**1**), Me (**18**)]-cocatalyst systems[a]. Effect of cocatalyst.

run	cat. [(μmol)]	Cocat.	Al [mmol] (Al/Ti)[b]	time [min]	yield [mg]	activity[c]	M_n[d] ×10^{-4}	M_w/M_n[d]	2M1P[e] [mol%]
25	**1** (0.5)	MAO	4.5 (9000)	10	480	5760	10	1.8	5.7
77	**1** (0.5)	MMAO-3BH	4.5 (9000)	10	170	2040	11	2.1	4.7
78	**1** (0.5)	MMAO-3AH	4.5 (9000)	20	150	900	12	2.0	4.5
79	**1** (0.5)	MMAO-3AT	4.5 (9000)	30	163	652	12	2.0	4.6
80	**18** (0.5)	Al(^{i}Bu)$_3$/B1[f]	0.5 (1000)	10	293	3520	14	2.1	4.1
81	**18** (0.5)	Al(^{i}Bu)$_3$/B2[f]	0.5 (1000)	10	252	3020	16	2.1	4.0

[a] Conditions: 2M1P + toluene total 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 6 or 10 min. [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] 2M1P content in copolymer (mol %) estimated by ^{13}C NMR spectra. [f] [B]/[Ti] = 1.

It was revealed that the copolymerization by the all catalyst systems took place and the resultant copolymers possessed similar molecular weights with unimodal molecular weight destributions (runs 25, 77-81). The catalytic activities in the **1**/MAO or MMAO catalysts decreased with increasing the ratios of the ^{i}Bu group in the aluminoxane employed (runs 25, 77-79), whereas the activities were not highly influenced by the borate compounds employed (runs 80-81). No significant differences in both the 2M1P contents and microstructures were observed in the resultant copolymers. It is suggesting that the copolymerization by **1** or **18**-cocatalysts took place with the similar catalytically active species and the cocatalysts only affected the catalytic activities. Although the observed facts are similar to those observed in the ethylene/1-hexene copolymerization using $Cp^*TiCl_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$-cocatalyst systems[23] as well as by ordinary metallocenes,[1] the facts should be an interesting contrast to those reported in the copolymerization of ethylene with 1-octene, isobutene, or norbornene using linked half-titanocene complexes-cocatalyst systems, in which both the activities and the comonomer contents in the resultant copolymers were highly affected by the cocatalyst employed.[10,26]

Figure 9 shows the DSC thermograms of the copolymers prepared by **1** and **18**-cocatalysts under the same condition (ethylene 6 atm, 2M1P 2.70 M). A trace endothermic peak at around 120 ^{o}C was observed in the copolymers prepared by the MAO or MMAO cocatalysts. In contrast, the peak was not observed when the borate compounds were employed as the cocatalysts. This finding suggest that different active species with $Cp^*Ti^+R(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ would be generated by reaction with MAO during the polymerization. Therefore, It also suggested that the small endothermic peaks from 110 ^{o}C to 140 ^{o}C of the copolymers by $Cp'TiCl_2(O\text{-}2,6\text{-}^{i}Pr_2C_6H_3)$ [Cp' = 1,2,3,4-Me_4C_5H (**8**), 1,2,4-$Me_3C_5H_2$ (**9**), 1,3-$Me_2C_5H_3$ (**10**), indenyl (**12**), Cp (**13**)]-MAO catalysts (Figure 8) may be due to the same reason. Therefore, the use of the borate cocatalysts seems to be more suited for precise synthesis of the ethylene/2M1P copolymers.

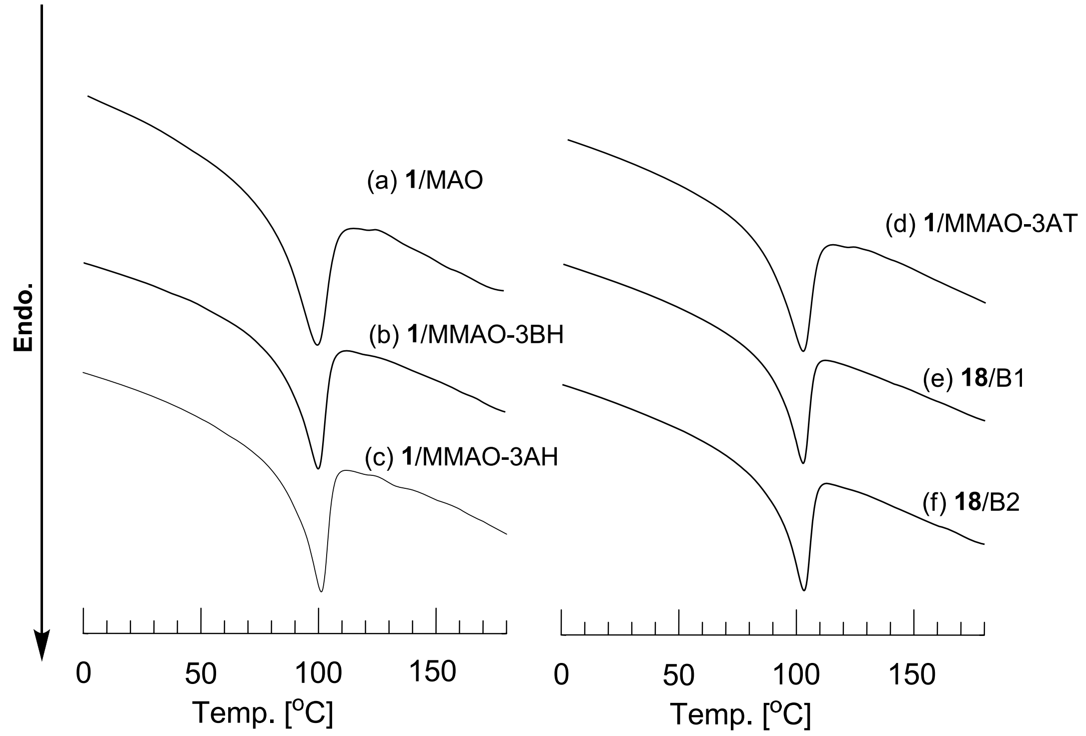
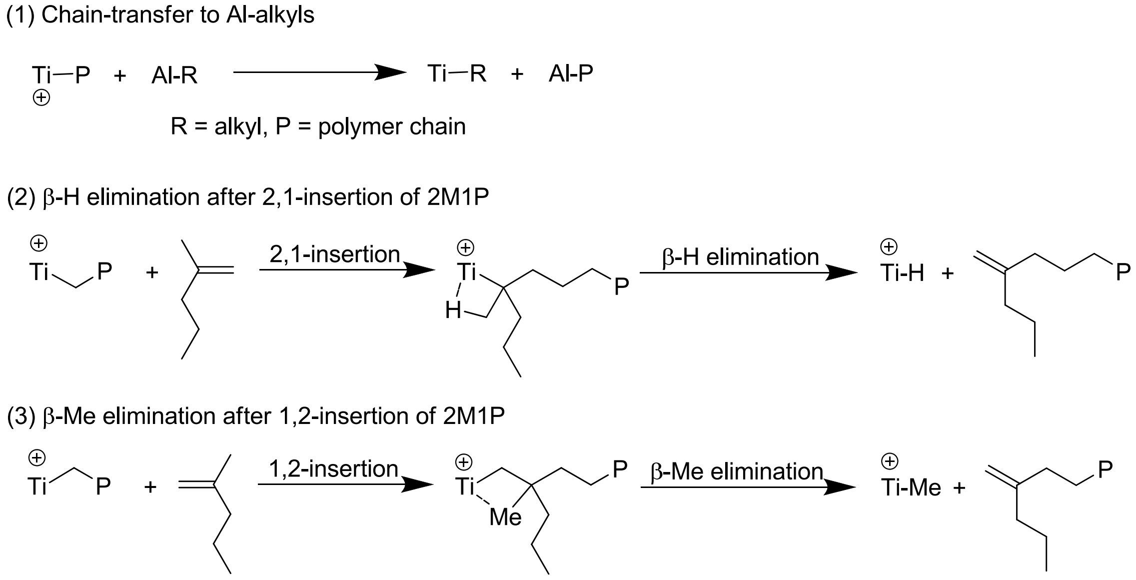


Figure 9. DSC thermograms of ethylene/2M1P copolymers prepared by Cp*$TiX_2(O\text{-}2,6\text{-}{}^{i}Pr_2C_6H_3)$ [X = Cl (**1**), Me (**18**)]-cocatalysts [(a) MAO, run 25; (b) MMAO-3BH, run 77; (c) MMAO-3AH, run 78; (d) MMAO-3AT, run 79; (e) $[PhN(H)Me_2][B(C_6F_5)_4]$ (B1), run 80; (f) $[Ph_3C][B(C_6F_5)_4]$ (B2), run 81].

Mechanism of chain transfer step

Two pathways, (1) chain transfer to Al-alkyls and (2) β-H or β-Me elimination, would be considered as the main chain transfer reaction in the copolymerization (Scheme 5). As described above, the M_n values of the copolymers prepared by the **1**-MAO catalyst were not dependent on the Al/Ti molar ratios employed and decreased with increasing the 2M1P contents in the copolymers. Moreover, the employed cocatalysts, such as MMAOs and borates, also didn't affect to the M_n values. As shown in the ^{13}C NMR spectrum of the copolymer by the **1**-MAO catalyst (run 27, Figure 10), the resonance at 110 ppm ascribed to a vinylene was observed. These results suggested that the dominant chain-transfer pathway in the copolymerization by **1** would be the β-H elimination after 2,1-insertion of 2M1P or β-Me elimination after 1,2-insertion of 2M1P.

Scheme 5



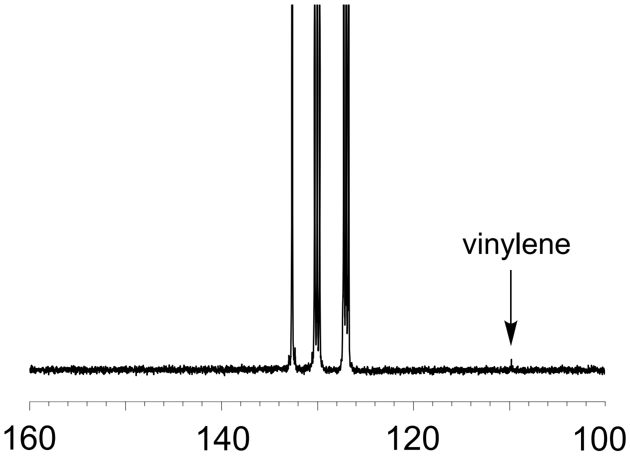


Figure 10. ^{13}C NMR spectrum of ethylene/2M1P copolymer prepared by **1**-MAO in *o*-dichlorobenzene-d_4 at 110 °C (run 27).

Conclusion

Efficient copolymerization of ethylene with VCH under moderate VCH/ethylene feed molar ratios was firstly achieved by using nonbridged half-titanocene of the type, Cp*$TiCl_2(O-2,6-{}^iPr_2C_6H_3)$ (**1**)-MAO catalyst system and the resultant copolymers had high molecular weights with uniform molecular weight distributions and VCH compositions. In addition, the **1**-MAO catalyst also afforded isotactic poly(VCH) with low catalytic activity, indicating that the catalyst would be able to prepare ethylene copolymers with 0-100 mol% VCH content. The effect of both the Cp' and mono-anionic ancillary donor ligands on the copolymerization was explored by using $^tBuCpTiCl_2(O-2,6-{}^iPr_2C_6H_3)$ (**2**) and $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp' = Cp* (**3**), Cp (**4**)]-MAO catalysts, and it was revealed that the aryloxo analogues (**1-2**) showed better VCH incorporations than the ketimide analogue (**3-4**), and the Cp* analogue (**1**) afforded higher molecular weight copolymer than the ^tBu analogue (**2**) as seen in ethylene/linear α-olefin copolymerization.

The **1**-MAO catalyst also achieved copolymerization of ethylene with 2M1P with high catalytic activity and afforded high molecular weight copolymers with unimodal molecular weight and comonomer distributions. And, the dominant chain transfer pathway in the copolymerization of the catalyst would be β-H elimination after 2,1-insertion of 2M1P or β-Me elimination after 1,2-insertion of 2M1P. In contrast, nonbridged half-titanocenes containing other ancillary donor ligands of the type, $Cp'TiCl_2(Y)$ [Y = $N{=}C^tBu_3$, Cp' = Cp* (**3**), Cp (**4**); L = Cl, Cp' = Cp* (**6**)] as well as the conventional catalysts, Cp_2ZrCl_2 (**7**) and $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**), exhibited negligible 2M1P incorporations under the same conditions. Exploration of the effect of substituents in the Cp' and aryloxide ligands on the copolymerization using $Cp'TiCl_2(O-2,6-{}^iPr_2C_6H_3)$ [Cp' = $1,2,3,4-Me_4C_5H$ (**8**), $1,2,4-Me_3C_5H_2$ (**9**), $1,3-Me_2C_5H_3$ (**10**), $1,3-{}^tBu_2C_5H_3$ (**11**), $^tBuC_5H$ (**2**) indenyl (**12**), Cp (**13**)] and Cp*$TiCl_2(O-2,6-R^1_2-4-R^2C_6H_2)$ [R^2 = H, R^1 = H (**15**), Me (**16**), ^iPr (**1**), ^tBu (**17**); R^2 = ^tBu, R^1 = ^iPr (**14**)] turned out that both the Cp* and 2,6-diisopropylphenoxy ligands were essential to exhibit the high catalytic activity and the efficient 2M1P incorporation with a single catalytically active species. In contrast, no distinct difference in the 2M1P incorporation was seen in the copolymerization by $Cp^*TiX_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [X = Cl (**1**), Me (**18**)] in the presence of the various cocatalysts such as MAO, MMAOs, borates.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous grade toluene (Kanto Chemical Co., Inc.), vinylcyclohexane (Aldrich) and 2-methyl-1-pentene (TCI Co., Ltd.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Ethylene of polymerization grade (Sumitomo Seika Chemicals Co., Ltd.) was used as received without further purification procedures.

Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 ºC for removing toluene, $AlMe_3$, and then heated at >100 ºC for 1 h for completion) in the drybox to give white solids. Other MMAO samples such as MMAO-3BH (Me/^{i}Bu= 3.54), MMAO-3AT (Me/^{i}Bu= 2.33), MMAO-3AH (Me/^{i}Bu= 2.67) were supplied from Tosoh Finechem Co., and were used as the white solids after removing solvent and $AlMe_3$, Al^iBu_3 *in vacuo* according to the analogous procedure as that in PMAO-S except that the resultant solid was re-dissolved in toluene (or in hexane) and then removed *in vacuo* to remove Al^iBu_3 completely. Reagent grade $[Ph_3C][B(C_6F_5)_4]$, $[PhN(H)Me_2][B(C_6F_5)_4]$ (Asahi Glass Co., Ltd.), and Al^iBu_3 (Kanto Chemical Co., Inc.) were stored in the dry box and were used as received.

(Aryloxo)(cyclopentadienyl)titanium(IV) complexes of the type, $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp' = Cp* (**1**, C_5Me_5),[16a] $^tBuC_5H_4$ (**2**),[16a] 1,2,4-$Me_3C_5H_2$ (**9**),[17b] 1,3-$Me_2C_5H_3$ (**10**),[16a] 1,3-$^tBuC_5H_3$ (**11**),[16a] indenyl (**12**) [18a], Cp (**13**) [16a]] and $Cp^*TiCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [R = H (**15**),[27] Me (**16**),[27] ^{t}Bu (**17**) [15c]], $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**18**)[15a] and $Cp^*TiCl_2(O\text{-}4\text{-}{}^tBu\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**14**)[15c] were prepared according to the previous reports. $Cp^*TiCl_2(N{=}C^tBu_2)$ (**3**),[28] $CpTiCl_2(N{=}C^tBu_2)$ (**4**),[28] $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**5**) [29] were prepared according to the published procedures. Cp^*TiCl_3 (**6**, Aldrich) and Cp_2ZrCl_2 (**7**, Wako Pure Chemical Ind., Ltd.) were used as received.

All ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^{1}H and 100.53 MHz for ^{13}C). All spectra were obtained in the indicated solvents at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^{1}H, ^{13}C). ^{13}C NMR spectra for poly(ethylene-*co*-2M1P)s and poly(ethylene-*co*-VCH)s were measured at 110 ^{o}C in C_6D_6/1,2,4-trichlorobenzene (1/4 v/v). The relaxation delay was 5.2 sec, the acquisition time was 1.3 sec, the pulse angle was 90^o, and the number of transients accumulated was ca. 6000.

Molecular weights and molecular weight distributions for the polyethylenes, poly(ethylene-*co*-2M1P)s, poly(ethylene-*co*-VCH)s were measured by a gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $< 2.8\times10^8$ MW) at 140 ºC using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weights were calculated by a standard procedure based on the calibration with standard polystyrene samples.

Differential scanning calorimetric (DSC) data for the polymers were recorded by a DSC6200 (Seiko Instruments Co.) under a N_2 atmosphere [Preheating: from 25 to 200 ºC (20 ºC/min), cooling to -100 ºC under N_2, and measurement from -100 to 200 ºC (20 ^{0}C/min) under N_2].

Synthesis of (1,2,3,4-Me_4C_5H)$TiCl_2$(O-2,6-$^i Pr_2C_6H_3$) (8). Into a Et_2O solution (30 mL) containing (1,2,3,4-Me_4C_5H)$TiCl_3$ (281 mg, 1.02 mmol), LiO-2,6-$^i Pr_2C_6H_3$ (189 mg, 1.03 mmol) was added in one portion at -30 ºC. The reaction mixture was warmed slowly to room temperature, and was stirred for 10 h. The resultant solid, which was prepared by removing Et_2O *in vacuo* after filtration through celite pad, was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled (-30 ºC) solution gave orange microcrystals (247 mg, 1st crop). Yield 58.0%. ^{1}H NMR ($CDCl_3$): δ 7.10 and 7.08 (d or dd, 2H), 7.03, 7.01 (d), and 6.99 (total 1H), 5.93 (s, 1H), 3.21 (m, 2H, Me_2CH-), 2.24 and 2.16 (s, Me-Cp, 12H), 1.20 (d, 12H, J = 6.8 Hz). ^{13}C NMR ($CDCl_3$): δ 161.3, 138.9, 134.1, 133.6, 123.7, 123.2, 119.1, 26.8, 23.7, 14.7, 12.9.

Ethylene homopolymerization, copolymerizations of ethylene with vinylcyclohexane (VCH) or 2-methyl-1-pentene (2M1P) in the presence of MAO (MMAO) cocatalysts. A typical reaction procedure for ethylene homopolymerization (run 1, Table 1) is as follows. Toluene (29 mL), and MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 ºC. A toluene solution (1.0 mL) containing **1** (0.1 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total ethylene pressure 4 atm). The mixture was magnetically stirred for 10 min, ethylene remained was purged after the reaction, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo*. Basic experimental procedures in ethylene/2M1P and ethylene/VCH copolymerizations were the same as that in the ethylene homopolymerization except that various amounts of comonomers (5 or 10 mL) were added in place of toluene partially (total 29 mL).

Ethylene/2-methyl-1-pentene (2M1P) copolymerization by $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (<u>18</u>) in the presence of borate cocatalysts. A typical procedure for copolymerization of ethylene with 2M1P by $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**18**)-$[PhN(H)Me_2][B(C_6F_5)_4]$ or $[Ph_3C][B(C_6F_5)_4]$ catalyst system (run 80) are as follows. Toluene (18 mL), 2M1P (10 mL) and Al^iBu_3 (0.50 mmol) were added into the autoclave in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 ºC. A toluene solution (1.0 mL) containing **18** (0.5 μmol) was then added, immediately followed by addition of a toluene solution (1.0 mL) containing $[PhN(H)Me_2][B(C_6F_5)_4]$ (0.5 μmol) or $[Ph_3C][B(C_6F_5)_4]$ (0.5 μmol). The reaction apparatus was then immediately pressurized to 5 atm (total ethylene pressure 6 atm), and the mixture was magnetically stirred for 10 min. After the reaction, the remaining ethylene was purged upon cooling in a ice bath, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo*.

Polymerization of vinylcyclohexane (VCH). A typical procedure for polymerization of VCH was as follows. MAO (290 mg, 5.0 mmol), VCH (5.0 mL) were added into a round bottom flask (25 mL) in the drybox, and the polymerization was started by addition of a toluene solution (0.5 mL) containing precatalyst (5.0 μmol). The reaction mixture was stirred at 25 ^{o}C for 1 hour, and the polymerization was terminated by addition of MeOH (5 mL). The reaction product was extracted with $CHCl_3$ at 3 times and the $CHCl_3$ layer was washed with distilled water. The $CHCl_3$ extract was dried over Na_2SO_4, and then was concentrated to 1 mL and the solution was dropped into MeOH (50 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo*.

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Chapter 3

Precise synthesis of ethylene copolymers containing unsaturated side chains by using nonbridged half-titanocene catalysts and introduction of polar functionality to the side chains

Introduction

Precise and efficient synthesis of new polyolefins that have never been prepared by conventional catalysts in one of the most attractive subjects in the field of transition metal catalyzed coordination polymerization because unique properties owing to the new structures can be highly expected.[1-3] Recently, considerable attention has been paid to precise controlled synthesis of ethylene copolymers containing olefinic side chain through copolymerization of ethylene with nonconjugated dienes, because the unsaturated polyethylenes are expected to show good rubber property like ethylene-propylene-diene rubber. Moreover, introduction of polar functional group to the side chain by chemical reaction enables to afford polar functionalized ethylene copolymers[4] that have been difficult to prepare by direct copolymerization of ethylene with polar olefins owing to the poisoning and interaction of the metal center with the polar functional groups.[2a,2e] However, the copolymerization has a significant problem that side reactions consisting of cyclization and cross-linking, intra- and intermolecular reactions of the olefinic side chain with the active metal center, compete with repeated monomer coordination-insertion.[4g,4k,6,7] Therefore, nonconjugated dienes containing two big different reactive olefins are utilized for excluding these side reactions by the one low reactive olefin,[4b-e,4g-j,4l,5i-k,7] however, examples concerning the copolymerization with both high catalytic activity and high content of the unsaturated side chain have been limited so far.

Nonbriged half-titanocene of the type, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$, is a promising candidate for precise synthesis of the ethylene copolymers containing unsaturated side chain because the catalyst favors repeated monomer insertion rather than the side reactions in 1,5-hexadiene and 1,7-octadiene homopolymerizations compared to ordinary metallocenes and linked-amide catalysts, and the resultant polymers contain terminal olefins with uniform composition.[8] Additionally, the catalyst exhibits notable catalytic activity in ethylene/1-octene/1,7-octadiene copolymerization and affords unsaturated ethylene copolymers without the side reactions.[8c]

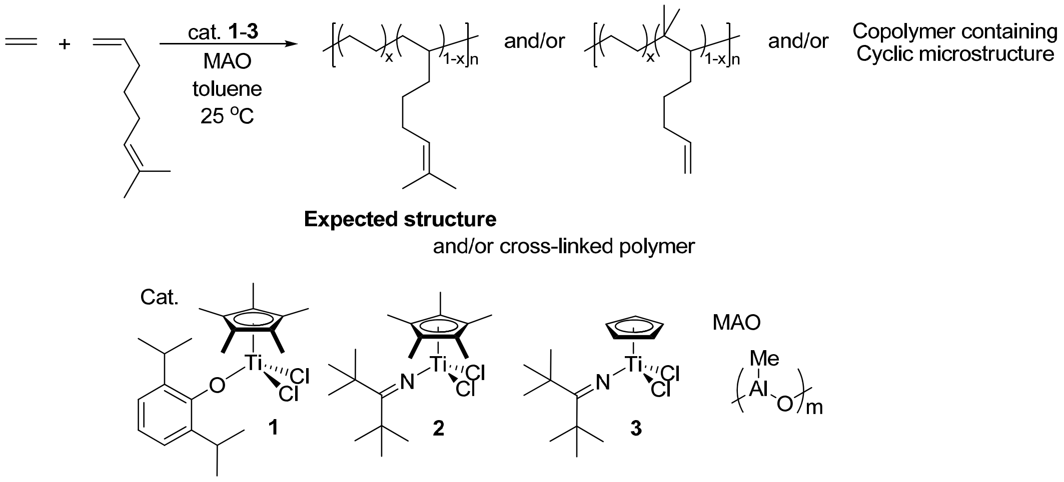
This chapter describes precise and efficient synthesis of the ethylene copolymers containing olefinic side chains by copolymerization of ethylene with nonconjugated dienes using combination of the nonbridged half-titanocenes with the nonconjugated dienes containing two different reactive olefins. Polar functionalization of the unsaturated side chains in the resultant copolymers is also dealt.

Results and Discussion

1. Copolymerization of ethylene with 7-methyl-1,6-octadiene (MOD)

Copolymerization of ethylene with 7-methyl-1,6-octadiene (MOD) using the nonbridged half-titanocenes of the type, $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**1**) and $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp' = Cp* (**2**) and Cp (**3**)], was conducted at 25 °C in toluene in the presence of methylaluminoxane (MAO) cocatalyst (Scheme 1) and ethylene/1-octene (OC) copolymerization was also conducted for comparison. The combination of **1-3** and MOD was chosen as the catalysts and nonconjugated diene respectively, because these catalysts exhibit both high catalytic activity and efficient comonomer incorporation in ethylene/α-olefin copolymerization[9-10] and especially the **1**-MAO prefers repeated monomer insertion rather than side reactions in the homo and copolymerization of nonconjugated dienes as described above.[8] The results are summarized in Table 1, and a typical ^{13}C NMR spectrum of poly(ethylene-*co*-MOD) is shown in Figure 1. The MOD and OC contents in the resultant copolymers were estimated from ^{13}C NMR spectra according to previous reports.[4d,11]

Scheme 1



It was revealed that the MOD copolymerization using the **1**-**3**/MAO catalysts took place and the resultant polymers possessed relatively high molecular weights with unimodal molecular weight distributions (runs 1-7, 11-12, 15-16). And the ^{13}C NMR spectra of the copolymers clearly indicate that MOD was incorporated only the mono-olefin without side reaction of the trisubstituted olefin in the all cases (Figure 1).

The **1**-MAO catalyst showed high catalytic activities in the ethylene/MOD copolymerization (38,800-97800 kg-polymer/mol-Ti·h) and the resultant polymers possessed unimodal molecular weight distributions (ca. 2) (runs 1-7). Both the catalytic activities and M_n values of the resultant polymers were not strongly dependent on the Al/Ti molar ratios employed (runs 1-3). The MOD contents in the copolymers increased with increasing the MOD/ethylene feed molar ratios (runs 4-7). These results strongly suggest that the copolymerization by **1** took place with a single catalytically active species.

Table 1. Copolymerization of ethylene (E) with 7-methyl-1,6-octadiene (MOD) or 1-octene (OC) by various half-titanocenes, Cp'TiCl$_2$(Y) [Y = O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp' = Cp* (**1**); Y = N=C^{t}Bu$_2$, Cp' = Cp* (**2**), Cp (**3**)]-MAO catalyst systems.[a]

run	cat. ([μmol])	MAO [mmol] (Al/Ti x 10^{-3})[b]	E [atm]	comonomer ([M])	yield [mg]	activity[c]	M_n[d] $\times 10^{-4}$	M_w/M_n[d]	MOD[e] [mol%]
1	**1** (0.05)	1.5 (30)	6	MOD (1.01)	400	80,000	12	2.2	
2	**1** (0.05)	3.0 (60)	6	MOD (1.01)	489	97,800	10	2.2	28.7
3	**1** (0.05)	4.5 (90)	6	MOD (1.01)	483	96,600	12	2.2	
4	**1** (0.05)	3.0 (60)	6	MOD (1.01)	486	97,200	12	2.3	29.2
5	**1** (0.05)	3.0 (60)	6	MOD (2.02)	367	73,400	12	2.2	40.6
6	**1** (0.05)	3.0 (60)	4	MOD (1.01)	231	46,200	11	2.2	37.4
7	**1** (0.05)	3.0 (60)	4	MOD (2.02)	194	38,800	13	2.1	49.0
8	**1** (0.02)	3.0 (150)	6	OC (1.06)	308	154,000	13	2.1	27.9
9[f]	**1** (0.02)	3.0 (150)	6	OC (1.06)	190	95,000	16	2.2	28.0
10	**1** (0.02)	3.0 (150)	4	OC (1.06)	158	79,000	12	2.0	33.2
11	**2** (0.2)	3.0 (15)	6	MOD (1.01)	253	12,700	31	3.2	23.2
12	**2** (0.2)	3.0 (15)	4	MOD (1.01)	151	7,550	22	2.3	28.6
13	**2** (0.2)	3.0 (15)	6	OC (1.06)	256	12,800	25	3.4	19.4
14	**2** (0.2)	3.0 (15)	4	OC (1.06)	118	5,900	18	2.5	27.9
15	**3** (0.05)	4.5 (90)	6	MOD (1.01)	220	44,000	35	2.8	22.6
16	**3** (0.05)	4.5 (90)	4	MOD (1.01)	117	23,400	25	2.6	32.3
17	**3** (0.02)	3.0 (150)	6	OC (1.06)	257	129,000	49	3.6	22.6
18	**3** (0.02)	3.0 (150)	4	OC (1.06)	188	94,000	40	3.2	31.2

[a] Conditions: MOD or OC + toluene total 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 25 °C, 6 min. [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Comonomer content in copolymer (mol %) estimated by ^{13}C NMR spectra. [f] Copolymerization of ethylene with OC in the presence of 2-methyl-2-butene (3.14M) although 2-methyl-2-butene was not incorporated in the resultant copolymer.

The **1**-MAO exhibited the highest catalytic activity in the copolymerization and the MOD contents of the resultant copolymers were higher than these by **2-3** under the same conditions (runs 4, 6, 11-12, 15-16) as seen in the ethylene/OC copolymerization (runs 8, 10, 13-14, 17-18). No significant differences in the M_n values as well as the comonomer contents in the resultant copolymers were observed between the OC and MOD copolymerizations under the similar conditions by **1-3** (ex: run 4 vs run 8, run 11 vs run 13, run 15 vs run 19). In contrast, the catalytic activities by the **1, 3**-MAO for the ethylene/MOD copolymerization were lower than these for the ethylene/OC copolymerization under the similar conditions (**1**: run 4, 6, 8, 10; cat **3**: run 15, 17, 19-20). The reason may be due to coordination of the trisubstituted olefin to the active metal center. In fact, the catalytic activity for the ethylene/OC copolymerization using the **1**-MAO catalyst in the presence of 2-methyl-2-butene decreased without significant differences of the M_n value and the OC content in the resultant copolymer (runs 9). In contrast, the activities of the Cp*-ketimide analogue (**2**) in the OC and MOD copolymerizations were similar (runs 9-12).

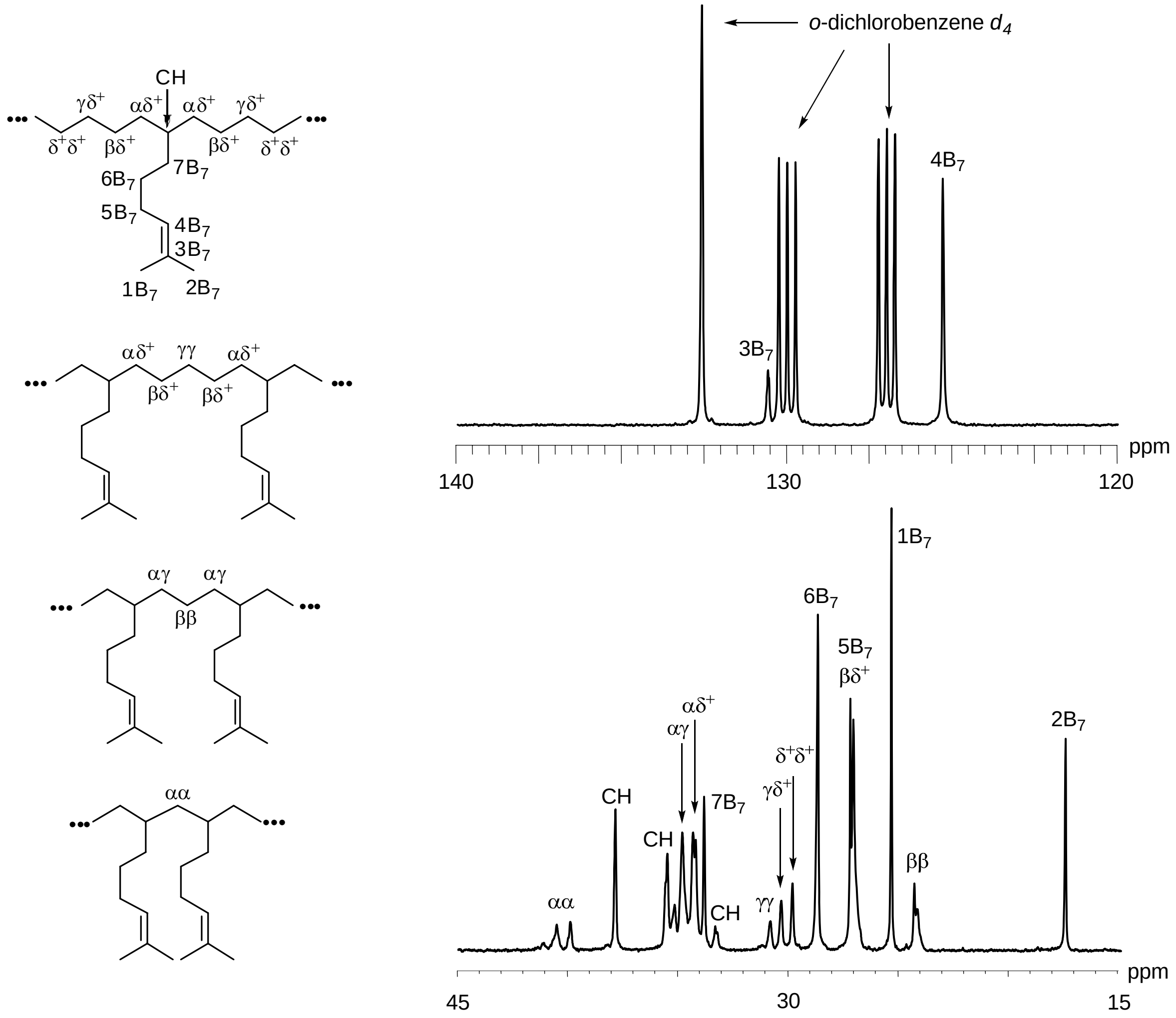


Figure 1. ^{13}C NMR spectra for poly(ethylene-*co*-MOD) in *o*-dichlorobenzene-d_4 at 110 ^{o}C, run 10).

Triad and diad distributions, r_E, r_C, $r_E \cdot r_C$ (E = ethylene; C = MOD, or OC) values estimated on the basis of ^{13}C NMR spectra for poly(ethylene-*co*-MOD)s[4i] and poly(ethylene-*co*-OC)s[11] by the **1-3**/MAO catalysts are summarized in Table 2 and Table 3. It is noted that the Cp*-aryloxo analogue (**1**) showed the lowest r_E value in the ethylene/MOD copolymerization as seen in the ethylene/OC copolymerization. No significant difference in the r_E values between OC and MOD copolymerizations was observed in **1-3**. These results indicate that the trisubstituted olefin in MOD should affect to only catalytic activity by coordination to the active metal center and should not affect to incorporation of the mono-olefin. It implies that ethylene copolymerization with trisubstituted olefins might be achieved by designing better catalysts.

Table 2. Triad sequence distributions in poly(ethylene-*co*-7-methyl-1,6-octadiene)s prepared by **1**-**3**-methylaluminoxane (MAO) catalyst systems.[a]

run	cat.	[MOD]/[E][b]	MOD cont.[c] [mol%]	triads[d]						diads[e]			r_{E}[f]	r_{M}[f]	$r_{\mathrm{E}}\cdot r_{\mathrm{M}}$[g]
				EEE	EEM+MEE	MEM	EME	MME+EMM	MMM	EE	EM+ME	MM			
2	**1**	1.39	28.7	0.334	0.309	0.070	0.219	0.068	0	0.49	0.48	0.03	2.8	0.10	0.29
4	**1**	1.39	29.2	0.353	0.279	0.075	0.222	0.071	0	0.49	0.47	0.04	2.9	0.11	0.31
11	**2**	1.39	23.2	0.416	0.296	0.056	0.184	0.043	0.005	0.56	0.41	0.03	3.8	0.09	0.35
15	**3**	1.39	22.6	0.426	0.292	0.055	0.185	0.042	0	0.57	0.41	0.02	3.9	0.07	0.28

[a] Detailed polymerization conditions, see Table 1 (MOD, M = 7-methyl-1,6-octadiene, E = ethylene). [b] Initial molar ratio of MOD/ethylene in the reaction mixture. [c] MOD content in mol% estimated by ^{13}C NMR spectra. [d] Estimated by ^{13}C NMR spectra. [e] [EE] = [EEE] + 1/2[EEM+MEE], [EM+ME] = [MEM] + [EME] + 1/2{[EEM+MEE] + [MME+EMM]}, [MM] = [MMM] + 1/2[MME+EMM]. [f] $r_{\mathrm{E}} = [\mathrm{M}]_0/[\mathrm{E}]_0 \times 2[\mathrm{EE}]/[\mathrm{EM+ME}]$, $r_{\mathrm{M}} = [\mathrm{E}]_0/[\mathrm{M}]_0 \times 2[\mathrm{MM}]/[\mathrm{EM+ME}]$. [g] $r_{\mathrm{E}}\cdot r_{\mathrm{M}} = 4[\mathrm{EE}][\mathrm{MM}]/[\mathrm{EM+ME}]^2$.

Table 3. Triad sequence distributions in poly(ethylene-*co*-1-octene)s prepared by **1**-**3**-methylaluminoxane (MAO) catalyst systems.[a]

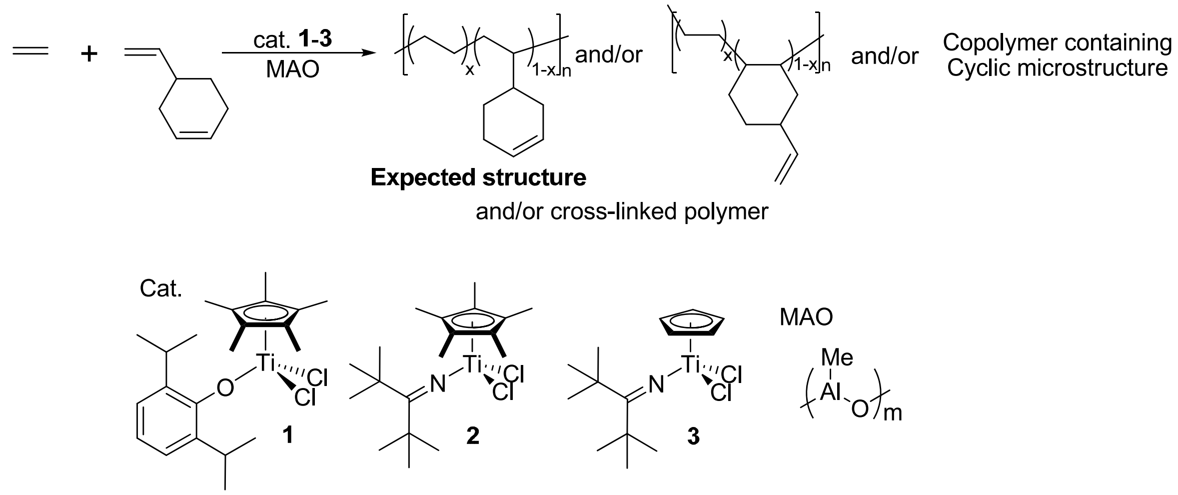
Run	cat.	[OC]/[E][b]	OC cont.[c] / mol%	triads[d]						diads[e]			r_{E}[f]	r_{O}[f]	$r_{\mathrm{E}}\cdot r_{\mathrm{O}}$[g]
				EEE	EEO+OEE	OEO	EOE	OOE+EOO	OOO	EE	EO+OE	OO			
8	**1**	1.47	27.9	0.307	0.334	0.080	0.203	0.068	0.008	0.48	0.48	0.04	2.9	0.12	0.34
9	**1**[h]	1.47	28.0	0.310	0.334	0.076	0.203	0.069	0.008	0.48	0.48	0.04	2.9	0.12	0.36
13	**2**	1.47	19.4	0.481	0.281	0.044	0.154	0.036	0.004	0.62	0.36	0.02	5.1	0.09	0.44
17	**3**	1.47	22.6	0.421	0.295	0.057	0.180	0.038	0.009	0.57	0.40	0.03	4.2	0.09	0.39

[a] Detailed polymerization conditions, see Table 1 (OC, O = 1-octene, E = ethylene). [b] Initial molar ratio of OC/ethylene in the reaction mixture. [c] 1-Octene content in mol% estimated by ^{13}C NMR spectra. [d] Estimated by ^{13}C NMR spectra. [e] [EE] = [EEE] + 1/2[EEO+OEE], [EO+OE] = [OEO] + [EOE] + 1/2{[EEO+OEE] + [OOE+EOO]}, [OO] = [OOO] + 1/2[OOE+EOO]. [f] $r_{\mathrm{E}} = [\mathrm{O}]_0/[\mathrm{E}]_0 \times 2[\mathrm{EE}]/[\mathrm{EO+OE}]$, $r_{\mathrm{O}} = [\mathrm{E}]_0/[\mathrm{O}]_0 \times 2[\mathrm{OO}]/[\mathrm{EO+OE}]$. [g] $r_{\mathrm{E}}\cdot r_{\mathrm{O}} = 4[\mathrm{EE}][\mathrm{OO}]/[\mathrm{EO+OE}]^2$ [h] Copolymerization in the presence of 2-methyl-2-butene.

2. Copolymerization of ethylene with 4-vinylcyclohexene (VCHen)

Copolymerization of ethylene with 4-vinylcyclohexene (VCHen) using the nonbridged half-titanocene **1-3** was conducted at 25 °C in toluene in the presence of MAO (Scheme 2), and hydrogenation of the resultant polymers by $RhCl(PPh_3)_3$ was also conducted to identify the microstructure. The combination of **1-3** and VCHen was chosen as the catalysts and nonconjugated diene respectively, because these catalysts not only exhibit high catalytic activities in ethylene/vinylcyclohexane (VCH) copolymerization with efficient VCH incorporations as described in chapter 2 in this thesis,[12] but also show negligible incorporation of cyclohexene in ethylene/cyclohexene copolymerization.[13] The results are summarized in Table 4, and the results of the ethylene/VCH copolymerization under the same conditions in chapter 2 are also shown for comparison.

Scheme 2



It turned out that copolymerization of ethylene with VCHen using **1-3**/MAO catalysts took place, and the resultant polymers possessed unimodal molecular weight distributions (runs 19-20, 23-24, 26-27). In the **1, 2**-MAO catalyst systems, the decreases of the activities in the VCHen copolymerization compared to the VCH copolymerization were observed (runs 19-25). The M_n values of the resultant copolymers prepared by **1** were much lower than these of the ethylene/VCH copolymers under the same conditions (runs 19-22). In contrast, the **3**-MAO exhibited higher catalytic activity in the VCHen copolymerization compared to the VCH copolymerization, and the M_n value of the resultant copolymer was higher than the VCH copolymer prepared under the same condition (runs 27-28).

Table 4. Copolymerization of ethylene with 4-vinylcyclohexene (VCHen) or vinylcyclohexane (VCH) by various half-titanocenes, Cp’TiCl$_2$(Y) [Y = O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp’ = Cp* (**1**); Y = N=C^{t}Bu$_2$, Cp’ = Cp* (**2**), Cp (**3**)]-MAO catalyst systems.[a]

run	cat. ([µmol])	comonomer ([M])	yield [mg]	activity[b]	$M_n \times 10^{-4}$ (M_w/M_n)[c]	*after hydrogenation* M_n(M_w/M_n)[c] $\times 10^{-4}$
19	**1** (2.0)	VCHen (1.22)	264	1,320	4.4 (2.1)	3.8 (2.4)
20	**1** (2.0)	VCHen (2.43)	194	970	2.6 (2.3)	3.1 (2.0)
21	**1** (0.2)	VCH (1.22)	334	16,700	18.7 (2.0)	
22	**1** (0.2)	VCH (2.43)	282	14,100	10.0 (2.3)	
23	**2** (1.0)	VCHen (1.22)	371	3,710	38.8 (2.4)	39 (2.5)
24	**2** (1.0)	VCHen (2.43)	185	1,850	25.6 (2.6)	24 (2.9)
25	**2** (1.0)	VCH (2.43)	522	5,220	31.6 (3.1)	
26	**3** (0.1)	VCHen (1.22)	218	21,800	-[d]	insoluble
27	**3** (0.1)	VCHen (2.43)	233	23,300	50.8 (2.0)	41 (2.0)
28	**3** (0.2)	VCH (2.43)	143	7,150	27.8 (2.9)	

[a] Conditions : VCHen or VCH + toluene total 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO) 3 mmol, ethylene 6 atm, 25 °C, 6 min. [b] Activity in kg-polymer/mol-Ti·h. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Insoluble.

Figure 2 shows typical ^{13}C NMR and DEPT spectra of the resultant copolymer and the resonances were identified by both the DEPT analysis and comparison with the published literature.[5d] As expected, the resonances ascribed to not only the cyclohexenyl side chain (CH, a, b, c, d, olefinic bond), but also the polyethylene backbone around the side chain ($\alpha\delta^+$, $\beta\delta^+$, $\gamma\delta^+$, $\alpha\gamma$, $\beta\beta$) were observed in the all copolymers. However, the unexpected resonances that are considered to be derived from side reaction were also observed in all cases.

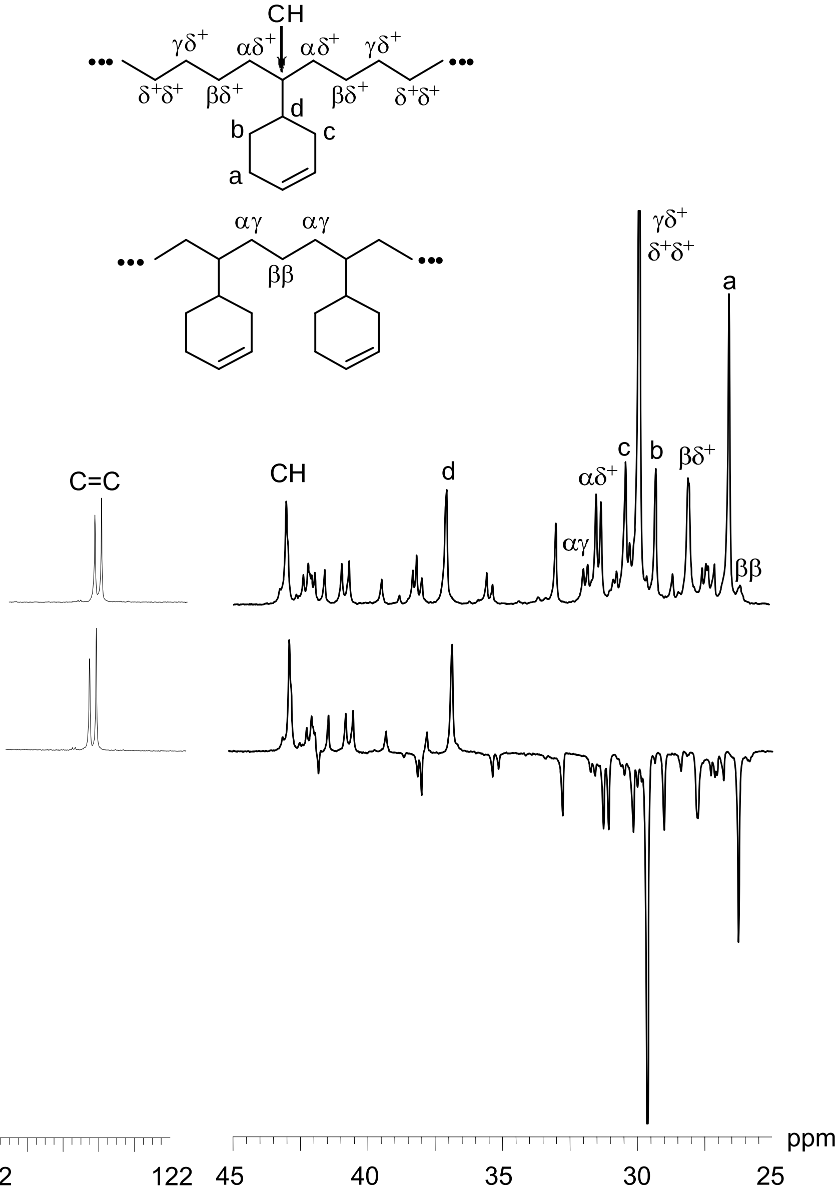


Figure 2. ^{13}C NMR and DEPT spectra for poly(ethylene-*co*-VCHen) by **1**-MAO (run 20) in tetrachloroethane-d_2 at 110 °C.

Typical ^{13}C NMR spectra of the resultant copolymers before and after hydrogenation are shown in Figure 3, and a ^{13}C NMR spectrum of ethylene/VCH copolymer is also shown as comparison. After hydrogenation, the resonances ascribed to the unsaturated side chain (olefin, CH, a, b, c, d, olefinic bond) and the polyethylene backbone around the side chain ($\alpha\delta^+$, $\beta\delta^+$, $\alpha\gamma$, $\beta\beta$) were disappeared, and the new resonances were agreement with these of the ethylene/VCH copolymer. In contrast, the resonances of the unexpected structure were unchanged after hydrogenation. Moreover, no significant changes in the M_n and M_w/M_n values between the copolymers before and after hydrogenation were observed (Table 4). These results strongly suggest that the unexpected microstructure would be saturated hydrocarbon derived from intramolecualr cyclization of the unsaturated cyclohexenyl side chain with the active metal center.

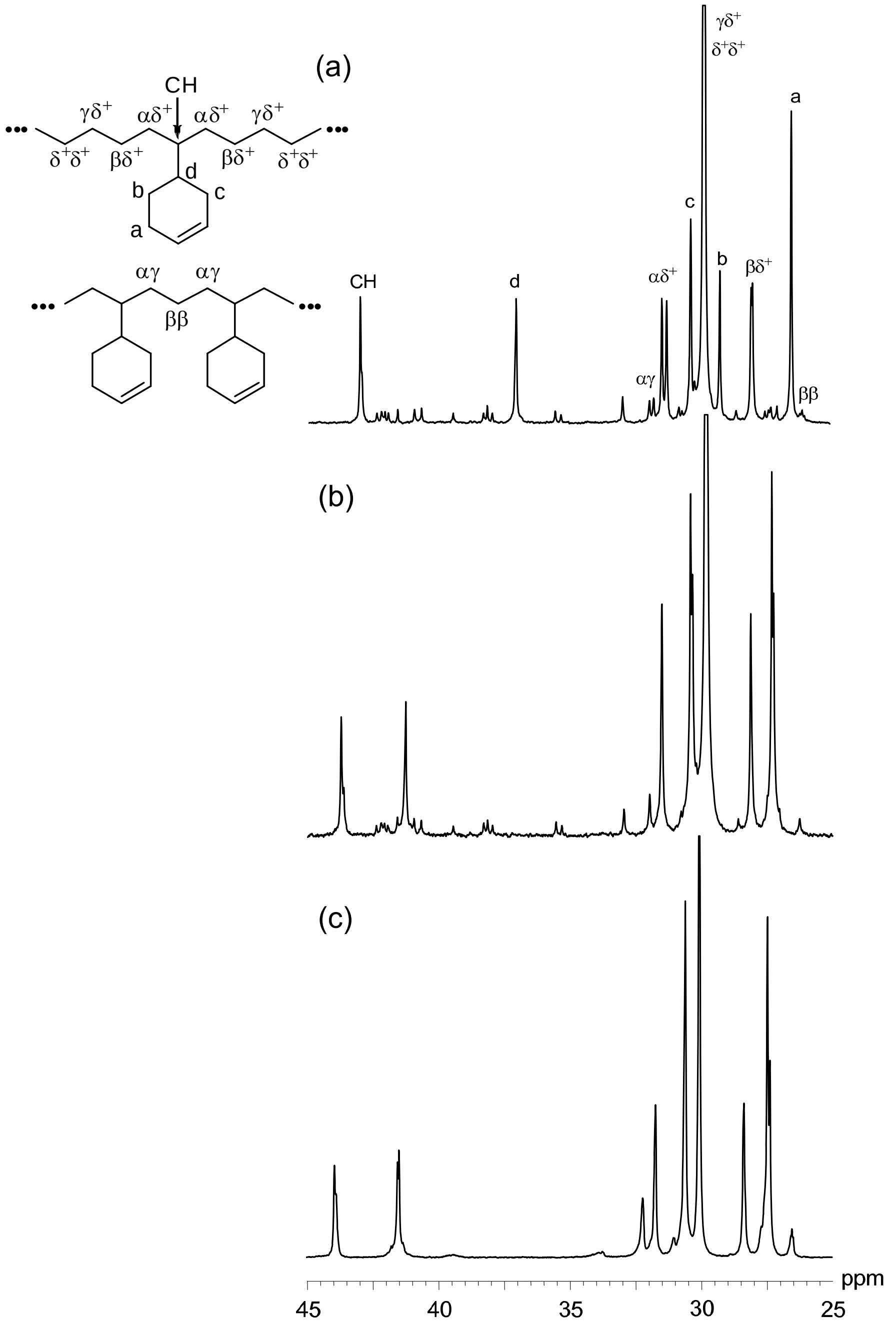
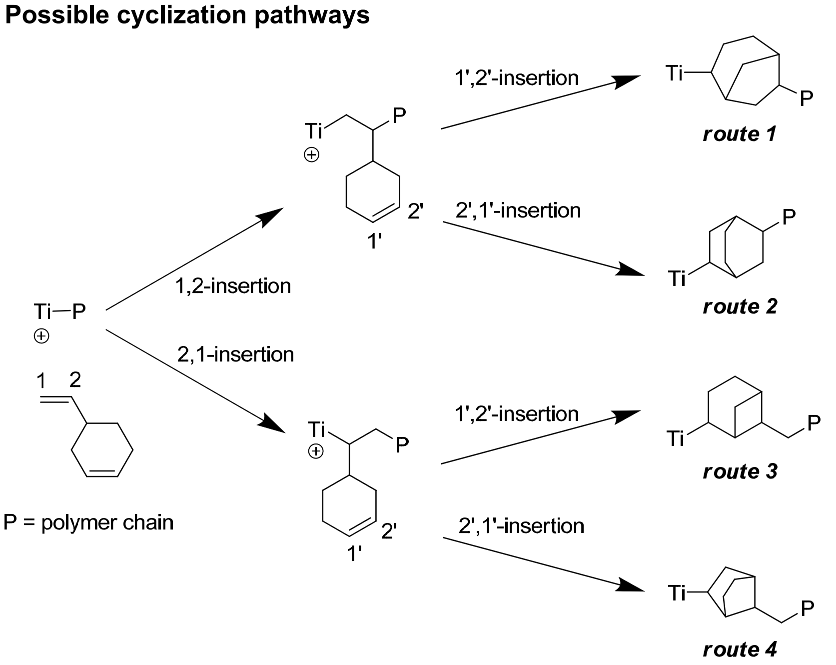


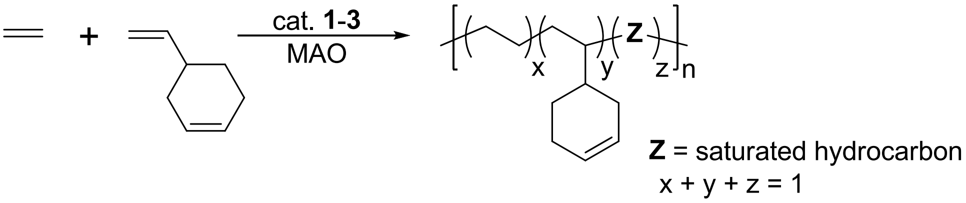
Figure 3. ^{13}C NMR spectra for poly(ethylene-*co*-VCHen) by **3** (run 27) (a) before and (b) after hydrogenation in tetrachloroethane-d_2 at 110 °C and (c) poly(ethylene-*co*-vinylcyclohexane) by **3** (run 28) in C_6D_6/1,2,4-trichlorobenzene at 110 °C.

Four routes would be considered as the cyclization pathway in the copolymerization (scheme 3). The many methine signals from 38.0 to 42.5 ppm in the ^{13}C NMR spectra imply that the route 3 or route 4 in scheme 3, cyclization of the cyclohexenyl side chain after 2,1-insertion of the mono-olefin in VCHen, may be the dominant cyclization pathway. However, there are no evidence for 2,1-insertion of the mono-olefin of VCHen, and thus the true structure has not been identified yet (Scheme 4).

Scheme 3



Scheme 4



On the basis of the assumption, the contents of VCHen containing cyclohexenenyl side chain in the copolymers (y × 100, y in scheme 4) and the extent of the side reaction were estimated by ^{1}H and ^{13}C NMR spectra. The results are summarized in Table 5, and the extent of the side reaction was defined by the integration ratio of the resonances at 36 ppm to that of "CH" at 43 ppm in ^{13}C NMR spectra.

Table 5. VCHen contents and extent of side reaction in ethylene/VCHen copolymers prepared by Cp'TiCl$_2$(Y) [Y = O-2,6-^{i}Pr$_2$C$_6$H$_3$, Cp' = Cp* (**1**); Y = N=C^{t}Bu$_2$, Cp' = Cp* (**2**), Cp (**3**)]-MAO catalyst systems.[a]

run	comonomer [M]	VCHen[b] [mol%]	side reaction[c] [-]	$T_m(T_g)$[d] [°C]
19	VCHen (1.22)	9.3	0.39	
20	VCHen (2.43)	15.5	0.35	(-13)
21	VCH (1.22)	22.5[e]	-	(-27)
22	VCH (2.43)	31.9[e]	-	(-12)
23	VCHen (1.22)	-	1.37	105
24	VCHen (2.43)	2.5	1.17	90
25	VCH (2.43)	10.9[e]	-	65
26	VCHen (1.22)	4.8	0.17	82
27	VCHen (2.43)	10.0	0.13	57
28	VCH (2.43)	24.5[e]	-	(-25)

[a] The details of polymerization were described in Table 4. [b] Content of VCHen containing cyclohexenyl side chain in copolymer (y × 100, y in scheme 4) by ^{1}H and ^{13}C NMR spectra. [c] Extent of side reaction estimated by ^{1}H and ^{13}C NMR spectra. [d] Measured by DSC. [e] VCH content (mol%) in copolymer.

It was revealed that the contents of VCHen containing cyclohexenyl side chain in the copolymers under the same conditions increased in the order: **1** (runs 19, 20) > **3** (runs 23, 24) >**2** (runs 26, 27) and the contents was lower than the corresponding VCH contents of the ethylene/VCH copolymers prepared under the same condition (run 20 vs run 21, run 24 vs run 25, run 27 vs run 28). On the other hand, the extent of the side reaction of the copolymer prepared by **3** was much lower than these by **1-2**. Moreover, as mentioned above, **3**-MAO exhibited the highest catalytic activity and afforded the highest molecular weight copolymers with unimodal molecular weight distributions. These results strongly indicate that the **3**-MAO catalyst would be the most suited for precise synthesis of the ethylene copolymer containing cyclohexenyl side chain in the copolymerization.

Effect of reaction condition on copolymerization of ethylene with 4-vinylcyclohexene by 3-MAO catalyst

Ethylene/VCHen copolymerization using the **3**-MAO catalyst under various conditions was conducted to explore the effect of the conditions on the copolymerization. This is because the polymerization conditions strongly affect not only the catalytic activity, but also the microstructures of the resultant polymers such as the comonomer content and extent of side reaction in the nonconjugated diene polymerization.[4-8] The results of the copolymerization are summarized in Table 6.

It was revealed that the copolymerization using the **3**-MAO catalyst under various conditions took place with high catalytic activities and the resultant copolymers possessed high molecular weights with unimodal molecular weight and comonomer distributions. The polymerization time, MAO concentration, and catalyst concentration didn't strongly affect to the catalytic activity, the extent of the side reaction, the contents of VCHen containing cyclohexenyl side chain, and the T_m values of the resultant copolymers (runs 27, 29-34).

The contents of VCHen containing cyclohexenyl side chain in the copolymers increased with decreasing the ethylene pressures, however, the notable decrease of the catalytic activities as well as the increase of the extent of the side reaction were observed. (runs 27, 35-36). In contrast, the contents also increased with increasing the VCHen concentrations without both decreasing the catalytic activities and increasing of the extent of the side reaction (runs 26-27, 38-39).

Table 6. Effect of polymerization condition on copolymerization of ethylene (E) with 4-vinylcyclohexene (VCHen) by $CpTiCl_2(N{=}C^tBu_2)$ (**3**)-MAO catalyst system.[a]

run	cat. ([μmol])	MAO [mmol] (Al/Ti x 10^{-3})[b]	E [atm]	VCHen [M]	temp. [°C]	time [min]	yield [mg]	activity[c]	M_n[d] × 10^{-4}	M_w/M_n[d]	VCHen[e] [mol%]	side reaction[f] [-]	T_m (T_g)[g] [°C]
29	**3** (0.1)	3.0 (30)	6	2.43	25	**3**	117	23,400	41.9	2.0	10.3	0.14	60
27	**3** (0.1)	3.0 (30)	6	2.43	25	**6**	233	23,300	50.8	2.0	10.0	0.13	57
30	**3** (0.1)	3.0 (30)	6	2.43	25	**10**	311	18,700	45.4	2.2	10.2	0.16	58
31	**3** (0.1)	**1.5 (15)**	6	2.43	25	6	210	21,000	44.1	2.3	10.5	0.14	55
27	**3** (0.1)	**3.0 (30)**	6	2.43	25	6	233	23,300	50.8	2.0	10.0	0.13	57
32	**3** (0.1)	**4.5 (45)**	6	2.43	25	6	246	24,600	28.6	2.4	10.1	0.14	55
33	**3** (**0.05**)	3.0 (60)	6	2.43	25	6	114	22,800	50.4	2.0	10.1	0.12	57
27	**3** (**0.1**)	3.0 (30)	6	2.43	25	6	233	23,300	50.8	2.0	10.0	0.13	57
34	**3** (**0.2**)	3.0 (15)	6	2.43	25	6	325	16,300	46.2	2.2	9.6	0.14	55
35	**3** (0.1)	3.0 (30)	**4**	2.43	25	6	74	7,400	30.7	2.0	15.2	0.22	35
27	**3** (0.1)	3.0 (30)	**6**	2.43	25	6	233	23,300	50.8	2.0	10.0	0.13	57
36	**3** (0.1)	3.0 (30)	**8**	2.43	25	6	456[h]	45,600	53.5	2.0	7.6	0.13	70
37	**3** (0.1)	3.0 (30)	6	**0**	25	6	118	11,800	46.7	2.0	-	-	137
38	**3** (0.1)	3.0 (30)	6	**0.61**	25	6	184	18,400	49.0	1.7	2.6	0.23	104
26	**3** (0.1)	3.0 (30)	6	**1.22**	25	6	218	21,800	- [i]	- [i]	4.8	0.17	82
27	**3** (0.1)	3.0 (30)	6	**2.43**	25	6	233	23,300	50.8	2.0	10.0	0.13	57
39	**3** (0.1)	3.0 (30)	6	**4.86**	25	6	195	19,500	54.8	2.1	16.1	0.13	(-18)
27	**3** (0.1)	3.0 (30)	6	2.43	**25**	6	233	23,300	50.8	2.0	10.0	0.13	57
40	**3** (0.1)	3.0 (30)	6	2.43	**40**	6	202	20,200	38.4	2.2	8.2	0.21	65
41	**3** (0.1)	3.0 (30)	6	2.43	**55**	6	154	15,400	29.6	2.2	7.0	0.34	72

[a] Conditions: VCHen + toluene total 30 mL, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO). [b] Al/Ti molar ratios. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standards. [e] Content of VCHen containing cyclohexenyl side chain in the copolymer by ^1H and ^{13}C NMR spectra. [f] Extent of side reaction estimated by ^{13}C NMR spectra. [g] Measured by DSC. [h] Stirring was stopped during polymerization due to the aggregation of polymer to the stirred tip. [i] Insoluble.

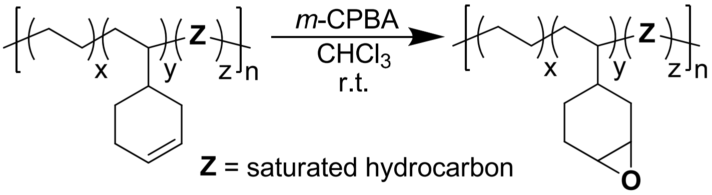
Despite comonomer contents in ethylene copolymers usually increase at higher temperature due to the decrease of the ethylene solubility into solvent, the contents of VCHen containing cyclohexenyl side chain in the copolymers decreased with increasing the polymerization temperatures employed (runs 27, 40-41). Moreover, the extent of the side reaction also increased with increasing the temperature. These indicate that the olefinic side chains were consumed by the side reaction.

In summary of the results, the increase of the monomer concentrations, especially ethylene concentration, suppresses the side reaction. It means that coordination or insertion of the monomers to the active metal center could compete with the side reaction. Therefore, both higher ethylene pressure (> 6 atm) and lower reaction temperature (25 ^{o}C) would be necessary for precise synthesis of the ethylene copolymers containing cyclohexenyl side chain with both the high catalytic activity and the low extent of the side reaction.

Introduction of polar functionality to olefinic side chain in ethylene/4-vinylcyclohexene copolymer

Epoxidation of the cyclohexenyl side chain in the ethylene/VCHen copolymer prepared by **3** was conducted in $CHCl_3$ at room temperature by using *m*-chloroperbenzoic acid (*m*-CPBA) (Scheme 5). The ^{13}C NMR spectra of the copolymer before and after epoxidation are shown in Figure 4. After epoxidation, the resonances at 128 ppm ascribed to the olefinic bond were disappeared and four new resonances ascribed to the epoxy group were observed at 52-54 ppm. The result clearly indicates that the functionalization proceeded in quantitative yield and the resultant polymer would be ethylene copolymer containing epoxy group in the side chain as expected.

Scheme 5



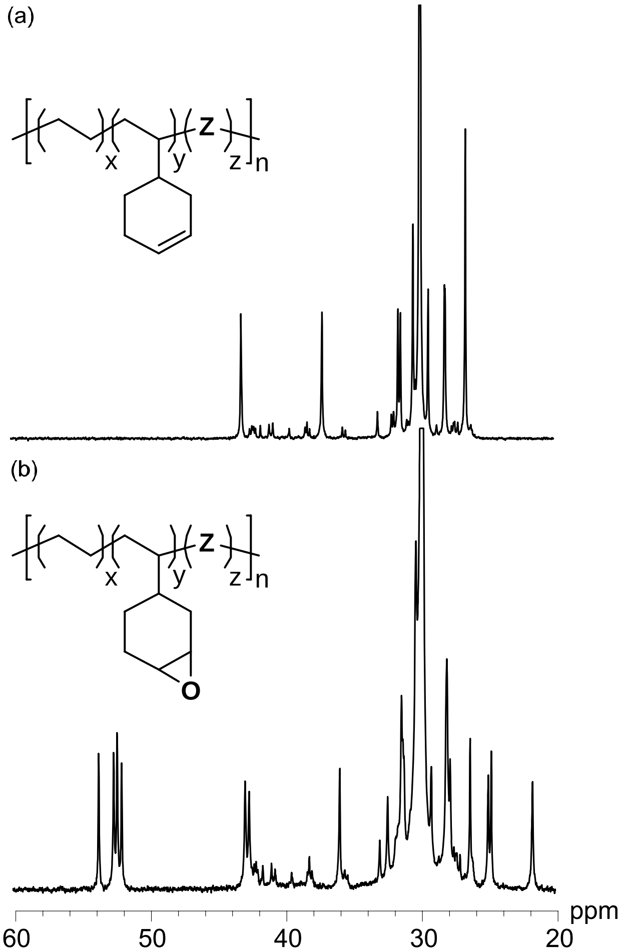


Figure 4. ^{13}C NMR spectra for poly(ethylene-*co*-VCHen) (a) before and (b) after epoxidation in tetrachloroethane-d_2 at 110 °C.

Conclusion

Copolymerization of ethylene with 7-methyl-1,6-octadiene (MOD) by using Cp'TiCl$_2$(Y) [Y = 2,6-^{i}Pr$_2$C$_6$H$_3$ (**1**), Cp' = Cp*; Y = N=C^{t}Bu$_2$, Cp' = Cp*(**2**), Cp(**3**)] in the presence of MAO afforded the ethylene copolymer containing trisubstituted olefin side chain without the side reactions. Especially, the **1, 3**-MAO catalysts exhibited notable catalytic activities with efficient MOD incorporations. The MOD contents in the resultant copolymers prepared by **1-3**, were similar with those in the ethylene/1-octene copolymerization under the similar conditions.

Copolymerization of ethylene with 4-vinylcyclohexene (VCHen) by using the **1-3**/MAO catalysts also afforded copolymers containing cyclohexenyl side chains with some extent of the side reaction, probably cyclization. The contents of the cyclohexenyl side chain in the resultant copolymers by **1-3** were lower than the comonomer content in ethylene/vinylcyclohexane copolymerization under the same condition. Especially, the **3**-MAO catalyst exhibited the highest catalytic activity with the lowest extent of the side reaction, however, suitable both ethylene pressure (> 6 atm) and polymerization temperature (25 ^{o}C) were essential for precise synthesis of the ethylene copolymer containing unsaturated side chain with the high catalytic activity and the low extent of the side reaction. Epoxidation of the side chain by peroxide afforded the ethylene copolymer containing expoxy group in the side chain with quantitative yield. These demonstrated the possibilities of the polar functionalization under mild conditions for ethylene copolymers.

Experimental Section

General Procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous grade toluene (Kanto Chemical Co., Inc.), 1-octene (Wako Pure Chemical Ind., Ltd.) 4-vinyl-1-cyclohexene (Merck & Co., Inc.), 7-methyl-1,6-octadiene (Aldrich), and 2-methyl-2-butene (Aldrich) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. *Meta*-chloroperbenzoic acid, with water (69-75% purity, Wako Pure Chemical Ind., Ltd.) was used as received. Ethylene of polymerization grade (Sumitomo Seika Chemicals Co., Ltd.) was used as received without further purification procedures.

Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 ºC for removing toluene, $AlMe_3$, and then heated at >100 ºC for 1 h for completion) in the drybox to give white solids.

(Cyclopentadienyl)titanium(IV) complexes of the type, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**)[14] and $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp' = Cp*(**2**)[15] and Cp(**3**)[15]], were prepared according to the previous reports.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^1H and 100.53 MHz for ^{13}C). All spectra were obtained in the solvents indicated at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C). ^{13}C NMR spectra for polyethylenes, poly(ethylene-*co*-1-octene)s, poly(ethylene-*co*-MOD)s and poly(ethylene-*co*-VCHen)s were measured at 110 ^oC in C_6D_6/1,2,4-trichlorobenzene (1/4 v/v), 1,1,2,2-tetrachloroethane-d_2 or *o*-dichlorobenzene-d_4. The relaxation delay was 5.2 sec, the acquisition time was 1.3 sec, the pulse angle was 90º, and the number of transients accumulated was ca. 6000.

Molecular weights and molecular weight distributions for the polyethylenes and poly(ethylene-*co*-VCHen)s were measured by a gel permeation chromatography (GPC, Tosoh

HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH$_{HR}$-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $< 2.8\times10^8$ MW at 140 ºC using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weights were calculated by a standard procedure based on the calibration with standard polystyrene samples.

Differential scanning calorimetric (DSC) data for the polymers were recorded by a DSC6200 (Seiko Instruments Co.) under a N_2 atmosphere [Preheating: from 25 to 200 ºC (20 ºC/min), cooling to -100 ºC under N_2, and measurement from -100 to 200 ºC (20 ºC/min) under N_2].

Copolymerizations of ethylene with 7-methyl-1,6-octadiene (MOD), 1-octene (OC), or 4-vinylcyclohexene (VCHen). A typical reaction procedure for copolymerization of ethylene with MOD (run 1, Table 1) is as follows. Toluene (24 mL), MOD (5 mL), and MAO solid (87 mg, 3.0 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 ºC. A toluene solution (1.0 mL) containing **1** (0.05 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 5 atm (total ethylene pressure 6 atm). The mixture was magnetically stirred for 6 min, ethylene remained was purged after the reaction, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo*. Basic experimental procedures in the ethylene/OC and ethylene/VCHen copolymerizations were the same as that in the ethylene/MOD copolymerization except that various amounts of the comonomers were added in place of MOD partially (total 29 mL).

Hydrogenation of poly(ethylene-*co*-VCHen). A general procedure is as follow. Into a 10 mL scale stainless-autoclave, toluene (5 mL), $RhCl(PPh_3)_3$ (5 mg) and poly(ethylene-*co*-VCHen) (50 mg) were added. The reaction apparatus was pressurized to 4 atm, and was magnetically stirred at 100 ºC for overnight. The reaction mixture was then poured into MeOH, and the resultant polymer was collected on a filter paper by filtration. The polymer was purified by reprecipitation, was collected, and then dried *in vacuo*.

Epoxidation of poly(ethylene-*co*-VCHen). To a $CHCl_3$ solution containing poly(ethylene-*co*-VCHen) 1.154 g (M_n = 668,000, M_w/M_n = 1.97, T_m = 58 °C, VCHen content = 10 mol%), *m*-CPBA·xH_2O 1.63 g was added. The reaction solution was stirred at room temperature for overnight, and then the mixture was dropped into MeOH with vigorous stirring after passing through a cotton plug. The resultant polymer was collected on a filter paper and was then dried *in vacuo*. Yield 1.17 g.

References

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Part II

Design and synthesis of new transition metal complex catalysts for olefin coordination polymerization

Chapter 4

Synthesis of group 4 half-metallocene complexes containing an aryloxo ligand and their use for ethylene polymerization and ethylene copolymerization

Introduction

Design and synthesis of efficient transition metal complex catalysts for precise olefin coordination polymerization have attracted considerable attention in the fields of catalysis, oganometallic chemistry and polymer chemistry.[1-6] As described in chapter 1-3, nonbridged half-titanocenes containing an aryloxo ligand of the type Cp'TiX$_2$(OAr) [Cp' = cyclopentadienyl; X = halogen, alkyl; OAr = aryloxo], have been one of the promising catalysts for ethylene copolymerization.[5b,7-14] Especially, Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) catalyst exhibits both high catalytic activity and efficient comonomer incorporation in ethylene copolymerizations with α-olefin[9c] and 2-methyl-1-pentene,[12] and the substituents at 2,6-position of the aryloxo ligand play an important role especially toward the catalytic activity as well as the comonomer incorporation.

In contrast, examples concerning synthesis of a series of group 4 nonbridged half-metallocenes containing an aryloxo ligand of the type Cp'MX$_2$(O-2,6-R$_2$C$_6$H$_3$) [M = Ti, Zr, Hf], especially the Zr and Hf complexes, were limited. Moreover, the studies concerning the effect of the centered metal not only on the catalytic activity in ethylene polymerization, but also on the comonomer incorporation in ethylene copolymerization have not been reported. Only the synthesis of Cp*ZrCl$_2$(O-2,6-^{t}Bu$_2$C$_6$H$_3$) and the use as the catalyst precursor for ethylene polymerization in the presence of methylaluminoxane (MAO) cocatalyst were reported.[15]

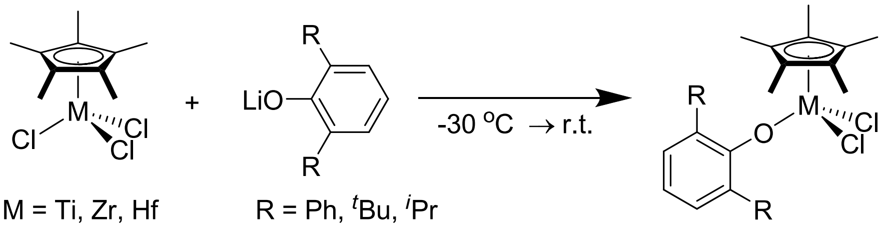
This chapter describes synthesis of a series of Cp*MCl$_2$(O-2,6-R$_2$C$_6$H$_3$) and the effect of the centered metal and the subsituents in the aryloxo ligand on ethylene homo- and copolymerization using these complexes in the presence of MAO cocatalyst.

Results and discussion

Synthesis and structural analysis of $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$.

Syntheses of the group 4 metal (IV) nonbriged half-metallocene complexes of the type, $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), ^{t}Bu (**b**), ^{i}Pr (**c**)] were attempted by treating Cp^*MCl_3 with $LiO\text{-}2,6\text{-}R_2C_6H_3$ in various solvents (Scheme 1). The complexes reported previously, $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Ti, R = Ph (**1a**),[16] R = ^{t}Bu (**1b**)[7c]; M = Zr, R = ^{t}Bu (**2b**)[15]], were prepared according to the published conditions. $Cp^*ZrCl_2(O\text{-}2,6\text{-}Ph_2C_6H_3)$ (**2a**) could be synthesized by the same procedure with **2b**, and the Hf analogues, $Cp^*HfCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [R = Ph (**3a**), ^{t}Bu (**3b**)], could be also prepared similarly by using toluene or Et_2O as the solvents. In contrast, the reaction of Cp^*ZrCl_3 with $LiO\text{-}2,6\text{-}{}^iPr_2C_6H_3$ afforded the mixture of $Cp^*ZrCl_{3-n}(OAr)_n$ [n = 0-3]. This may be due to the large Zr atomic radius compared to Ti. The new complexes (**2a**, **3a-b**) were identified based on ^1H, ^{13}C NMR spectra and elemental analyses.

Scheme 1



M = Ti, R = Ph (**1a**), R = ^{t}Bu (**1b**), R = ^{i}Pr (**1c**);
M = Zr, R = Ph (**2a**), R = ^{t}Bu (**2b**);
M = Hf, R = Ph (**3a**), R = ^{t}Bu (**3b**).

Suitable single crystals for X-ray crystallographic analysis were grown from chilled CH_2Cl_2/*n*-hexane solution containing **2a-b**, **3a-b**. The determined molecular structures are shown in Figure 1. The selected bond distances and angles are summarized in Table 1, and these values of the Ti analogues (**1a-c**) that were reported previously are also shown for comparison.[7a,7c,16]

The Zr and Hf complexes (**2-3,a-b**) fold a rather distorted tetrahedral geometry around the metal centers as seen in the Ti analogues (**1a-c**). The Zr-Cl bond distances [**2a**-**b**: 2.3881(5)-2.4008(4) Å] are slightly longer than the Hf-Cl bond distances [**3a**-**b**: 2.3640(78)-2.3751(7) Å], and are longer than the Ti-Cl bond distances [**1a**-**b**: 2.2674(10)-2.2865(14) Å].[7c, 16] The Zr-O bond distances [1.9349(12), 1.9431(9) Å] are also slightly longer than the Hf-O [1.9224(15), 1.9280(19) Å] and the Ti-O [1.811(3), 1.804(2) Å] bond distances.[7c, 16] These should be due to the influence by the atomic radii.[17]

In contrast, no significant difference was observed in the Cl(1)-M-Cl(2) bond angles, except that the angles of the Ph analogues (**1**-**3a**) are larger than those of the corresponding *ᵗ*Bu analogues (**1**-**3b**). The M-O-C(phenyl) bond angles of the Zr-Ph (**2a**) and the Hf-Ph (**3a**) analogues are smaller than those of the *ᵗ*Bu analogues (**2**-**3b**), whereas the opposite trend was observed in the Ti analogues (**1a**-**b**).

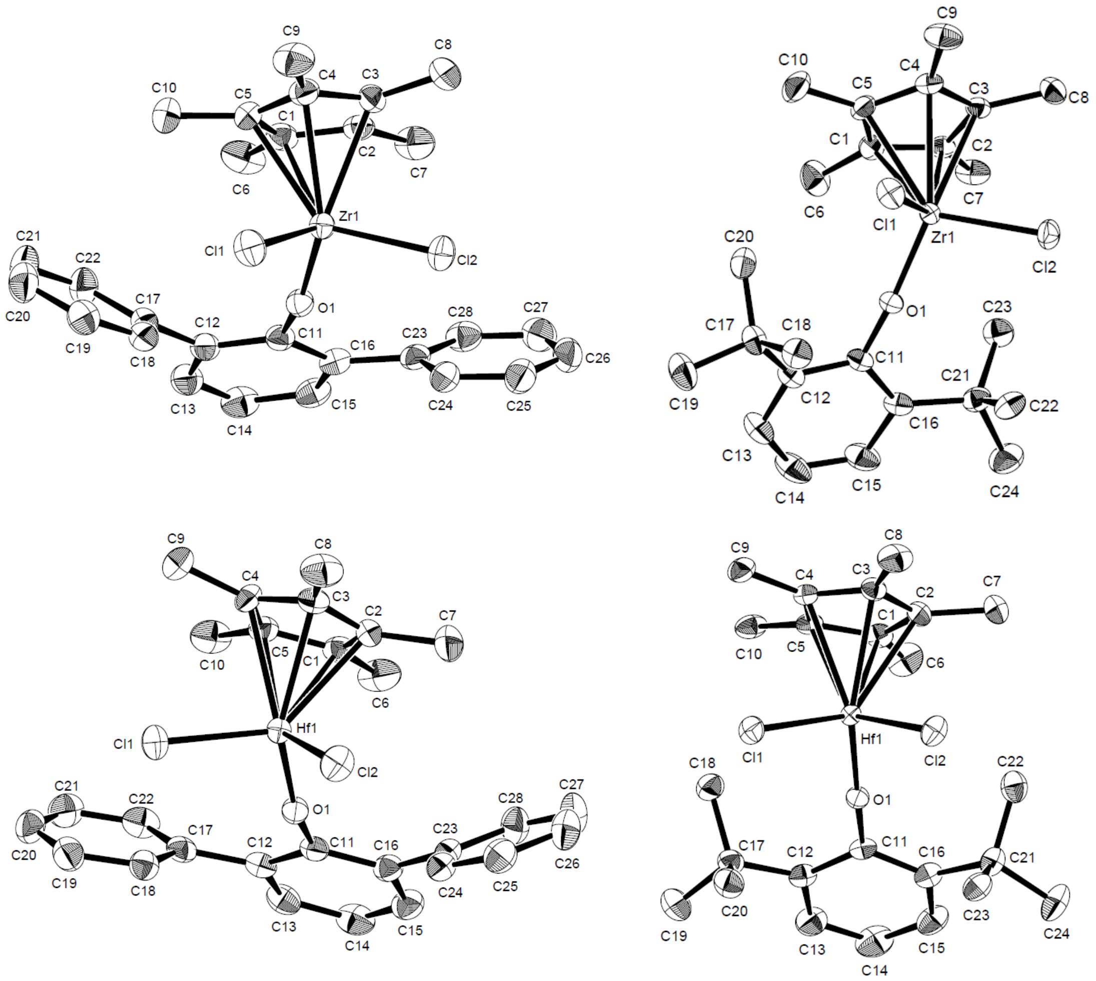


Figure 1. ORTEP drawings for Cp*MCl$_2$(O-2,6-R$_2$C$_6$H$_3$) [top: M = Zr, R = Ph (**2a**, left), ^{t}Bu, (**2b**, right); bottom: M = Hf, R = Ph (**3a**, left), ^{t}Bu (**3b**, right)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1. Selected bond distances (Å) and angles (°) for Cp*MCl$_2$(O-2,6-R$_2$C$_6$H$_3$) [M = Ti, R = Ph (**1a**), ^{t}Bu (**1b**), ^{i}Pr (**1c**); M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, R = Ph (**3a**), ^{t}Bu (**3b**)].

Complex (M, R)	**1a**[a] (Ti, Ph)	**1b**[b] (Ti, ^{t}Bu)	**1c**[c] (Ti, ^{i}Pr)	**2a** (Zr, Ph)	**2b** (Zr, ^{t}Bu)	**3a** (Hf, Ph)	**3b** (Hf, ^{t}Bu)
			Selected bond distances (Å)				
M(1)-Cl(1)	2.2693(13)	2.2674(10)	2.305(2)	2.4008(4)	2.3961(3)	2.3640(7)	2.3714(6)
M(1)-Cl(2)	2.2865(14)	2.2674(10)	2.239(2)	2.3881(5)	2.3963(3)	2.3751(7)	2.3710(8)
M(1)-O(2)	1.811(3)	1.804(2)	1.772(3)	1.9349(12)	1.9431(9)	1.9224(15)	1.9280(19)
			Selected bond angles (°)				
M(1)-O(1)-C (Phe)	160.6(3)	155.5(2)	173.0(3)	160.99(11)	169.95(8)	160.97(14)	169.64(16)
Cl(1)-M(1)-Cl(2)	98.70(5)	98.10(4)	103.45(5)	99.629(17)	98.234(12)	99.40(2)	98.04(2)
Cl(1)-M(1)-O(1)	104.33(10)	103.22(6)	99.1(2)	107.37(3)	103.72(2)	104.71(4)	104.60(6)
Cl(2)-M(1)-O(1)	105.20(10)	103.22(6)	104.1(2)	105.73(3)	105.52(3)	106.25(4)	103.10(5)

[a] Cited from ref 16. [b] Cited from ref 7c. [c] Cited from ref 7a

Ethylene polymerization by Cp*MCl_2(O-2,6-$R_2C_6H_3$)/MAO catalyst systems: Effect of Al/M molar ratios and polymerization temperature.

Ethylene polymerization using a series of Cp*MCl_2(O-2,6-$R_2C_6H_3$) [M = Ti, R = Ph (**1a**), ^{t}Bu (**1b**), ^{i}Pr (**1c**); M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, R = Ph (**3a**), ^{t}Bu (**3b**)] was conducted in the presence of MAO cocatalyst (Scheme 2). MAO white solid prepared by removing toluene and $AlMe_3$ from commercially available MAO solution was chosen, because it was effective for the preparation of high molecular weight ethylene/α-olefin and ethylene/2M1P copolymers with unimodal molecular weight distributions when **1c** was used as the catalyst precursor.[9a,12] The results are summarized in Table 2 and 3.

Scheme 2

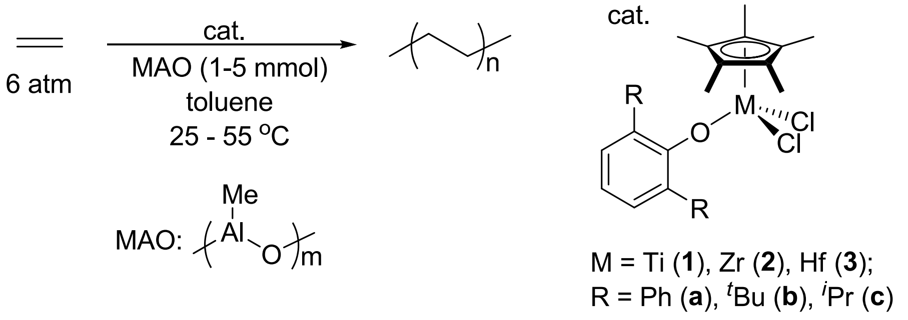


Table 2 summarizes the results of ethylene polymerization at 25 °C in toluene under various Al/M molar ratios. The catalytic activities with a series of Cp*MCl_2(O-2,6-$R_2C_6H_3$) (**1-3,a-b**) under optimized Al/M molar ratios increased in the order: **1a** (96600 kg-PE/mol-Ti·h, run 4) >> **2a** (8850, run 15), **1b** (8400, run 9) > **2b** (3340, run 19) > **3a** (750, run 26) > **3b** (78, run 28). This result indicates that the Ti analogues (**1a-b**) exhibited higher activities than the corresponding Zr analogues (**2a-b**), and the Hf analogues (**3a-b**) are the lowest. It was also revealed that the Ph analogues (**1-3a**) showed higher catalytic activities than the corresponding ^{t}Bu analogues (**1-3b**) owing to the steric bulk around the metal centers probably.

Table 2. Ethylene polymerization by Cp*MCl$_2$(O-2,6-R$_2$C$_6$H$_3$) [M = Ti, R = Ph (**1a**), ^{t}Bu (**1b**), ^{i}Pr (**1c**); M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, R = Ph (**3a**), ^{t}Bu (**3b**)]-MAO catalyst systems: Effect of Al/M molar ratio.[a]

run	cat. ([μmol])	MAO [mmol] (Al/M × 10^{-3})[b]	yield [mg]	activity [kg-PE/mol-M·h]	M_n[c] × 10^{-4}	M_w/M_n[c]
1	**1a** (0.01)	1.0 (100)	133	79,800	120	3.2
2	**1a** (0.01)	2.0 (200)	145	87,000		
3	**1a** (0.01)	3.0 (300)	144	86,400	67.8[d]	3.3
4	**1a** (0.01)	4.0 (400)	161	96,600	67.0[d]	2.9
5	**1a** (0.01)	5.0 (500)	151	90,600	54.4[d]	3.4
6	**1b** (0.1)	1.0 (10.0)	93	5,580	3.74	2.9
7	**1b** (0.1)	2.0 (20.0)	113	6,780	2.63[e]	2.5
8	**1b** (0.1)	3.0 (30.0)	127	7,620	1.78[e]	2.3
9	**1b** (0.1)	4.0 (40.0)	140	8,400	2.67[e]	2.4
10	**1b** (0.1)	5.0 (50.0)	125	7,500	2.35[e]	2.9
11	**1c** (0.01)	3.0 (300)	72	43,200	189	2.4
12	**2a** (0.2)	1.0 (5.0)	5	200		
13	**2a** (0.2)	2.0 (10.0)	3	90		
14	**2a** (0.2)	2.5 (12.5)	85	2,600	0.59	2.1
15	**2a** (0.2)	3.0 (15.0)	295	8,850	2.31	2.2
16	**2a** (0.2)	4.0 (20.0)	205	6,150	2.43	2.0
17	**2a** (0.2)	5.0 (25.0)	14	420		
18	**2b** (0.5)	1.0 (2.0)	181	2,170	35.1	1.9
19	**2b** (0.5)	2.0 (4.0)	278	3,340	21.3	2.3
20	**2b** (0.5)	3.0 (6.0)	217	2,600	16.3	2.3
21	**2b** (0.5)	4.0 (8.0)	81	970	13.4	2.2
22	**2b** (0.5)	5.0 (10.0)	103	1,240	13.5	2.0
23	**3a** (1.0)	1.0 (1.0)	20	120	0.79	2.8
24	**3a** (1.0)	2.0 (2.0)	24	140	0.56	2.0
25	**3a** (1.0)	3.0 (3.0)	108	648	0.49	2.0
26	**3a** (1.0)	4.0 (4.0)	125	750	0.50	1.9
27	**3a** (1.0)	5.0 (5.0)	86	520	0.40	2.0
28	**3b** (5.0)	3.0 (0.6)	65	78	2.33	4.2

[a] Conditions: toluene 30 mL, MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO) 1-5 mmol, ethylene 6 atm, 25 °C, 10 min. [b] Molar ratio of Al/M. [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] Low molecular weight shoulder was observed in small amount in the GPC trace. [e] High molecular weight shoulder was observed in small amount in the GPC trace.

The Ti-Ph analogue (**1a**) showed notable catalytic activities in the ethylene polymerization (runs 1-5), and the activity was somewhat higher than that by the Ti-^{i}Pr analogue (**1c**, run 11) under the same condition. As reported previously,[7c] the activities by the Ti-^{t}Bu analogue (**1b**) were lower (runs 6-10) than those by **1c**. The catalytic activities by **1a-b** were not strongly dependent upon the Al/Ti molar ratios employed, whereas the molecular weight distributions of the resultant polyethylenes by **1a** were affected by the Al/Ti molar ratios and polymerization temperature employed. As exemplified in Figure 2 (GPC charts in the resultant polyethylenes prepared, runs 1, 3, 5, and 30), peaks corresponding to trace or small amount of low molecular weight polymers were observed when the polymerizations were conducted at the high Al/Ti molar ratios (> 300,000) or at 55 ºC.

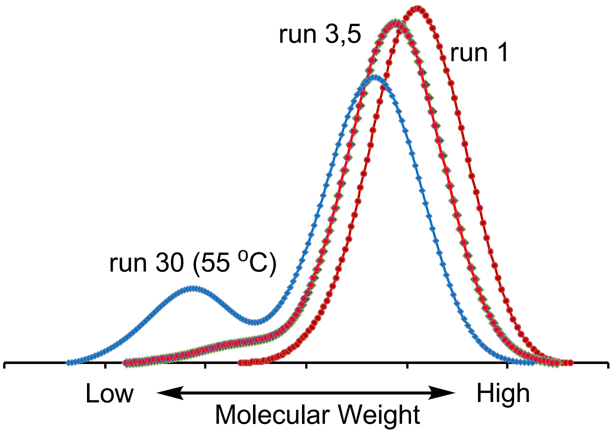


Figure 2. GPC traces for polyethylenes prepared by Cp*$TiCl_2(O\text{-}2,6\text{-}Ph_2C_6H_3)$ (**1a**)-MAO catalyst.

In contrast, the activity of the Zr-Ph analogue (**2a**) were sensitive toward the Al/Zr molar ratios employed (runs 12-17). The molecular weights in the resultant polymers prepared by the Zr and Hf analogues (**2-3,a-b**) were lower than those prepared by the Ti-Ph (**1a**) and Ti-^{i}Pr (**1c**) analogues (runs 12-28), although the polymers possessed unimodal molecular weight distributions.

Table 3 summarizes the results in the ethylene polymerization under various temperatures.

The catalytic activities of the Ti complexes (**1a**-**b**) decreased at higher temperature (40-55 ºC, runs 4, 9, 29-32), and significant decreases in the activities were observed in case of the Zr complex catalysts (**2a**-**b**, runs 15, 19, 33-36). In contrast, the activity of the Hf-Ph complex (**3a**) increased at higher temperature (40-55 °C, runs 26, 37-38).

Table 3. Ethylene polymerization by Cp*$MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Ti, R = Ph (**1a**), ^{t}Bu (**1b**); M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, R = Ph (**3a**)] - MAO catalyst systems: Effect of polymerization temperature.[a]

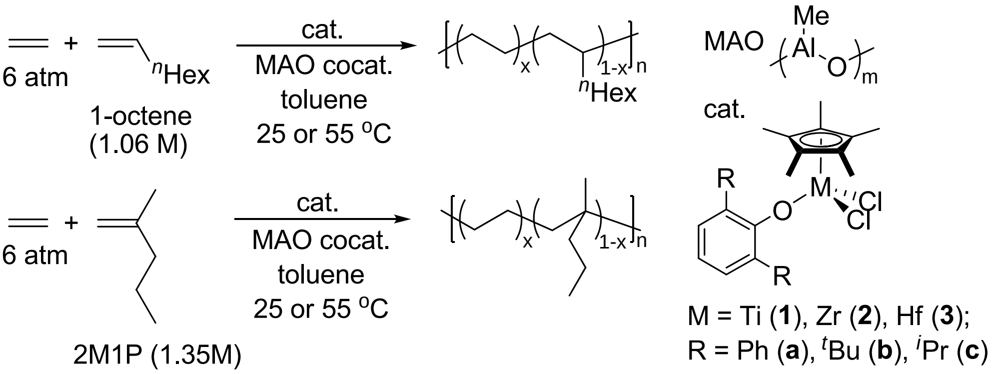
run	cat. ([μmol])	MAO [mmol] (Al/M)[b]	temp. [°C]	yield [mg]	activity [kg-PE/mol-M·h]	M_n[c] × 10^{-4}	M_w/M_n[c]
4	**1a** (0.01)	4.0 (400)	25	161	97,000	67.7[d]	2.9
29	**1a** (0.01)	4.0 (400)	40	88	53,000	61.1[d]	2.9
30	**1a** (0.01)	4.0 (400)	55	67	40,000	40.7[d]	3.2
9	**1b** (0.1)	4.0 (40.0)	25	140	8,400	2.67[e]	2.4
31	**1b** (0.1)	4.0 (40.0)	40	63	3,780	2.54[e]	2.2
32	**1b** (0.1)	4.0 (40.0)	55	82	4,920	2.32[e]	1.7
15	**2a** (0.2)	3.0 (15.0)	25	295	8,850	2.31	2.2
33	**2a** (0.2)	3.0 (15.0)	40	20	600	Insoluble	
34	**2a** (0.2)	3.0 (15.0)	55	15	450	Insoluble	
19	**2b** (0.5)	2.0 (4.0)	25	278	3,340	21.3	2.3
35	**2b** (0.5)	2.0 (4.0)	40	36	430	Insoluble	
36	**2b** (0.5)	2.0 (4.0)	55	37	440	Insoluble	
26	**3a** (1.0)	4.0 (4.0)	25	125	750	0.50	1.9
37	**3a** (1.0)	4.0 (4.0)	40	140	840	0.38	2.1
38	**3a** (1.0)	4.0 (4.0)	55	270	1,620	0.41	2.0

[a] Conditions : toluene 30 mL, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO) 1-5 mmol, ethylene 6 atm, 25 °C, 10 min. [b] Molar ratio of Al/M. [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] Low molecular weight shoulder was observed in small amount in the GPC trace. [e] High molecular weight shoulder was observed in small amount in the GPC trace.

Copolymerization of ethylene with 1-octene and 2-methyl-1-pentene by Cp*$MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$-MAO catalyst systems.

Copolymerizations of ethylene with 1-octene, and 2-methyl-1-pentene (2M1P) using a series of Cp*MCl_2(O-2,6-$R_2C_6H_3$) [M = Ti, R = Ph (**1a**), ^{t}Bu (**1b**), ^{i}Pr (**1c**); M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, R = Ph (**3a**)]-MAO catalysts were conducted at 25 °C and 55 °C (Scheme 3). The results are summarized in Table 4, and the OC[18] and 2M1P[12] contents in the resultant copolymers were estimated from ^{13}C NMR spectra according to the previous reports.

Scheme 3



It turned out that copolymerization of ethylene/1-octene using a series of Cp*MCl_2(O-2,6-$R_2C_6H_3$) (**1-2,a-b**, and **3a**)-MAO catalysts afforded the copolymers with unimodal molecular weight distributions (M_w/M_n = ca. 2) except **1b**. However, notable increases of activity in the copolymerization compared to the ethylene homopolymerization as seen in **1c**[9b-c, 12] were not observed in the other cases. Note that the 1-octene contents in the resultant copolymers were dependent upon the centered metal employed rather than the substituents on the aryloxo ligand, and the Ti complexes (**1a-c**) showed better 1-octene incorporations than the Zr and Hf analogues (**2a-b**, **3a**).

Table 4. Copolymerizations of ethylene with 1-octene (OC), 2-methyl-1-pentene (2M1P) by $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Ti (**1**), Zr (**2**), Hf (**3**); R = Ph (**a**), R = ^{t}Bu (**b**), ^{i}Pr (**c**)]-MAO catalyst systems.[a]

run	cat. ([μmol])	MAO [mmol] (Al/M ×10^{-3})[b]	comonomer [M]	temp. [°C]	yield [mg]	activity [kg-PE/mol-M·h]	M_n[c] ×10^{-4}	M_w/M_n[c]	comonomer[d] [mol%]
4	**1a** (0.01)	4.0 (400)	-	25	161	97000	67.0[e]	2.9	--
39	**1a** (0.01)	4.0 (400)	OC (1.06)	25	53	32000	4.70	1.9	27.0
40	**1a** (0.01)	4.0 (400)	OC (1.06)	55	trace	-	-	-	
41	**1a** (0.01)	4.0 (400)	2M1P (1.35)	25	trace	-	-	-	
42	**1a** (0.01)	4.0 (400)	2M1P (1.35)	55	222	133000	1.64	4.8	trace
9	**1b** (0.1)	4.0 (40.0)	-	25	140	8400	2.67[f]	2.4	--
43	**1b** (1.0)	4.0 (4.0)	OC (1.06)	25	68	410	3.86	3.8	27.8
44	**1b** (1.0)	4.0 (4.0)	OC (1.06)	55	127	762	3.70	3.3	34.3
45	**1b** (5.0)	4.0 (0.8)	2M1P (1.35)	25	99	120	1.50	5.6	trace
11	**1c** (0.01)	3.0 (300)	-	25	72	43200	189	2.4	--
46[g]	**1c** (0.02)	3.0 (150)	OC (1.06)	25	308	154000	12.8	2.1	27.9
47[h]	**1c** (0.5)	4.5 (9.0)	2M1P (1.35)	25	705	8460	11.8	2.1	3.3
15	**2a** (0.2)	3.0 (15.0)	-	25	295	8850	2.31	2.2	--
48	**2a** (0.2)	3.0 (15.0)	OC (1.06)	25	trace	-	-	-	
49	**2a** (0.2)	3.0 (15.0)	OC (1.06)	55	431	12900	1.41	2.2	3.2
50	**2a** (0.2)	3.0 (15.0)	2M1P (1.35)	25	24	720	insoluble		
51[i]	**2a** (0.1)	3.0 (30.0)	2M1P (1.35)	55	400	48000	194[j]	2.2	none
19	**2b** (0.5)	2.0 (4.0)	-	25	278	3340	21.3	2.3	--
52	**2b** (0.5)	2.0 (4.0)	OC (1.06)	25	263	3200	26.1	2.3	9.4
53	**2b** (0.5)	2.0 (4.0)	OC (1.06)	55	219	2600	1.24	2.9	15.9
54	**2b** (0.5)	2.0 (4.0)	2M1P (1.35)	25	150	1800	6.80	13	none
55	**2b** (0.5)	2.0 (4.0)	2M1P (1.35)	55	204	2450	156	2.4	
26	**3a** (1.0)	4.0 (4.0)	-	25	125	750	0.50	1.9	--
56	**3a** (1.0)	4.0 (4.0)	OC (1.06)	25	128	768	0.50	2.0	9.9
57	**3a** (1.0)	4.0 (4.0)	OC (1.06)	55	139	834	0.65	1.8	16.4
58	**3a** (1.0)	4.0 (4.0)	2M1P (1.35)	25	80	480	0.42	2.2	none
59	**3a** (1.0)	4.0 (4.0)	2M1P (1.35)	55	206	1240	0.32[f]	2.6	

[a] Conditions : toluene + 1-octene or 2M1P total 30 mL, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), ethylene 6 atm, 25 °C, 10 min. [b] Molar ratio of Al/M. [c] GPC data in *o*-dichlorobenzene vs polystyrene standard. [d] Comonomer content in copolymer (mol%) estimated by ^{13}C NMR spectra. [e] Low molecular weight shoulder was observed in small amount in the GPC trace [f] High molecular weight shoulder was observed in small amount in the GPC trace. [g] Cited from chapter 3 (run 8 in Table 1), polymerization 6 min. [h] Cited from chapter 2 (run 24 in Table 3). [i] Polymerization time 5 min. [j] Sample was hardly soluble even in hot *o*-dichlorobenzene (140 °C).

As shown in chapter 3, the Ti–^{i}Pr complex (**1c**) exhibited notable catalytic activity in ethylene/1-octene copolymerization (run 46) and the resultant copolymer possessed high molecular weight with unimodal molecular weight distribution (M_n = 128,000, M_w/M_n = 2.1). The 1-octene contents in the resultant copolymers prepared by **1a-b** were very close to that prepared by **1c** at 25 °C (runs 39, 43, 46). The activities in the copolymerization by **1a-b** were lower than these in ethylene polymerization, and the activity of **1a** dramatically decreased at 55 °C. Moreover, the M_n value in the copolymer prepared by **1a** at 25 °C was much lower than that in the polyethylene (runs 4 vs 39) and the resultant copolymers prepared by **1b** possessed broad molecular weight distributions (runs 43-44).

Both the catalytic activities and 1-octene contents in the copolymers by the Zr (**2a-b**) and Hf (**3a**) complexes increased at 55 ºC (runs 49, 53, 57) although the activities in the ethylene homopolymerization by the Zr analogues (**2a-b**) dramatically decreased at 55 °C (runs 15, 19, 26, 34). The Zr-^{t}Bu complex (**2b**) showed similar 1-octene incorporation with the Hf-Ph analogue (**3a**), however, these showed less efficient 1-octene incorporations than the Ti complexes (**1a-c**) under the same conditions. The Zr-Ph analogue (**2a**) showed the lowest 1-octene incorporation (run 49). No significant difference in the microstructures of the resultant copolymers prepared by the Ph analogues **1-3a** was observed (Figure 3), although some resonances were not seen owing to the low 1-octene contents in the copolymers prepared by **2-3a** and resonances ascribed to the polymer chain ends were seen owing to the low molecular weight in the copolymer by **3a**. These results suggest that the Ti analogues (**1a-c**) seem to be more suited as the catalyst precursors than the Zr and Hf analogues (**2a-b**, **3a**) in terms of both the activity and the 1-octene incorporation in the ethylene/1-octene copolymerization.

And it is reported that the Ti complexes also show more efficient comonomer incorporations compared with the Zr or Hf complexes in ethylene/propylene copolymerization using the group 4 metallocene of the type Cp_2MCl_2 (M = Ti, Zr, Hf)[19] and ethylene/1-octene copolymerization using bridged half-metallocene of the type $[Me_2Si(C_5Me_4)(N^tBu)]MCl_2$ (M

= Ti, Zr)[2b]. These facts indicate that Ti should be the most suitable metal center to design a new efficient group 4 catalyst for ethylene copolymerizations in term of comonomer incorporation.

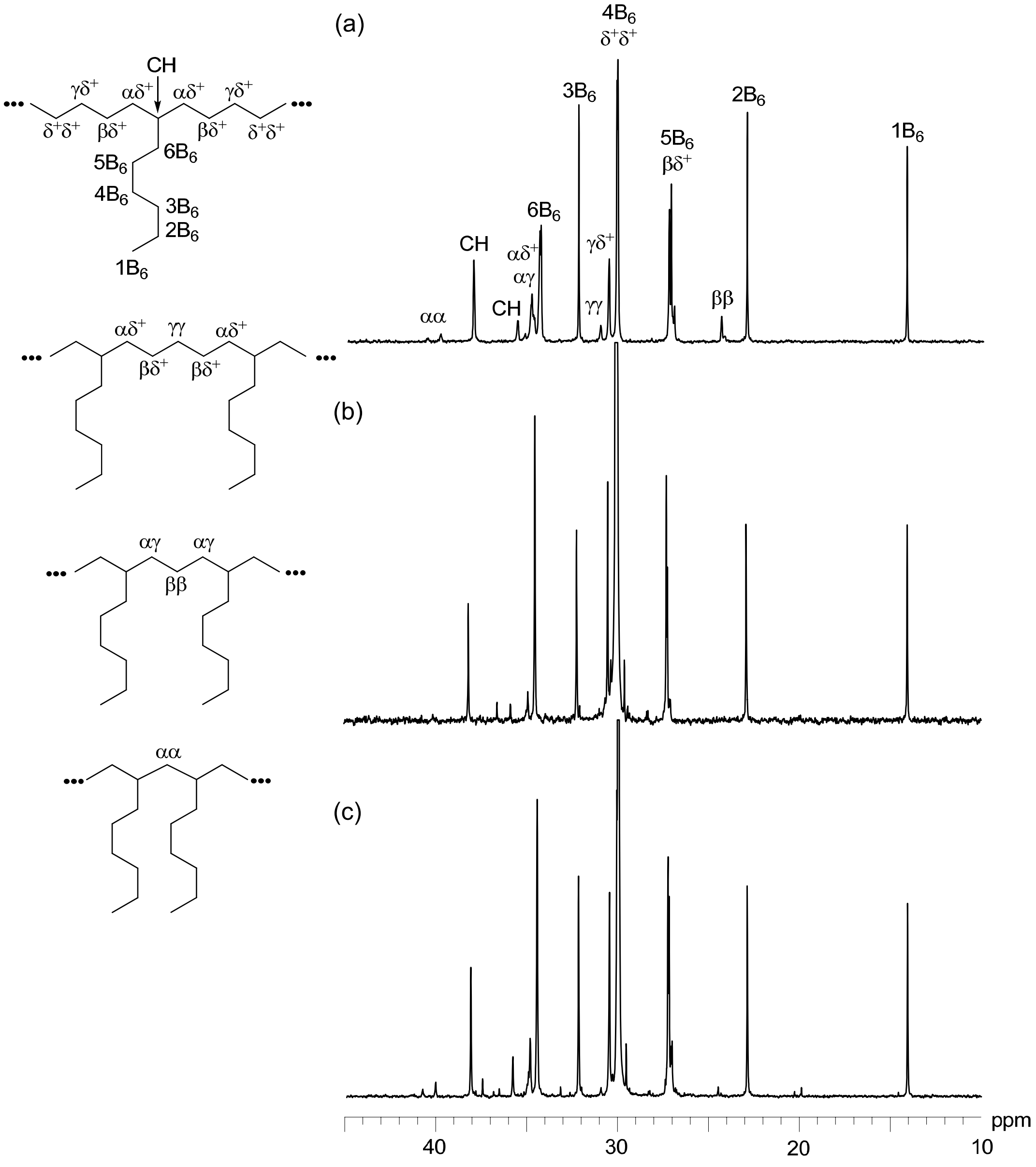


Figure 3. ^{13}C NMR spectra in C_6D_6/1,2,4-trichlorobenzene 1/4 (v/v) at 110 °C for poly(ethylene-*co*-1-octene)s prepared by $Cp^*MiCl_2(O\text{-}2,6\text{-}Ph_2C_6H_3)$-MAO catalysts [(a) M = Ti (**1a**, run 39), (b) M = Zr (**2a**, run 49), (c) M = Hf (**3a**, run 56)].

As revealed in the chapter 2, the Ti-^{i}Pr analogue **1c** showed high catalytic activity in the ethylene/2M1P copolymerization, and the resultant polymer was poly(ethylene-*co*-2M1P) that possessed rather high molecular weight with uniform molecular weight distribution (run 47, $M_n = 1.18\times10^5$, $M_w/M_n = 2.1$, 2M1P content = 3.3 mol%). In contrast, the 2M1P contents in the polymers prepared by the Ti-Ph and Ti-^{t}Bu analogues (**1a-b**) were negligible (runs 42, 45) although the **1a**-MAO exhibited much higher catalytic activity at 55 °C compared to 25 °C (runs 41-42). Moreover, the Zr and Hf analogues (**2a-b**, **3a**) afforded linear polyethylenes without 2M1P incorporation (run 51, 54, 58) in all cases. Taking into account of these results, the Ti-^{i}Pr (**1c**) analogue should be the most suited catalyst precursor for the copolymerization in terms of both the catalytic activity and the comonomer incorporation.

Conclusion

A series of $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Ti, R = Ph (**1a**), ^{t}Bu (**1b**), ^{i}Pr (**1c**); M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, R = Ph (**3a**), ^{t}Bu (**2b**)] were synthesized, and the effect of both the substituent in the aryloxo ligand and the centered metal on the catalytic activity as well as the comonomer incorporation in ethylene homo- and co-polymerization was explored using these complexes in the presence of MAO cocatalyst. The structures for **2-3,a-b** determined by X-ray crystallography were a rather distorted tetrahedral geometry around the metal centers. The catalytic activity in ethylene polymerization at 25 °C increased in the order: Ti > Zr > Hf, and the complexes containing 2,6-diphenylphenoxy ligand (**1-3a**) showed higher catalytic activities than the corresponding analogues containing 2,6-di-*tert*-butylphenoxy ligand (**1-3b**). The activities decreased at higher temperature except **3a**. The molecular weights in the resultant polymers prepared by the Zr and the Hf analogues (**2-3,a-b**) were lower than those prepared by the Ti-Ph (**1a**) and the Ti-^{i}Pr (**1c**) analogues. In the ethylene/1-octene copolymerization, both the catalytic activities and 1-octene incorporations were highly affected by the centered metal employed, and the resultant copolymers possessed uniform molecular weight distributions except **1b**. The Ti analogues (**1a-c**) exhibited much better 1-octene incorporations than the Zr and Hf analogues (**2a-b**, **3a**). The Ti-^{i}Pr analogue (**1c**) seems to be the most suited in terms of both the catalytic activity and the 1-octene incorporation. Moreover, only the Ti-^{i}Pr analogue (**1c**) efficiently incorporated 2M1P in the ethylene/2M1P copolymerization. The results indicate that both the Ti metal center and the ^{i}Pr group on the aryloxo ligand should be essential for the efficient copolymerization. Thus, I believe that the introduction of electron donating or withdrawing groups at 4-position in 2,6-diisopropylphenoxy ligand in $Cp^*TiX_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ would be a promising approach for more efficient catalysts for the ethylene copolymerizations.

Experimental Section

General procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous grade toluene and *n*-hexane (Kanto Chemical Co., Inc.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Anhydrous dichloromethane and diethyl ether (Kanto Chemical Co., Inc.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16). Cp*$ZrCl_3$ (Aldrich) and Cp*$HfCl_3$ (Aldrich) were used as received. Cp*$TiCl_3$,[20] Cp*$TiCl_2$(O-2,6-$Ph_2C_6H_3$) (**1a**),[16] Cp*$TiCl_2$(O-2,6-$^tBu_2C_6H_3$) (**1b**)[7c] Cp*$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (**1c**)[7a] and Cp*$ZrCl_2$(O-2,6-$^tBu_2C_6H_3$) (**2b**)[15] were prepared according to the publish procedures.

Ethylene of polymerization grade (Sumitomo Seika Chemicals Co., Ltd.) was used as received without further purification procedures. 1-Octene (Wako Pure Chemical Ind., Ltd.) and 2-methyl-1-pentene (TCI Co., Ltd.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 ºC for removing toluene, $AlMe_3$, and then heated at >100 ºC for 1 h for completion) in the drybox to give white solids.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^1H and 100.53 MHz for ^{13}C). All spectra were obtained in the solvents indicated at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C). ^{13}C NMR spectra for polyethylenes, poly(ethylene-*co*-1-octene)s and poly(ethylene-*co*-2-methyl-1-pentene)s were measured at 110 ^oC in C_6D_6/1,2,4-trichlorobenzene (1/4 v/v). The relaxation delay was 5.2 sec, the acquisition time was 1.3 sec, the pulse angle was 90^o, and the number of transients accumulated was ca. 6000.

Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.), and some analytical runs were performed twice to confirm the reproducibility in the independent analysis/synthesis runs. Certain C values were somewhat lower than those calculated, whereas their N, H, values were close; this is due to incomplete combustion (to form titanium carbide).

Molecular weights and molecular weight distributions for the polyethylenes poly(ethylene-*co*-2-methyl-1-pentene)s and poly(ethylene-*co*-1-octene)s were measured by a gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH$_{HR}$-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $< 2.8\times10^8$ MW at 140 ºC using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weights were calculated by a standard procedure based on the calibration with standard polystyrene samples.

Synthesis of Cp*ZrCl$_2$(O-2,6-Ph$_2$C$_6$H$_3$) (2a). Into a toluene/*n*-hexane suspension containing Cp*ZrCl$_3$ (303 mg, 0.910 mmol), LiO-2,6-Ph$_2$C$_6$H$_3$ (234 mg, 0.928 mmol) was added at -30 ^{o}C. The reaction mixture was warmed slowly up to room temperature, and the mixture was stirred for 5 hour. The solvent was removed *in vacuo* after addition of CH_2Cl_2, and the resultant residue was extracted with hot toluene. The toluene extract was then removed *in vacuo* to give a pale yellow solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled solution gave colorless crystal. Yield: 359 mg (72.7%). ^{1}H NMR (CDCl$_3$): δ 7.55 (d, 4H, *J* = 8.1), 7.44 (t, 4H, *J* = 7.5), 7.32 (t, 2H, *J* = 7.3), 7.27 (d, 2H, *J* = 7.7), 7.11 (t, 1H, *J* = 7.5), 1.57 (s, 16H). ^{13}C NMR (CDCl$_3$): δ. 154.9, 138.8, 133.3, 130.4, 130.3, 128.9, 127.1, 126.2, 122.3, 10.9. Anal. Calcd. for $C_{28}H_{28}Cl_2ZrO$: C, 61.97; H, 5.20; N, 0%. Found: C, 61.20; H, 5.31; N, 0%.

Synthesis of Cp*HfCl$_2$(O-2,6-Ph$_2$C$_6$H$_3$) (3a). To a toluene solution (10 mL) containing Cp*HfCl$_3$ (506 mg, 1.20 mmol), LiO-2,6-Ph$_2$C$_6$H$_3$ (313 mg, 1.24 mmol) was added at -30 ^{o}C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for additional 12 hour. The solvent was removed in *vacuo* after addition of CH_2Cl_2, and the resultant white tan residue was extracted with hot toluene. The toluene extract was then dried *in vacuo*, and the resulting white was dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled solution gave colorless crystal. Yield 430 mg (56.7 %). ^{1}H NMR ($CDCl_3$): δ 7.52 (dd, 4H, *J* = 7.5, 1.4), 7.41 (t, 4H, *J* = 7.5), 7.31 (tt, 2H, *J* = 7.5, 1.4), 7.26 (d, 2H, *J* = 7.4), 7.08 (t, 1H, *J* = 7.4), 1.61 (s, 15H). ^{13}C NMR ($CDCl_3$): δ 154.9, 138.3, 133.4, 130.4, 130.3, 128.8, 127.1, 123.8, 122.1, 10.7. Anal. Calcd. for $C_{28}H_{28}Cl_2HfO$: C, 53.39; H, 4.48; N, 0%. Found: C, 52.62; H, 4.27; N, 0.05%.

Synthesis of Cp*HfCl$_2$(O-2,6-^{t}Bu$_2$C$_6$H$_3$) (3b). Synthesis of **3b** was carried out by the same procedure as that for **1b** except that Cp*HfCl$_3$ (250 mg, 0.595 mmol), LiO-2,6-^{t}Bu$_2$C$_6$H$_3$ (132 mg, 0.622 mmol) and Et_2O as solvent were used. Yield: 94 mg (27%). ^{1}H NMR ($CDCl_3$): δ 7.19 (d, 2H, *J* = 7.7 Hz), 6.82 (t, 1H, *J* = 7.7 Hz), 2.10 (s, 15H), 1.37 (s, 18H). ^{13}C NMR ($CDCl_3$): δ. 160.6, 139.2, 125.5, 124.8, 120.8, 35.3, 31.9, 12.2. Anal. Calcd. for $C_{24}H_{36}Cl_2HfO$: C, 48.86; H, 6.15; N, 0%. Found: C, 49.12; H, 6.25; N, 0.10%.

Ethylene homopolymerization and copolyemerizations with 1-octene or 2-methyl-1-pentene (2M1P) in the presence of MAO cocatalyst. A typical reaction procedure for ethylene homopolymerization (run 1, Table 1) is as follows. Toluene (29 mL), and MAO solid (58 mg, 1.0 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 ºC. A toluene solution (1.0 mL) containing **1a** (0.01 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 5 atm (total ethylene pressure 6 atm). The mixture was magnetically stirred for 10 min, the remaining ethylene was purged after the reaction, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo* at 60^{o}C. Basic experimental procedures in ethylene/1-octene and ethylene/2M1P copolymerizations were the same as that in the ethylene homopolymerization except that 1-octene or 2M1P (5 mL) were added in place of toluene partially (total 29 mL).

Crysllographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. Suitable single crystals of **2a-b** and **3a-b** were prepared from CH_2Cl_2/*n*-hexane solution at -30 °C. The selected crystal collection parameters are summarized in Table 5. All structures were solved by direct methods and expanded using Fourier techniques,[21] and the non-hydrogen atoms were included but not refined. All calculations for complexes were performed using the Crystal Structure [22] crystallographic software package.

Table 5. Crystal and data collection parameters for $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Zr, R = Ph (**2a**), ^{t}Bu (**2b**); M = Hf, Ph (**3a**), ^{t}Bu (**3b**)].[a]

Complex (M, R)	**2a** (Zr, Ph)	**2b** (Zr, ^{t}Bu)	**3a** (Hf, Ph)	**3b** (Hf, ^{t}Bu)
Formula;	$C_{28}H_{28}Cl_2OZr$;	$C_{24}H_{36}Cl_2OZr$;	$C_{28}H_{28}Cl_2HfO$;	$C_{24}H_{36}Cl_2HfO$;
Formula weight	542.65	502.67	629.92	589.94
Habits	colorless, block	colorless, block	colorless, block	colorless, block
Crystal size (mm)	0.35 × 0.1 ×0.15	0.40 × 0.30 × 0.18	0.30 × 0.25 × 0.18	0.40 × 0.40 ×0.30
Crystal system	monoclinic	monoclinic	monoclinic	monoclinic
Space group	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)	$P2_1/n$ (#14)
a (Å)	9.0510(3)	9.6805(4)	9.0287(3)	9.6678(3)
b (Å)	7.5984(2)	15.5345(5)	7.61072(18)	15.5309(4)
c (Å)	36.2051(10)	17.0748(5)	36.2190(8)	17.0507(4)
β (deg)	93.0128(12)	107.1917(11)	92.9237(12)	107.1726(8)
V ($Å^3$)	2486.51(13)	2453.01(15)	2485.54(12)	2446.02(11)
Z value	4	4	4	4
D_{calcd} (g/cm^3)	1.449	1.361	1.683	1.602
F_{000}	1112.00	1048.00	1240.00	1176.00
Temp (K)	193	193	193	193
μ (Mo Kα) (cm^{-1})	6.747	6.773	44.223	44.871
No. of reflns measd	Total: 33034 Unique: 5624 R_{int} = 0.027	Total: 23994 Unique: 5594 R_{int} = 0.020	Total: 19782 Unique: 5361 R_{int} = 0.026	Total: 19523 Unique: 4464 R_{int} = 0.042
No. of observations ($I > -3.00\delta(I)$)	4870	5117	4823	4327
No. of variables	317	289	317	289
Residuals: R1; Rw	0.0290; 0.0891	0.0209; 0.0719	0.0195; 0.0529	0.0261; 0.073
GOF	1.004	1.009	1.006	1.008
Max (minimum) peak in final diff. map (e-/ $Å^3$)	0.55 (-0.61)	0.30 (-0.35)	0.99 (-0.84)	0.80 (-2.53)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (*w* = Least squares weights, Chebychev polynomial). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (No = number of observations, N_v = number of variables).

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Chapter 5

Synthesis of hydrotris(pyrazolyl)borate titanium complexes containing an aryloxo ligand and their use for ethylene polymerization

Introduction

Design and synthesis of efficient transition metal complex catalysts for olefin coordination polymerization have attracted considerable attention in the fields of oganometallic chemistry and polymer chemistry.[1-3] As described in chapter 1-4, nonbridged half-titanocenes containing an anionic donor ligand of type Cp'TiX_2(Y) [Cp' = cyclopentadienyl; X = halogen, alkyl; Y = aryloxo, ketimide], have been one of the promising catalysts for precise synthesis of new ethylene copolymers.[3b]

Tris(pyrazolyl)borate (Tp') ligands have been considered as one of the most promising alternative of Cp' ligands because they are the same mono-anionic 5-electron donors with Cp' ligands, and their electronic and steric properties are tunable by introduction of substituents on the pyrazolyl rings.[4-5] Additionally, the strong σ-electron donor property of Tp' is expected to stabilize the catalytically active species and the Tp' complexes would fold octahedral geometry that may form a more suitable steric environment for insertion than tetrahedral geometry like the Cp' analogues.[4-5]

It is known that group 4 metal tris(pyrazolyl)borate complexes, Tp'MCl_3 [M = Ti, Zr, Hf; Tp' = Tp^{Mes} = HB(3-mesitylpyrazolyl)$_3$], Tp^{Mes*} = HB(3-mesitylpyrazolyl)$_2$(5-mesitylpyrazolyl)], exhibited high catalytic activity for ethylene polymerization in the presence of methylaluminoxane (MAO),[6] and the cationic alkyl species, generated from Tp*Zr$(CH_2Ph)_3$ [Tp* = HB(3,5-Me_2-pyrazolyl)$_3$] or $Tp^{Mes*}Hf(CH_2Ph)_3$ with $[Ph_3C][B(C_6F_5)]$, polymerize ethylene.[7] And, the effect of substituents in Tp' ligand on the ethylene polymerization behavior by Tp'$TiCl_3$-MAO catalysts was also known.[6,8-9] In contrast, examples for olefin polymerization using group 4 metal Tp’ complexes containing an anionic donor ligand of the type Tp’MX$_2$(Y) have been limited,[6e,8-9] although these are highly expected to be efficient olefin polymerization catalysts like Cp’TiX$_2$(Y). Especially, studies including structural analysis and effect of ligand on the activity in olefin polymerization as well as isolation of thermal stable cationic alkyl complex have never been reported so far.

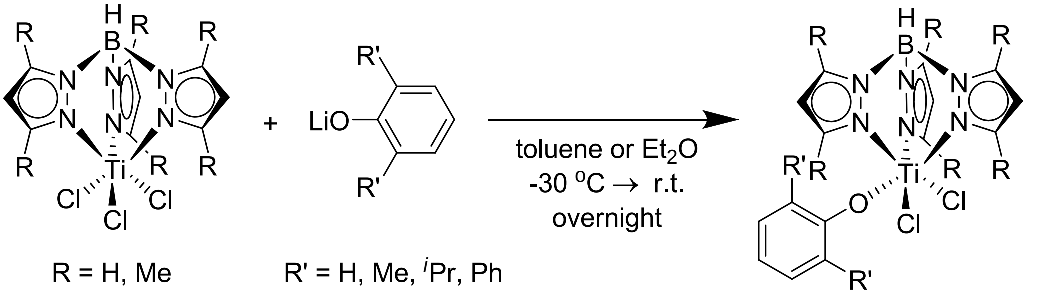
This chapter describes synthesis and structural analysis of a series of Tp’TiX$_2$(OAr) [OAr = aryloxo], and their use in ethylene polymerization including isolation of stable cationic alkyl complex.

Results and Discussion

Synthesis and structural analysis of tris(pyrazolyl)borate Ti(IV) dichloride complexes containing aryloxo ligands , Tp’TiCl$_2$(O-2,6-R’$_2$C$_6$H$_3$).

A series of hydrotris(pyrazoly)borate(aryloxo)titanium (IV) dichloro complexes of the type Tp’TiCl$_2$(O-2,6-R’$_2$C$_6$H$_3$) [Tp’ = HB(pyrazolyl)$_3$ = Tp, R’ = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**); Tp = Tp*, R’ = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)], were synthesized by treating TpTiCl$_3$ or Tp*TiCl$_3$ with LiOAr in toluene or Et$_2$O (Scheme 1). These complexes were isolated in 56-88% yields and were identified by ^{1}H and ^{13}C NMR spectra, elemental analyses, and all their structures were determined by single crystal X-ray crystallography. **1a-b**, **2a** were isolated as CH$_2$Cl$_2$ or toluene adducts and the solvent molecules per titanium were estimated on the basis of both the ^{1}H NMR spectra and elemental analyses.

Scheme 1



R = H, R' = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**);
R = Me, R' = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)

Suitable single crystals for X-ray crystallographic analysis were grown from chilled CH_2Cl_2/*n*-hexane solution containing **1a-d**, **2b-d** and from chilled toluene containing **2a**. The determined structures are shown in Figure 1 and the selected bond distances and angles are summarized in Table 1-2. These complexes fold a rather distorted octahedral geometry around the Ti and the two Cl atoms are placed in *cis*-form. The Ti-O bond distances in the Tp analogues (**1a-d**) [**1a** 1.7667(12), **1b** 1.764(2), **1c** 1.7687(15), **1d** 1.7944(12) Å] are somewhat shorter than those in the corresponding Tp* analogues (**2a-d**) [**2a** 1.773(2), **2b** 1.7752(8), **2c** 1.7820(15), **2d** 1.7941(18) Å]. These distances are longer than that in $Tp^*TiCl_2(O^tBu)$ [1.741(2) Å][6b] and are similar with that in $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ [1.772(3) Å].[10] These findings suggest that electron donation of the aryloxo ligands to the Ti metal centers should be weaker than that of the alkoxo ligand. The Ti-Cl bond distances in the Tp analogues (**1a-d**) are also slightly shorter than the corresponding Tp* analogues (**2a-d**), and those in Tp* analogues are somewhat longer than that in Tp^*TiCl_3 [Ti-Cl(1) = 2.258(1), Ti-Cl(2) = 2.271 Å].[11] In these complexes (**1a-d**, **2a-d**), the Ti-N(2) bond distances positioning *trans* to the aryloxo ligands are longer than the Ti-N(4) and Ti-N(6) bond distances positioning *cis* due to *trans* influence of the aryloxo ligands.

The Ti-O-C (phenyl) angles in **1a-c** and **2b-d** [168.65(17)-175.70(10)] are similar with that in $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ [173.0(3)°],[10] whereas the angles in **1d** and **2a** are somewhat small [**1a** 149.69(11)°, **2a** 159.2(2)°]. The Cl(1)-Ti-Cl(2) angles in the Tp* analogues (**2a-d**) decreased with increasing steric bulk of the substituents of the aryloxo ligands, whereas these in the Tp analogues increased in the order: **1d** < **1a** < **1c** < **1b**.

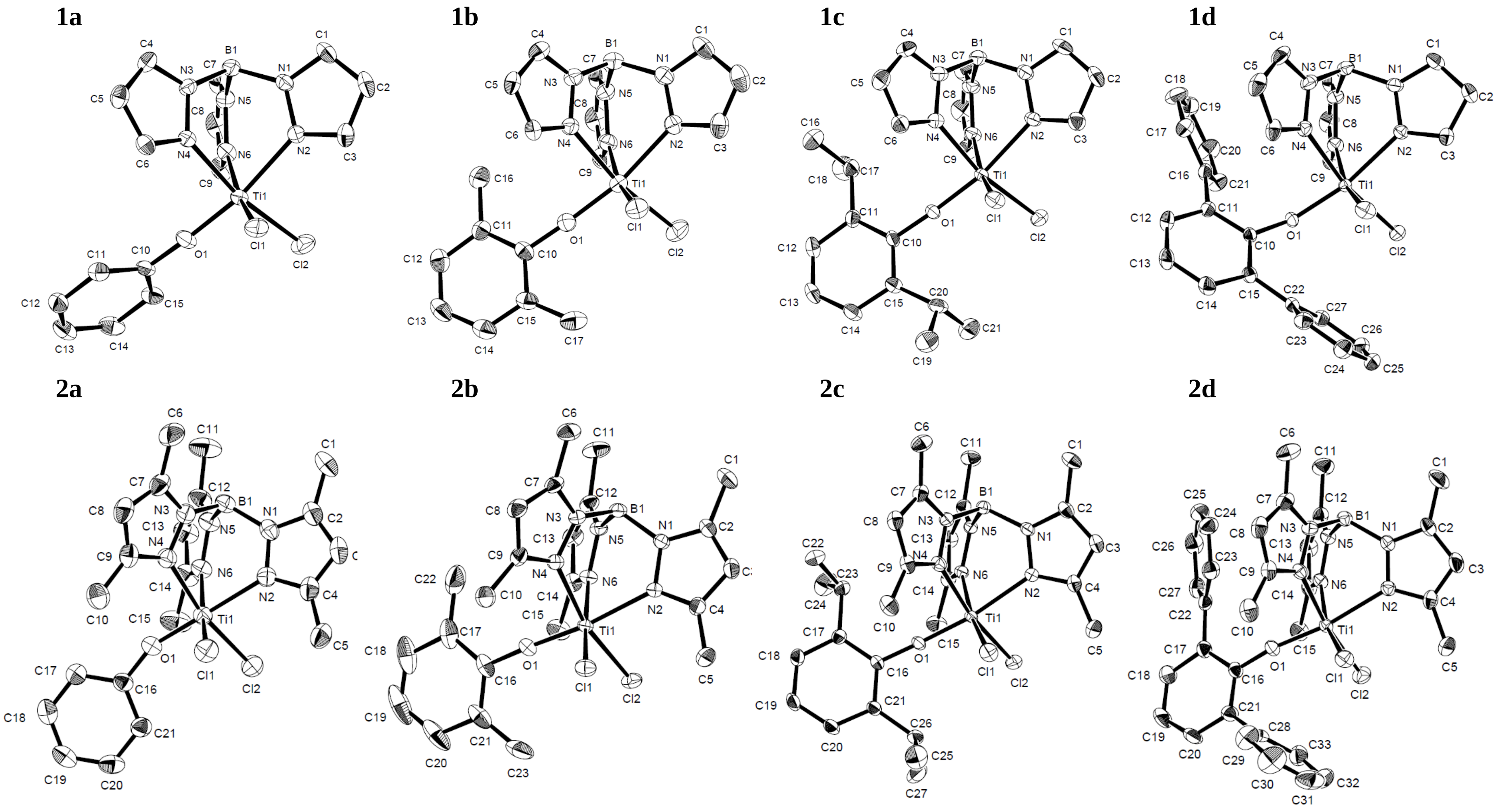


Figure 1. ORTEP drawings for Tp’TiCl$_2$(O-2,6-R’$_2$C$_6$H$_3$) [top: Tp’ = Tp, R’ = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**); bottom: Tp’ = Tp*, R’ = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 1. Selected bond distances (Å) and angles (^{o}) for TpTiCl$_2$(O-2,6-R'$_2$C$_6$H$_3$) [R' = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**)].

Complex (R')	**1a** (H)	**1b** (Me)	**1c** (^{i}Pr)	**1d** (Ph)
Selected bond distances (Å)				
Ti(1)-Cl(1)	2.2895(5)	2.2932(10)	2.2867(5)	2.2734(5)
Ti(1)-Cl(2)	2.2958(6)	2.3034(9)	2.2918(6)	2.2996(4)
Ti(1)-O(1)	1.7667(12)	1.764(2)	1.7687(15)	1.7940(12)
Ti(1)-N(2)	2.1882(14)	2.184(2)	2.1890(18)	2.1975(14)
Ti(1)-N(4)	2.1481(16)	2.153(2)	2.1550(19)	2.1484(15)
Ti(1)-N(6)	2.1734(15)	2.157(2)	2.1690(16)	2.1428(15)
Selected bond angles (^{o})				
Ti(1)-O(1)-C(Phe)	170.86(11)	174.59(18)	173.52(11)	149.69(11)
Cl(1)-Ti(1)-Cl(2)	97.20(2)	98.02(3)	97.98(2)	96.671(19)
Cl(1)-Ti(1)-O(1)	97.83(4)	97.84(7)	97.53(4)	96.65(4)
Cl(2)-Ti(1)-O(1)	96.94(5)	98.27(7)	99.00(5)	100.33(4)
N(2)-Ti(1)-N(4)	80.98(5)	81.02(9)	80.22(7)	79.75(5)
N(2)-Ti(1)-N(6)	80.12(5)	80.22(9)	80.55(6)	79.73(5)
N(4)-Ti(1)-N(6)	81.66(6)	81.96(8)	81.59(6)	83.09(5)
N(2)-Ti(1)-O(1)	169.71(5)	169.89(9)	170.18(7)	168.98(5)
N(4)-Ti(1)-O(1)	91.76(6)	89.94(9)	91.20(7)	89.52(5)
N(6)-Ti(1)-O(1)	91.67(5)	94.09(9)	93.56(6)	96.60(5)

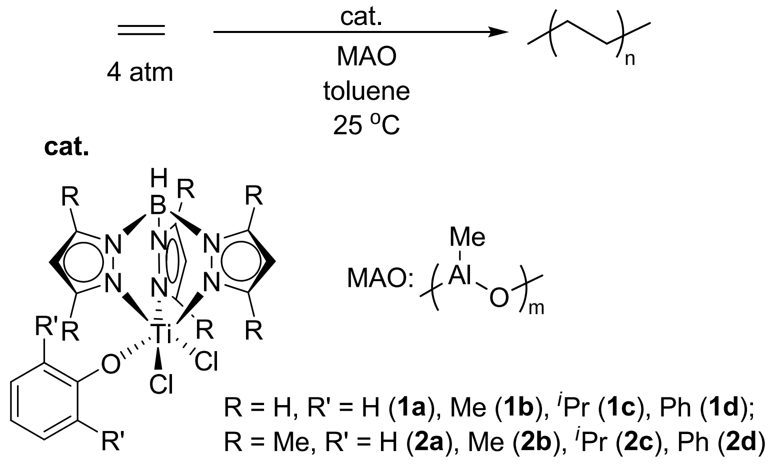
Table 2. Selected bond distances (Å) and angles (^{o}) for Tp*TiCl$_2$(O-2,6-R'$_2$C$_6$H$_3$) [R' = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)].

Complex (R')	**2a** (H)	**2b** (Me)	**2c** (^{i}Pr)	**2d** (Ph)
Selected bond distances (Å)				
Ti(1)-Cl(1)	2.3216(10)	2.3070(4)	2.3057(5)	2.2883(7)
Ti(1)-Cl(2)	2.3164(9)	2.3097(4)	2.3089(5)	2.2849(8)
Ti(1)-O(1)	1.773(2)	1.7752(8)	1.7820(15)	1.7941(18)
Ti(1)-N(2)	2.214(2)	2.2132(10)	2.2240(19)	2.215(2)
Ti(1)-N(4)	2.136(2)	2.1672(12)	2.1747(13)	2.162(2)
Ti(1)-N(6)	2.155(2)	2.1697(11)	2.1461(16)	2.182(2)
Selected bond angles (^{o})				
Ti(1)-O(1)-C(Phe)	159.2(2)	175.70(10)	171.45(10)	168.65(17)
Cl(1)-Ti(1)-Cl(2)	97.82(3)	96.709(13)	95.90(2)	95.23(3)
Cl(1)-Ti(1)-O(1)	93.89(7)	95.34(3)	96.89(5)	100.33(6)
Cl(2)-Ti(1)-O(1)	93.66(7)	96.96(3)	97.39(4)	95.44(6)
N(2)-Ti(1)-N(4)	84.23(9)	81.70(4)	83.06(5)	83.00(8)
N(2)-Ti(1)-N(6)	84.59(9)	83.96(4)	82.31(6)	79.63(8)
N(4)-Ti(1)-N(6)	80.61(9)	83.00(4)	83.38(5)	84.78(8)
N(2)-Ti(1)-O(1)	179.14(9)	173.01(4)	172.35(5)	171.24(8)
N(4)-Ti(1)-O(1)	95.62(10)	93.73(4)	90.80(6)	91.82(8)
N(6)-Ti(1)-O(1)	94.55(9)	90.25(4)	92.50(6)	92.90(8)

Ethylene polymerization by Tp'$TiCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$-MAO catalyst systems.

Ethylene polymerization using Tp'$TiCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ (**1a-d**, **2a-d**) was conducted at 25 °C in the presence of dried MAO (Scheme 2) and the results are summarized in Table 3.

Scheme 2



R = H, R' = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**);
R = Me, R' = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)

$TpTiCl_2(OPh)$ (**1a**) exhibited notable high catalytic activities under the optimized Al/Ti molar ratios [48,700-73,200 kg-PE/mol-Ti·h (runs 7, 10, 12)], and the activities were highly dependent on the Al/Ti molar ratios employed (runs 1-9). A significant decrease of the catalytic activity was observed at 40 °C (runs 10-11). Note that the activity of **1a** was comparable to that of Cp_2ZrCl_2 (runs 12, 34) and was 4 times higher than that of $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (runs 7, 33) under the much lower Al/Ti molar ratio (200 vs 30000). The activities of **1b-d** and **2a-d** under the optimized conditions were much lower than that of **1a** (90-645 kg-PE/mol-Ti·h, runs 13, 17-18, 20, 25, 29-30). The M_w/M_n values in the resultant polymers were broad and the values were highly dependent on the Al/Ti molar ratios employed. These results suggest that several catalytically active species would be generated in the presence of excess MAO. In contrast, the resultant polyethylenes prepared by **1a** under the optimized Al/Ti molar ratios possessed unimodal molecular weight distributions (runs 7, 10, Figure 2), suggesting that the polymerization should proceed with a single catalytically active species under these optimized conditions.

Table 3. Ethylene polymerization by Tp'$TiCl_2(O-2,6-R'_2C_6H_3)$ [Tp' = Tp, R' = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**); Tp' = Tp*, R' = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)]-MAO catalyst systems: Effect of Al/Ti molar ratio.[a]

run	cat. ([μmol])	Al/Ti[b]	yield [mg]	activity[c]	M_w[d] x 10^{-4}	M_w/M_n[d]
1[e]	**1a** (2.0)	100	507[g]	5,070	156	8.4
2	**1a** (2.0)	250	164	492		
3	**1a** (2.0)	500	175	525		
4	**1a** (2.0)	1000	127	381		
5	**1a** (2.0)	1500	60	180		
6	**1a** (0.1) [f]	100	138	16,600	182	7.3
7	**1a** (0.1) [f]	200	459	55,100	229	2.9
8	**1a** (0.1) [f]	300	442	53,000	182	5.9
9	**1a** (0.1) [f]	400	96	12,000	133	6.2
10	**1a** (0.05) [f]	400	203	48,700	221	2.9
11	**1a** (0.05) [k]	400	32	3,800	108	3.6
12	**1a** (0.01)	2000	122	73,200	132	4.2
13	**1b** (2.0)	100	92	280	96.3	20
14	**1b** (2.0)	250	95	280	62.5	8.8
15	**1b** (2.0)	500	61	180	56.0	27
16	**1b** (2.0)	1000	48	140		
17	**1b** (2.0)	1500	49	150		
18	**1c** (2.0)	100	55	330	82.5	168
19	**1d** (2.0)	100	160	480	103	24
20	**2a** (2.0)	100	147	441	42.7	118
21	**2a** (2.0)	250	215	645	33.0	57
22	**2a** (2.0)	500	136	408	29.4	36
23	**2a** (2.0)	1000	42	130	37.7	48
24	**2a** (2.0)	1500	17	51		
25	**2b** (2.0)	100	97	240	49.8	69
26	**2b** (2.0)	250	138	414	38.3	40
27	**2b** (2.0)	500	118	354	38.5	26
28	**2b** (2.0)	1000	20	60	43.4	19
29	**2b** (2.0)	1500	20	60		
30	**2c** (2.0)	250	34	100	79.8	189
31	**2d** (2.0)	250	30	90	34.8	61
32	**Ti**[h] (0.1)	10000	145	7,250	232[j]	3.0[j]
33	**Ti**[h] (0.1)	30000	205	12,300	293[j]	2.9[j]
34	**Zr**[i] (0.01)	300000	134	80,400		

[a] Conditions: MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), toluene 30 mL, ethylene 4 atm, 25 °C, 10 min. [b] Molar ratio of Al/Ti. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polyethylene standard. [e] Polymerization time 3 min. [f] Polymerization time 5 min. [g] Stirring was stopped due to aggregation of polymer to the stirrer tip. [h] $Cp^*TiCl_2(O-2,6-{}^iPr_2C_6H_3)$. [i] Cp_2ZrCl_2. [j] GPC data in *o*-dichlorobenzene vs polystyrene standard. [k] 40 °C.

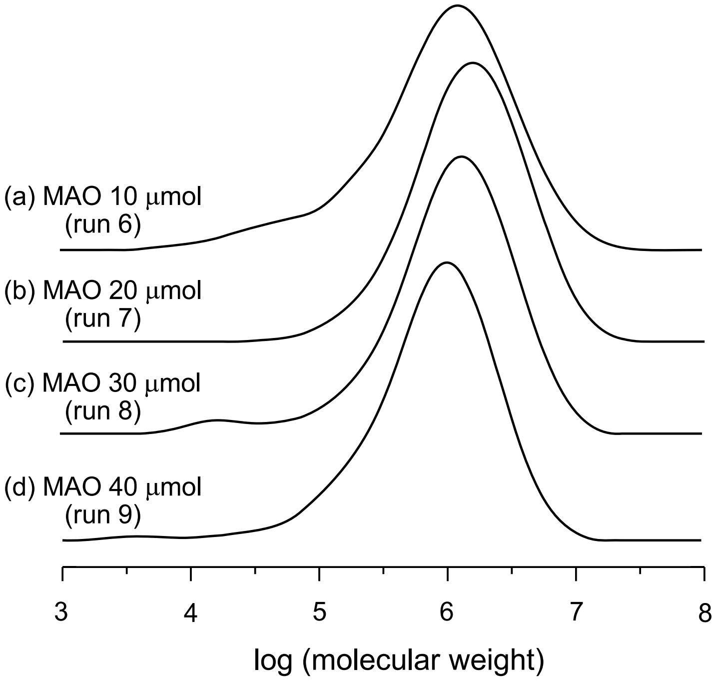


Figure 2. GPC traces of polyethylenes prepared by **1a**-MAO catalyst system. The detailed conditions and results are shown in Table 4.

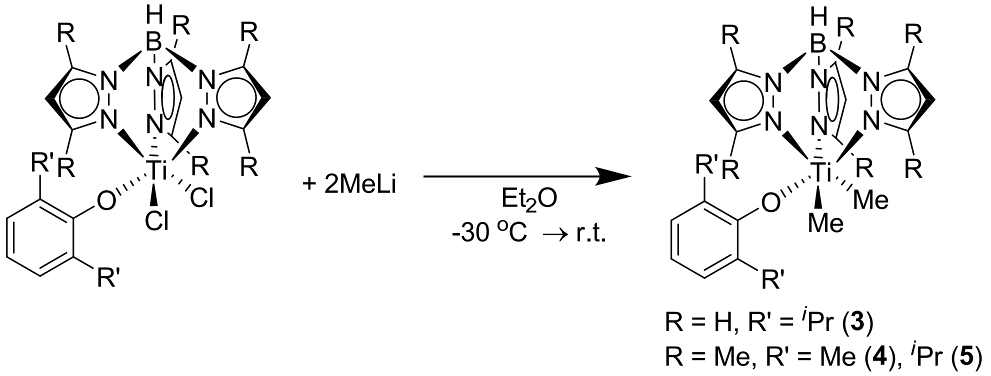
Synthesis and structural analysis of dialkyl complexes, Tp'TiR"$_2$(O-2,6-R'$_2$C$_6$H$_3$), and isolation of the cationic Ti(IV) alkyl complexes, [Tp'TiR"$_2$(O-2,6-R'$_2$C$_6$H$_3$)]$^+$.

Identification of catalytically active species is an essential process both to consider polymerization mechanism and to design efficient catalysts. It is widely known that cationic alkyl species has been proposed to be a catalytically active species in group 4 metal complex catalysts, which are usually synthesized from its di- or trialkyl analogues by reacting with boranes and borates.[2c] Therefore, synthesis and isolation of the dialkyl complexes, Tp'TiR"$_2$(O-2,6-R'$_2$C$_6$H$_3$), and the cationic alkyl complexes, Tp'Ti$^+$R"(O-2,6-R'$_2$C$_6$H$_3$), were investigated.

Syntheses of a series of dimethyl complexes of the type Tp'TiMe$_2$(O-2,6-R'$_2$C$_6$H$_3$) were attempted by treating Tp'TiCl$_2$(O-2,6-R'$_2$C$_6$H$_3$) (**1a-d, 2a-d**) with 2 equivalent of MeLi in Et$_2$O (Scheme 3). The three dimethyl complexes, Tp'TiMe$_2$(O-2,6-R'$_2$C$_6$H$_3$) [Tp' = Tp, R' =

^{i}Pr (**3**); Tp = Tp*, R' = Me (**4**), ^{i}Pr (**5**)], were able to be prepared by the reaction and were identified by ^{1}H and ^{13}C NMR spectra, elemental analyses, and all their structures were determined by single crystal X-ray crystallography. In contrast, other dimethyl analogues have not been able to be prepared by the procedure and attempts for isolation of the dimethyl analogues from **2a** by treatments with MeMgBr, $ZnMe_2$, and $SnMe_4$ were also unsuccessful at this moment.

Scheme 3



Suitable single crystals for X-ray crystallographic analysis were grown from chilled Et_2O containing **3-5**. The determined structures are shown in Figure 3, and the selected bond distances and angles are summarized in Table 4. These crystal structures fold a rather distorted octahedral geometry around Ti, and the two methyl groups are placed in *cis*-form. The Ti-C bond distances and the C(1)-Ti-C(2) bond angle in the Tp analogue (**3**) are similar with those in the Tp* analogues (**4-5**). The Ti-O bond distances and the Ti-O-C(phenyl) angles in **3-5** are similar with those in the corresponding dichloro complexes (Table 1-2, **1c**, **2b-c**). The Ti-N(2) bond distances positioning *trans* to the aryloxo ligands in **3-5** are close to the Ti-N(4) and Ti-N(6) bond distances positioning *cis*, although the Ti-N(2) bond distances in the dichloro analogues (**1c**, **2b-c**) are longer than the other Ti-N bond distances. This result suggests that the methyl groups may exhibit similar *trans* influence with the aryloxo groups.

In comparison to Cp'$TiMe_2$(O-2,6-$^{i}Pr_2C_6H_3$) [Cp' = Cp (**A**), Cp* (**B**)], Tp'TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Tp' = Tp (**3**), Tp* (**5**)], had the similar Ti-C and Ti-O bond distances as well as Ti-O-C(phenyl) and C-Ti-C bond angles.[9-10] In contrast, resonances ascribed to the Ti-*<u>Me</u>* of the Tp' analogues (**3,5**) in both the ^{1}H and ^{13}C NMR spectra were observed in the much lower magnetic field than these for Cp' analogues [chemical shifts in ppm (^{1}H, ^{13}C): **3** (1.72, 66.5), **5** (1.78, 65.2) > **A** (0.94, 54.2),[10] **B** (0.75, 54.2)[11]]. This result implies that the Ti-Me bonds in the Tp' analogues are lower nucleophilic than those in the Cp' analogues.

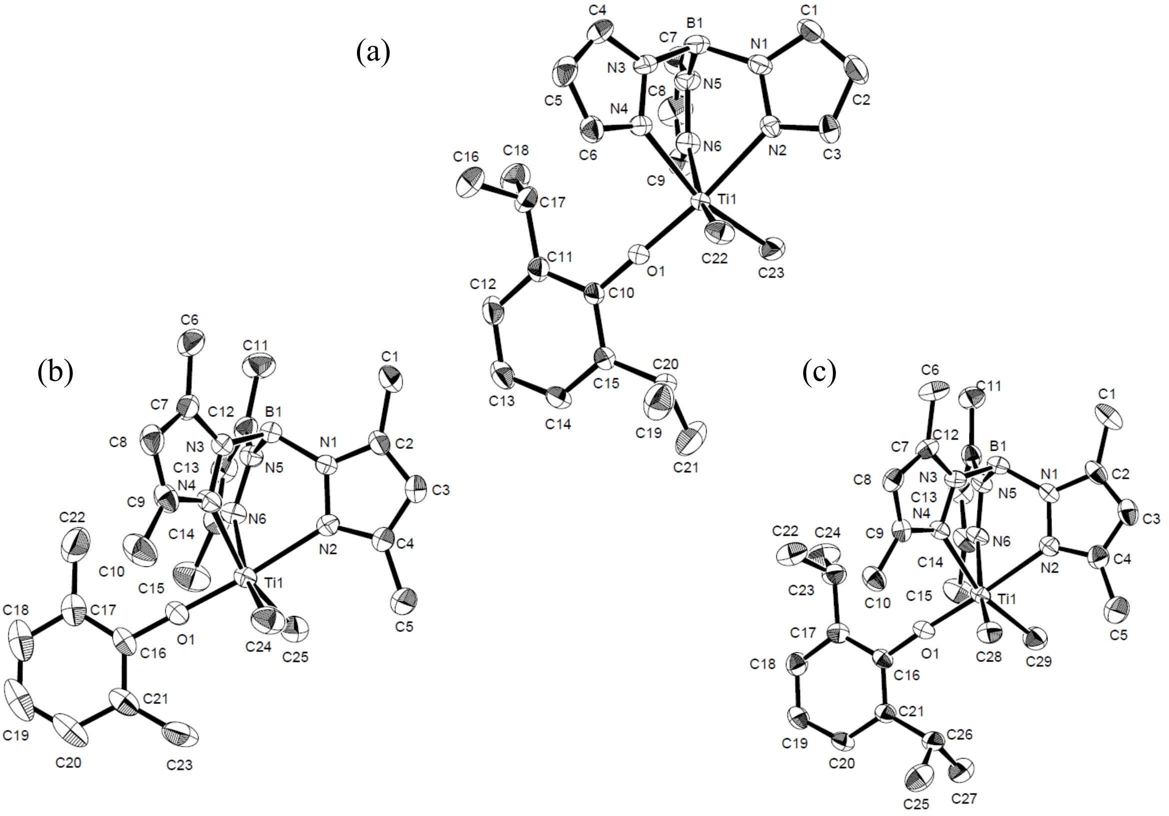


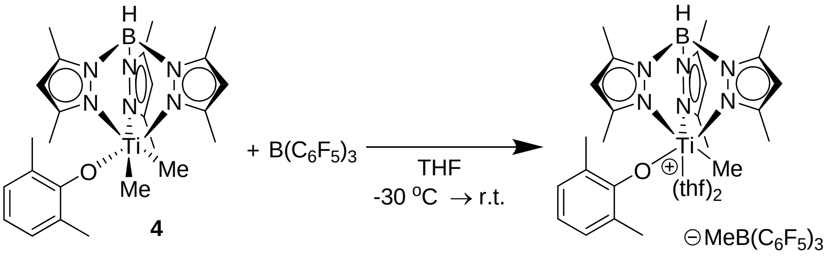
Figure 3. ORTEP drawings for Tp'TiMe$_2$(O-2,6-R'$_2$C$_6$H$_3$) [Tp' = Tp, R' = ^{i}Pr (**3**, a); Tp = Tp*, R' = Me (**4**, b), ^{i}Pr (**5**, c)]. Thermal ellipsoids are drawn at the 50% probability level and H atoms are omitted for clarity.

Table 4. Selected bond distances (Å) and angles (°) for Tp'TiMe$_2$(O-2,6-R'$_2$C$_6$H$_3$) [Tp' = Tp, R' = ^{i}Pr (**3**); Tp' = Tp*, R' = Me (**4**), ^{i}Pr (**5**)].

Complex (Tp', R')	**3** (Tp, ^{i}Pr)	**4** (Tp*, Me)	**5** (Tp*, ^{i}Pr)
	Selected bond distances (Å)		
Ti(1)-C(1)	2.102(3)	2.126(3)	2.124(2)
Ti(1)-C(2)	2.123(3)	2.130(3)	2.130(2)
Ti(1)-O(1)	1.794(2)	1.7775(18)	1.7938(15)
Ti(1)-N(2)	2.236(2)	2.254(2)	2.2628(18)
Ti(1)-N(4)	2.229(2)	2.251(2)	2.2528(17)
Ti(1)-N(6)	2.233(2)	2.238(2)	2.2503(18)
	Selected bond angles (°)		
Ti(1)-O(1)-C(Phe)	172.85(16)	174.75(17)	176.86(13)
C(1)-Ti(1)-C(2)	99.33(13)	99.03(12)	98.98(10)
C(1)-Ti(1)-O(1)	98.29(11)	95.47(11)	96.57(8)
C(2)-Ti(1)-O(1)	96.88(10)	97.46(10)	96.56(8)
N(2)-Ti(1)-N(4)	79.06(8)	80.79(8)	80.06(6)
N(2)-Ti(1)-N(6)	78.89(9)	80.90(8)	81.61(6)
N(4)-Ti(1)-N(6)	80.00(8)	80.58(8)	81.15(6)
N(2)-Ti(1)-O(1)	173.08(10)	175.67(8)	176.73(7)
N(4)-Ti(1)-O(1)	96.82(8)	95.45(8)	97.74(6)
N(6)-Ti(1)-O(1)	94.98(9)	96.44(8)	95.69(6)

Note that the reaction of **4** with one equivalent of B(C$_6$F$_5$)$_3$ in THF afforded the cationic methyl complex, [Tp*TiMe(O-2,6-Me$_2$C$_6$H$_3$)(THF)$_2$][MeB(C$_6$F$_5$)$_3$] in quantitative yield (Scheme 4), and the product was identified by ^{1}H and ^{13}C NMR spectra and elemental analysis. The formation of MeB$^-$(C$_6$F$_5$)$_3$ was conformed by the resonance at 0.48 ppm ascribed to the B-*Me* in the ^{1}H NMR spectrum and the two remained THF molecules per titanium were based on the results of both ^{1}H NMR and elemental analysis.

Scheme 4



Ethylene polymerization and ethylene copolymerization with 1-octene by $Tp^{*}TiX_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ [X = Cl (2b), Me (4)] and $[Tp^{*}TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)(THF)_2][MeB(C_6F_5)_3]$ (6) catalysts.

Ethylene polymerization and ethylene copolymerization with 1-octene (OC) using $Tp^{*}TiX_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ [X = Cl (**2b**), Me (**4**)] and $[Tp^{*}TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)(THF)_2][MeB(C_6F_5)_3]$ (**6**) were conducted at 25 °C in the presence of various cocatalysts (Scheme 5). $Al^{i}Bu_3$ was chosen as scavenger to remove the THF molecules from the Ti metal center of **6** and to remove impurities in the polymerization system. The results are summarized in Table 5.

Scheme 5

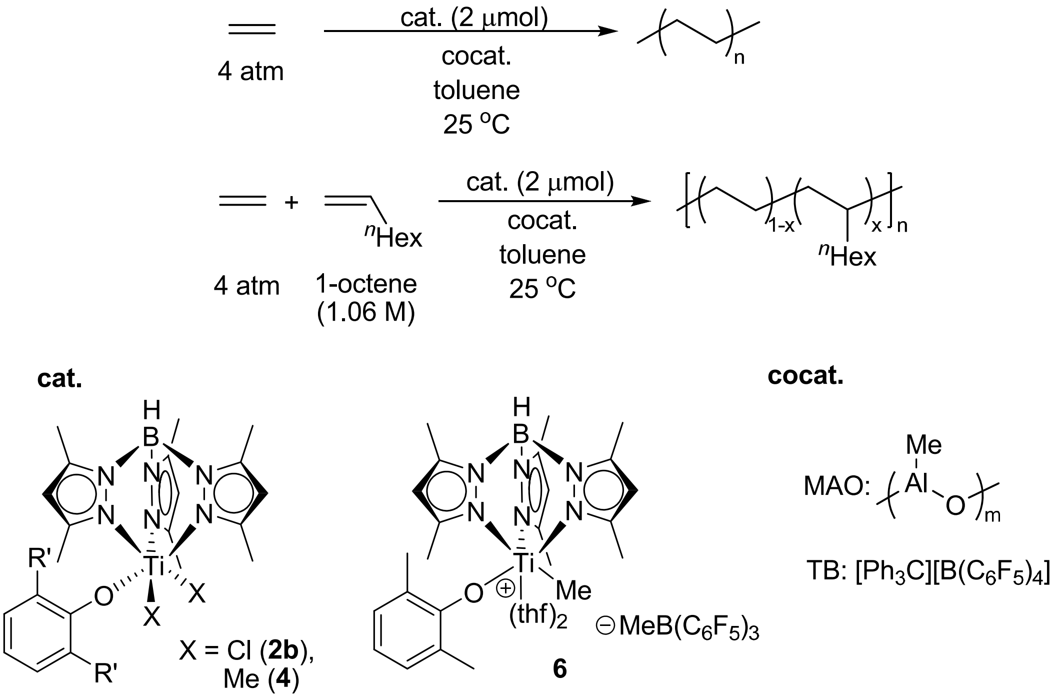


Table 5. Ethylene polymerization and ethylene copolymerization with 1-octene (OC) by Tp*TiX_2(O-2,6-$Me_2C_6H_3$) [X = Cl (**2b**), Me (**4**)] and [Tp*TiMe(O-2,6-$Me_2C_6H_3$) $(THF)_2$][MeB$(C_6F_5)_3$] (**6**)-cocatalysts.[a]

run	cat.	cocat.	Al/Ti[b]	comonomer ([M])	yield [mg]	activity[c]	M_w (M_n)[d] × 10^{-4}	M_w/M_n[d]	OC content[f] [mol%]
26	**2b**	MAO	250	-	138	410	38.3[e]	40[e]	-
35	**2b**	MAO	250	OC (1.06)	84	250	82.9	3.8	2.0
36	**4**	MAO	250	-	98	290	19.7 (15.0)	1.3	-
37	**4**	MAO	250	OC (1.06)	88	260	11.9	2.0	trace
38	**4**	TB	0	-	trace	-	-	-	-
39	**4**	TB/Al^{i}Bu$_3$	25	-	trace	-	-	-	-
40	**4**	TB/Al^{i}Bu$_3$	50	-	27	81	32.9	2.8	-
41	**4**	TB/Al^{i}Bu$_3$	50	OC (1.06)	27	81	225	7.2	1.9
42	**4**	TB/Al^{i}Bu$_3$	100	-	20	60	129	4.1	-
43	**4**	TB/Al^{i}Bu$_3$	200	-	18	54	100	3.7	-
44	**6**	-	0	-	trace	-	-	-	-
45	**6**	(Al^{i}Bu$_3$)	25	-	90	270	39.5 (20.1)	2.0	-
46	**6**	(Al^{i}Bu$_3$)	25	OC (1.06)	34	100	17.8	2.0	trace
47	**6**	(Al^{i}Bu$_3$)	50	-	34	100	33.8	3.5	-
48	**6**	(Al^{i}Bu$_3$)	100	-	43	129	42.5	3.8	-
49	**6**	(Al^{i}Bu$_3$)	200	-	18	54	58.3	36	-

[a] Conditions: toluene + 1-octene total 30 mL, cat. 2.0 μmol, MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO) or $[Ph_3C][B(C_6F_5)_4]$ (TB) cocatalysts ([TB]/[Ti] = 1), ethylene 4 atm, 25 °C, 10 min. [b] Molar ratio of Al/Ti. [c] Activity in kg-polymer/mol-Ti·h. [d] GPC data in *o*-dichlorobenzene vs polystyrene standard. [e] GPC data in *o*-dichlorobenzene vs polyethylene standard. [f] OC content (mol%) in copolymer estimated by ^{13}C NMR spectra.

As described above, the dichloro analogue (**2b**)-MAO catalyst showed the moderate catalytic activities in the ethylene polymerization, and the resultant polymers possessed high molecular weights with broad molecular weight distributions (runs 25-29 in Table 3, Figure 4). In contrast, the dimethyl analogue (**4**)-MAO catalyst afforded a rather lower molecular weight polyethylene with narrow molecular weight distribution (M_w = 197,000, M_w/M_n = 1.3, run 36, Figure 4). These results strongly indicate that several catalytically active species would be generated during activation process in the **2b**-MAO catalyst system.

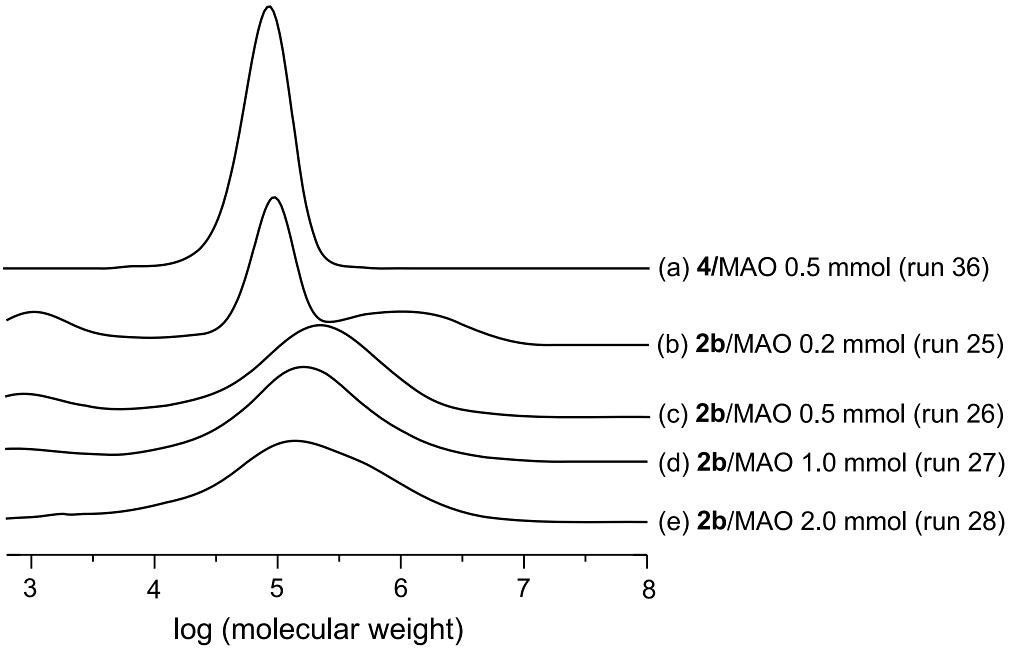


Figure 4. GPC traces of polyethylenes prepared by (a) **4**-MAO and (b)-(e) **2b**-MAO catalyst systems.

The dimethyl analogue (**4**)-$[Ph_3C][B(C_6F_5)_4]$ catalyst exhibited a rather low catalytic activities in ethylene polymerization in the presence of Al^iBu_3 (runs 40, 42-43). The resultant polymers prepared under the high Al concentrations (Al/Ti = 100-200) possessed much higher M_w values and more broad M_w/M_n values compared to that under the low one (Al/Ti = 25). These suggest that several active species should be generated in the mixture owing to the excessive Al^iBu_3.

The cationic methyl analogue (**6**) showed moderate catalytic activities for ethylene polymerization in the presence of Al^iBu_3 without MAO (runs 45, 47-49), and the increase of the Al/Ti molar ratios led to the decreasing of the catalytic activity as well as broadening of the molecular weight distributions. Importantly, the activity under the optimized condition was close to that of the **4**-MAO under the same condition, the M_n value of the resultant polymer was also close to that prepared by the **4**-MAO (runs 36, 45). In addition, these catalysts showed similar catalytic activities as well as negligible OC incorporations in ethylene/1-octene copolymerization (runs 37, 46). These results clearly indicate that the cationic alkyl species would be the catalytically active species.

Conclusion

A series of hydrotris(pyrazolyl)borate titanium complexes containing aryloxo ligands of the type, $Tp'TiCl_2(O\text{-}2,6\text{-}R'_2C_6H_3)$ [Tp' = Tp, R' = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**); Tp' =Tp*, R' = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)] and $Tp'TiMe_2(O\text{-}2,6\text{-}R'_2C_6H_3)$ [Tp' = Tp, R' = ^{i}Pr (**3**); Tp' =Tp*, R' = Me (**4**), ^{i}Pr (**5**)], were synthesized and identified by NMR, elemental analyses and X-ray crystallographic analyses. Moreover, isolation of the thermal stable tris(pyrazolyl)borate titanium (IV) cationic alkyl species, $[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)(THF)_2][MeB(C_6F_5)_3]$ (**6**), was firstly succeeded. The dichloro complexes **1b-c** and **2a-d** exhibited moderate catalytic activities for ethylene polymerization in the presence of MAO, and both the activities and the molecular weights of the resultant polymers were highly dependent on the Al/Ti molar ratios employed. The complex **1a** exhibited high catalytic activity and afforded high molecular weight polyethylenes with unimodal molecular weight distributions in the presence of small amount of MAO (Al/Ti molar ratio = 200). The dimethyl complex (**4**)-MAO and the cationic methyl complex (**6**) catalysts polymerized ethylene with the cationic Ti(IV) species, and the resultant polyethylenes possessed unimodal molecular weight distributions. Thus, I believe that further modifications of the Tp' and anionic donor ligand (Y) in Tp'MX_2(Y) should be a promising approach for more efficient catalysts for precise olefin polymerization.

Experimental Section

General procedure. All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques. Anhydrous grade toluene and *n*-hexane (Kanto Chemical Co., Inc.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Anhydrous dichloromethane, diethyl ether and tetrahydrofuran (Kanto Chemical Co., Inc.) were stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16). $TpTiCl_3$ and Tp^*TiCl_3 were prepared according to the publish procedures.[12] Reagent grade $B(C_6F_5)_3$ (Aldrich), $[Ph_3C][B(C_6F_5)_4]$ (Asahi Glass Co., Ltd.), and Al^iBu_3 (Kanto Chemical Co., Inc.) were stored in the dry box and were used as received.

Ethylene of polymerization grade (Sumitomo Seika Chemicals Co., Ltd.) was used as received without further purification procedures. 1-Octene (Wako Pure Chemical Ind., Ltd.) was stored in the drybox in the presence of molecular sieves (mixture of 3A 1/16 and 4A 1/8, and 13X 1/16) after passing through an alumina short column under nitrogen. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 ºC for removing toluene, $AlMe_3$, and then heated at >100 ºC for 1 h for completion) in the drybox to give white solids.

All ^1H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.78 MHz for ^1H and 100.53 MHz for ^{13}C). All spectra were obtained in the solvents indicated at room temperature unless otherwise noted. Chemical shifts are given in ppm and are referenced to $SiMe_4$ (δ 0.00, ^1H, ^{13}C). ^{13}C NMR spectra for poly(ethylene-*co*-1-octene)s were measured at 110 ^oC in C_6D_6/1,2,4-trichlorobenzene (1/4 v/v). The relaxation delay was 5.2 sec, the acquisition time was 1.3 sec, the pulse angle was 90º, and the number of transients accumulated was ca. 6000.

Elemental analyses were performed by using a PE2400II Series (Perkin-Elmer Co.), and some analytical runs were performed twice to confirm the reproducibility in the independent analysis/synthesis runs. Certain C values were somewhat lower than those calculated, whereas their N, H, values were close; this is due to incomplete combustion (to form titanium carbide).

Molecular weights and molecular weight distributions for the polyethylenes and poly(ethylene-*co*-1-octene)s were measured by a gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $< 2.8\times10^8$ MW at 140 ºC using *o*-dichlorobenzene containing 0.05 wt/v% 2,6-di-*tert*-butyl-*p*-cresol as eluent. The molecular weights were calculated by a standard procedure based on the calibration with standard polystyrene or polyethylene samples.

Synthesis of $TpTiCl_2(OPh)$ (1a). Into a Et_2O suspension containing $TpTiCl_3$ (402 mg, 1.09 mmol), LiOPh (114 mg, 1.14 mmol) was added at -30 °C. The reaction mixture was warmed slowly up to room temperature, and the mixture was stirred overnight. The solvent was removed *in vacuo* after addition of CH_2Cl_2, and the resultant residue was extracted with hot toluene. The toluene extract was then removed *in vacuo* to give a red solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled solution placed in a freezer gave a red crystal of $TpTiCl_2(OPh)\cdot0.25(CH_2Cl_2)$. Yield: 429 mg (87.8%). ^{1}H NMR ($CDCl_3$): δ 8.38 (d, 1H, *J* = 2.2), 7.82 (d, 2H, *J* = 2.2), 7.65 (d, 1H, *J* = 2.2), 7.63 (d, 2H, *J* = 2.2), 7.3-7.0 (m, 5H), 6.28 (d, 1H, *J* = 2.2), 6.14 (d, 2H, J = 2.2). ^{13}C NMR ($CDCl_3$): δ 167.4, 144.3, 142.6, 134.0, 133.9, 129.2, 125.0, 119.6, 104.9, 104.8. Anal. Calcd. for $C_{15.25}H_{15.5}BCl_{2.5}N_6OTi$: C, 41.06; H, 3.50; N, 18.84%. Found: C, 41.19; H, 3.49; N, 18.85%.

Synthesis of $TpTiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (1b): Method 1. Into a toluene suspension containing $TpTiCl_3$ (400 mg, 1.09 mmol), $LiO\text{-}2,6\text{-}Me_2C_6H_3$ (147 mg, 1.15 mmol) was added at -30 °C. The reaction mixture was warmed slowly up to room temperature, and the mixture was stirred overnight. The solvent was removed *in vacuo* after addition of CH_2Cl_2, and the resultant residue was extracted with hot toluene. The toluene extract was then removed *in vacuo* to give a red solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled solution placed in the freezer gave a red crystal of $TpTiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)\cdot 0.5(CH_2Cl_2)\cdot 0.1(n\text{-hexane})$. Yield: 459 mg (83.6%). ^{1}H NMR ($CDCl_3$): δ 8.38 (d, 1H, *J* = 2.2), 7.81 (d, 2H, *J* = 2.2), 7.67 (d, 2H, *J* = 2.2), 7.62 (d, 1H, *J* = 2.2), 6.9-6.8 (m, 3H), 6.26 (d, 1H, *J* = 2.2), 6.14 (d, 2H, *J* = 2.2), 2.10 (s, 6H). ^{13}C NMR ($CDCl_3$): δ. 166.9, 144.3, 143.0, 134.1, 133.8, 131.2, 128.5, 124.6, 104.9, 104.8, 16.5. Anal. Calcd. for $C_{18.1}H_{21.4}BCl_3N_6OTi$: C, 43.13; H, 4.28; N, 16.67%. Found (1): C, 43.33; H, 4.12; N, 16.49%. Found (2): C, 43.35; H, 4.20; N, 16.53%.

Synthesis of $TpTiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (1b): Method 2. Synthesis of **1b** was carried out by the same procedure as that for **1b** (method 1) except that $TpTiCl_3$ (774 mg, 2.11 mmol) and $LiO\text{-}2,6\text{-}Me_2C_6H_3$ (284 mg, 2.22 mmol) were used, and $TpTiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)\cdot 0.67(CH_3C_6H_5)$ was obtained by recrystallization in toluene at -30 °C. Yield: 817 mg (75%). $C_{21.7}H_{24.4}BCl_3N_6OTi$: C, 50.62; H, 4.77; N, 16.33%. Found (1): C, 50.53; H, 4.91; N, 16.60%. Found (2): C, 50.54; H, 5.07; N, 16.43%.

Synthesis of $TpTiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1c). Synthesis of **1c** was carried out by the same procedure as that for **1b** (method 1) except that $TpTiCl_3$ (400 mg, 1.09 mmol) and $LiO\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (209 mg, 1.13 mmol) were used. Yield: 435 mg (78.5%). ^{1}H NMR ($CDCl_3$): δ 8.36 (d, 1H, *J* = 2.0), 7.79 (d, 2H, *J* = 2.2), 7.67 (d, 2H, *J* = 2.2), 7.61 (d, 1H, *J* = 2.0), 7.03 (m, 3H), 6.24 (d, 1H, *J* = 2.0), 6.15 (d, 2H, *J* = 2.2), 3.49 (sep, 2H, *J* = 6.9), 1.00 (d, 12H, *J* = 6.9). ^{13}C NMR ($CDCl_3$): δ 164.0, 144.3, 143.3, 142.3, 134.1, 133.7, 125.2, 123.8, 104.9, 104.8, 26.1, 24.7. Anal. Calcd. for $C_{21}H_{27}BCl_2N_6OTi$: C, 49.55; H, 5.35; N, 16.51%. Found: C, 49.16; H, 5.34; N, 16.22%.

Synthesis of $TpTiCl_2(O\text{-}2,6\text{-}Ph_2C_6H_3)$ (1d). Synthesis of **1d** was carried out by the same procedure as that for **1b** (method 1) except that $TpTiCl_3$ (401 mg, 1.09 mmol) and $LiO\text{-}2,6\text{-}Ph_2C_6H_3$ (281 mg, 1.11 mmol) were used. Yield: 551 mg (87.4%). ^{1}H NMR ($CDCl_3$): δ 8.04 (d, 1H, *J* = 2.2), 7.58 (d, 2H, *J* = 2.2), 7.42 -7.35 (m, 7H), 7.27 – 7.23 (m, 2H), 7.20-7.05 (m, 7H), 6.04 (t, 1H, *J* = 2.2), 6.01 (t, 2H, *J* = 2.2). ^{13}C NMR ($CDCl_3$): δ 163.5, 143.8, 143.3, 138.1, 135.2, 133.4, 133.0, 130.9, 130.1, 127.4, 126.9, 124.2, 104.9, 104.3. Anal. Calcd. for $C_{27}H_{23}BCl_2N_6OTi$: C, 56.19; H, 4.02; N, 14.56%. Found: C, 55.27; H, 3.85; N, 14.30%.

Synthesis of Tp*TiCl$_2$(OPh) (2a): Method 1. Synthesis of **2a** was carried out by the same procedure as that for **1b** (method 1) except that Tp*TiCl$_3$ (216 mg, 0.479 mmol) and LiOPh (50 mg, 0.50 mmol) were used, and Tp*TiCl$_2$(OPh)·0.8(CH_2Cl_2) was obtained. Yield 228 mg (82.6%). ^{1}H NMR ($CDCl_3$): δ 7.3-7.2 (m, 4H), 7.07 (tt, 1H, *J* = 6.8, 1.6), 5.82 (s, 1H), 5.67 (s, 2H), 2.82 (s, 3H), 2.37 (s, 3H), 2.35 (s, 6H), 2.24 (s, 6H). ^{13}C NMR ($CDCl_3$): δ 167.7, 154.0, 152.4, 143.7, 143.2, 129.3, 124.7, 120.6, 107.4, 106.2, 16.3, 15.1, 12.6, 12.5. Anal. Calcd. for $C_{21.8}H_{28.6}BCl_{3.6}N_6OTi$: C, 45.38; H, 5.00; N, 14.56%. Found (1): C, 45.29; H, 5.02; N, 14.39%. Found (2): C, 45.49; H, 4.99; N, 14.39%.

Synthesis of Tp*TiCl$_2$(OPh) (2a): Method 2. Synthesis of **2a** was carried out by the same procedure as that for **2a** (method 1) except that Tp*TiCl$_3$ (279 mg, 0.618 mmol) and LiOPh (65 mg, 0.65 mmol) were used, and Tp*TiCl$_2$(OPh)·($CH_3C_6H_5$) was obtained by recrystallization from toluene at -30 ^{o}C. Yield 302 mg (81.3%). Anal. Calcd. for $C_{28}H_{35}BCl_2N_6OTi$: C, 55.94; H, 5.87; N, 13.98%. Found (1): C, 56.00; H, 5.94; N, 13.96%. Found (2): C, 56.01; H, 5.71; N, 13.97%.

Synthesis of Tp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (2b). Synthesis of **2b** was carried out by the same procedure as that for **1b** (method 1) except that Tp*TiCl$_3$ (352 mg, 0.780 mmol) and LiO-2,6-Me$_2$C$_6$H$_3$ (103 mg, 0.804 mmol) were used. Yield: 355 mg (84.8%). ^{1}H NMR ($CDCl_3$): δ 7.01 (d, 1H, *J* = 7.3), 6.81 (t, 1H, *J* = 7.3), 6.76 (d, 1H, *J* = 7.3), 3.12 (s, 3H), 2.88 (s, 3H), 2.38 (s, 9H), 2.26 (s, 6H), 1.44 (s, 3H). ^{13}C NMR ($CDCl_3$): δ167.4, 154.0, 152.8, 143.6, 142.9, 133.2, 129.9, 128.6, 128.0, 124.3, 107.3, 106.0, 18.1, 16.4, 15.2, 14.9, 12.6, 12.5. Anal. Calcd. for $C_{23}H_{31}BCl_2N_6OTi$: C, 51.43; H, 5.82; N, 15.65%. Found: C, 50.56; H, 5.94; N, 15.29%.

Synthesis of Tp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (2c). Synthesis of **2c** was carried out by the same procedure as that for **1b** (method 1) except that Tp*TiCl$_3$ (202 mg, 0.447 mmol) and LiO-2,6-^{i}Pr$_2$C$_6$H$_3$ (86 mg, 0.47 mmol) were used. Yield: 203 mg (76.4%). ^{1}H NMR (CDCl$_3$): δ 7.18 (dd, 1H, J = 7.5, 1.7), 7.00 (t, 1H, J = 7.5), 6.88 (dd, 1H, J = 7.5, 1.7), 5.80 (s, 1H), 5.70 (s, 2H), 4.93 (sep, 1H, J = 6.6), 2.87 (s, 3H), 2.40 (s, 6H), 2.37 (s, 3H), 2.34 (m, 1H), 2.26 (s, 6H), 1.44 (d, J = 6.6), 0.62 (d, J = 6.6). ^{13}C NMR (CDCl$_3$): δ 164.5, 153.8, 152.5, 143.9, 143.3, 142.9, 141.2, 124.9, 124.3, 123.5, 107.2, 106.7, 26.3, 25.3, 25.1, 24.3, 16.5, 15.9, 12.6, 12.5. Anal. Calcd. for $C_{27}H_{39}BCl_2N_6OTi$: C, 54.67; H, 6.63; N, 14.17%. Found: C, 53.53; H, 6.73; N, 13.89%.

Synthesis of Tp*TiCl$_2$(O-2,6-Ph$_2$C$_6$H$_3$) (2d). Synthesis of **2d** was carried out by the same procedure as that for **1b** (method 1) except that Tp*TiCl$_3$ (244 mg, 0.540 mmol) and LiO-2,6-Ph$_2$C$_6$H$_3$ (140 mg, 0.555 mmol) were used. Yield: 199 mg (55.7%). ^{1}H NMR (CDCl$_3$): δ 7.84 (d, 2H, J = 7.7), 7.52 (t, 2H, J = 7.7), 7.44 (t, 1H, J = 7.3), 7.28 (dd, 1H, J = 7.3, 1.8), 7.08 (t, 1H, J = 7.7), 7.01 (dd, 1H, J = 7.3, 1.8), 6.84 (m, 1H), 6.66 – 6.55 (m, 4H), 5.65 (s, 1H), 5.42 (s, 2H). ^{13}C NMR (CDCl$_3$): δ 163.6, 153.5, 152.0, 142.6, 142.3, 138.5, 138.4, 138.3, 134.5, 131.6, 131.5, 129.1, 128.0, 127.6, 126.5, 126.1, 123.6, 106.9, 16.5, 15.9, 12.5, 12.4. Anal. Calcd. for $C_{33}H_{35}BCl_2N_6OTi$: C, 59.94; H, 5.33; N, 12.71%. Found: C, 58.51; H, 5.22; N, 12.39%.

Synthesis of TpTiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (3). To a Et$_2$O solution (10 mL) containing TpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1c**, 311 mg, 0.611 mmol), MeLi in Et$_2$O (1.09 M, 1.05 mL, 1.14 mmol) was added at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 30 min. Then the dark green suspension was passed thorough celite pad, the resultant red solution was concentrated to 2 mL. The chilled solution gave red microcrystal. Yield 120 mg (41.9%). ^{1}H NMR (C$_6$D$_6$): δ 7.48 (d, 3H, J = 2.2), 7.33 (d, 3H, J = 2.2), 7.24 (d, 2H, J = 7.6), 7.12 (t, 1H, J = 7.6), 5.73 (t, 3H, J = 2.2), 3.95 (sept, 2H, J = 7.0), 1.71 (s, 6H), 1.21 (d, 12H, J = 7.0). ^{13}C NMR (CDCl$_3$): δ 161.1, 142.3, 140.5, 134.0, 124.1, 123.0, 104.9, 66.5, 26.5, 24.9. Anal. Calcd. For $C_{23}H_{33}BCl_2N_6OTi$: C, 59.00; H, 7.10; N, 17.95%. Found: C, 58.80; H, 7.37; N, 17.96%.

Synthesis of Tp*TiMe$_2$(O-2,6-Me$_2$C$_6$H$_3$) (4). Synthesis of **4** was carried out by the same procedure as that for **3** except that Tp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**2b**, 879 mg, 1.64 mmol) and MeLi in Et$_2$O (1.09 M, 3.3 ml, 3.6 mmol) were used. Yield: 650 mg (80.0% yield). ^{1}H NMR (C$_6$D$_6$): δ 7.17 (d, 1H, *J* = 7.3), 6.94 (d, 2H, *J* = 7.3), 6.89 (t, 2H, *J* = 7.3), 5.83 (s, 1H), 5.37 (s, 2H), 3.29 (s, 3H), 2.76 (s, 3H), 2.27 (s, 3H), 2.12 (s, 6H), 2.05 (s, 6H), 1.81 (s, 3H), 1.77 (s, 6H). ^{13}C NMR (CDCl$_3$): δ 164.2, 152.4, 151.2, 143.5, 142.8, 130.5, 129.6, 129.1, 128.7, 122.2, 107.9, 106.1, 65.0, 18.6, 16.4, 16.0, 14.2, 12.9, 12.3. Anal. Calcd. For $C_{25}H_{37}BCl_2N_6OTi$: C, 60.50; H, 7.51; N, 16.93%. Found: C, 60.42; H, 7.70; N, 16.78%.

Synthesis of Tp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (5). Synthesis of **5** was carried out by the same procedure as that for **3** except that Tp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2c**, 429 mg, 0.723 mmol) and MeLi in Et$_2$O (1.09 M, 1.45 ml, 1.58 mmol) were used. Yield: 370 mg (92.6 %). ^{1}H NMR (C$_6$D$_6$): δ 7.35 (dd, 1H, *J* = 7.0, 2.2), 7.13 (dd, 1H, *J* = 7.7, 2.2), 7.09 (t, 1H, *J* = 7.7), 5.80 (s, 1H), 5.41 (sept, 1H, *J* = 7.0), 5.37 (s, 2H), 2.88 (sept, 1H, *J* = 7.0), 2.77 (s, 3H), 2.27 (s, 3H), 2.12 (s, 6H), 2.08 (s, 6H), 1.78 (s, 6H), 1.71 (d, 6H, *J* = 7.0 Hz), 0.86 (d, 6H, *J* = 7.0 Hz). ^{13}C NMR (CDCl$_3$): δ 161.2, 152.5, 151.1, 143.2, 142.7, 141.6, 140.7, 124.4, 124.3, 123.1, 107.9, 106.4, 65.2, 27.1, 25.6, 25.4, 24.6, 16.0, 15.2, 13.0, 12.4. Anal. Calcd. For $C_{29}H_{45}BCl_2N_6OTi$: C, 63.06; H, 8.21; N, 15.21%. Found: C, 62.95; H, 8.55; N, 15.13%.

Synthesis of [Tp*TiMe(O-2,6-Me$_2$C$_6$H$_3$)][Me(BC$_6$F$_5$)$_3$](THF)$_2$ (6). To a THF solution (10 mL) containing Tp*TiMe$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**4**, 322 mg, 0.649 mmol), B(C$_6$F$_5$)$_3$ (332 mg, 0.648 mmol) was added at -30 °C. The reaction mixture was warmed slowly to room temperature, and the mixture was stirred for 1 hour. The solvent in the mixture was then removed *in vacuo*, yielding analytically pure product (743 mg, quantitative yield) ascribed to **6**. ^{1}H NMR (CDCl$_3$): δ 7.16 (d, 3H, *J* = 7.0 Hz), 6.99 (t, 3H, *J* = 7.5 Hz), 6.93 (d, 3H, *J* = 7.0 Hz), 6.07 (s, 1H), 5.77 (s, 1H), 5.72 (s, 1H), 3.74 (br s), 3.49 (br s), 2.98 (s, 3H), 2.52 (s, 3H), 2.43 (s, 3H), 2.42 (s, 3H), 2.40 (s, 3H), 2.25 (s, 3H), 2.13 (br s), 2.09 (s, 3H), 1.85 (br s), 1.83 (s, 3H), 1.64 (br s), 1.45 (s, 3H), 0.49 (s, 3H). Anal. Calcd. For $C_{51}H_{53}B_2F_{15}N_6O_3Ti$: C, 53.15; H, 4.64; N, 7.29%. Found: C, 53.24; H, 4.50; N, 7.23%.

Ethylene polymerization using MAO as cocatalyst. A typical reaction procedure for ethylene homopolymerization using MAO cocatalyst (run 5, Table 3), is as follows. Toluene (29 mL), and MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale, stainless steel) in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at 25 ºC. A toluene solution (1.0 mL) containing **1** (2.0 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total ethylene pressure 4 atm). The mixture was magnetically stirred for 10 min, ethylene remained was purged after the reaction, and the mixture was then poured into MeOH (300 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with MeOH, and was then dried *in vacuo* at 60^{o}C.

Ethylene polymerization using borate as cocatalyst. A typical procedure for ethylene polymerization using $[Ph_3C][B(C_6F_5)_4]$ (run 39, Table 5) is as follows. Toluene (28 mL) and $Al^{i}Bu_3$ (100 μmol) were added into the autoclave in the drybox, and the reaction apparatus was then replaced and filled with ethylene (1 atm) at 25 °C. A toluene solution (1.0 mL) containing **3** (2.0 μmol) was then added, immediately followed by addition of a toluene solution (1.0 mL) containing $[Ph_3C][B(C_6F_5)_4]$ (2.0 μmol). The reaction apparatus was then immediately pressurized to 3 atm (total ethylene pressure 4 atm), and the mixture was magnetically stirred for 10 min. After the reaction, the remaining ethylene was purged upon cooling in a ice bath, and the mixture was then poured into MeOH (150 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, was adequately washed with MeOH, and then was dried *in vacuo* at 60 ^{o}C

Crysllographic Analysis. All measurements were made on a Rigaku RAXIS-RAPID imaging plate diffractometer with graphite-monochromated Mo Kα radiation. The selected crystal collection parameters are summarized in Table 6-8. All structures were solved by direct methods and expanded using Fourier techniques,[13] and the non-hydrogen atoms were included but not refined. All calculations for complexes were performed using the Crystal Structure[14] crystallographic software package.

Suitable single crystals of **1a-d**, **2b-d** were prepared at -30 ^{o}C in CH_2Cl_2/*n*-hexane solution and that of **2a** were grown by slow evaporation of a toluene solution. And these of **3-5** were grown by slow evaporation of Et_2O.

Table 6. Crystal and data collection parameters for $TpTiCl_2(O\text{-}2,6\text{-}R'_2C_6H_3)$ [R' = H (**1a**), Me (**1b**), ^{i}Pr (**1c**), Ph (**1d**)].[a]

Complex (R')	**1a** (H)	**1b** (Me)	**1c** (^{i}Pr)	**1d** (Ph)
Formula;	$C_{15}H_{15}BCl_2N_6OTi$	$C_{17}H_{19}BCl_2N_6OTi$	$C_{21}H_{27}BCl_2N_6OTi$	$C_{27}H_{23}BCl_2N_6OTi$
Formula weight	424.94	452.99	509.10	577.13
Habits	Red, block	Red, block	Red, block	Red, block
Crystal size (mm)	0.40 × 0.38 × 0.30	0.15 × 0.10 × 0.06	0.37 × 0.32 × 0.10	0.35 × 0.32 × 0.25
Crystal system	Monoclinic	Monoclinic	Triclinic	Orthorhombic
Space group	$P2_1/c$ (#14)	$P2_1/n$ (#14)	P-1 (#2)	$P2_12_12_1$(#19)
a (Å)	9.4610(4)	9.9436(6)	9.7436(4)	11.6472(3)
b (Å)	16.7774(7)	20.7533(10)	9.8171(4)	13.6516(3)
c (Å)	12.0042(5)	10.0498(5)	14.1166(5)	17.3088(5)
β (deg)	102.2595(14)	97.2040(17)	74.4772(11)	
α (deg)			71.4051(11)	
γ (deg)			76.4601(12)	
V ($Å^3$)	1862.00(13)	2057.52(18)	1216.66(8)	2752.14(12)
Z value	4	4	2	4
D_{calcd} (g/cm^3)	1.516	1.462	1.390	1.393
F_{000}	864.00	928.00	528.00	1184.00
Temp (K)	193	193	193	193
μ (Mo Kα) (cm^{-1})	7.634	6.958	5.967	5.372
No. of reflns measd	Total: 17801	Total: 19870	Total: 12037	Total: 27327
	Unique: 4235 (R_{int} = 0.023)	Unique: 4664 (R_{int} = 0.073)	Unique: 5548 (R_{int} = 0.016)	Unique: 3518 (R_{int} = 0.019)
No. of observations (I > -3.00δ(I))	3664	2873	4964	3386
No. of variables	250	272	316	366
Residuals: R1; Rw	0.0300; 0.01121	0.0430; 0.0922	0.0341; 0.0877	0.0224; 0.0726
GOF	1.005	1.001	1.004	1.017
Max (minimum) peak in final diff. map (e-/ $Å^3$)	0.50 (-0.30)	0.43 (-0.44)	0.42 (-0.34)	0.20 (-0.29)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (*w* = Least squares weights, Chebychev polynomial). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (No = number of observations, N_v = number of variables).

Table 7. Crystal and data collection parameters for Tp*$TiCl_2(O\text{-}2,6\text{-}R'_2C_6H_3)$ [R' = H (**2a**), Me (**2b**), ^{i}Pr (**2c**), Ph (**2d**)].[a]

Complex (R')	**2a** (H)	**2b** (Me)	**2c** (^{i}Pr)	**2d** (Ph)
Formula;	$C_{21}H_{27}BCl_2N_6OTi$	$C_{23}H_{31}BCl_2N_6OTi$	$C_{27}H_{39}BCl_2N_6OTi$	$C_{33}H_{35}BCl_2N_6OTi$
Formula weight	509.06	537.15	593.26	661.30
Habits	Red, block	Red, block	Red, block	Red, block
Crystal size (mm)	0.20 × 0.12 × 0.08	0.42 × 0.35 × 0.30	0.40 × 0.30 × 0.20	0.44 × 0.30 × 0.08
Crystal system	Monoclinic	Monoclinic	Monoclinic	Orthorhombic
Space group	$P2_1/n$ (#14)	$P2_1/c$ (#14)	Cc (#9)	$P2_12_12_1$(#19)
a (Å)	9.7007(4)	14.7492(4)	17.8222(7)	19.7106(6)
b (Å)	20.3442(7)	9.9928(3)	9.5655(3)	20.0977(4)
c (Å)	17.2797(8)	19.0194(5)	19.4654(9)	8.0599(2)
β (deg)	106.3583(15)	106.0602(8)	115.8357(14)	
V ($Å^3$)	3272.1(2)	2693.78(11)	2986.7(2)	3192.84(14)
Z value	2	4	4	4
D_{calcd} (g/cm^3)	1.306	1.324	1.319	1.376
F_{000}	1340.00	1120.00	1248.00	1376.00
Temp (K)	193	193	193	193
μ (Mo Kα) (cm^{-1})	4.591	5.428	4.964	4.727
No. of reflns meads	Total: 32024 Unique: 7498 (Rint = 0.040)	Total: 25703 Unique: 6136 (Rint = 0.022)	Total: 14521 Unique: 3409 (Rint = 0.023)	Total: 31298 Unique: 4096 (Rint = 0.033)
No. of observations ($I > -3.00\delta(I)$)	5275	5364	3381	3798
No. of variables	432	338	382	432
Residuals: R1; Rw	0.0523; 0.1638	0.0284; 0.1022	0.0212; 0.0628	0.0324; 0.0941
GOF	1.001	1.015	1.004	1.002
Max (minimum) peak in final diff. map (e-/ $Å^3$)	0.52 (-0.58)	0.28 (-0.32)	1.7 (-0.25)	0.55 (-0.35)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (w = Least squares weights, Chebychev polynomial). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (No = number of observations, N_v = number of variables).

Table 8. Crystal and data collection parameters for Tp’TiMe$_2$(O-2,6-R’$_2$C$_6$H$_3$) [Tp’ = Tp, R’ = ^{i}Pr (**3**); Tp’ = Tp*, R’ = Me (**4**), ^{i}Pr (**5**)].[a]

Complex (Tp’ R’)	**3** (Tp, ^{i}Pr)	**4** (Tp*, Me)	**5** (Tp*, ^{i}Pr)
Formula	$C_{23}H_{33}BN_6OTi$	$C_{25}H_{37}BN_6OTi$	$C_{29}H_{45}BN_6OTi$
Formula weight	468.28	496.32	552.42
Habits	red, block	red, block	red, block
Crystal size (mm)	0.45 × 0.25 × 0.20	0.20 × 0.15 × 0.10	0.15 × 0.15 × 0.14
Crystal system	triclinic	orthorhombic	monoclinic
Space group	P-1 (#2)	Pbca (#61)	$P2_1/n$ (#14)
a (Å)	9.7967(7)	16.4059(4)	10.1593(3)
b (Å)	9.9965(7)	15.9210(4)	16.0503(6)
c (Å)	14.1515(11)	20.6856(6)	19.4198(7)
β (deg)	74.558(2)		99.4513(11)
α (deg)	72.676(2)		
γ (deg)	77.002(2)		
V (Å^3)	1259.20(16)	5403.0(2)	3123.60(18)
Z value	2	8	4
D_{calcd} (g/cm^3)	1.235	1.220	1.175
F_{000}	496.00	2112.00	1184.00
Temp (K)	193	193	193
μ (Mo Kα) (cm^{-1})	3.658	3.447	3.047
No. of reflns meads	Total: 10332 Unique: 4569 (Rint = 0.022)	Total: 42685 Unique: 4921 (Rint = 0.054)	Total: 25590 Unique: 5682 (Rint = 0.043)
No. of observations (I > -3.00δ(I))	4174	3072	4062
No. of variables	322	344	424
Residuals: R1; Rw	0.0461; 0.1255	0.0396; 0.0994	0.0374; 0.0984
GOF	1.001	1.013	1.007
Max (minimum) peak in final diff. map (e-/ Å^3)	0.39 (-0.76)	0.23 (-0.28)	0.23 (-0.29)

[a] Diffractometer: Rigaku RAXIS-RAPID Imaging Plate. Structure solution: direct methods. Refinement: full-matrix least-squares. Function minimized: $\Sigma w(|F_o|-|F_c|)^2$ (w = Least squares weights, Chebychev polynomial). Standard deviation of an observation of unit weight: $[\Sigma w(|F_o|-|F_c|)^2/(N_o-N_v)]^{1/2}$ (No = number of observations, N_v = number of variables).

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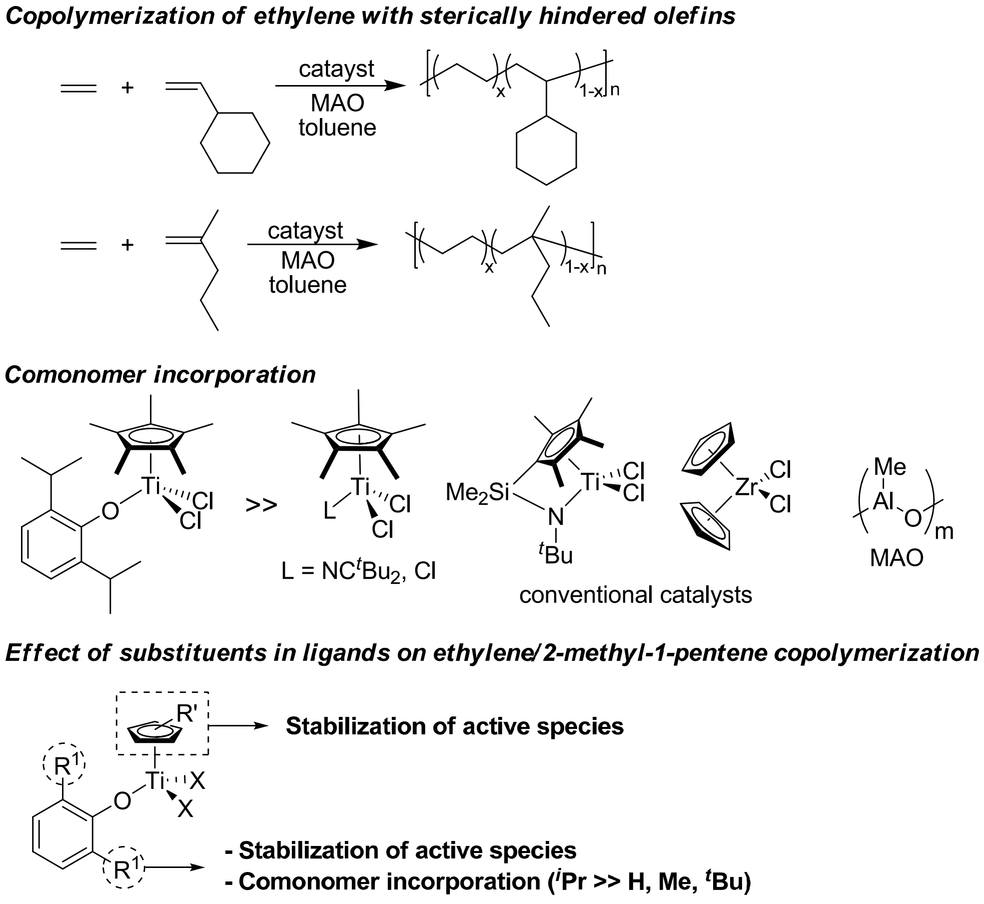
Chapter 6

Concluding Remarks

In this thesis, (1) precise and efficient synthesis of new ethylene copolymers by using nonbridged half-titanocene catalysts of type Cp'TiX$_2$(Y) [Cp' = cyclopentadienyl; X = halogen, alkyl; Y = anionic donor ligand such as OAr, N=CR$_2$] and (2) design and synthesis of new transition metal complex catalysts for coordination polymerization were studied. In chapter 2, ethylene copolymerizations with γ-branched-α-olefin and 2,2-disubstituted-α-olefin, sterically hindered monomers that have been difficult to incorporate due to the steric bulk, were explored. In chapter 3, precise and efficient synthesis of ethylene copolymers containing unsaturated side chains was investigated by ethylene copolymerization with nonconjugated dienes containing two different reactive olefins. On the basis of the results in chapter 2-3, transition metal catalysts, group 4 half-metallocene complexes containing an aryloxo ligand of the type Cp'MCl$_2$(OAr) (M = Ti, Zr, Hf) and tris(pyrazolyl)borate titanium complexes containing an aryloxo ligand of the type Tp'TiX$_2$(OAr) [Tp' = tris(pyrazolyl)borate], were designed, and their synthesis and their potential as olefin polymerization catalysts were investigated in chapter 4-5.

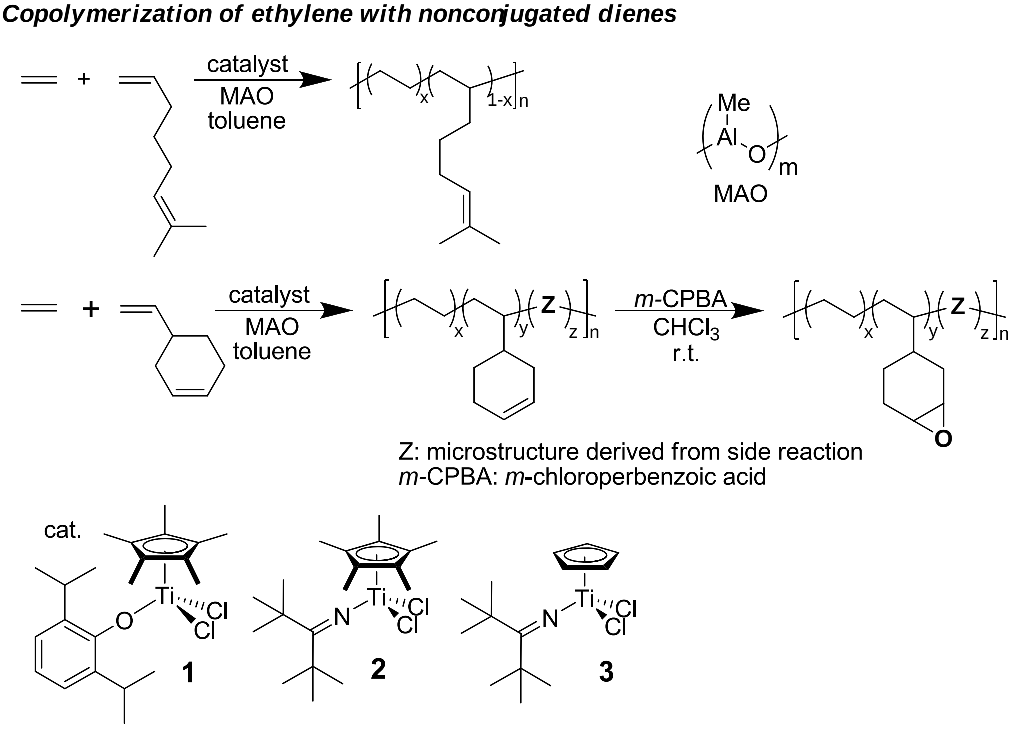
In chapter 2, copolymerizations of ethylene with vinylcylohexane and 2-methyl-1-pentene were explored by using the half-titanocene catalysts (Scheme 1). The Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)-MAO catalyst exhibited high catalytic activities for the copolymerizations with a single catalytically active species and afforded copolymers containing much higher comonomer contents compared to conventional catalysts. Especially in the 2M1P copolymerization, the use of both Cp* and 2,6-diisopropylphenoxy ligands was essential to obtain copolymers with high catalytic activity as well as with high and uniform 2M1P incorporation.

Scheme 1



In chapter 3, copolymerizations of ethylene with nonconjugated dienes, 7-methyl-1,6-octadiene (MOD) and 4-vinylcyclohexene (VCHen), using the half-titanocene complexes (**1-3**) were explored for precise and efficient synthesis of the ethylene copolymers containing unsaturated side chains (Scheme 2). The **1-3**/MAO catalysts copolymerized ethylene with MOD and the resultant copolymers possessed unsaturated side chain without side reaction. These catalysts also copolymerized ethylene with VCHen and the afforded copolymers contained cyclohexenyl side chain although some degree of side reaction was accompanied in all cases. In particular, $CpTiCl_2(N{=}C^tBu_2)$ (**3**)-MAO catalyst exhibited the highest catalytic activity with the lowest degree of side reaction. The subsequent introduction of polar functionality, epoxy group, into the cyclohexenyl side chain of the copolymer was also succeeded.

Scheme 2

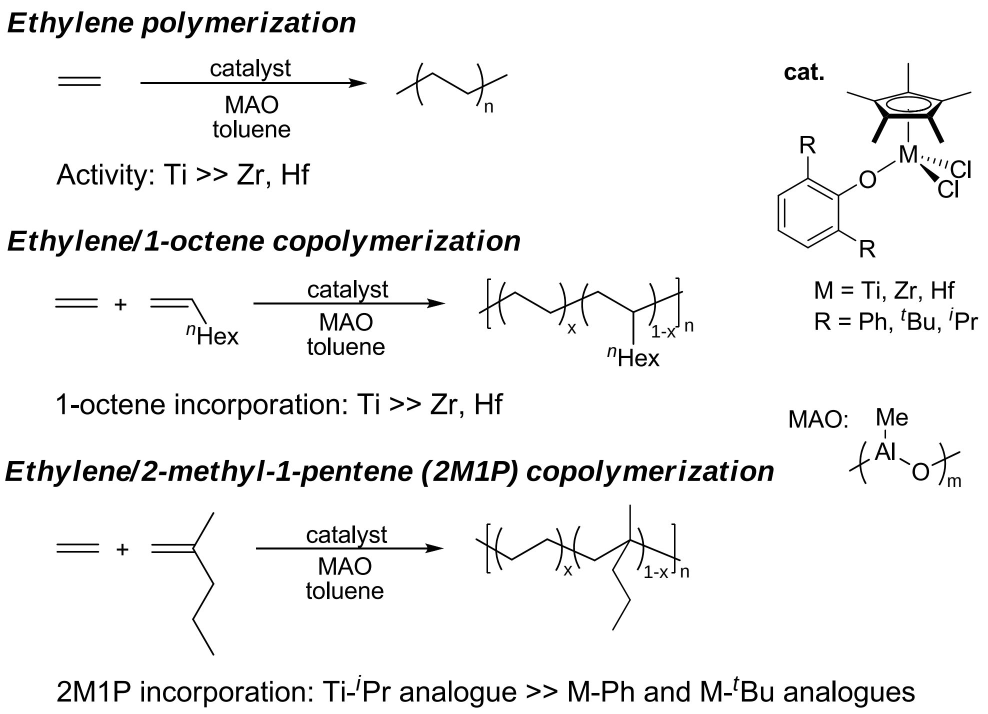


Copolymerization of ethylene with nonconjugated dienes

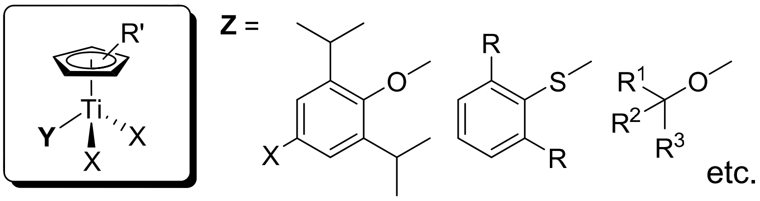
Z: microstructure derived from side reaction
m-CPBA: *m*-chloroperbenzoic acid

In chapter 4, a series of group 4 half-metallocene complexes containing an aryloxo ligand of the type, $Cp^*MCl_2(O\text{-}2,6\text{-}R_2C_6H_3)$ [M = Ti, Zr, Hf; R = Ph, ^{t}Bu, ^{i}Pr], were synthesized by reactions of Cp^*MCl_3 with $LiO\text{-}2,6\text{-}R_2C_6H_3$, and ethylene polymerization and ethylene copolymerizations with 1-octene and 2-methyl-1-pentene (2M1P) using these complexes in the presence of MAO were investigated (Scheme 3). It turned out that Ti metal center is more suitable for ethylene polymerization and ethylene/1-octene copolymerization than Zr and Hf metal centers in terms of both the catalytic activity and comonomer incorporation. Moreover, both the Ti metal center and the ^{i}Pr groups at 2,6-position on the aryloxo ligand are essential for the efficient 2M1P incorporation in the ethylene/2M1P copolymerization. Therefore, a detail exploration of the mono-anionic donor ligands (Y) in the nonbridged half-titanocenes $Cp'TiX_2(Y)$ would be a promising approach to find more efficient catalysts for ethylene copolymerizations (Scheme 4). Especially, ethylene copolymerizations by using $Cp'TiX_2(O\text{-}2,6\text{-}4\text{-}Z\text{-}^iPr_2C_6H_3)$ [Z = electron donating and withdrawing groups] would reveal the electronic effect of the active metal center on ethylene copolymerization and the resultant knowledge should lead to design of new efficient catalysts.

Scheme 3



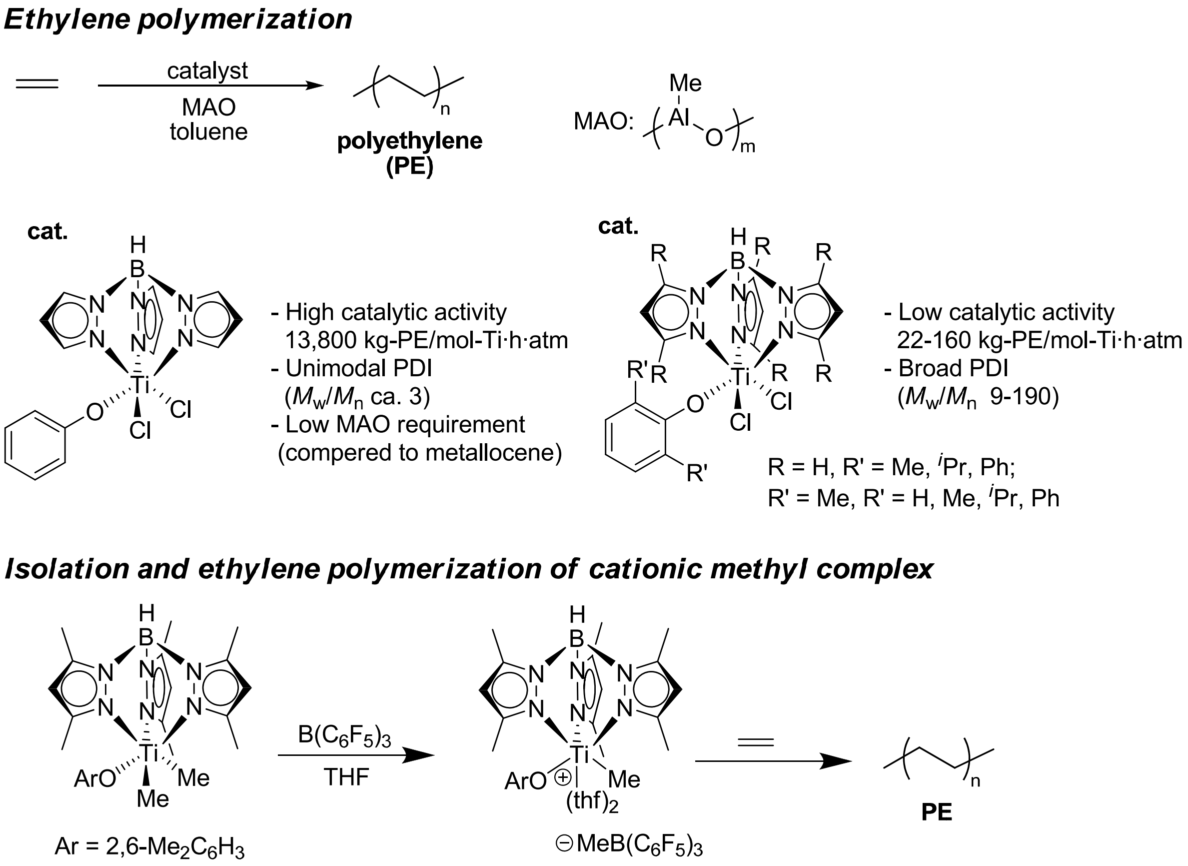
Scheme 4



In chapter 5, a series of hydrotris(pyrazolyl)borate titanium complexes containing an aryloxo ligand of the type, Tp'$TiCl_2$(O-2,6-$R_2C_6H_3$) [Tp' = Tp = HB(pyrazolyl)$_3$ or Tp* = HB(3,5-Me_2-pyrazolyl)$_3$; R = H, Me, ^{i}Pr, Ph] were synthesized by reactions of Tp'$TiCl_3$ with LiO-2,6-$R_2C_6H_3$, and ethylene polymerization using these complexes were investigated

(Scheme 5). $TpTiCl_2(OPh)$-MAO catalyst exhibited the highest catalytic activity and the activity was 4 times higher than that of $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$. The required amount of MAO was 150 times lower compared to $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ under a optimized condition. The cationic alkyl species of the type, $[Tp^*TiMe(O\text{-}2,6\text{-}Me_2C_6H_3)(THF)_2]\text{-}[MeB(C_6F_5)_3]$, was successfully isolated and the complex polymerized ethylene without MAO.

Scheme 5



- High catalytic activity 13,800 kg-PE/mol-Ti·h·atm
- Unimodal PDI (M_w/M_n ca. 3)
- Low MAO requirement (compered to metallocene)

- Low catalytic activity 22-160 kg-PE/mol-Ti·h·atm
- Broad PDI (M_w/M_n 9-190)

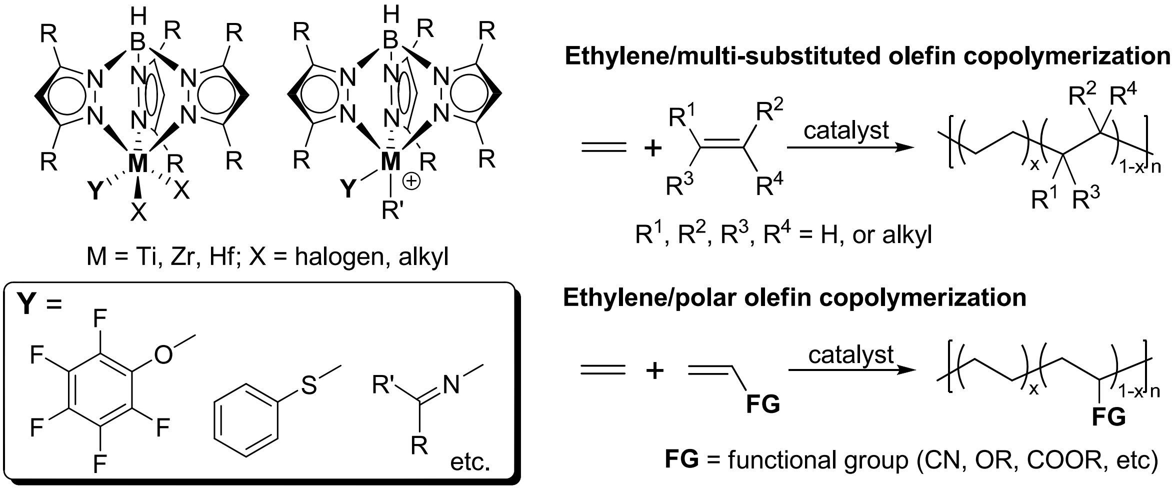
R = H, R' = Me, ^{i}Pr, Ph;
R' = Me, R' = H, Me, ^{i}Pr, Ph

Ar = $2,6\text{-}Me_2C_6H_3$

$\ominus MeB(C_6F_5)_3$

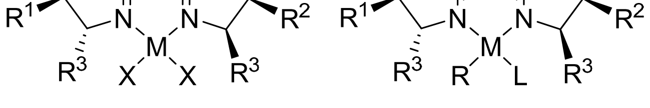
These low or no MAO requirements in these catalysts are significant advantages from the aspect of the industrial application of homogeneous catalysts. And, a simple replacement of both the anionic donor ligand and metal center in $Tp'MX_2(Y)$ complexes would be highly expected to lead to more efficient catalysts for the ethylene/sterically hindered olefin copolymerizations as seen in $Cp'MX_2(Y)$ (Scheme 6). Moreover, the catalysts may be able to copolymerize ethylene with polar olefins directly because a rather wide cone angle of Tp’ ligands compared to Cp’ ligands may lead to improvement in tolerance toward the polar functional groups.

Scheme 6



Recently, design and synthesis of late transition metal complex catalysts for the direct copolymerization of ethylene with polar olefins have been investigated actively, because these complexes exhibit higher tolerance toward the functional groups compared to early transition metal catalysts. I have been also exploring the possibility using nickel and palladium complexes containing 2,2-bisoxazoline derivatives (Scheme 7), although effective catalysts have not been found yet.

Scheme 7



M = Ni, Pd; X = alkyl, halogen; L = neutral ligands

In this thesis, the efficient ethylene copolymerizations of γ-branched-α-olefin and 2,2-disubstituted-α-olefin by using the Cp'MX_2(Y) catalysts were firstly achieved, and the effects of the metal center, anionic ligand (Y), and substituents in ligands on the copolymerizations were revealed. The possibility of the Tp'TiX_2(Y) complexes as efficient catalysts for precise olefin polymerization was also demonstrated. I highly believe that the proposal mentioned above would lead to a discovery of efficient catalysts for the production of new polyolefins.

List of Publications

学位論文の主たる部分を公表した論文

(1) “Efficient incorporation of 2-methyl-1-pentene in copolymerization of ethylene with 2-methyl-1-pentene catalyzed by nonbridged half-titanocenes”

Nomura, K.; Itagaki, K.; Fujiki, M.

Macromolecules **2005**, *38*, 2053-2055.

(2) “Efficient incorporation of vinylcylohexane in ethylene/vinylcyclohexane copolymerization catalyzed by nonbridged half-titanocenes”

Nomura, K.; Itagaki, K.

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(3) “Ethylene/2-methyl-1-pentene copolymerization catalyzed by half-titanocenes containing aryloxo ligand: Effect of cyclopentadienyl fragment.

Nomura, K.; Itagaki, K.

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(4) “Effect of cyclopentadienyl and anionic donor ligands on monomer reactivities in copolymerization of ethylene with 2-methyl-1-pentene by nonbridged half-titanocenes - cocatalyst systems”

Itagaki, K.; Fujiki, M.; Nomura, K.

Macromolecules **2007**, *40*, 6489-6499.

(5) “Ethylene polymerization and ethylene/1-octene copolymerization using group 4 half metallocenes containing aryloxo ligands, $Cp^*MCl_2(OAr)$ [M = Ti, Zr, Hf; Ar = $O\text{-}2,6\text{-}R_2C_6H_3$, R = ^{t}Bu, Ph], - MAO catalyst systems”

Itagaki, K.; Hasumi, S.; Fujiki, M.; Nomura, K.

J. Mol. Catal. A: Chem., in press.

(6) “Tris(pyrazolyl)borate Ti(IV) complexes containing phenoxy ligands: Effective catalyst precursors for ethylene polymerization that proceeds via cationic Ti(IV) species”

Itagaki, K.; Kakinuki, K.; Katao, S.; Khamnaen, T.; Fujiki, M.; Nomura, K.; Hasumi, S.

Organometallics ASAP.

総説

(1) “高機能ポリオレフィンの創製を指向した高性能分子触媒 －新しいエチレン系ポリマーの創製を可能とした研究例－“

野村琴広、板垣浩司

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(1) “Influence of steric and electronic perturbations on the polymerization activities of α-iminocarboxamide nickel complexes”

Azoulay, J. D.; Itagaki, K.; Wu, G.; Bazan, G. C.

Organometallics **2008**, *27,* 2273-2280.

(2) “Direct precise functional group introduction into polyolefins: Efficient incorporation of vinyltrialkylsilanes in ethylene copolymerizations by nonbridged half-titanocenes”

Nomura, K.; Kakinuki, K.; Fujiki, M.; Itagaki, K.

Macromolecules **2008**, *41*, 8974-8976.

学位論文の主たる部分を公表した学会発表 (本人発表分)

－国際学会－

(1) ”Effect of ligands in copolymerization of ethylene with 1,1-disubstituted-α-olefins catalyzed by half-titanocenes containing aryloxo ligands”

K. Itagaki, M. Fujiki, K. Nomura

The 10th Japan-Korea Symposium on Catalysis, YP131, 松江市, 5/’05.

(2) “Efficient incorporation of 1,1-disubstituted-α-olefins, cyclohexene in ethylene copolymerization by nonbridged half-titanocenes”

K. Itagaki, W. Wang, M. Fujiki, K. Nomura

2005 USA-Japan Forum: “Advances in Polymer Chemistry and Their Impacts upon Society”,

South Lake Tahoe, California (USA), 6/’05.

(3) “Efficient incorporation of some ‘traditionally unreactive’ olefins in ethylene copolymerizations using nonbridged half-titanocenes”

K. Itagaki, W. Wang, K. Nomura

13th IUPAC International Symposium on Organometallic Chemistry directed towards Organic Synthesis (OMCOS 13), P482, Geneva, Switzerland, 7/’05.

(4) “Copolymerization of ethylene with ‘traditionally unreactive’ monomers by nonbridged half-titanocenes”

K. Itagaki, K. Nomura

Asian Polyolefin Workshop 2005 (APO2005), P13, 奈良市, 12/’05.

(5) “Copolymerization of ethylene with disubstituted α-olefins catalyzed by nonbridged half-titanocene”

K. Itagaki, J. Liu, M. Fujiki, K. Nomura

5th International Workshop on Heterogeneous Ziegler-Natta Catalysts, P18, 北陸先端大, 3/’07. Poster Award.

(6) “Precise copolymerization of ethylene with sterically encumbered olefins by nonbridged half-titanocenes”

K. Itagaki, K. Kakinuki, M. Fujiki, K. Nomura

International Symposium on Catalysis and Fine Chemicals 2007 (C&FC2007), MC-A0116, Singapore, 12/’07

(7) “Precise synthesis of functionalized polyethylene via copolymerization of ethylene with nonconjugated diene”

K. Itagaki, A. Takemoto, J. Liu, M. Fujiki, K. Nomura

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(8) “Ethylene polymerization by hydrotris(pyrazolyl)borate titanium(IV) complexes containing phenoxy ligands”

K. Itagaki, K. Kakinuki, M. Fujiki, K. Nomura

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(3) “ハーフチタノセン錯体触媒を用いるエチレン共重合による不飽和ポリオレフィンの精密合成”
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第 37 回石油・石油化学討論会, IC02, 札幌, 2007 年 10 月.

(4) “各種フェノキシ配位子を有するヒドロトリス(ピラゾリル)ボラン配位チタン錯体の合成・同定およびエチレン重合”
板垣浩司、垣貫健一、藤木道也、野村琴広
第 55 回有機金属化学討論会, P2C-21, 大阪府立大学, 2008 年 9 月. ポスター賞.

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(2) “オレフィンの精密共重合のためのチタン錯体触媒の設計・創製”
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(3) “フェノキシ配位子を有する第 4 族ハーフメタロセン錯体の合成とオレフィン重合”
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Koji Itagaki