Studies on Stereospecific Polymerization of Polar Monomer with Zirconium Complexes

Department of Chemistry, Gaduate School of Science and Engineering

SAITAMA UNIVERSITY

Yusuke Saito

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Chapter 1

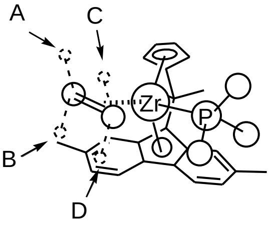
General Introduction

Introduction

Polyolefins including polyethylene (PE), polypropylene (PP), poly(4-methyl-1-pentene) (PMP), and ethylene-propylene elastomer (EPR) have useful characters with excellent mechanical strength, flexibility, processability, chemical inertness, and recyclability. Their materials are essential goods such as plastic bag, wrap, water pipe, electronic heating coating material, rope, and car bumper in everyday life. For example, about 60% of thermoplastics are made from homopolymers which consist of ethylene or propylene and from copolymers incorporating ethylene or propylene produced by coordination polymerization reactions with organometallics catalysts. Thus, organometallic catalysts have contributed to the development of polyolefin industry controlling macrostructures of stereoregularity and branch. Today, two types of catalysts have mainly applied to industrial productions of polyethylene and polypropylene mainly has been applicated two types of catalysts.

One is Ziegler-Natta catalysts based on $TiCl_4$ with Et_2AlCl as a cocatalyst that were discovered by Ziegler, Natta demonstrated that an appropriate catalytic system that is heterogeneous multi-site catalysts provides polypropylene with semi-crystalline in 1950s.[1] Generally, polyethylene synthesized by Ziegler-Natta catalysts is called as high-density polyethylene (HDPE) and exhibits higher melting point and crystallinity than low-density polyethylene (LDPE) synthesized by radical polymerization under high temperature and pressure. The discovery of the catalysts took much advantage in basis of industrial and academic research, and the development of the catalytic system utilizing Group 4 metal and aluminum reagents that exhibit high performance have been attracting much attention.

The other is metallocene catalysts developed by Kaminsky and co-worker in 1980s that have only one type of active species called single site catalyst to give polymer with special structures, for example, isotactic and syndiotactic polyolefins, linear polyethylene, ethylene-propylene elastomer, and cycloalkene copolymer.[2] In particular, the degree of the stereoregularity of stereoselective polyolefins such as isotactic or syndiotactic polypropylene can be evaluated from configurations of two neighboring substituents (so called diad) as *m* (*meso*) for syn or *r* (*racemo*) for anti stereochemistries, which are directly related to physical properties of polyolefin. For example, atactic polypropylene having methyl groups with irregular configuration for main chain adopts amorphous structure lacking crystallinity. In contrast, isotactic polypropylene that has regular arrangement of methyl groups laying in the same side to the polymer chain shows high melting points (160–165 ºC) and high crystallinity to form helical structure. The generation of stereoselectivity which affects properties of polyolefin has greatly relations with the framework of the ligand in catalysts. When a metallocene complex reacts with α-olefin, four different coordination modes (A–D) are assumed for a prochiral olefin (Scheme 1).[3] According to the NOE difference NMR spectroscopy of a model compound that has a structure similar to polymerization active species, the position A is preferential at ambient temperature providing a wide space without steric repulsion.



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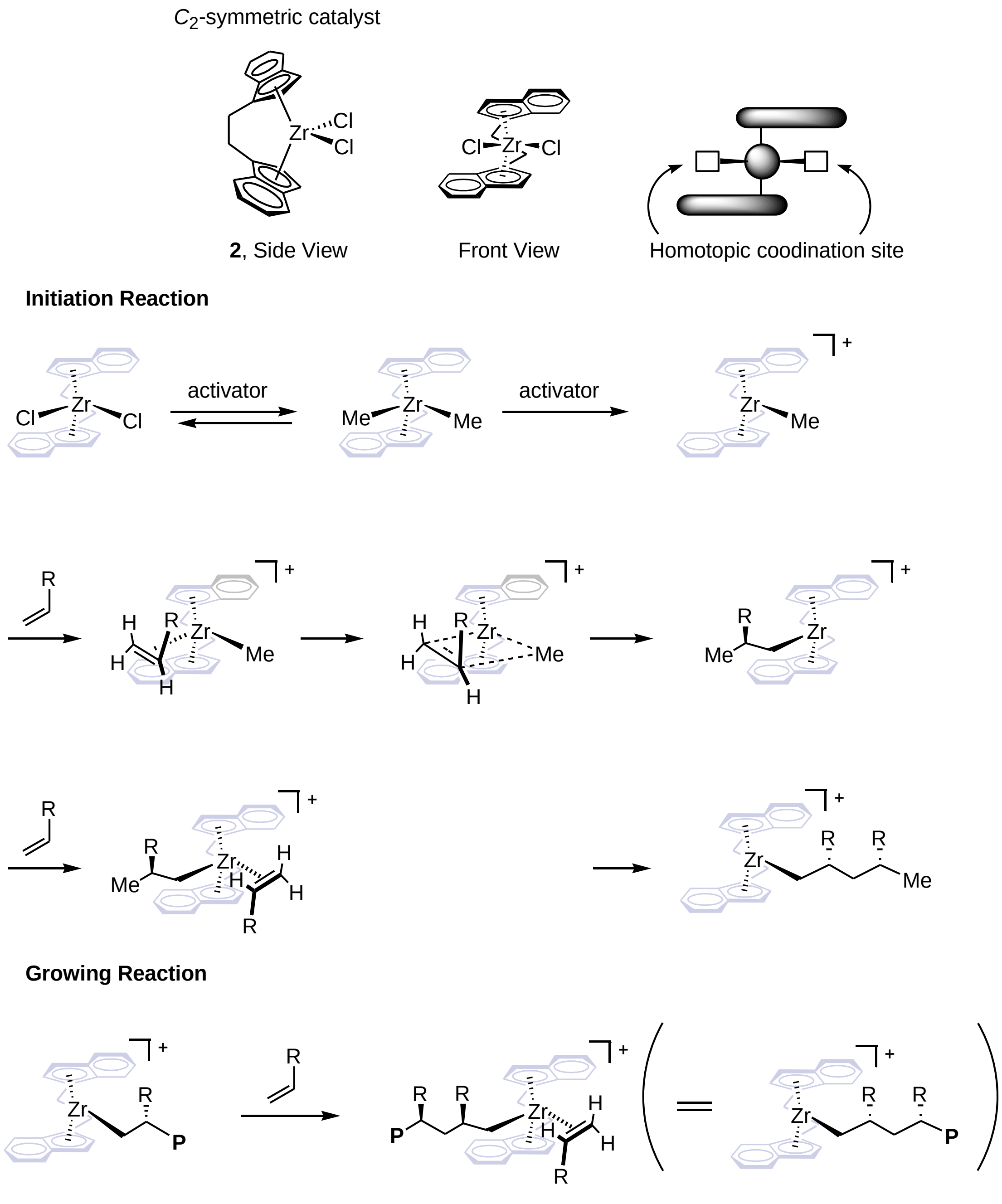
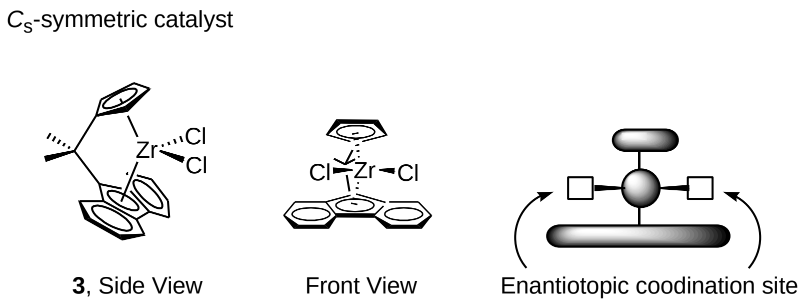
Scheme 1. Coordination possibilities for an α-olefin in the complex (C_5H_4–CMe_2–$C_{13}H_6Me_2$)Zr(PMe_3)(α-olefin) **1**.

Taking the report into considerations, the mechanism for the isospecific α-olefin polymerization with *ansa*-zirconium complex **2** having a C_2-symmetric ligand such as ethylene bis(indenen) ligand has been proposed as shown in Scheme 2. First of all, the pre-catalyst is activated by an activator such as aluminum compounds or dMAO (dried methylaluminoxane), followed by the insertion of monomer into generated cationic monoalkyl species. The polymer chain adopts a proper configuration to avoid steric repulsion against the indenyl ligand, and an α-olefin molecule coordinates/inserts into the central metal from a suitable direction (*re*-face or *si*-face) to minimize steric repulsion between the polymer chain and the alkyl group of α-olefin in the four membered transition state. In the growing step, since coordination site of α-olefin is homotopic before and after the monomer insertion, α-olefin can be always inserted with maintaining a same configuration. Thus, metallocene catalysts with a C_2-symmetric ligand produce isotactic polyolefins by the enantiomorphic site control mechanism.



Scheme 2. A proposed mechanism for isospecific α-olefin polymerization with C_2-symmetric zirconocene.

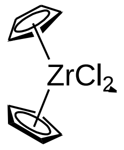
In the case of an *ansa*-zirconium complex **3** with C_s-symmetric ligand having fluorenyl and cyclopentadienyl rings bridged by a methylene linker, the two active species generated from the precatalyst **3** for α-olefin polymerization have enantiotopic relations to provide syndiotactic polyolefin owing to the C_s-symmetric character (Scheme 3).



Scheme 3. Coordination site of C_s-symmetric zirconocene.

The propylene polymerization performances of some metallocene catalysts and Ziegler-Natta catalyst are summarized in Table 2.[3] There are mainly three methods about design of metallocene catalysts for more advanced and precise stereocontrol: They are to bridge cyclopentadienyl or indenyl rings, to introduce a substituent at the 2-position on indenyl rings, and to innovate the 4-aryl substituent on indenyl rings. For example, in comparison between non-bridged metallocene **4** and ethylene-bridged metallocene **2** that has a more rigid ligand, the catalyst **2** produced more highly isotactic polypropylene with [*mmmm*] = 78.5%. By introducing substituents on the 2- and 4-substituents of indenyl rings, isotacticity of polypropylene reached up to [*mmmm*] = 99.9%. The precatalyst promoted completely isospecific polypropylene on the same level with heterogenerous Ziegler-Natta catalysts, and the melting point (T_m) of 171 ºC outstandingly transcended those of isotactic polypropylene derived from Ziegler-Natta catalysts.

Table 2. Polymerization of propylene with metallocene catalysts.[3]



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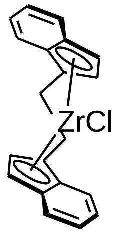

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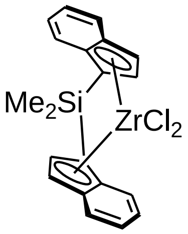

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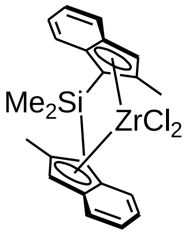

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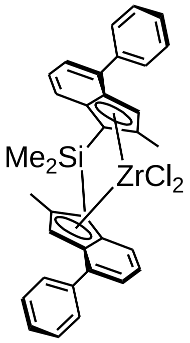

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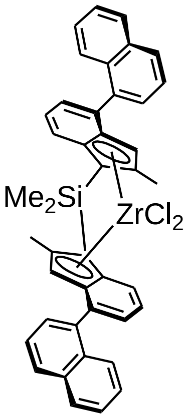

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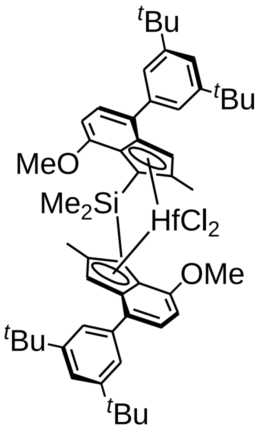

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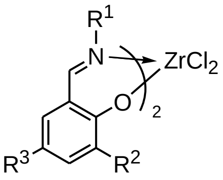
Cat.	Activity [kg mmol^{-1} h^{-1}]	M_w [g mol^{-1}]	[*mmmm*] [%]	T_m [ºC]
4	140	2,000	7	–
2	188	24,000	78.5	132
5	190	36,000	81.7	137
6	99	195,000	88.5	145
7	245	213,000	95.2	150
8	875	920,000	99.1	161
9	1.8	5,800,000	99.9	171
Ziegler-Natta	20	900,000	99	162

However, these modifications of metallocenes made sacrifices of productivity to gain isotactic polymers. Therefore, development of more highly active catalysts for isospecific α-olefin polymerization has been greatly aspired for future polyolefin chemistry.

This interest expanded to new single site catalysts without cyclopentadienyl ligands, the so-called post-metallocene catalyst. The development led to tremendous impacts on academic and industrial research in regard to ligand design to control α-olefin polymerization.

Fujita et al. developed phenoxy-imine bidentate ligands composed by nitrogen and oxygen donor atoms, and synthesized early transition metal complexes (known as FI catalysts) based on titanium and zirconium with the two [NO]-type ligands, which were applied to extremely highly active ethylene polymerization.[4] The ethylene polymerization performances of FI catalysts are compiled in Table 3. It is acharacteristic feature that their structures and electronic states of ligands can be modified easily by introduction of heteroatom and steric substituent. If R^1 and R^2 substituents in catalysts are appropriate, the coordination site to insert monomer can be controlled and the catalytic activity drastically changes. For example, when R^1 = cyclohexyl and R^2 = ^{t}Bu (**16**), the catalytic activity is 82 kg(PE) mmol(**16**)$^{-1}$ h^{-1} bar^{-1}. In contrast, when R^1 = cyclohexyl and R^2 = CPh_2Me (**19**), the catalytic activity reached 6,552 kg(PE) mmol(**19**)$^{-1}$ h^{-1} bar^{-1}.

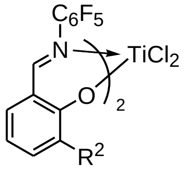
Table 3. Polymerization of ethylene with FI catalysts.[4]



10–**19**

Complex	R^1	R^2	R^3	Activity [kg mmol^{-1} h^{-1}]
10	Ph	Me	H	0.4
11	Ph	^{i}Pr	H	0.9
12	Ph	^{t}Bu	H	519
13	Ph	^{t}Bu	Me	331
14	Ph	1-Adamantyl	Me	714
15	Ph	Cumyl	Me	2,096
16	Cy	^{t}Bu	Me	82
17	Cy	1-Adamantyl	Me	434
18	Cy	Cumyl	Me	4,315
19	Cy	CPh_2Me	H	6,552

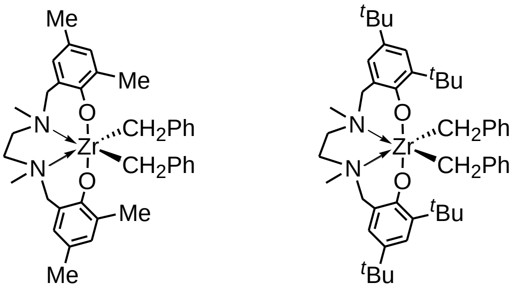
Table 4. Propylene polymerization with FI catalysts.[4]



20–**24**

Complex	R^2	Activity [kg mmol^{-1} h^{-1}]	M_n [g mol^{-1}]	M_w/M_n	T_m [°C]	[*rr*] [%]
20	H	30.7	189,000	1.51	n.d.	43
21	Me	68.8	260,200	1.22	n.d.	52
22	^{i}Pr	31.1	153,700	1.16	n.d.	75
23	^{t}Bu	3.7	28,500	1.11	137	87
24	TMS	5.9	47,000	1.08	152	93

The effect of substituents in FI catalysts for syndiotactic propylene polymerization is shown in Table 4. To avoid steric repulsion between methyl group of propylene and R^2 substituent, selective *re*/*si* insertion of propylene monomer takes place. Consequently, as R^2 substituent in catalysts becomes more bulky, the syndiotacticity of polypropylene increases from 43% to 93% strikingly. However, in 1-hexene polymerization, the FI catalysts furnished non-stereoselective poly(1-hexene) with significant regioerrors (50 mol%). Thus, the catalysts had not succeeded in stereospecific polymerization of higher α-olefins.



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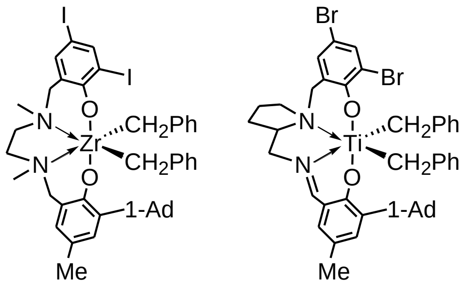
Scheme 4. [ONNO]-type zirconium complexes

Kol et al. developed ethylene-linked [ONNO]-type bis(phenolate) tetradentate ligand with a C_2 symmetric structure to improve flexible phenoxy imine bidentate ligands (Scheme 4).[5] The zirconium complex **25** bearing an [ONNO]-type ligand with a methyl group at the *ortho* position in the phenoxide served as a 1-hexene polymerization catalyst, leading to an atactic poly(1-hexene) (activity = 35 g(PH) mmol(**25**)$^{-1}$ h^{-1}). When zirconium complex **26** with a ligand having a *tert*-butyl group at the *ortho*-position was used with an initiator for the polymerization of 1-hexene, the polymerization proceeded in a living manner to afford isotactic polymer (activity = 18 g(PH) mmol(**26**)$^{-1}$ h^{-1}) with narrow dispersity. These results indicated that bulkiness of the substituent at the *ortho* position affects the activity and stereospecificity of polymer formation due to the control of coordination site for monomer. However, these catalysts exhibited low activity in 1-hexene polymerization albeit success in the synthesis of isotactic poly(1-hexene).

To develop the catalyst to allow excellent isotactic polyolefin with high activity, ligands having substituents that give influence on not only steric factor but also electronic factor have been recently designed.

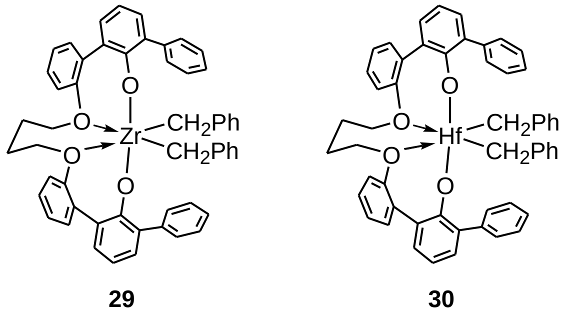


27 **28**

Scheme 5. C_1-symmetric [ONN'O]-type Group 4 metal complexes with an improved [ONNO]-type ligand.

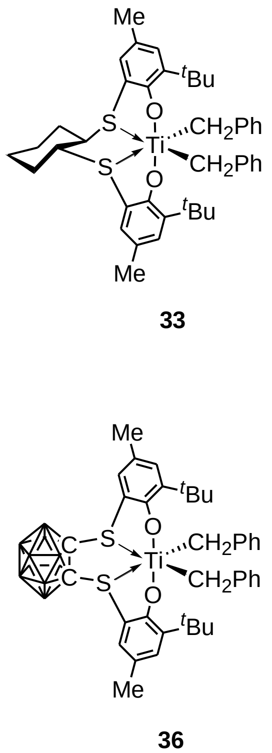
Kol *et al.* reported zirconium complexes with a pseudo C_2 symmetric [ONN'O] ligand with iodine substituents as an electron-withdrawing group **27** in 1-hexene polymerization to record the high activity of 300 g(PH) mmol(**27**)$^{-1}$ h^{-1} among post-metallocene-type zirconium complexes that achieve completely isospecific polymerization (Scheme 5).[6] Moreover, use of zirconium complex **28** having [ONN'O]-type ligand, with a bulky 1-adamantyl group at the *ortho*-position which has a more rigid ethylene bridge moiety, in 1-hexene polymerization gave highly isotactic poly(1-hexene) with 1,500 g(PH) mmol(**28**)$^{-1}$ h^{-1} ([*mmmm*] > 95%).

Quite recently, the activity of 1-hexene polymerization with [OOOO]-type bis(phenolato) hafnium complex **30** in 1-hexene polymerization has reached up to 4,900 g(PH) mmol(**30**)$^{-1}$ h^{-1} (M_w = 81,600 g mol^{-1}, PDI = 2.0, [*mmmm*] = 89%) (Scheme 6).[7] The value did record the highest activity in 1-hexene polymerization among post-metallocene catalysts. However the polymer showed slightly decrease of isospecificity to 89%. Thus, only a few catalysts that achieve high activity and precise isospecificity in polymerization of α-olefin have been reported.



Scheme 6. C_2-symmetric [OOOO]-type Group 4 metal complexes.

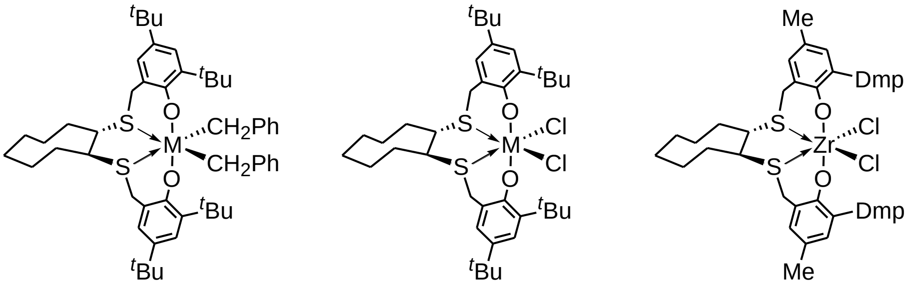
According to HSAB rule, hard zirconium atom has tendency to be strongly coordinated by hard donors such as nitrogen atom, leading to decrease of the Lewis acidity. In constant, it can be expected that soft sulfur atom coordinates more weakly to zirconium atom than nitrogen atom does.



Scheme 7. [OSSO]-type Group 4 metal complexes.

A Group 4 metal complexes with a series of [OSSO]-type ligands forming compact 5-5-5 and 5-6-5 chelate rings were innovated by Okuda *et al.*.[8] In particular, titanium complex **31** incorporating 1,4-dithiabutanediyl-linked [OSSO]-type ligand affords isotactic polystyrene with high activity in styrene polymerization (Scheme 7). In contrast, the complex **31** performed as a 1-hexene oligomerization catalyst to give oligo(1-hexene) with high catalytic activity (1,750 g(PH) mmol(**27**)$^{-1}$ h^{-1}). On the other hand, the titanium complex **32** with 1,5-dithiapentanediyl-bridged [OSSO]-type ligand produced syndiotactic polystyrene with quite low activity. In the polymerization of styrene in the presence of 1-hexene, the catalytic system using titanium complex **33**, bearing an [OSSO]-type ligand featuring the fusion of a *trans*-cyclooctane-1,2-diyl ring with the (Λ^*,R^*,R^*)-configuration, afforded isotactic polystyrene terminated by regio- and stereoirregular oligohexene. In addition, Kol *et al.* reported that ethylene-bridged [OSSO]-type zirconium complex **34** with 6-5-6 chelate ring polymerized 1-hexene at room temperature to provide poly(1-hexene) with regioregular and stereoirregular (atactic) structure (activity = 80 g(PH) mmol(**34**)$^{-1}$ h^{-1}, M_w = 7,400 g mol^{-1}) despite of its C_2 symmetry.[9] Di-*tert*-butoxy zirconium complex **35** showed interconversion behavior between enantiomers ($\Delta G^\ddagger$ = 71 ± 1 kJ mol^{-1}), indicating that the complex **35** could not maintain C_2-symmetric structure in solution because of the high flexibility of the ethylene bridge due to low coordination avility of sulfur atoms. Miyatake *et al.* reported the complex **35** played a role as a polymerization catalyst of vinylcyclohexane to give isotactic poly(vinylcyclohexane). Jin *et al.* demonstrated that Group 4 metal complexes **36** bearing an *o*-carborane linked [OSSO]-type ligand had abilities to polymerize ethylene and to copolymerize ethylene with 1-hexene.

Our laboratory established a convenient synthetic method of a series of mixed donor based bis(phenolato) [OSSO]-type tetradentate ligands with a *trans*-cyclooctane-1,2-diyl platform and synthesized a dibenzyl zirconium complex **37** with one of the [OSSO]-type ligand (Scheme 8).[10] The zirconium complex adopted the C_2-symmetric, *cis*-α structure unlike Group 4 metal complexes with [ONNO]-type ligand such as salan, salen, and salalen complexes. The results of 1-hexene polymerization was summarized in Table 5. Upon activation with $B(C_6F_5)_3$ or $(Ph_3C)[B(C_6F_5)_4]$, the complex **37** acted as an excellent polymerization catalyst for 1-hexene to provide isotactic poly(1-hexene) ([*mmmm*] > 95%) with higher activity (activity = 2,500 g(PH) mmol(**37**)$^{-1}$ h^{-1}) than reported [ONNO]-type and [OSSO]-type zirconium complexes. Moreover, we also reported the synthesis of dichloro zirconium complex **39** with the same ligand that performed as a 1-hexene polymerization catalyst involving the highest activity of 18,100 g(PH) mmol(**39**)$^{-1}$ h^{-1} among the reported post-metallocene catalysts.[11] Furthermore, 4-methyl-1-pentene polymerization catalyzed by the **39**/dMAO system produced completely isotactic poly(4-methyl-1-pentene) (PMP) with good activity (1,220–1,690 g(PMP) mmol(**39**)$^{-1}$ h^{-1}) and relatively narrow polydispersities. Additionally, hafnium complex **40** showed as a high potential for 1-hexene polymerization to give remarkably higher molecular weight of poly(1-hexene) than zirconium complexes with high activity and excellent isospecificity. Hafnium precatalyst **38** was found to lead to isospecific polymerizations of 1-hexene or 4-methyl-1-pentene with good activity to produce isotactic poly(1-hexene)s and poly(4-MP)s, respectively, with significantly larger molecular weights than any polymers ever obtained by group 4 metal complexes with other [OSSO]-type ligands. Moreover, the complex **38** upon activation with dMAO promoted the propylene polymerization accompanying high activity and controlled isotacticity at a range of temperatures. In particular, the highest isotacticity ([*mmmm*] = 93.7%) and melting transition temperature (T_m = 156.2 °C) were observed for polypropylene produced at 0 °C. Zirconium complex **41** with the [OSSO]-type ligand having 2,6-dimethylphenyl groups at the *ortho* position in phenyl moiety is an active styrene polymerization catalyst, leading to highly isotactic polystyrene.



37 (M = Zr)
38 (M = Hf)

39 (M = Zr)
40 (M = Hf)

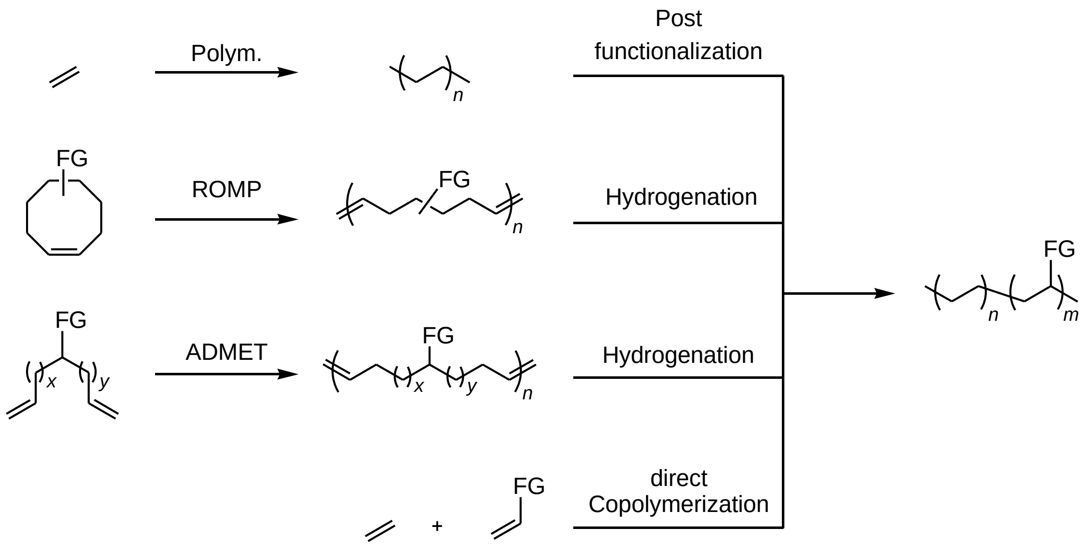
41

Scheme 8. Group 4 metal complexes having [OSSO]-type ligand with a *trans*-cyclooctane-1,2-diyl platform.

Table 5. Comparison among post-metallocene catalysts for 1-hexene polymerization

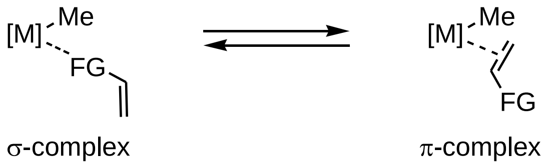
Cat.	Activity g(polymer) mmol(cat)$^{-1}$ h^{-1}	M_w (g mol^{-1})	PDI	[*mmmm*] [%]
25 (Zr)	35	23,000	1.57	0
26 (Zr)	18	12,000	1.15	>95
29 (Zr)	1,800	94,500	1.9	66
30 (Hf)	4,900	81,600	2.0	89
27 (Zr)	300	155,000	1.9	95
28 (Ti)	1,500	353,000	1.03	>95
31 (Ti)	1,750	458	1.30	–
34 (Zr)	80	7,400	1.6	–
37 (Zr)	2,500	43,000	1.9	>95
38(Hf)	420	102,200	1.2	>95
39 (Zr)	18,100	40,000	1.9	95
40 (Hf)	1,050	58,600	1.6	>95

Meanwhile, functionalized polyolefins are strongly desired as new materials possesing beneficial properties such as adhesion, toughness, print/paintability, miscibility, and rheological properties unlike those of hydrocarbon-based polyolefins.[12] General synthetic routes for functionalized high-density polyethylene (HDPE) are principally developed as post functionalization of polyethylene, ring-opening metathesis polymerization (ROMP) of functionalized cyclooctenes, acyclic diene metathesis (ADMET) of functionalized terminal dienes, and direct copolymerization of ethylene with functionalized α-olefins in radical, anionic, or coordination polymerizations (Scheme 9). However, these synthetic methods except the direct copolymerization hold serious problems which are the necessity of multi-step procedures and specially functionalized monomers. For example, radical copolymerizations such as atom-transfer radical polymerization (ATRP) and reversible addition-fragmentation chain-transfer (RAFT) are suitable to control the molecular weight, narrow distribution, and wide scope of polar vinyl monomer, but they cannot control stereospecificity in copolymer and show low reactivity for non-polar monomer due to the lack of conjugated stabilization of generated radicals and require quite harsh conditions (high pressures and temperature). On the other hand, coordination polymerization with transition metal complex, which enables to achieve copolymerization of ethylene with polar monomer without harsh conditions in radical or anionic polymerization, has much attention to develop new materials.



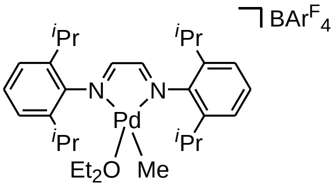
Scheme 9. Synthetic methods for functionalized HDPE.

Since early transition metal complexes possess high Lewis acid nature, they have a tendency to form σ-complex with functional groups of polar monomers, which prevents the formation of the π-complex coordinating the C=C double bond on the transition metal (Scheme 10). In sharp contrast, late metal complexes have an inclination to form π-complex against σ-complex due to low oxophilicity. Therefore, as they are more tolerant to functional moieties to be Lewis base, directly copolymerization has been examined employing late transition metal catalysts.



Scheme 10. Equilibrium between σ-coordination and π-coordination of polar vinyl monomer into a central metal.

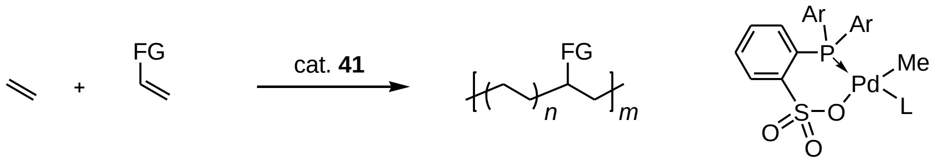
As the first example of Group 10 metal complex, palladium complexes incorporating α-diimine ligand by Brookhart et al. has expanded to copolymerization of ethylene or propylene with polar functional monomers such as acrylates ($CH_2=CHCO_2R$), acrylic acid ($CH_2=CHCO_2H$), and methyl vinyl ketone to yield highly branched copolymers (Scheme 11).[13] As the catalysts normally tend to promote chain walking that repeats rapid β-hydride elimination to produce olefin and 2,1-reinsertion of the produced olefin, linear functional polyethylene or polypropylene could not be obtained.



Scheme 11. Pd(II) diimine catalyst reported by Brookhart.

Palladium phosphino-sulfonate catalyst **41** provided functionalized polyethylene from copolymerization of ethylene with various vinyl polar monomers such as acrylates ($CH_2=CHCO_2R$), acrylic acid ($CH_2=CHCO_2H$), vinyl acetate ($CH_2=CHOAc$), acrylonitrile ($CH_2=CHCN$), vinyl fluoride ($CH_2=CHF$), vinyl esters ($CH_2=CHOR$), acrylamide ($CH_2=CHCONR_2$), and vinyl sulfones ($CH_2=CHSO_2R$) (Table 6).[14]

Table 6. Copolymerization of ethylene with polar vinyl monomer catalyzed by a palladium complex **41**.[14]



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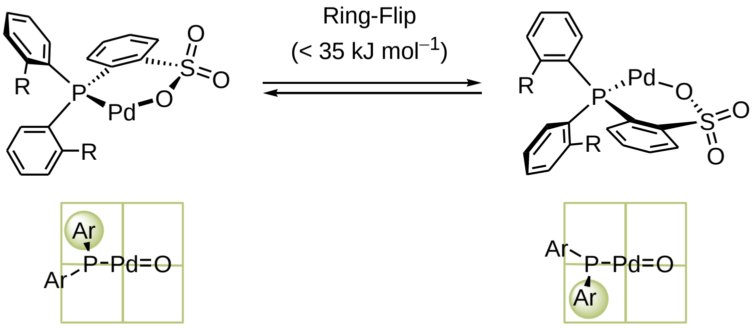
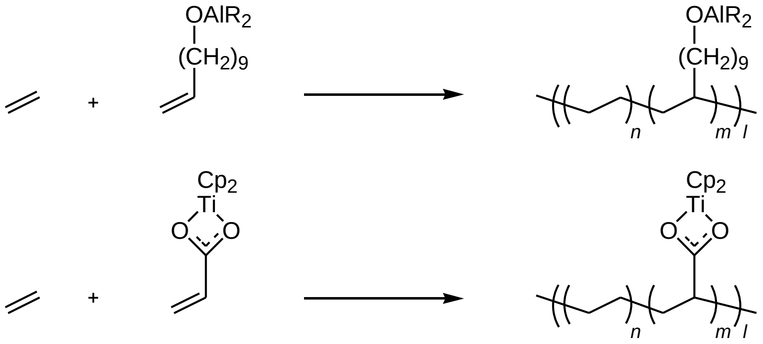
FG	M_n [10^3 g mol^{-1}]	Incorporation 1/(m+1) [%]
COOMe	~41.2	~52
COOH	6–8	3-10
OAc	5–11	0.6–1.9
CN	~12.3	2–9
F	4.5–14.5	0.1–3.6
OBu	0.9–4.8	1–7
CONH^{i}Pr	1.2–1.3	3.2–4.1
SO_2Me	~3.6	~13.9

However, polymerization of methyl acrylate in the presence of a catalytic amount of the palladium complex **41** affords only heptamer. In addition, stereospecificity of the resulting oligomer cannot be controlled. That is due to the low-energy ring flip of six membered metal-ligand chelate (Scheme 12). Thus, late transition metal complexes in homo- and copolymerization of polar monomer is suitable to incorporation of polar monomer into copolymer but is incompatible with generation of stereospecific homo- and copolymer.



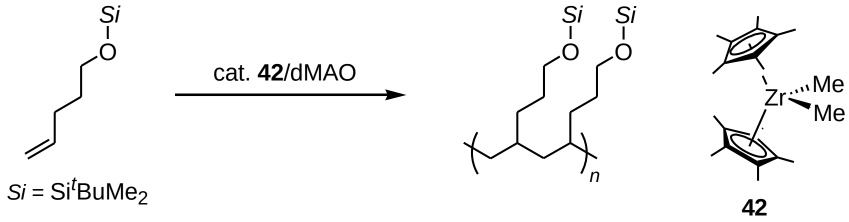
Scheme 12. Ring-flip motion of the six-membered metal-ligand chelate.

Meanwhile, as Group 4 metal complexes have strong Lewis acid character and high oxophilicity, a solution to achieve the polymerization of polar monomer is to transform the monomer into innocuous species for the central metals. On the strategy, therefore, for the syntheses of functionalized polyethylenes or polypropylenes possessing –OH,[15] $–NR_2$,[16] –OR,[17] –C(O)OR,[18] –SR,[19] $–SiR_3$,[20] and $–BR_2$[21] by the their polymerization with Zeigler-Natta or metallocene catalysis, the polymerizations have been approached through masking or precomplexation of the functionality with the stoichiometric amount of Lewis acidic species (Scheme 13).



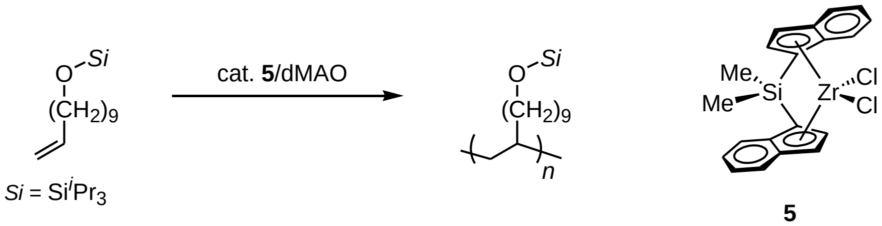
Scheme 13. Selected examples of functionalized HDPE containing heteroatom fragments.

Recently, Waymouth et al. reported the homopolymerization of α-olefin, the hydroxy group of which is protected by a silyl group such as ${}^{t}BuMe_2Si$ (Scheme 14). Polymerization of the siloxy-substituted α-olefin with a catalyst prepared by the treatment of $Cp^*{}_2ZrMe_2$ **42** with $B(C_6F_5)_3$ afforded oligomer of M_n = 1,800 g mol^{-1} with 40.0 g $mmol^{-1}$ h^{-1}.[22] A different catalytic system generated from the combination of *rac*-(EBTHI)$ZrMe_2$ (EBTHI = ethylene-1,2-bis(η^5-4,5,6,7-tetrahydro-1-indenyl) and $B(C_6F_5)_3$ was not active in the siloxy-substituted α-olefin polymerization.



Scheme 14. Polymerization of siloxy-substituted α-olefin with **42**/dMAO.

10-Undecen-1-oxytriisopropylsilane has been polymerized by the combination of *rac*-dimethylsilylbis(1-indenyl)zirconium dichloro complex [$Me_2Si(Ind)_2ZrCl_2$] **5** and dMAO to give the polymer with M_w = 23,300 g mol^{-1} (Scheme 15).[23] Thus these results indicated that ligand framework is an important factor in terms of hindrance to the poison of active species.



Scheme 15. Polymerization of siloxy-substituted α-olefin with **5**.

Against metallocene catalysts, post-metallocene catalysts, which can be poisoned by the coordination of donor atoms such as nitrogen, oxygen, and sulfur atoms on central metal, have low tolerance for polar functional group. It is assumed that the coordination of functional moieties in vinyl polar monomer on metal center is more stable than that of olefinic moiety in polar monomer or α-olefin. According to this idea, to reveal the effect of post-metallocene catalysts in polar monomer copolymerization, Fujita *et al.* estimated the energy difference (ΔE) between ethylene-coordinated and carbonyl-coordinated cationic complexes by DFT calculations (Table 4).[24] The ΔE value for titanium complex with phenoxy imine ligand and metallocene complex are 55.7 and 104.6 kJ mol^{-1}, respectively, indicating that the FI catalyst displays much higher functional group tolerance than the metallocene catalysts owing to the coordination of [O^-, N] ligands, that is, FI catalysts are promising for more facile introduction of polar monomer in copolymer. In fact, though metallocene catalysts show no copolymerization ability of ethylene with 5-hexen-1-yl acetate, FI catalysts have achieved the synthesis of functionalized polyethylene in the same polymerization.

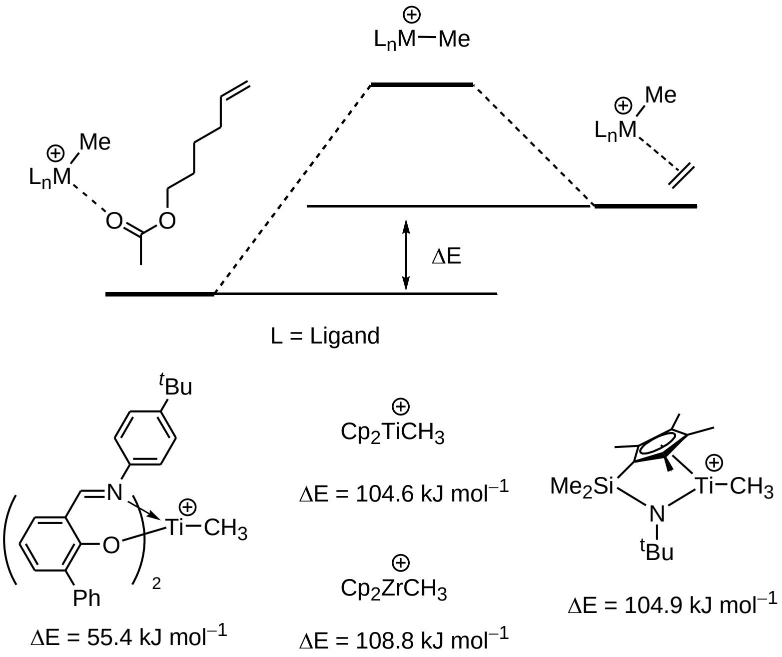
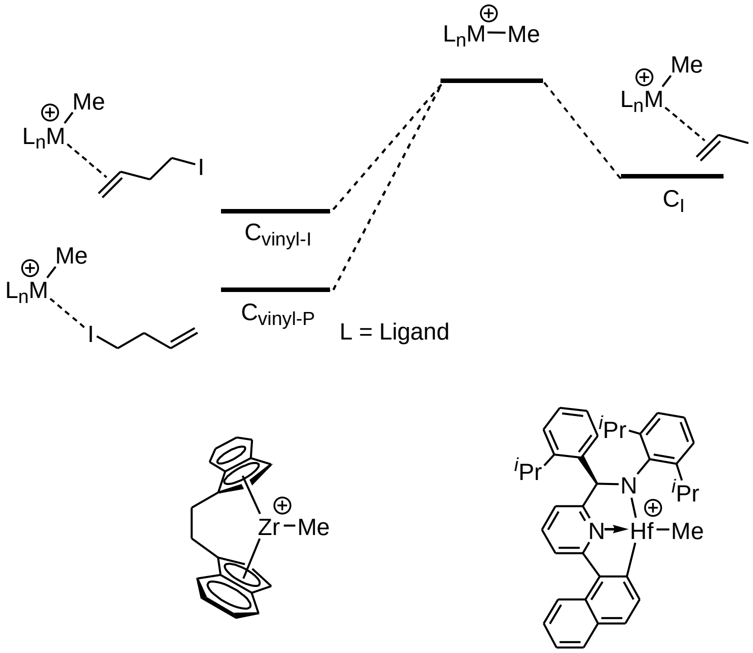


Table 4. The energy of cationic species coordinated with 5-hexene-1-yl-acetate or ethylene, computed by DFT calculations.

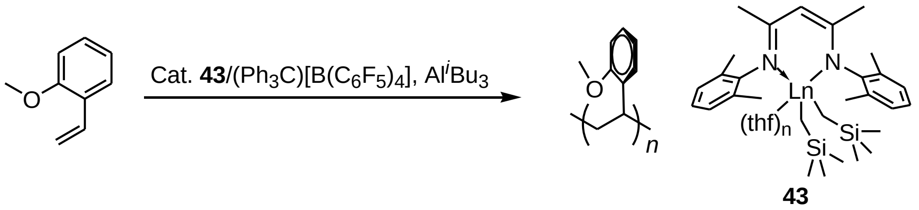
In addition, Li *et al.* also reported the comparison of energy gaps between 4-iodo-1-butene- and propylene-coordinated metallocene catalyst (Zr) and post-metallocene catalyst (Hf) by the DFT calculations (Table 5). The ΔE value of $C_{vinyl\text{-}I}$–C_I and $C_{vinyl\text{-}I}$–$C_{vinyl\text{-}P}$ for zirconium complexes are 21.94 and 7.57 kJ mol^{-1}, respectively, while the corresponding ΔEs are 12.93 and 5.97 kJ mol^{-1}, respectively. These results indicate that the hafnium complex is more likely to be coordinated by 4-iodo-1-butene than the zirconocene. Consequently, copolymerization of propylene with ω-halo-α-olefin with the hafnium complex gives halogenated *i*PP with 11.7 mol % of functional monomer incorporation (zirconocene: 3.5 mol %).[25]



Cat.	$E_{\text{vinyl-P}}$ (kJ mol^{-1})	$E_{\text{vinyl-I}}$ (kJ mol^{-1})	E_{I} (kJ mol^{-1})
Zr	−78.81	−71.24	−93.18
Hf	−38.85	−32.38	−45.31

Table 5. The energy of propylene- or 4-iodo-1-butene-coordinated cationic complexes, computed by DFT calculations.

Quite recently, Cui *et al.* presented that rare-earth metal complexes **43** featuring β-diketiminato ligand as precatalyst achieved the first isospecific polymerization of *ortho*-methoxystyrene, which was activated through σ-π chelation of polar monomer instead of poisoning by Lewis basic methoxy group (Scheme 16).[26]

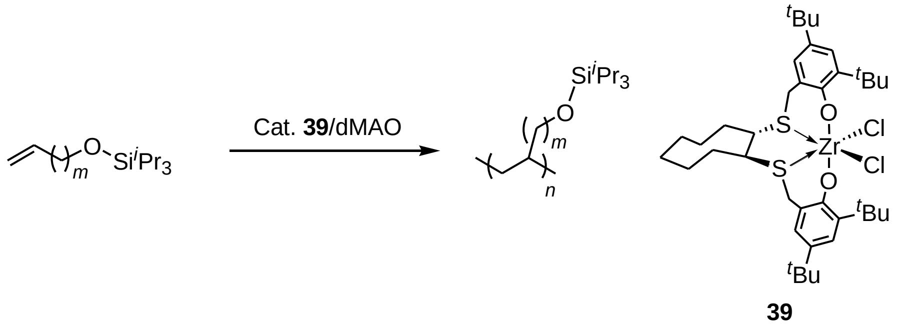


Scheme 16. Isospecific polymerization of polar monomer with **43**

However, isospecific polymerization of polar α-olefins by coordination polymerization with transition metal complexes has never been explored. In addition, the corresponding copolymer with high polar-monomer incorporation has not been synthesized yet.

Since [OSSO]-type zirconium complexes can be postulated to be poisoned by oxygen and sulfur atoms from the ligand, it would be expected that the energy difference (ΔE) between coordination of vinyl moiety and functional group into the cationic center is lower than that of metallocene catalysts. In addition, since our [OSSO]-type zirconium complex is one of the most highly active catalyst in α-olefin polymerization among the reported post-metallocene catalysts, the author guesses that the polar monomer polymerization using the [OSSO]-type complex affords isotactic functional polyolefin retaining high activity. As mentioned as above, when α-olefin containing hydroxyl moiety is polymerized with transition metal complex, aluminum and silicon compounds are usually used as the protection group to prevent poison into the central metal. It is difficult to treat aluminum compounds owing to air- and moisture-sensitivity. However, silicon compounds are superior compared with aluminum compound because of: (1) stability (basically, silicon compounds are quite stable toward air and moisture than aluminum ones), (2) low price [for example, in contrast to chlorotrimethylsilane ($23.40/100 mL), trimethylalumium is considerably expensive ($226.50/100 g) in Sigma-Aldrich Co.], (3) wide choice of substituent, and (4) facile transformation.

Thus, the author focuses on two points in order to achieve hydroxy-containing α-olefin polymerization evolving complete stereospecificity. The first one is to use high performance of our catalyst precursor, [OSSO]-type dichloro zirconium complex. The second one is to protect the terminal hydroxy group with a silicon group. In this doctor's thesis, the author investigated the details of the isospecific polymerization of ω-siloxy-α-olefin using [OSSO]-type zirconium in Chapter 1.



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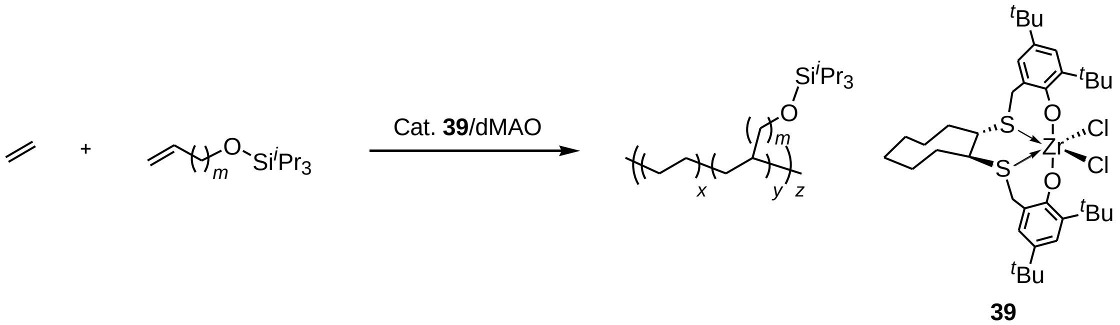
In Chapter 2, on the basis of the results obtained in Chapter 1, the author tried the copolymerization of siloxy-substituted α-olefin with ethylene and 1-hexene with the [OSSO]-type zirconium complex.



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Finally, the author studied the transformation of isotactic siloxy-containing polyolefins to the corresponding new types of isotactic polar polyolefins in Chapter 3.

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Chapter 2

Isospecific Polymerization of ω-alken-α-oxytriisopropylsilane with zirconium complex with [OSSO]-type ligand

2-1 Introduction

Polyolefins such as polyethylene and polypropylene are widely used as useful materials, and it is well known that a factor controlling their crystallinity and melting point is related to the tacticity of polymers.[1] In spite of their high utility and versatility, further application is actually limited owing to their poor properties regarding adhesion, dye retention, and toughness. As introduction of functional groups into polyolefins is expected to be able to improve their properties, therefore, much attention has been paid to design direct polymerization methods of polar monomer.[2] However, coordination polymerization of polar monomer catalyzed by transition metal complex hardly occur owing to toxification of active species by coordination of functional moiety in polar monomer during polymerization reaction, and it remains a challenging task to break through them.

Recently, as for a strategy for this problem, a method that masks the functional groups of a polar monomer with Lewis acid has been published.[3] On the other hand, in the case of unprotected polar monomer, less oxophilic late-transition metal complexes[4] and early-transition metal complexes, Lewis acidity of which are reduced by electron-donating ancillary ligands[5], have been quite recently reported to enable copolymerize ethylene or propylene with functional monomer. In particular, copolymerizations of propylene with polar monomer using Group 4 metal complexes achieved to afford functionalized iPP.[6] Moreover, *Cui* et al. reported that rare-earth metal species achieve isospecific and syndiotactic coordination polymerization of *ortho*-methoxystyrene.[7] but, to the best of our knowledge, isospecific polymerization of functionalized α-olefin has never been pursued.

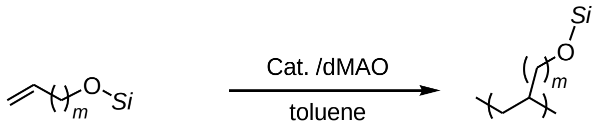
Meanwhile, we have invented a class of group 4 metal complexes 2with the bis(phenolate) ligand containing a *trans*-cyclooctane-1,2-bis(thio) platform,[8] which perform as a powerful polymerization catalyst of α-olefin to give excellent isospecificity of poly(α-olefin) with high activity in comparison with conventional post-metallocene catalysts.[9] In this chapter, the author report that the zirconium complex can operate as the polymerization catalyst of terminal siloxy-subsituted α-olefin **1** with moderate activity to produce highly isospecific polymer with functional group.

2-2 Polymerization of siloxy-substituted α-olefin

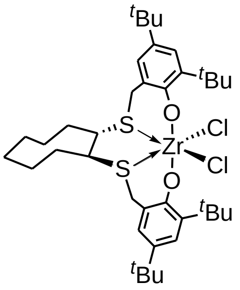
We have found that dichloro zirconium complex **2** showed an excellently potential as a pre-catalyst for the α-olefin polymerizations, which promotes highly isospecific polymerizations of 1-hexene, 4-methyl-1-pentene, or propylene with high activities. To evaluate the catalytic ability of **2** for the polymerization of the polar monomer, we examined the polymerization of terminal siloxy-substituted α-olefin **1** as the target monomer. According to the literature, the starting terminal triisopropylsiloxy α-olefins **1** were prepared by the treatment of the corresponding ω-alken-α-ol with chlorotriisopropylsilane in the presence of imidazole.[10] The results of the polymerization of ω-alken-α-oxytriisopropylsilane catalyzed by zirconium complexes **2–4** upon activation with dMAO (dried methylaluminoxane) were summarized in Table 1.

First, the polymerization of 5-hexen-1-oxytriisopropylsilane **1c** (1.0 g, 4.0 mmol) catalyzed by zirconium complex **2** (0.0020 mmol) with 250 equivalents of dMAO (0.50 mmol) as an activator proceeded efficiently at 25 ºC for 12 h to produce 170 mg of a viscous polymer showing 7.3 g mmol(**2**)$^{-1}$ h^{-1} of activity (Run 3). The GPC analysis showed that the resulting polymer possessed a weight-average molecular weight (M_w) of 42,700 g mol^{-1} with a monomodal polydispersity (PDI = 2.0), implicating that the catalyst system behaved as a single site catalyst. In the ^{1}H NMR spectrum of the obtained polymer, a characteristic triplet signal assigned to $-CH_2O-$ fragment was observed at δ 3.66. We measured the ^{13}C{^{1}H} NMR to determine the isospecificity [*mmmm*] of the obtained polymer. The ^{13}C{^{1}H} NMR spectrum of the obtained polymer was shown in Figure 1. The ^{13}C{^{1}H} NMR spectrum exhibited eight sharp signals.

Table 1. Polymerization of terminal substituted α-olefin with zirconium complexes 2–4 upon the activation with dMAO.



1 *m* = 2, 3 4, 9



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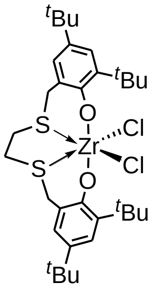

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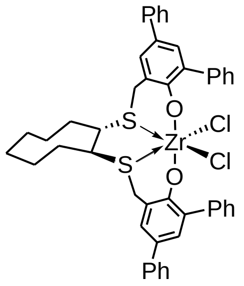
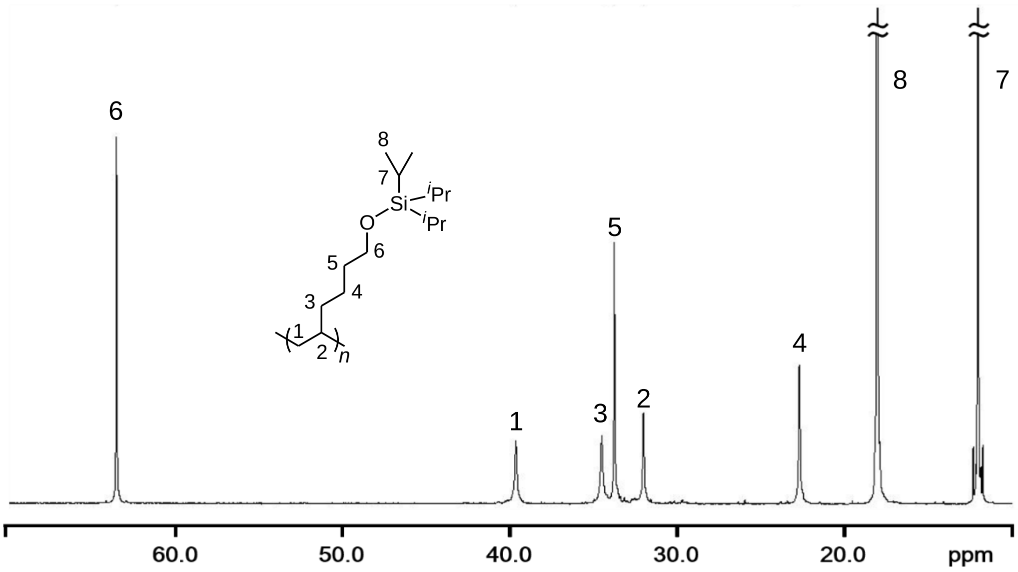


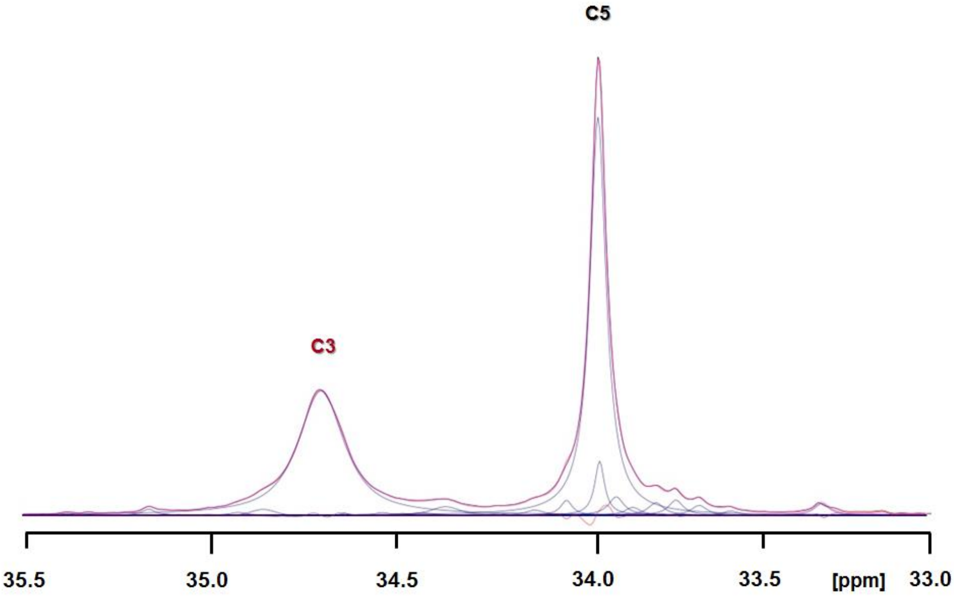
4

Run[a]	Cat.	Monomer (m+2, *Si*)	Yield [mg]	Activity [g mmol^{-1} h^{-1}]	M_w[b] [g mol^{-1}]	PDI[b,c]	[*mmmm*][d] [%]
1	**2**	**1a** (4, Si^{i}Pr$_3$)	N. R.[e]	–	–	–	–
2	**2**	**1b** (5, Si^{i}Pr$_3$)	27	0.56	8,900	1.7	85
3	**2**	**1c** (6, Si^{i}Pr$_3$)	170	7.3	42,700	2.0	>95
4[f]	**2**	**1d** (11, Si^{i}Pr$_3$)	171	81	23,300	1.9	>95
5	**2**	**1e** (6, SiMe$_3$)	N. R.	–	–	–	–
6	**2**	**1f** (6, ^{t}BuMe$_2$Si)	9.4	0.4	3,000	1.2	–
7	**2**	**1g** (6, SiPh$_3$)	N. R.	–	–	–	–
8	**2**	**1c**	200	8.5	13,900	2.0	>95
9	**2**	**1c**	160	6.8	8,700	1.9	92
10[g]	**2**	**1c**	110	315	7,300	1.5	85
11[h]	**2**	**1d**	269	1,620	10,700	1.5	94
12[i]	**3**	**1c**	300	0.62	1,540	1.2	–
13[j]	**4**	**1a**	N. R.	–	–	–	–

[a]Polymerization of **1** (1.0 g) was performed with **2** (2.0 μmol) and dMAO (0.50 mmol) in toluene (5 mL) at 25 ºC for 12 h. [b]Determined by GPC. [c]PDI = $M_\mathrm{w}/M_\mathrm{n}$. [d]Determined by ^{13}C NMR spectroscopy. [e]No reaction. [f]Poylmerization time was 1 h. [g]Polymerization was performed with **2** (2.0 μmol) and dMAO (4.40 mmol) in toluene (5 mL) at 25 ºC for 10 min. [h]Polymerization was performed with **2** (2.0 μmol) and dMAO (3.50 mmol) in toluene (5 mL) at 25 ºC for 5 min. [i]Polymerization was performed with **3** (20.0 μmol) and dMAO (5.0 mmol) in toluene (10 mL) at 25 ºC for 24 h. [h]Polymerization was performed with **4** (2.0 μmol) and dMAO (0.50 mmol) in toluene (5 mL) at 25 ºC for 24 h.

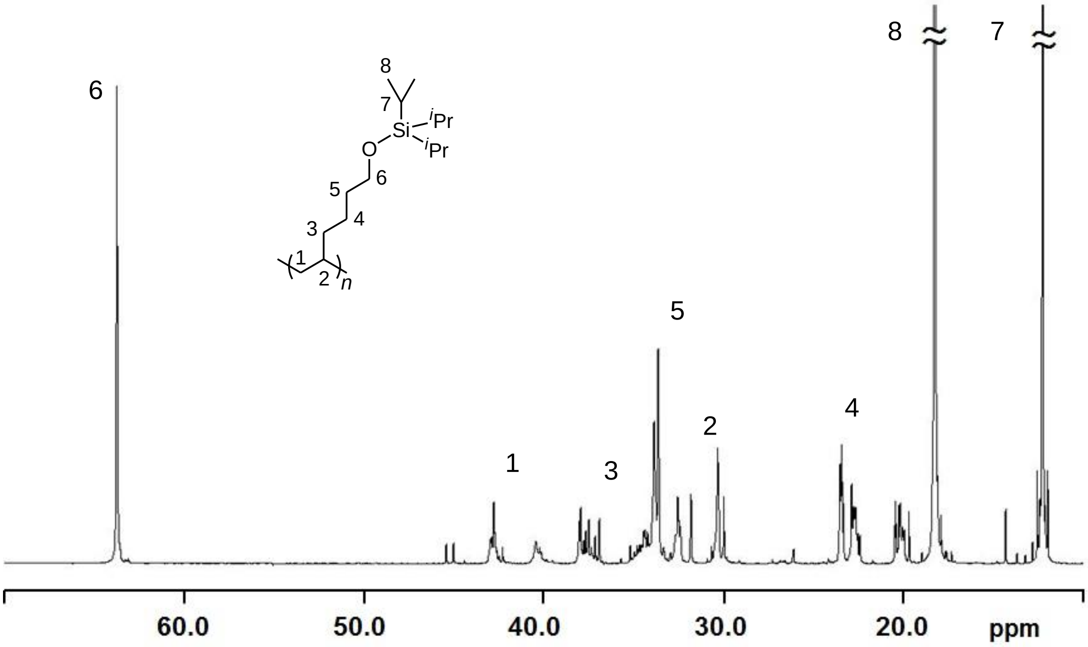
Figure 1. The ^{13}C{^{1}H} NMR spectrum ($CDCl_3$) of the obtained polymer (Run 3).





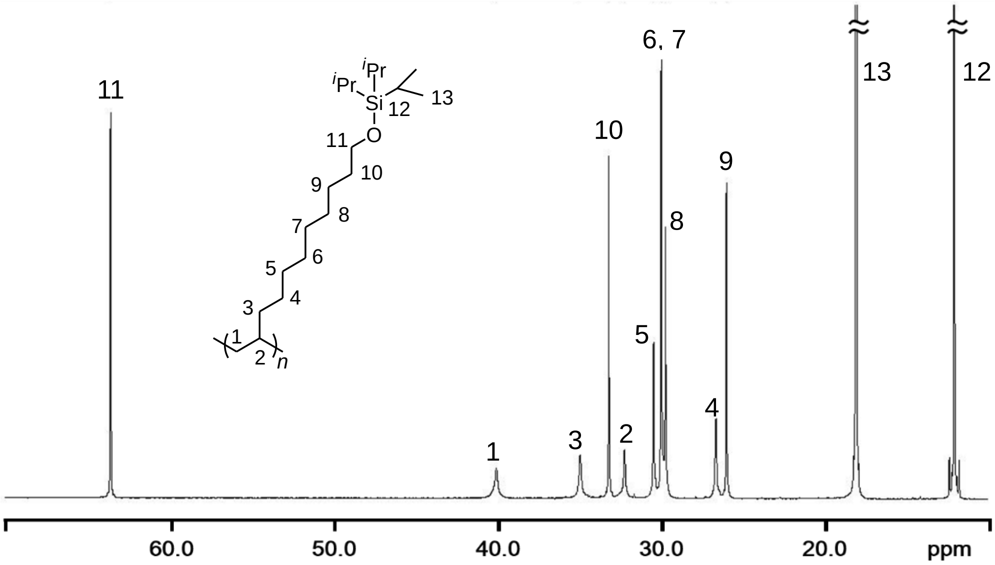
The signals due to methine and methyl carbon atoms in the triisopropyl group attached to the silicon atom were observed at δ 12.2 and 18.2, respectively. The main chain was identified by the resonances at δ 39.8 (C1) and 32.1 (C2), and the signals of the side chain were displayed at 63.5 (C6), 34.5 (C3), 33.8 (C5), and 22.7 (C4). Notably, the resulting polymer does possess an excellent isospecificity ([*mmmm*] > 95%), judged by the signal due to the carbon atom (C3) neighbored to the main chain, in reference to the $^{13}C\{^{1}H\}$ NMR analysis of an isotactic poly(1-hexene).[11] As far as we know, this achievement of the synthesis of the functionalized polyolefins with high isospecificity in coordination polymerization is the first instance except for a restrictive isospecific polymerization of *ortho*-methoxystyrene with the rare-earth metal species.[6] However, as there are no examples synthesizing poly(5-hexene-1-oxytriisopropylsilane), polymerization of **1c** using zirconium complex **3** with a 1,2-dithioethanediyl-linked [OSSO]-type ligand reported by Kol *et al.* and Miyatake *et al.*[12] was carried out to evaluate the magnitude of isospecificity for the resulting polymer (Run 12). The catalytic system of **3** (0.0020 mmol) with dMAO (0.50 mmol) for polymerization of **1c** (1.0 g, 4.0 mmol) showed lower activity [0.62 g mmol(**3**)$^{-1}$ h^{-1}] and provided quite less isoselective oligomer (M_w = 1,540 g mol) (Figure 2) than those of the **2**/dMAO system, suggesting that the generation of isospecificity are largely influenced by the bridge moieties. Meanwhile, the hafnium complex, which was expected to produce a polymer with higher molecular weight than **2** did in the presence of 250 equivalents of dMAO, did not polymerize **1c** under the same conditions. Next, we tried to polymerize polar monomers with different chain length, 3-buten-1-oxytriisopropylsilane **1a** was inert in coordination polymerization with the **2**/dMAO catalytic system, and **1a** was recovered (Run 1).

Figure 2. ^{13}C{^{1}H} NMR spectrum (CDCl$_3$) of atactic polymer obtained by ethylene bridged [OSSO] zirconium complex **3** (Run 12).

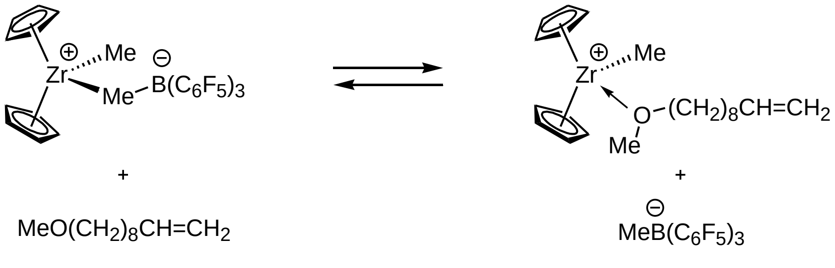


The reason why the insertion reaction of **1a** is prevented would be steric repulsions between the bulky triisopropylsilyl group in the polar monomer and the *tert*-butyl group in the *ortho*-position at the phenoxide in the active species. We have revealed that zirconium complex **4** having a modified [OSSO]-type ligand with 2,6-dimethylphenyl group at the *o*-position showed a character as an isospecific polymerization catalyst of styrene which is a bulkier than 1-hexene.^{13} However, **4** had no ability to polymerize **1a** (Run 13), although **4** seems to have a wider coordination space than **2** (Run 13). The catalytic system of zirconium complex **2** (0.0020 mmol) and dMAO (0.50 mmol) for the polymerization of 4-penten-1-oxytriisopropylsilane **1b** (1.0 g, 4.1 mmol) provided a viscous oily oligomer with low activity of 0.56 g mmol^{-1} h^{-1} with M_w = 8,900 g mol^{-1} (Run 2). Judged by the ^{13}C{^{1}H} NMR spectrum, the isospecificity of the gained polymer decreased to 85%. In the case of 10-undecen-1-oxytriisopropylsilane **1d** possessing a longer carbon chain than **1c**, the catalytic activity [81 g mmol(**2**)$^{-1}$ h^{-1}] was about 10 folds higher than that for **1c** (Run 4), implying that the steric repulsions between a bulky silyl moiety in a monomer and a growing chain hamper the polar monomer insertion (Run 4). In comparison of the polymerization of **1d** with another homogeneous polymerization catalyst, the zirconium pre-catalyst **2** performed slightly higher catalytic activity than a metallocene-type zirconium complex (activity = 42 g mmol(Cat)$^{-1}$ h^{-1}, M_w = 23,300 g mol^{-1}) affording the functional polyolefin of nearly the same molecular weight.[14] The ^{13}C{^{1}H} NMR spectrum of the polymer gained in Run 4 exhibited twelve sharp signals due to overlapping of two signals. The signal due to the carbon atom (C3) was identified as one observed at δ 34.9, and the isospecificity ([*mmmm*]) was estimated over 95% (Figure 3).

Figure 3. The $^{13}C\{^1H\}$ NMR spectrum ($CDCl_3$) of the isotactic polymer (Run 4).

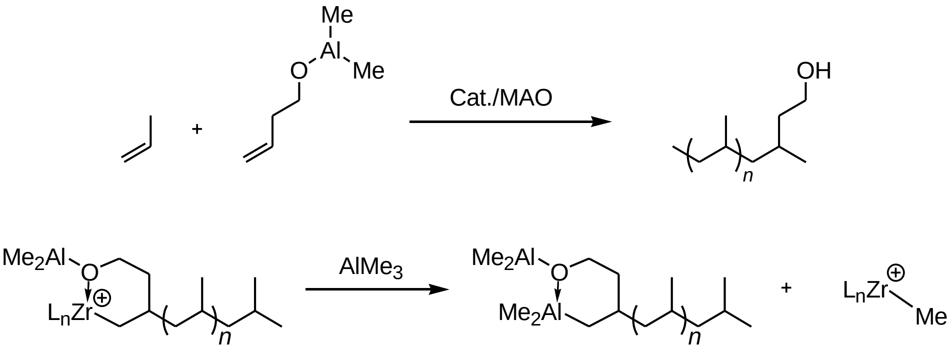


Next, to reveal the effect of the bulkiness of silyl substituents, we examined the polymerization of some silyl-protected monomers under the same conditions. In the case of 5-hexen-1-oxytrimethylsilane **1e**, the polymerization reaction did not proceed at all (Run 5). Baird *et al.* reported a rapid exchange between free and oxygen-coordinated monomer in the reaction of cationic $Cp_2ZrMe(\mu\text{-}Me)B(C_6F_5)_3$ with 5 equivalents of 1-methoxy-9-decene (Scheme 1).[15] Thus, it is assumed that in the case of Me_3Si as the protection group, the active cationic species generated from the **2** and dMAO was poisoned by the naked Lewis base moiety in **1e**.



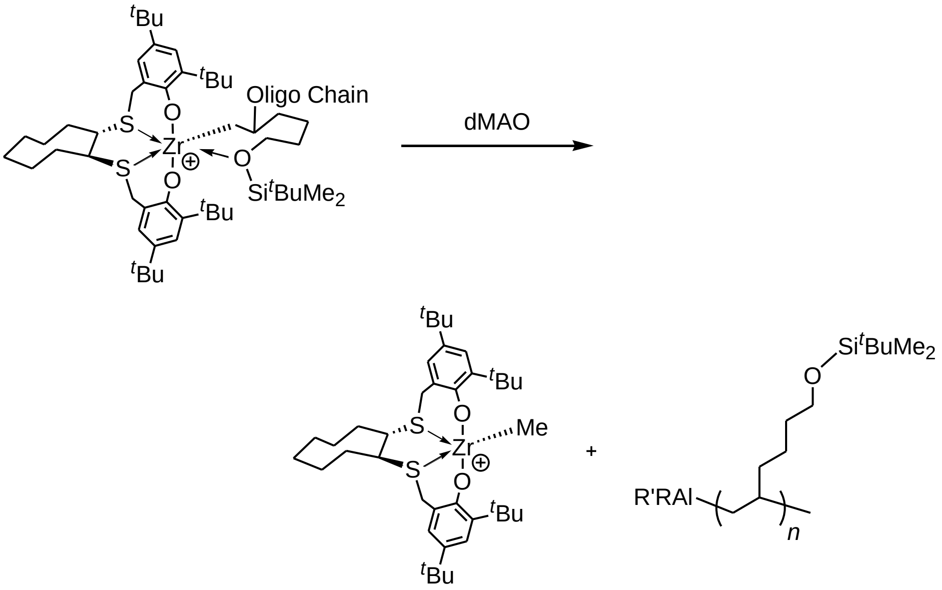
Scheme 1. Equilibrium between O- and borate-coordinated cationic species.

The catalytic system oligomerized 5-hexen-1-oxy-*tert*-butyldimethylsilane **1f** to provide the corresponding viscous oligomer with an activity of 0.4 g mmol(**2**)$^{-1}$ h^{-1}(Run 6). The GPC analysis showed a molecular weight of 3,000 g mol^{-1} matching to tetradecamers with PDI = 1.2. Shiono et al reported that $Me_2Si(1\text{-}Ind)_2ZrCl_2$ performs as a precatalyst for propylene/dimethyl(3-buten-1-oxy)aluminum copolymerization to afford end-hydroxylated polypropylene.[16] The formation mechanism was proposed; after insertion of polar monomer, the chain-transfer reaction of the generated dormant species occurred by trimethylaluminum in MAO to produce the corresponding polymer (Scheme 2). Therefore, if the protection substituent was small like $AlMe_2$ group, the polymerization reaction was hindered by the stabilization of the active species by coordination of the oxygen atom.



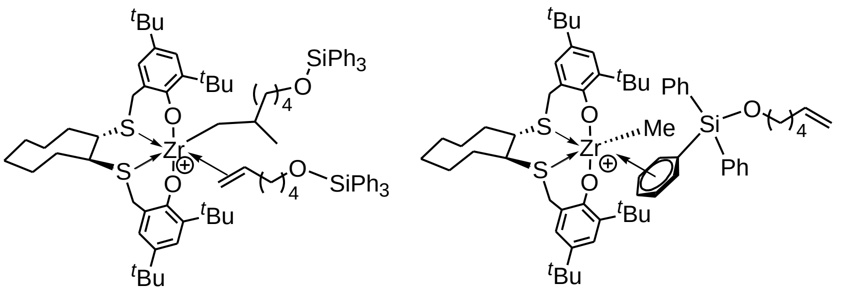
Scheme 2. Formation of polypropylene introduced aluminum species.

Taking the report into account, it is assumed that the oxygen atom adjacent to the *tert*-butyldimethylsilyl group in **1f** stabilizes the central metal to form a dormant species leading to weakening of coordination, which gives a chance of transmetallation (Scheme 3).



Scheme 3. Plausible intramolecular chelation and mechanism for oligomerization of **1f**.

In the case of 5-hexen-1-oxytriphenylsilane **1g**, **2**/dMAO system did not perform the polymerization (Run 7). The reason for the inhibition of the polymerization of **1g** is considered by two possibilities (Scheme 4). One is that, after the insertion of **1g**, the insertion of next **1g** is prevented by the steric hindrance between triphenylsilyl groups. The other is stabilization of the active species by the coordination of the phenyl group in **1g**.



Scheme 4. Prevention of **1g** polymerization by monomer **1g**.

Next, to reveal conditions to polymerize **1c** with high productivity, we attempted the polymerization of **1c** with **2**/dMAO system under different temperatures (Run 8, 9). Although the catalytic activity showed a small change at temperatures in the range from 25 to 70 °C, the molecular weight dramatically decreased to M_w = 8,700 g mol^{-1} in Run 9 from 13,900 g mol^{-1} in Run 8. The polymer obtained in Run 9 had vinylene $R^1CH{=}CHR^2$ and vinylidene $R^3R^4C{=}CH_2$ moieties as end groups at around δ 5.4 and 4.8, respectively, as shown in the ^{1}H NMR spectrum (Figure 4). Moreover, in the ^{13}C{^{1}H} NMR spectrum, the signals assignable to vinylene and vinylidene carbons were observed at δ 148.8 and 110.0 and δ 129.0 and 128.2, respectively (Figure 5).

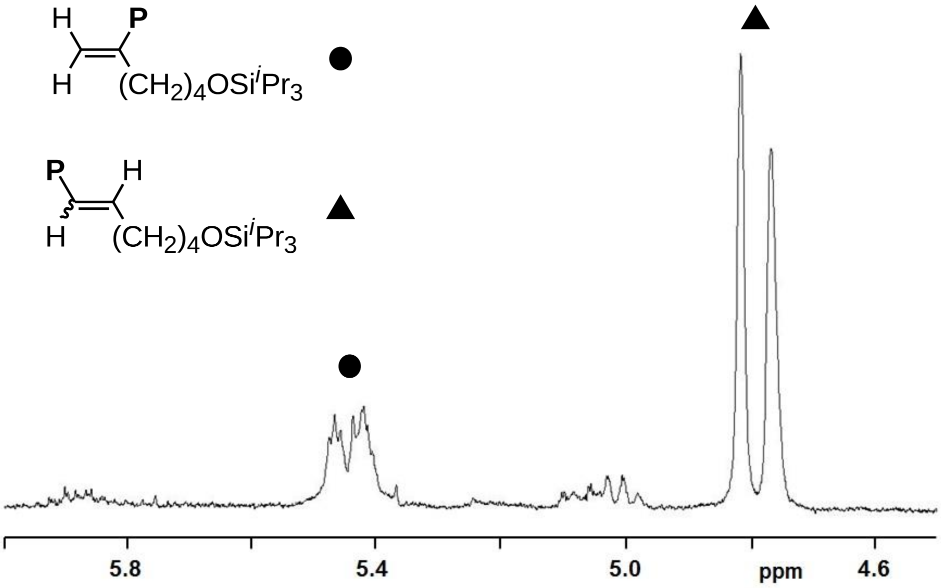


Figure 4. A part of the ^{1}H NMR spectrum of the polymer (Run 9).

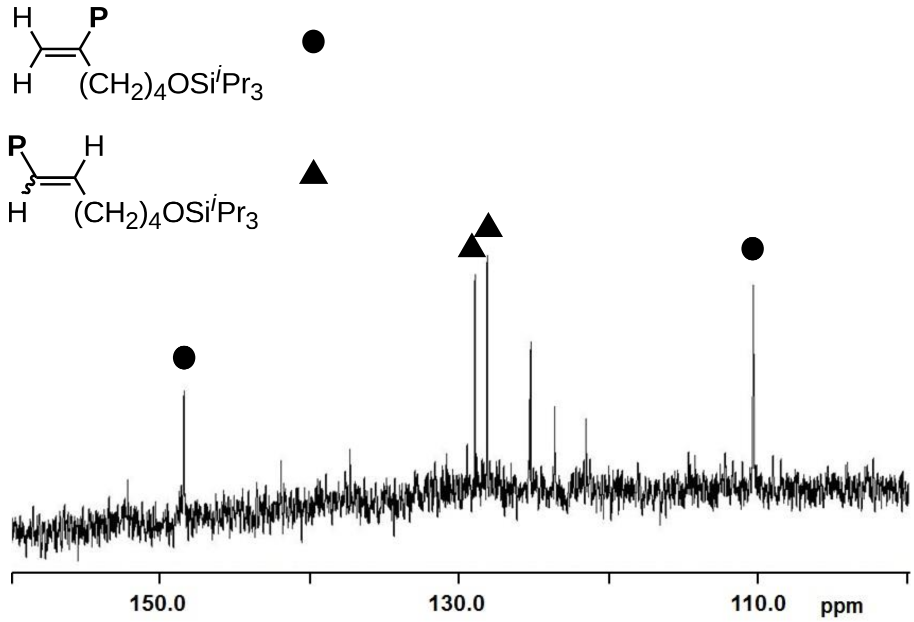
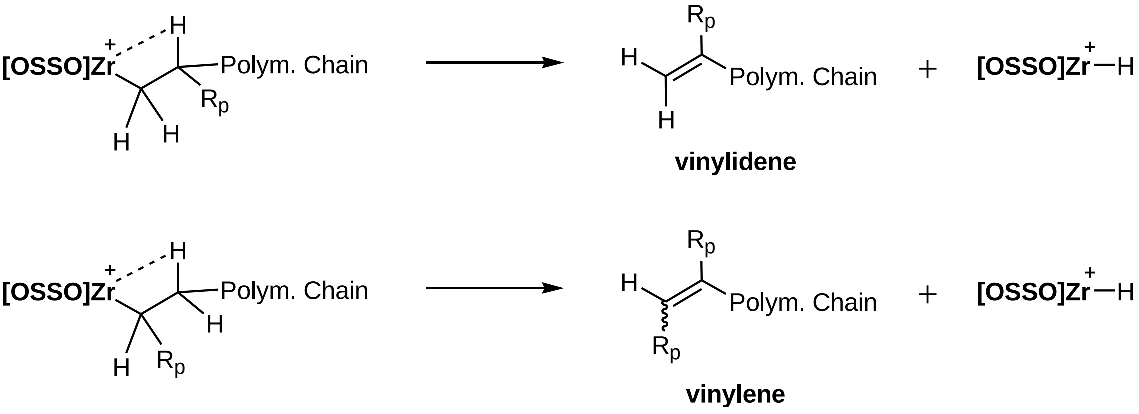


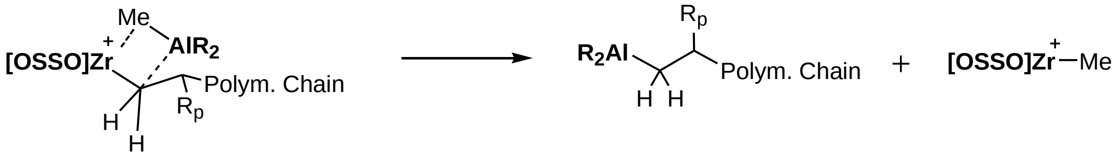
Figure 5. A part of the $^{13}C\{^{1}H\}$ NMR spectrum of the polymer (Run 9).

These results strongly suggest that the temperature factor participated in the process promoting β-hydride elimination (Scheme 4).



Scheme 4. The β-elimination processes of the polymer chain.

The condition employing approximately 2,000 equivalents of dMAO (4.0 mmol) as an activator for the precatalyst **2** (0.0020 mmol) was suitable to provide high production of the corresponding polymer [315 g mmol(**1**)$^{-1}$ h^{-1}] (Run 10) accompanying the decrease of the molecular weight to 7,300 g mol^{-1}. Interestingly, the signals due to vinylene and vinylidene protons were not observed in this case. Those results suggest that the production of the active species and the transmetallation are accelerated by using a large amount of dMAO.



Scheme 5. Transmetallation of the polymer chain from zirconium to aluminum species.

Moreover, polymerization of **1d** with complex **2** (0.0020 mmol) under a condition using excess dMAO (3.5 mmol) proceeded in the highest activity [1,620 g mmol(**1**)$^{-1}$ h^{-1}] among conditions using the combination of **2** and dMAO, producing the polymer with M_w of 10,700 g mol^{-1} dropped by the chain-transfer reaction.

2-3 Conclusion

We have demonstrated that the zirconium complex **2** having our [OSSO]-type ligand has a high potential to polymerize the terminal siloxy-substituted α-olefin **1**, which is a alkene having a silyl-protected hydroxy group, affording the corresponding isotactic polymer. This is the first example as the isospecific polymerization of functionalized polar α-olefin **1**. The polymerization of the siloxy-substituted α-olefin is dependent on the bulkiness of the silyl substituent, and triisopropyl silyl group is reveled to be appropriate under the catalytic system of **2** and dMAO to gain high-molecular-weight polymers. Complex **2** provided a polymer possessing terminal vinyl/vinylidene groups at 70 ºC. Moreover, polymerization of **1d** with **2**/dMAO produced the isospecific polymer with the highest activity.

2-4 Experimental Section

General Procedures.

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a Glovebox Japan E300 Gloveboxes under an inert atmosphere of argon. Anhydrous hexane and toluene were purchased from KANTO Chemical. Other chemicals were used as received. ^{1}H (400 MHz) and ^{13}C (100.5 MHz) NMR spectra were obtained with Bruker DRX400. The ^{13}C{^{1}H} NMR data of poly(ω-alken-α-oxytriiisopropylsilane)s were obtained in $CDCl_3$ at room temperature. The molecular weights and molecular weight distributions of polymers were determined against polystyrene standard by gel permeation chromatography on a SCL-10AVP/LC-10ATVP/DGU-14A/CTO-10ACVP/RID-10A apparatus (Shimadzu Corporation) using a GPC KF-804L (Shodex Corporation) column for poly(ω-alken-α-oxytriiisopropylsilane)s. Zirconium complexes with [OSSO]-type ligand[12], dMAO[18], and ω-alken-α-oxytriiisopropylsilanes[10] were prepared by the literature procedures.

General procedure for ω-alken-α-oxytriisopropylsilane polymerization.

A 50 mL Schlenk flask was charged sequentially with the catalyst precursor **1** (0.0020 mmol), cocatalyst (dMAO), and toluene (5.0 mL) at room temperature. After stirring for 1 min at room temperature, ω-alken-α-oxytriisopropylsilane (1.0 g) was added to the reaction mixture. The mixture was stirred for the desired time at the room temperature. The reaction was quenched by addition of MeOH and concentrated HCl aq.. The mixture was extracted with CH_2Cl_2, and the organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure at 140 °C during an overnight to leave the polymer.

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Chapter 3

Copolymerization of 5-hexen-1-oxytriisopropylsilane with ethylene or 1-hexene catalyzed by zirconium complex having [OSSO]-type ligand

3-1 Introduction

Polyolefins possessing polar functional groups are materials with special properties unlike non-functionalized polyolefin. The direct synthetic methods for functionalized polyolefins are copolymerized ethylene or propylene with polar functional monomers by radical copolymerization or coordination copolymerization. The radical polymerization was generally not suitable to control the molecular weight, the branching ratio, and the distribution of the functional groups in the polymer chain. Meanwhile, the coordination polymerization catalyzed by the post-metallocene catalysts is normally allowed to synthesize the stereoselective poly(α-olefin)s by stereospecific polymerization and copolymers with high content of α-olefins.[1] Recently, the early- and late-transition metal complexes as coordination polymerization catalysts have been shown to lead the copolymerization of ethylene or propylene with the polar monomer that has a protection group to prevent deactivation of central metals.[2] For example, Li *et al*. reported that a hafnium complex bearing a pyridyl-amido ligand catalyzed the copolymerization of propylene with ω-halo-α-olefin to afford the copolymer with a polar monomer incorporation ratio of up to 11.7 mol %.[3] In addition, Sun and Tang *et al*. demonstrated that the complexes containing [ONS] tridentate ligands showed high activity in the copolymerization of ethylene with 9-decen-1-ol and give the copolymer containing up to 8.8 mol % of 9-decen-1-ol units.[4] Although the functionalization of PE or PP has been achieved in coordination polymerization successfully, the synthesis of the functionalized polyolefins with high polar monomer contents has been rarely reported yet.

Quite recently, we have presented that zirconium complex **1** is an excellent catalyst for 1-hexene polymerization to produce poly(1-hexene) isospecifically with considerably large molecular weights.[5] Furthermore, we have also demonstrated the copolymerization of ethylene with 1-hexene catalyzed by the zirconium complex **1** with dMAO under atmospheric pressure to give random poly(ethylene-*co*-hexene)s with high 1-hexene contents (37.3–66.7 mol%) and activities of 1,100–2,700 g mmol(**1**)$^{-1}$ h^{-1}.[5] In addition, the catalytic system of the zirconium precatalyst **1** and dMAO operated the isospecific homopolymerzation of terminal siloxy substituted α-olefins. Therefore, the copolymerization performance of the zirconium complex **1** for the siloxy-substituted α-olefin and the non-polar alkenes attracts considerable attentions.

In chapter 3, the author demonstrates the copolymerization of ethylene/5-hexen-1-oxytriisopropylsilane with the zirconium precatalyst **1**. Moreover, the author also describes the copolymerization of 1-hexene as an α-olefin with 5-hexen-1-oxytriisopropylsilane in the same catalytic system.

3-2 Copolymerization of ethylene with 5-hexen-1-oxytriisopropylsilane

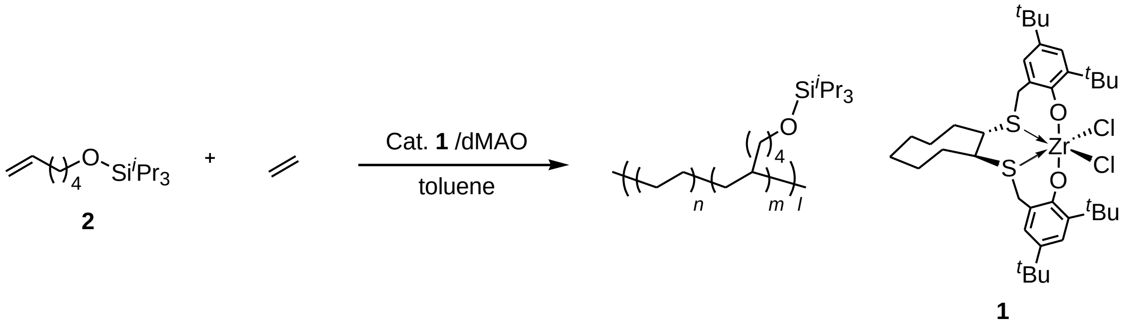
On the basis of the homopolymerization performance of the dichloro zirconium complex **1** for the terminal siloxy-substituted α-olefins as described in Chapter 2, we applied to the copolymerization of ethylene/5-hexen-1-oxytriisopropylsilane to reveal its potential for the copolymerization and to gain insight whether the precatalyst **1** controls a polar monomer content in a copolymer.

We carried out copolymerizations of ethylene with 5-hexen-1-oxytriisopropylsilane **2** (1.0 g, 3.9 mmol) catalyzed by the zirconium complex **1** (0.0020 mmol) under atmospheric pressure (Table 1). The results are summarized in Table 1. Upon activation with 250 equivalents of dMAO (0.50 mmol), the precatalyst **1** operated the copolymerization of ethylene with **2** at 25 ºC to afford a viscous poly(ethylene-*co*-5-hexen-1-1oxytriisopropylsilane) with 81 g mmol^{-1} h^{-1} of activity. Compared with ethylene/1-hexene copolymerization (activity = 1,110 g mmol^{-1} h^{-1}, M_w = 10,100 g mol^{-1}) by the same catalytic system, the catalytic activity drastically dropped down probably due to the bulkiness use of monomer **2**. The GPC analysis of the resulting copolymer exhibited 10,800 g mol^{-1} of a molecular weight (M_w). And, the molecular weight distribution showed a narrow value (PDI = 2.2), suggesting that the catalytic system performed as a single site catalyst in the copolymerization. Furthermore, the incorporation value of **2** in the copolymer can be estimated from integral values in the ^{1}H NMR spectrum (Figure 1) by using the following equation:

$$\text{Polar Monomer Incorpolation (mol\%)} = \frac{1}{1 + \dfrac{(\text{Integral of Alkyl Region}) - 30}{4}}$$

Equation 1. Equation to introduce the polar monomer incorporation

Table 1. Ethylene/5-hexen-1-oxytriisopropylsilane **2** copolymerization catalyzed by the [OSSO]$ZrCl_2$ complex **1** in the presence of dMAO



Run^a	Comonomer	dMAO	Yield	Activity	M_w^{b}	PDI^{b,c}	Incorp.^{d}
	[mmol]	[mmol]	[mg]	[g mmol^{-1} h^{-1}]	[g mol^{-1}]		[mol %]
1	4.0	0.50	162	81	10,800	2.2	17.5
2^e	4.0	0.50	770	77	10,200	1.9	21.4
3	4.0	4.0	933	470	7,800	1.8	19.0
4	3.2	0.50	238	119	4,300	2.5	13.0
5	2.4	0.50	242	121	3,800	2.7	7.5
6	1.6	0.50	246	123	429,700^f 3,600	1.1	5.2
7	0.8	0.50	211	105	2,900	2.4	4.7

[a] Copolymerization of **2** (1.0 g, 3.9 mmol) with ethylene under atmospheric pressure was performed with **1** (2.0 μmol) and dMAO (0.50 mmol) in toluene (5 mL) at 25 °C for 1 h. [b] Determined by HT-GPC. [c] PDI = M_w/M_n. [d] Determined by ^{1}H NMR spectroscopy. [e] Polymerization time was 5 h. [f] Bimodal distribution.

Applying the equation, the resulting copolymer was estimated to contain 17.5 mol % of polar monomer. In a similar manner, the contents of **2** in other runs are calculated. In the conditions injecting different amounts of **2**, the copolymerizations afforded the corresponding copolymers with different contents of **2** (Run 4–7). Notably, when 0.4 mmol of **2** was injected, the content of **2** in the copolymer decreased down to 4.7 mol%, indicating that the control of the incorporation of **2** is related with the amount of **2**.

The ^{1}H NMR analysis of the copolymer showed a characteristic triplet signal due to the methylene carbon attached to the oxygen atom at δ 3.67 (Figure 1). Additionally, a quite small singlet assigned to vinylidene protons appeared at δ 4.70, indicating that β-hydride elimination occurred after 5H1OSi insertion. In contrast, two small multiplet signals at δ 4.92–5.03 and 5.69–5.86 were assigned to the chain-end formed by β-hydride elimination after ethylene insertion.

In the ^{13}C{^{1}H} NMR spectrum, the two signals in 5-hexen-1-oxytriisopropylesilane unit at δ 23.0 (2B), 26.9 (3B) were slightly downfield shifted than those of poly(5-hexen-1-oxytriisopropylsilane) [δ 23.2 (2B), 28.7 (3B)] (Scheme 1, Figure 2, and Table 2). The signal due to 4B carbon, which is usually used for the estimation of stereospecificity of α-olefin polymerization shifted to by 1.4 ppm at δ 33.1 (4B) from that (δ 34.5) of a polymer obtained by the homopolymerization of 5-hexen-1-oxytriisopropylsilane, suggesting that the copolymer does not possess sequential units of 5-hexen-1-oxytriisopropylsilane. The structure of copolymer is assumed as follows. According to Wang group's paper, the repeated ethylene units of the copolymer resonated at δ 29.9 (EEE, $S_{\delta\delta}$) and terminal methyl and methylene carbons were observed at δ 14.3 (1S) and 22.9 (2S) and 32.1 (3S), respectively.[6] The signal at δ 37.6 ($T_{\delta\delta}$) was identified as the carbon in the main chain bonded with a side chain. The resonances at δ 18.2 (1Si) and

12.2 (2Si) were assigned to the carbons in the triisopropylsilyl group. The resonances of and $S_{\alpha\gamma}$ associated to the PEP alternative triad units due to appeared weakly at δ 24.2 and 35.0, respectively. In the HMQC and HMBC analyses, the signals due to the terminated carbons formed by the β-hydride elimination of ethylene units were observed at δ 114.3 ($1E_{vilyl}$), 138.9 ($2E_{vinyl}$), and the signal of the allylic carbon ($CH_2=CH-\underline{C}H_2-$, $3E_{allyl}$) resonated at δ 36.0.

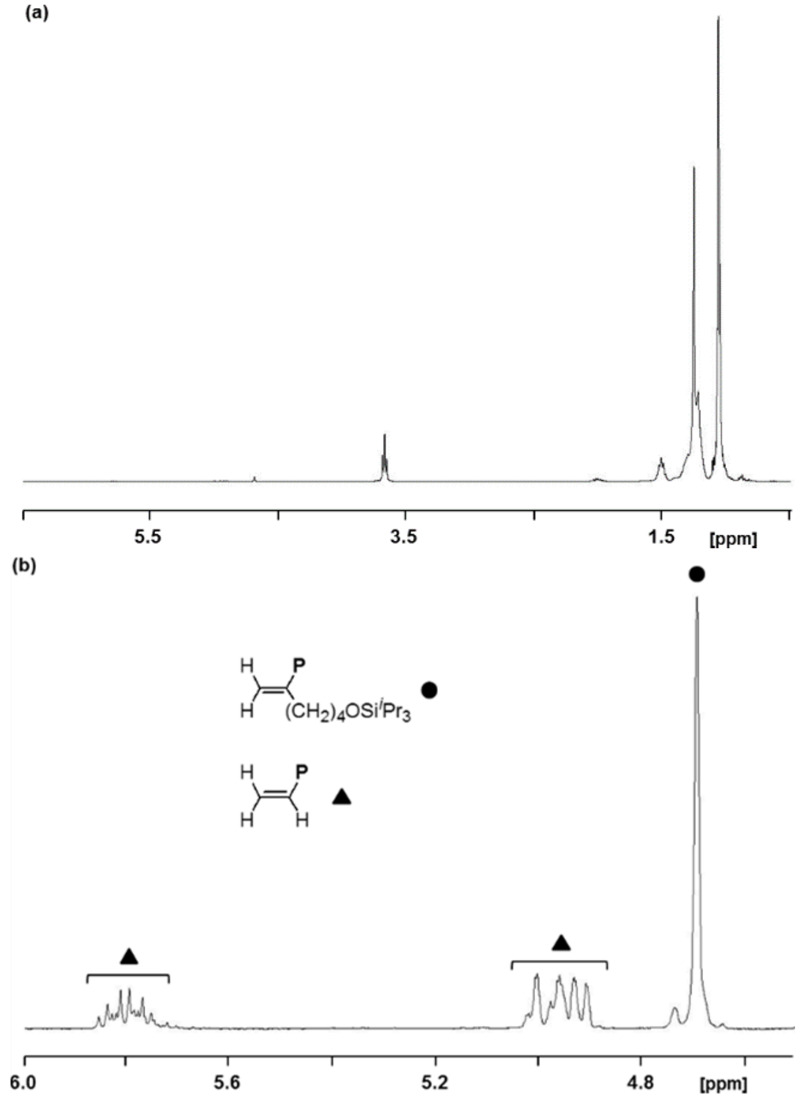
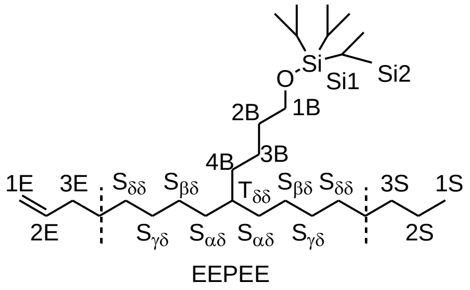
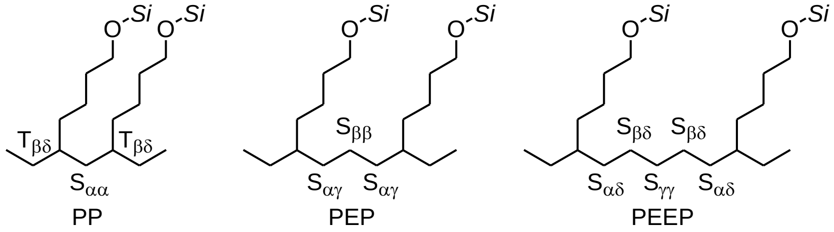


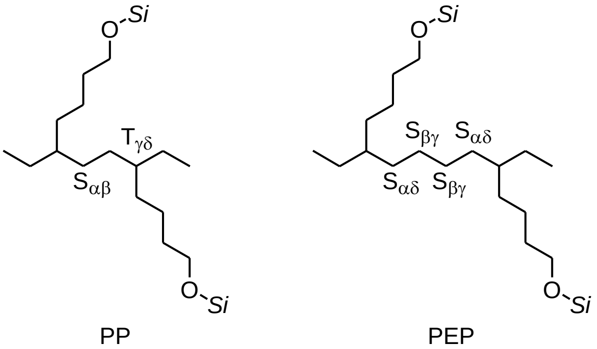
Figure 1. (a) A part of the ^{1}H NMR spectrum of the copolymer obtained in Run 1, Table 1, (b) the enlarged view of the region for vinyl protons.



1,2-insertion



2,1-insertion



Scheme 1. Possible structures of the copolymer.

The termination chain-end of vinylidene group which formed by β-hydride elimination after 1,2-insertion of 5H1OSi were detected at δ 108.6 ($1E_{\text{vinylidene}}$) and 149.9 ($2E_{\text{vinylidene}}$). It is assumed that PP dyad sequences were observed around δ 38.9–39.5. The results of the spectroscopic analysis are shown in Table 1.

Figure 2. Parts of the $^{13}C\{^{1}H\}$ NMR spectrum of the copolymer obtained (Table1, Run 1), (b) the enlarged view of the $^{13}C\{^{1}H\}$ NMR spectrum (Table 1, Run 1).

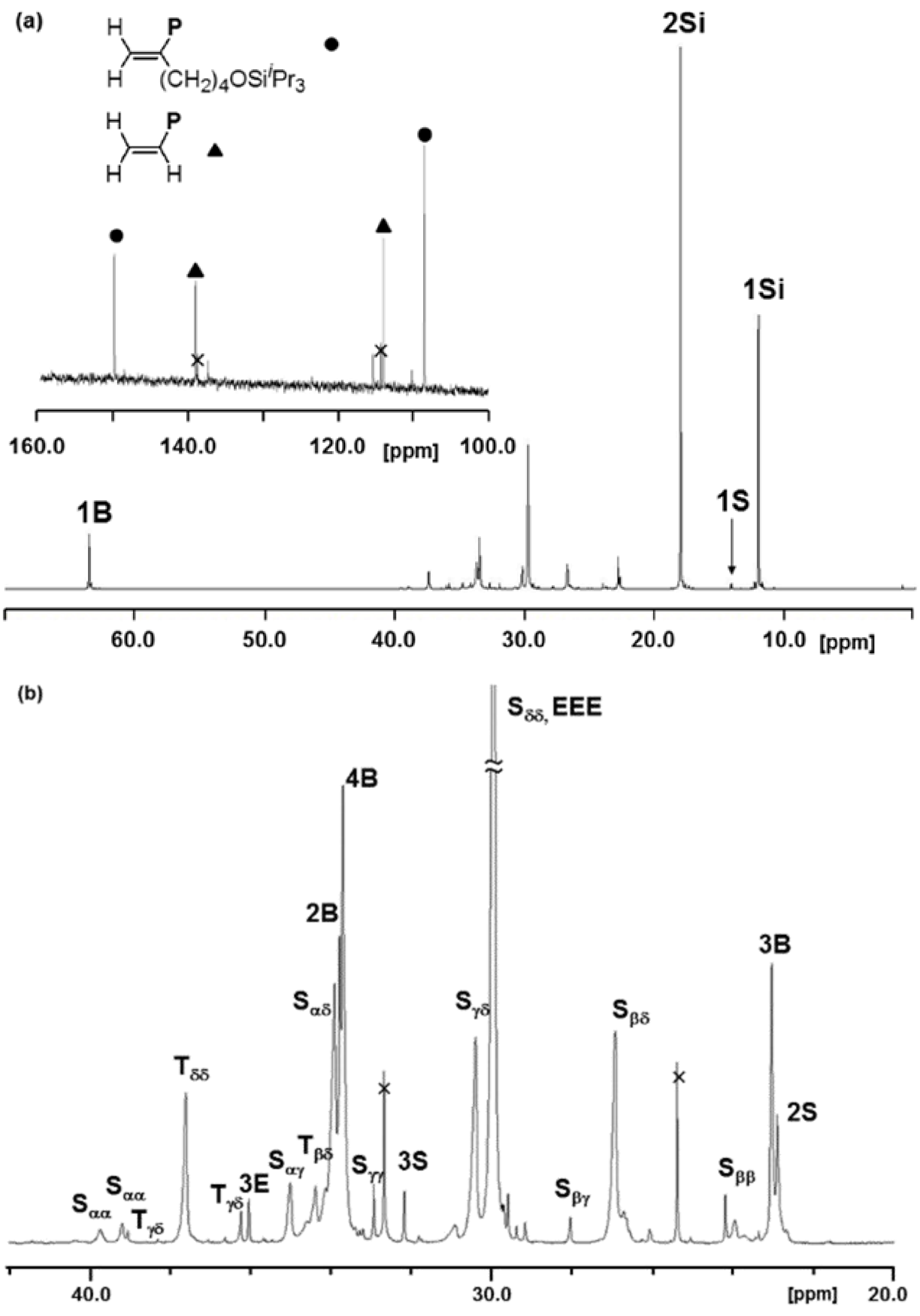


Table 2. The summary of chemical shifts for the copolymer.

Region	Carbon	Sequence	Chemical Shift [ppm]
	2E	–	150.0
	1E	–	108.5
H	1B	–	63.6
A	$S_{\alpha\alpha}$	PPP	39.7
	$S_{\alpha\alpha}$	PPE	39.2
B	$T_{\delta\delta}$	EPPE	39.0
	$T_{\beta\delta}$	EPE	37.6
C1	$S_{\alpha\gamma}$	PEP	36.2
	3E	–	36.0
	$T_{\beta\delta}$	PPE	35.0
	$S_{\alpha\delta}$	PEEP	34.1
	$S_{\alpha\delta}$	PEE	33.9
G	4B	–	33.7
C2	$S_{\gamma\gamma}$	PEEP	32.9
D1	$S_{\gamma\delta}$	PEE	30.3
	$S_{\delta\delta}$	EEE	29.9
	$S_{\beta\gamma}$	PEP	28.0
	2B	–	26.9
E	$S_{\beta\delta}$	EEP	26.7
F	$S_{\beta\beta}$	EPEPE–EPEPP	24.2–24.0
D2	3B	–	23.0

3S	–	32.1
2S	–	22.9
1S	–	14.3
2Si	–	18.2
1Si	–	12.2

Meanwhile, Randall and Hsieh have reported the ^{13}C NMR analysis of poly(ethylene-*co*-1-hexene) in terms of the sequences of the arrangement of ethylene and 1-hexene units.[7] According to the report, there are three possible diads (EE, EH, HH) and six possible triads (EEE, EEH, HEH, EHE, EHH, HHH) in the poly(ethylene-*co*-1-hexene). The diads are related with the triad segments and the tetrad segments as shown in the below equations.

$$[HH] = [HHHH] + [HHHE] + [EHHE]$$

$$= [HHH] + (1/2)[HHE]$$

$$[HE] = [EHEE] + [HHEE] + [EHEH] + [HHEH]$$

$$= 2[EHE] + [EHH]$$

$$[EE] = [EEEE] + [EEEH] + [HEEH]$$

$$= [EEE] + (1/2)[EEH]$$

As there are lots of the combinations of ethylene and comonomer unit in the copolymer, the signals in the copolymer are normally, complexly overlapped. Thus, it is generally impossible to analyze the copolymer completely in the ^{13}C NMR spectrum. However, to resolve the problem, Randall and Hsieh introduced a concept of collective assignments for quantitative estimation by dividing the spectrum into some parts. The parts consist of some triads units as following equations.

$$T_A = k([HHH] + (1/2)[HHE])$$

$$T_B = k[EHE])$$

$$T_C = k(2[HHH] + 3[HHE] + 3[EHE])$$

$$T_D = k(2[EEE] + (1/2)[HHE] + [EHE]+ [EHH] + [EHH] + [HHH])$$

$$T_E = k[HHE]$$

$$T_F = k[HEH]$$

$$T_G = k([HHH] + [HHE] + [EHE])$$

$$T_H = k([HHH] + [HHE] + [EHE])$$

The factor *k* is NMR constant, which is later removed through normalization. The following six equations representing ratios of triads sequence in copolymer can be derived by resolving the above equations:

$$k[\mathrm{EHE}] = T_\mathrm{B}$$

$$k[\mathrm{EHH}] = 2(T_\mathrm{G} - T_\mathrm{B} - T_\mathrm{A})$$

$$k[\mathrm{HHH}] = 2T_\mathrm{A} - T_\mathrm{B} - T_\mathrm{G}$$

$$k[\mathrm{HEH}] = T_\mathrm{B}$$

$$k[\mathrm{HEE}] = 2(T_\mathrm{G} - T_\mathrm{A} - T_\mathrm{F})$$

$$k[\mathrm{EEE}] = (1/2)(T_\mathrm{A} + T_\mathrm{D} - T_\mathrm{F} - 2T_\mathrm{G})$$

Applying the equations, the ratios of the triads, the diads, monomer contents, and the $\gamma_\mathrm{E}\gamma_\mathrm{P}$ value were obtained as summarized in Table 3. In Run 1, the copolymer contained 1.5% of the PPP triad. The ratios of the PPP and EPP units are quite low through the copolymerizations. With decrease of the feed of the polar monomer in the copolymerization, the ratio of the PPP triads decreased to 0.1%, indicating that it rarely occurs that the polar monomer inserts consecutively three times. On the other hand, the ratio of the EEE triads increased up to 96.2%. The value of the polar monomer content (17.5 mol %) judged by ^{1}H NMR spectrum is close to a value determined by ^{13}C NMR spectrum. Additionally, the $\gamma_\mathrm{E}\gamma_\mathrm{P}$ value can be shown by the below equation defined by the ratio of the diads units.

$$\gamma_\mathrm{E}\gamma_\mathrm{P} = \frac{4[\mathrm{HH}][\mathrm{EE}]}{[\mathrm{HE}]^2}$$

Table 3. The ratios of diads and triads in the copolymers.

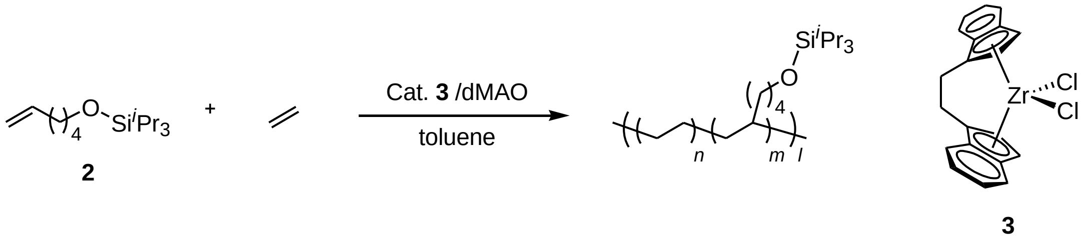
Run (M_p Incorp.)	EPE	EPP	PPP	PEP	PEE	EEE
1 (17.5)	13.1	3.0	1.5	4.5	20.3	57.6
2 (21.4)	12.7	2.1	1.9	4.8	17.8	60.7
3 (19.0)	14.4	1.7	2.1	5.0	20.5	56.3
4 (13.0)	12.5	0.6	1.3	3.0	19.7	63.0
5 (7.5)	9.8	1.1	0.7	2.9	15.1	70.4
6 (5.2)	6.2	1.4	0.1	0.5	12.9	78.9
7 (4.7)	1.3	0.1	0.1	0.3	20.0	96.2

Run (M_p Incorp.)	PP	EP	EE	P	E	$\gamma_E\gamma_P$
1 (17.5)	5.6	21.7	72.7	16.4	83.6	3.48
2 (21.4)	4.6	21.2	74.2	15.2	74.2	3.08
3 (19.0)	5.5	30.5	73.0	15.6	84.4	2.31
4 (13.0)	1.8	19.6	78.6	11.6	88.4	1.48
5 (7.5)	2.4	16.7	80.9	10.7	89.3	2.76
6 (5.2)	0.3	13.9	86.1	8.2	91.8	6.55
7 (4.7)	0.3	2.6	97.1	1.6	98.4	20.44

Applying the equation, the values of $\gamma_E\gamma_P$ are calculated and summarized in Table 3. A block copolymer shows more than 1 of the $\gamma_E\gamma_P$ value ($\gamma_E\gamma_P > 1$), in constant, if the $\gamma_E\gamma_P$ value is lower than 1 in a copolymerization ($\gamma_E\gamma_P < 1$), the copolymer adopts an alternative structure. The $\gamma_E\gamma_P$ values for the present ethylene/5-hexen-1-oxytriisopropylsiane copolymerization showed 1.48–20.44, indicating that these polymers form random structure with the slightly enriched EEE or PPP sequences.

When the precatalyst **1** (0.0020 mmol) was activated by 2,000 equivalents of dMAO (4.0 mmol), the copolymerization proceeded in about 6 fold higher activity than that in Run 1 (Run 3). In the GPC analysis, the resulting copolymer possessed the molecular weight of 7,800 g mol^{-1} with PDI = 2.05. In the comparison with the copolymerization performance of ethylene/5-hexen-1-oxytriisopropylsilane with the racemic ethylene-bridged bis(indenyl)-type zirconocene dichloride complex **1** (activity = 4,090 g mmol^{-1} h^{-1}, M_w = 136,000 g mol^{-1}, PDI = 2.05) reported by Japan Polypropylene Corp. and Japan Polypropylene Corp. (Scheme 2),[8] the precatalyst **1** showed one-order lower activity and smaller molecular weight, while our catalytic system produced the copolymer with higher polar monomer content (4.7–21.4 mol %).

Scheme 2. Copolymerization of ethylene/**2** catalyzed by **3**



The gained copolymer exhibited nearly the same polar monomer incorporation (19.0 mol%) as that in Run 1, indicating that the amount of dMAO is independent of the reaction of the polar monomer and, dMAO promotes the formation of the active species.

3-3 Copolymerization of 1-hexene with 5-hexen-1-oxytriisopropylsilane

In order to reveal the polymerization performance for other α-olefins, we examined the copolymerization of 1-hexene with 5-hexen-1-oxytriisopropylsilane **2** catalyzed by zirconium complex **1** in the presence of dMAO as an activator. The results of copolymerization are depicted in Table 4. In the case of the conditions employing equivalent amounts of 1-hexexe and **2**, the corresponding copolymer was produced with about 200 times higher activity (300 g mmol^{-1} h^{-1}) than that of homopolymerization of **2** (Run 1), suggesting that the insertion of 1-hexene to polymer chains occurs more rapidly to contribute to the higher activity than that of **2** that induces steric hindrance between the bulky triisopropylsliyl groups (Run 1). The content of **2** in the copolymer can be calculated by the ^{1}H NMR spectrum (Eq. 2).

$$\text{Incorpolation of } \mathbf{2} \text{ (mol\%)} = \frac{1}{1 + \dfrac{(\text{Integral of Alkyl Region}) - 30}{12}}$$

Equation 2. Equation to calculate the incorporation of **2**.

Calculating with the eq. 2, the copolymer is estimated to contain 29.0 mol% of **2**. In the ^{1}H NMR spectrum, the characteristic signal due to the methylene protons attached to the oxygen atom of the obtained copolymer were observed at δ 3.67 as a triplet signal.

Table 4. The 1-hexene/5-hexen-1-oxytriisopropylsilane **2** copolymerization with **1** with dMAO

Run[a]	[H]:[P]	dMAO [mmol]	Yield [mg]	Activity [g mmol^{-1} h^{-1}]	M_w[b] [g mol^{-1}]	PDI[b, c]	Incorp[d]. [mol%]
1	1:1	0.50	102.1	300	37,200	2.2	29.0
2[e]	1:1	0.50	133.9	1,340	6,700	1.8	46.6
3[f]	1:1	0.50	215.3	2,150	3,500	1.6	45.3
4	1:1	5.0	190.6	1,910	900	1.2	38.9
5	4:1	0.50	147.0	1,470	11,200	2.1	9.4
6	3:2	0.50	140.0	1,400	12,100	1.7	27.4
7	2:3	0.50	125.2	1,250	10,700	1.8	40.3
8	1:4	0.50	118.5	1,190	11,700	1.8	52.8

[a]Copolymerization of **2** with 1-hexene was performed with **1** (2.0 μmol) and dMAO (0.50 mmol) in toluene (5 mL) at 25 ºC for 10 min. [b]Determined by HT-GPC. [c]PDI = M_w/M_n. [d]Determined by ^{1}H NMR spectroscopy. [e]Polymerization performed at 40 ºC. [f]Polymerization performed at 70 ºC.

Figure 3. Parts of the $^{13}\mathrm{C}\{^{1}\mathrm{H}\}$ NMR spectrum of the obtaind copolymer (Table 4, Run 1).

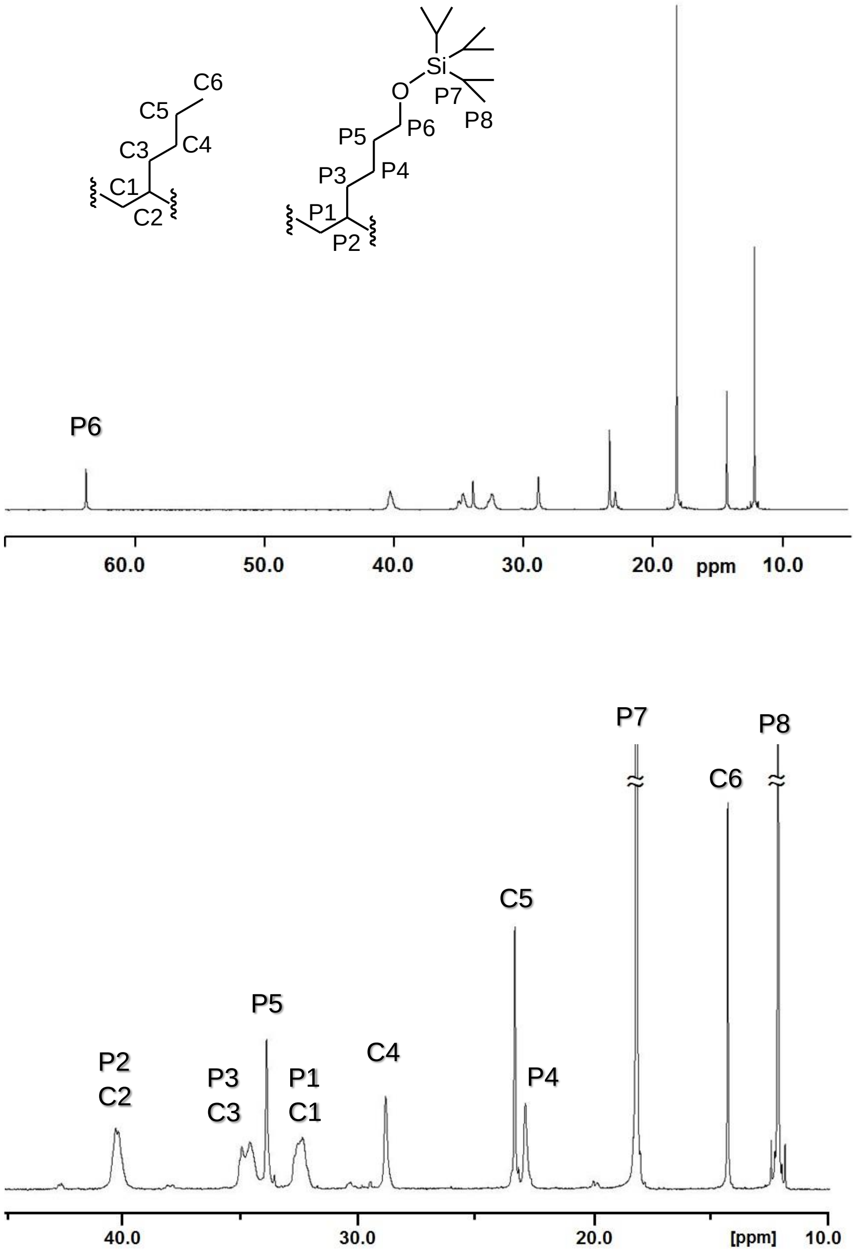
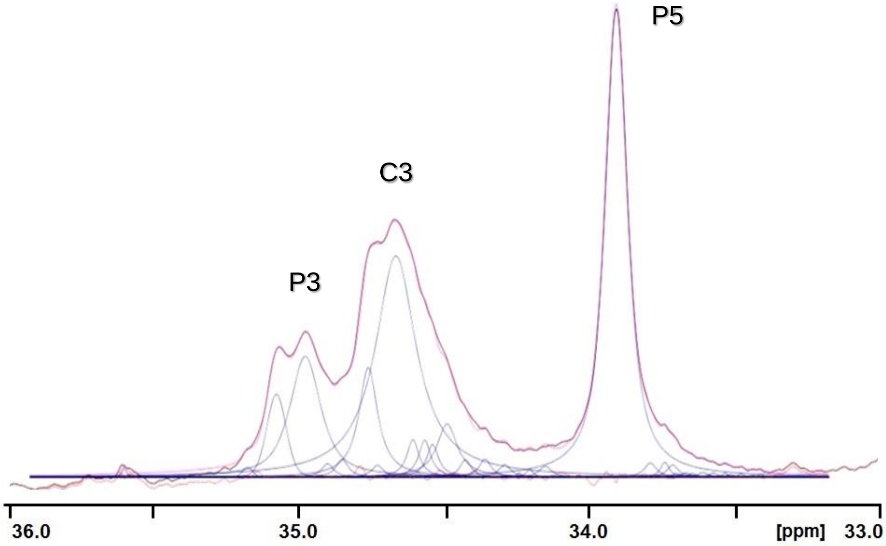
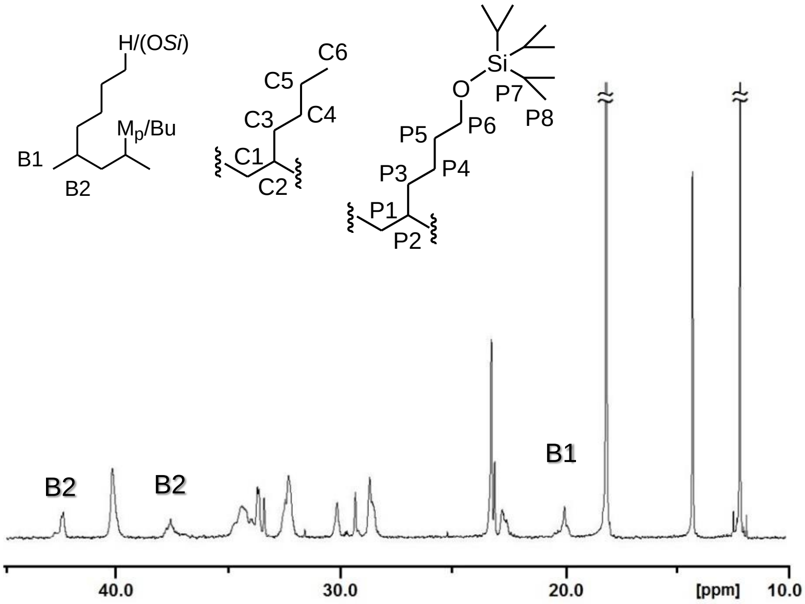


Figure 4. Peak separation of broad multimodal signals due to C3 and P3.



In the ${}^{13}C\{{}^{1}H\}$ NMR spectrum, the six peaks at δ 40.2 (C1), 35.0 (C3), 32.7(C2), 28.9 (C4), 23.4 (C5), and 14.3(C6) are attributed to the corresponding main 1-hexene units in copolymer (Figure 3). The eight peaks at δ 63.7 (P6), 40.2 (P1), 34.6 (P3), 33.9 (P2), 32.4 (P5), 22.9 (P4), 18.1 (P7), and 12.1 (P8) assigned to principle units of **2**. In order to calculate the isospecificity of the copolymer, broad signals due to C3 and P3 were divide into the some peaks (Figure 4). However, the isospcecificity of copolymer cannot be measured because existence of some peaks due to each C3 and P3. In Run 4, zirconium complex **1** (0.0020 mmol) was activated with 2,500 equivalents of dMAO (5.0 mmol) to result in highly active copolymerization of 1-hexene with **2** giving oligomers with molecular weight of 900 g mol^{-1}, which corresponds pentamer, and narrow PDI. This result indicates that the catalytic system accelerated the chain transfer of the growing polymer chain into the aluminum atom in dMAO. In addition, the HMQC and HMBC NMR spectra exhibited a signal due to the terminal methyl carbons (B1) at δ 20.0 and signals of the methine carbon (B2) attaching the terminal carbon B1 at δ 37.6 and 42.5.

Figure 5. A part of 13C NMR spectrum of the copolymer (Run 4, Table 1).



At 40 ºC, the zirconium complex **1**/dMAO system performed an increasing activity [1,340 g mmol(**1**)$^{-1}$ h^{-1}] (Run 2) that is more than 4 times larger than that at 25 ºC (Run 1). In contrast, the molecular weight decreased to 6,700 g mol^{-1} probably due to the chain transfer of polymer chain, because the signals due to the vinyl protons and carbons were not observed. Even at 70 ºC, the catalytic system showed higher activity [2,150 g mmol(**1**)$^{-1}$ h^{-1}] (Run 3); The molecular weight was drastically dropped down to 3,500 g mol^{-1}. When the feed concentration of **2** was increased, the contents of **2** increased from 9.4 mol% to 52.8 mol% drastically (Runs 5–8).

3-4 Conclusion

We have demonstrated that the zirconium complex **1** could serve as the high-potential copolymerization catalyst for ethylene and 5-hexen-1-oxytriisopropylsilane **2** to give the corresponding copolymer with molecular weight of 10,800 g mol^{-1} and narrow PDI value of 2.2. The NMR analyses exhibited that the obtained copolymer contained 17.5 mol% of 5-hexen-1-oxytriisopropylsilane unit and possessed terminal vinyl groups. In the ethylene/**2** copolymerization, the activity was almost independent of the feed concentration of the amount of dMAO.

Moreover, we have reported that the system of zirconium complex **1**/dMAO initiated copolymerization of 1-hexene with **2** to afford the corresponding the poly(1-hexene-*co*-5-hexen-1-oxytriisopropylsilane) with molecular weight of 37,200 g mol^{-1} and 29.0 mo l% of the incorporation of **2**. The contents of polar monomer **2** increased up to 52.8 mol %.

3-5 Experimental Section

General Procedures.

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a Glovebox Japan E300 Gloveboxes under an inert atmosphere of argon. Anhydrous toluene was purchased from KANTO Chemical. Other chemicals were used as received. ^{1}H (400 MHz) and ^{13}C (100.5 MHz) NMR spectra were obtained with Bruker DRX400. The ^{13}C NMR data of poly(ethylene-*co*-5-hexen-1-oxytriiisopropylsilane)s and poly(1-hexene-*co*-5-hexen-1-oxytriiisopropylsilane)s were obtained in $CDCl_3$ at room temperature. Zirconium complex **1** with [OSSO]-type ligand,[9] dMAO,[10] and 5-hexen-1-oxytriisopropylsilane[11] were prepared by literature procedures.

General procedure for ethylene/5-hexen-1-oxytriisopropylsilane polymerization.

A 50 mL Schlenk flask was charged sequentially with dMAO, ethylene (1.0 atm), 5-hexen-1-oxytriisopropyllsilane (1.0 g) and toluene (4.0 mL) at room temperature. After stirring for 1 min at room temperature, a solution of catalyst **1** (0.0020 mmol) in toluene (1.0 mL) was added to the reaction mixture. The mixture was stirred for a desired time at an appropriate temperature. The reaction was quenched by addition of methanol and concentrated hydrochloric acid. The mixture was extracted with dichloromethane, and the organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure at 140 °C during an overnight to leave polymer.

General procedure for 1-hexexe/5-hexen-1-oxytriisopropylsilane polymerization.

A 50 mL Schlenk flask was charged sequentially with **1** (0.0020 mmol), dMAO, and toluene (5.0 mL) at room temperature. After stirring for 1 min at room temperature, a mixture of 1-hexene and 5-hexen-1-oxytriisopropyllsilane with a desired concentration was added to the reaction mixture. The mixture was stirred for a desired time at an appropriate temperature. The reaction was quenched by addition of methanol and concentrated hydrochloric acid. The mixture was extracted with dichloromethane, and the organic layer was washed with water and dried over Na_2SO_4. The solvent was removed under reduced pressure at 140 °C during an overnight to leave polymer.

3-6. References

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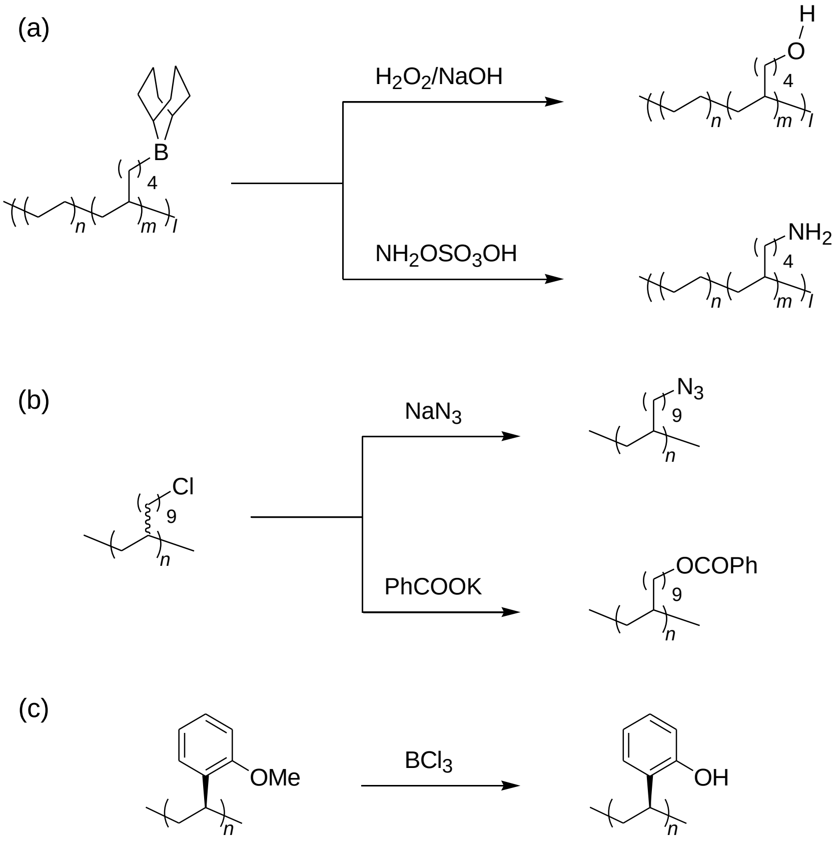
Chapter 4

Transformation of the terminal siloxy-substituted poly(α-olefin)s

4-1 Introduction

Polyolefins bearing various functional groups can change the characters drastically due to the functional substituents. For instance, poly(vinyl chloride)s are utilized as the material such as water pipes and films to show water resistance, incombustibility, and electric insulation. In addition, poly(vinyl alcohol)s are used as surface active agents and binders to display the characters of the high water solubility. However, poly(vinyl alcohol)s cannot synthesize directly by the polymerization of vinyl alcohol because of the isomerization of vinyl alcohol into more stable acetaldehyde. Therefore, stepwise methods that are combinations of the polymerization of vinyl acetate and the saponification of the resulting poly(vinyl acetate)s are used to synthesize poly(vinyl alcohol)s. Recently, functional group transformations of polyolefins synthesized by coordination polymerization have been reported.[1] For example, Chung *et al.* reported the syntheses of polyolefins bearing hydroxy group or amino group as the terminal substituents by the reactions of polyolefins having boryl groups (9-BBN moiety) with the appropriate organic reagents.[2] Defieux et al. reported the derivatization of chloro functions of poly(11-chloro-1-undecene) into the polyolefin with azido groups and aromatic ester groups.[3] Cui et al. demonstrated that isotactic poly(*o*-methoxystyrene) was transformed through the demethylation reaction into isotactic poly(*o*-hydroxystyrene).[4] However, the transformations of functional poly(α-olefin)s having a specific tacticity have not been investigated.

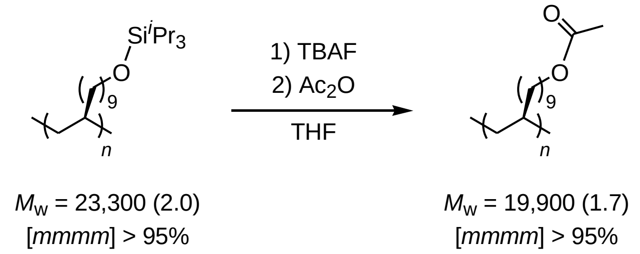
Scheme 1. The derivatizations of the functional polymer with (a) boryl, (b) chloro, and(c) methoxy substituents.



Meanwhile, we have succeeded in the synthesis of isotactic poly(α-olefin)s with terminal siloxy-substituents. Therefore, the author investigates the transformation of the isotactic, terminal siloxy-substituted poly(α-olefin) into poly(α-olefin)s having other substituents.

4-2 Transformation of siloxy-substituted polymer into acetoxy-substituted polymer

We tried transformations of siloxy-substituted poly(α-olefin)s into poly(α-olefin)s having acetoxy groups. First, the direct acetylation of isospecific poly(10-undecen-1-oxytriisopropylsilane) with a molecular weight of 23,300 g mol^{-1} and PDI = 2.0 by the desilylation reaction was carried out (Scheme 2). After the desilylation of the functionalized polymer with tetrabutylammonium fluoride (TBAF) in THF, the mixture was treated with acethyl anhydride to give the corresponding viscous polymer with the acetyl groups at the terminal positions almost quantitatively (99%). The GPC analysis exhibited the molecular weight of 19,900 g mol^{-1} and PDI = 1.7.



Scheme 2. Acetylation of isotactic poly(10-undecen-1-oxytriisopropylsilane) by treatment with TBAF and then acetic anhydride.

The IR spectra of the starting and the obtained polymers are shown in Figures 1 and 2, respectively. In the IR spectrum of the resulting polymer, new absorptions were observed at 1741 cm^{-1} (C=O) and 3442 cm^{-1} (O–H).

Figure 1. FT IR spectrum of poly(10-undecen-1-oxytriispropropylsilane).

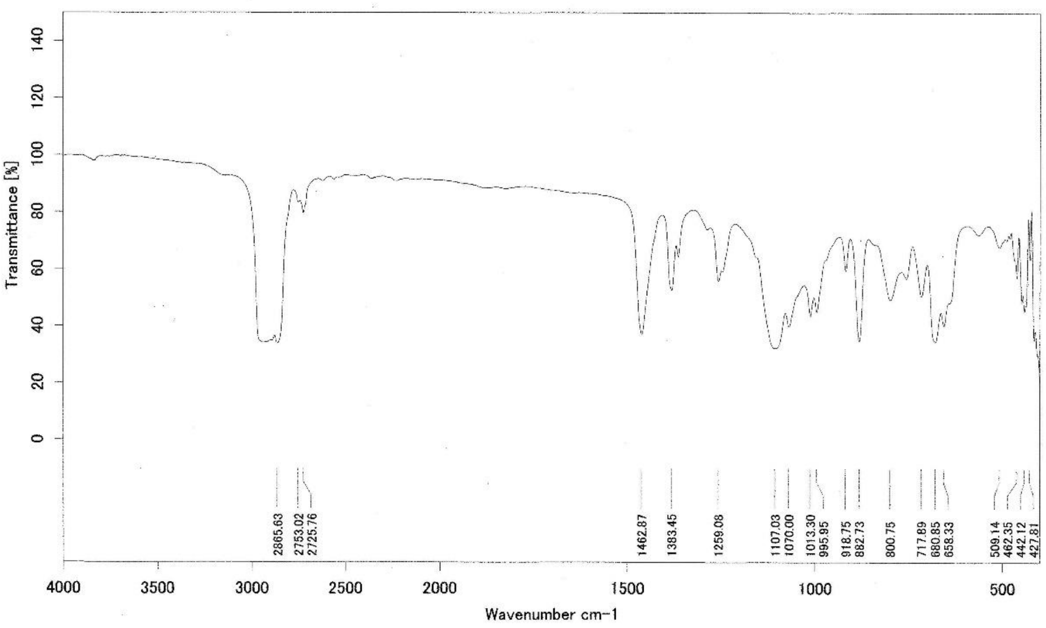


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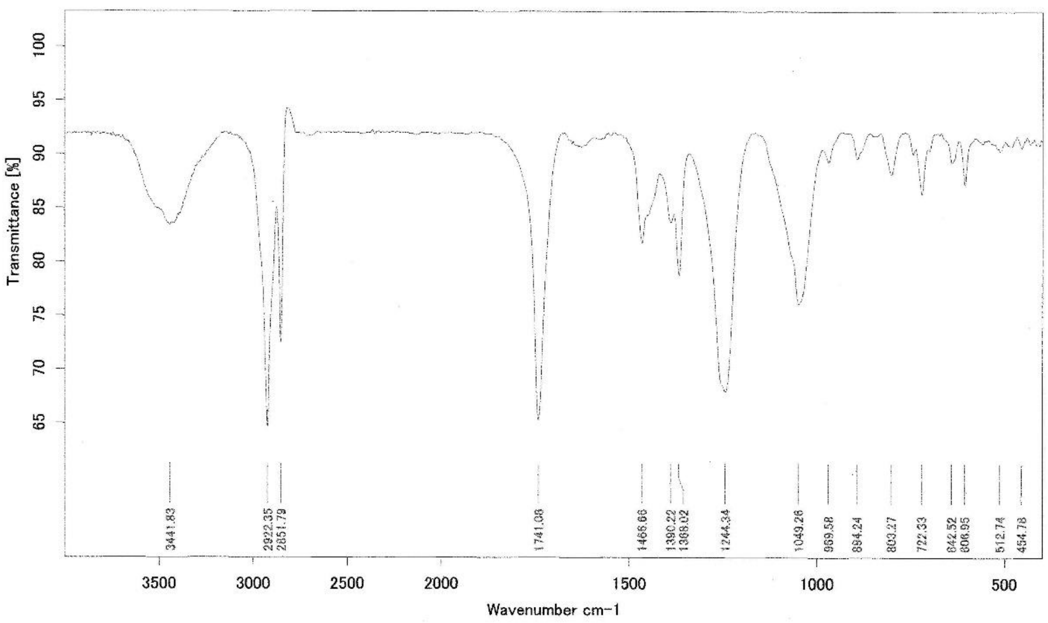
Figure 2. FT IR spectrum of poly(10-undecenyl acetate).



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The ^{1}H NMR spectrum of the acetyl-substituted polymer indicated a triplet at δ 4.04 due to –CH_2–OAc fragment, which is downfield-shifted compared with the corresponding signal of the reactant polymer, together with small signals attributed to –CH_2–OH fragment at δ 3.62 produced by the hydrolysis of the acetyl groups (Figure 3). The signal due to the methyl proton in the acetyl group resonated at δ 2.03. In the ^{13}C NMR spectrum, two signals attributed to the triisopropylsilyl group disappeared completely, and new signals due to the methyl and carbonyl carbons in the acetyl group appeared at δ 22.0 and 171.0, respectively, together with a signal at δ 64.6 due to the methylene carbon bonded to the acetyl group (Figure 4). In addition, a small signal due to the carbon attached to the terminal hydroxy group was displayed at δ 62.8.

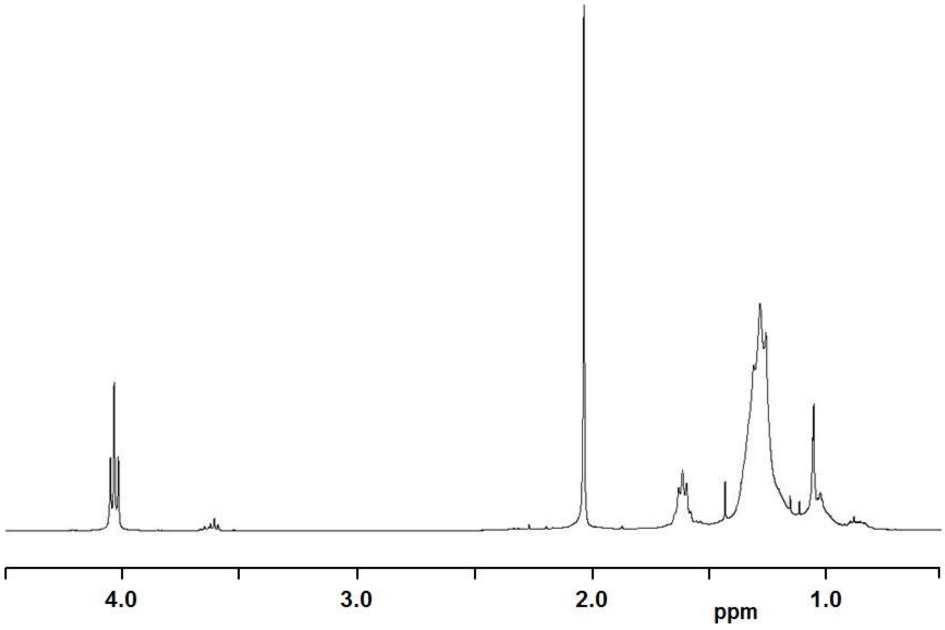


Figure 3. ^{1}H NMR spectrum of the obtained poly(10-undecenyl acetate).

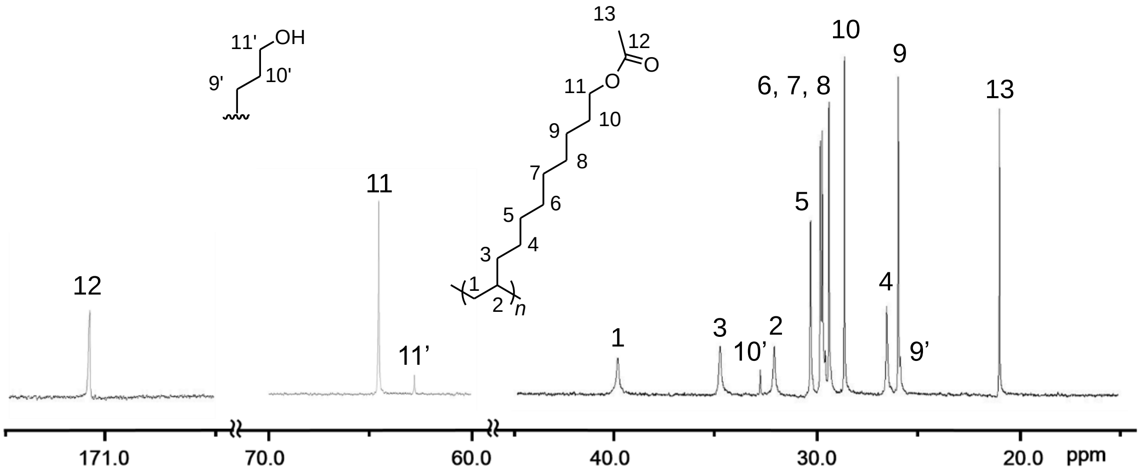
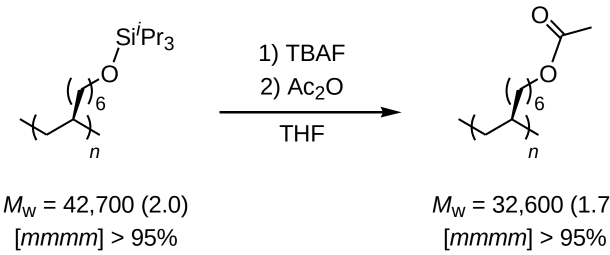


Figure 4. $^{13}C\{^{1}H\}$ NMR spectrum of the obtained poly(10-undecenyl acetate).

Next, we examined a similar acetoxylation of siloxy-substituted poly(5-hexen-1-oxytriisopropylilane). The isotactic polymer with molecular weight of 42,700 g mol^{-1} and PDI = 2.0 was transformed by the reaction with TBAF followed by the treatment with Ac_2O into a viscous oily polymer in 49% yield (Scheme 2). This low yield suggests that the polymer effect was operative there as the length of the side chain was shorter than that of the poly(10-undecen-1-oxytriisopropylsilane). The GPC analysis of the gained polymer exhibited the molecular weight of 32,600 g mol^{-1} and PDI = 2.0.

In the ^{1}H NMR spectrum, the acetoxy-substituted polymer showed the signal due to methylene protons at δ 4.05 (Figure 5). As similar as the case of poly(10-undecenyl acetate), the methyl proton resonated as a singlet at δ 2.04. In the ^{13}C NMR spectrum, the resonances of the methyl and the carbonyl carbons in the acetyl group were observed at δ 21.0 and 170.9, respectively (Figure 6).



Scheme 2. The reaction of isotactic poly(5-hexen-1-oxytriisopropylsilane) with TBAF, and then acetic anhydride.

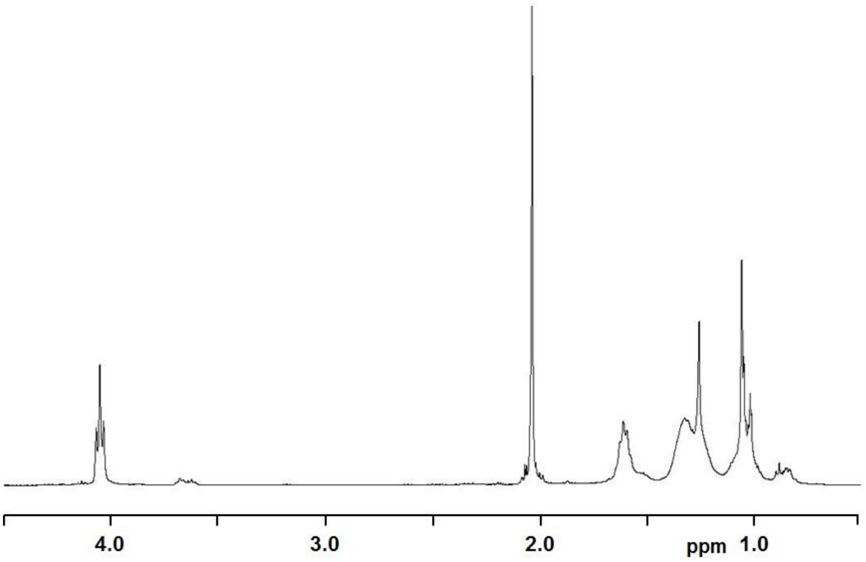


Figure 5. ^{1}H NMR spectrum of the obtained poly(5-hexenyl acetate).

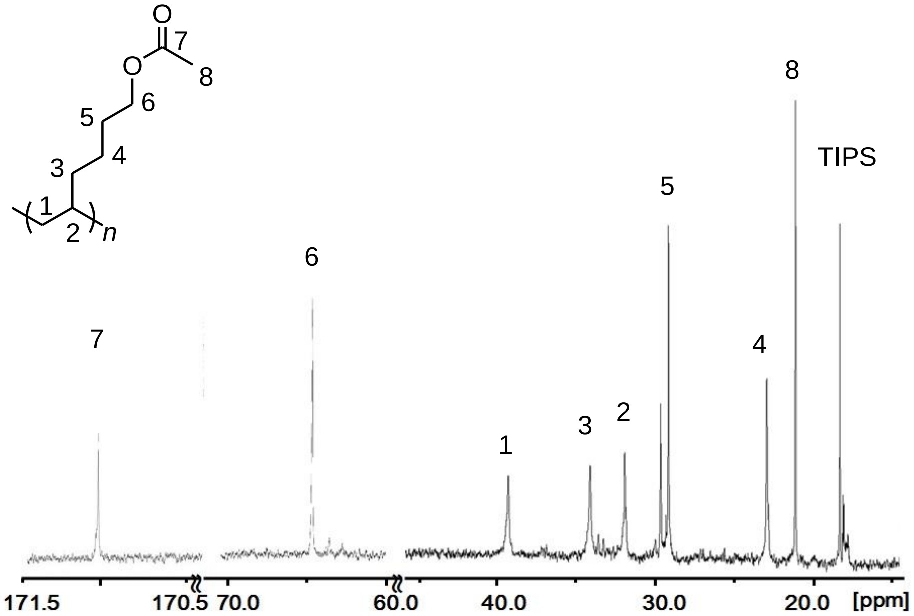


Figure 6. $^{13}C\{^{1}H\}$ NMR spectrum of the obtained poly(5-hexenyl acetate).

4-3 Conclusion

We have demonstrated the transformation of the silyl group in poly(5-hexen-1-oxytriisopropylsilane) into the acetyl group using TBAF/Ac_2O to afford the corresponding poly(5-hexenyl acetate) in a moderate yield. This result caused in the polymer effect. In contrast, poly(10-hexen-1-oxytriisopropylsilane) was easily transformed in a similar manner into the corresponding poly(10-hexenyl acetate) quantitatively.

4-4 Experimental Section

General Procedures.

All manipulations of air- and/or moisture-sensitive compounds were performed either using standard Schlenk-line techniques or in a Glovebox Japan E300 Gloveboxes under an inert atmosphere of argon. THF was dried over a potassium mirror prior to use. Other chemicals were used as received. ^{1}H (400 MHz) and ^{13}C{^{1}H} (100.5 MHz) NMR spectra were obtained with a Bruker DRX400. The ^{13}C{^{1}H} NMR data of the poly(ω-alkenyl acetate)s were obtained in $CDCl_3$ at room temperature. The IR spectra were recorded with a Brucker TENSOR II. The molecular weights and molecular weight distributions of polymers were determined against polystyrene standard by gel permeation chromatography on a SCL-10AVP/LC- 10ATVP/DGU-14A/CTO-10ACVP/RID-10A apparatus (Shimadzu Corporation) using a GPC KF-804L (Shodex Corporation) column for the poly(ω-alkenyl acetate)s.

Reaction of poly(10-undecen-1-oxytriisopropylsilane) with TBAF and then Ac_2O.

In a 50 mL two-necked flask, a solution of the polymer (30.5 mg, 0.093 mmol) in THF (5 mL) was added a solution of tetrabutylammonium fluoride (1.0 M, 1 mL, 1.0 mmol) at 0 ºC, and the mixture was stirred for 1 h at ambient temperature. To the mixture was added a solution of acetyl anhydride (100 μL, 1.0 mmol) for 12 h at ambient temperature. The mixture was extracted with Et_2O, washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. The crude mixture was washed with hexane, and the solvent was removed under reduced pressure to give a colorless viscous oily polymer (15.8 mg, 99%).

Reaction of poly(5-hexen-1-oxytriisopropylsilane) with TBAF and then Ac_2O.

In a 50 mL two-necked flask, a solution of the polymer (16.2 mg, 0.065 mmol) in THF (5 mL) was added a solution of tetrabutylammonium fluoride (1.0 M, 0.07 mL, 0.70 mmol) at 0 ºC, and the mixture was stirred for 6 h at ambient temperature. To the mixture was added a solution of acetyl anhydride (10 μL, 0.10 mmol), and the mixture was stirred for 16 h at ambient temperature. The mixture was extracted with Et_2O, washed with water, dried over anhydrous Na_2SO_4, and evaporated to dryness under reduced pressure. The crude mixture was subjected to column chromatography (silica gel, Ac_2O:hexane = 1:2). The solvent was removed under reduced pressure to give a colorless viscous oily polymer (4.0 mg, 49%).

4-5 References

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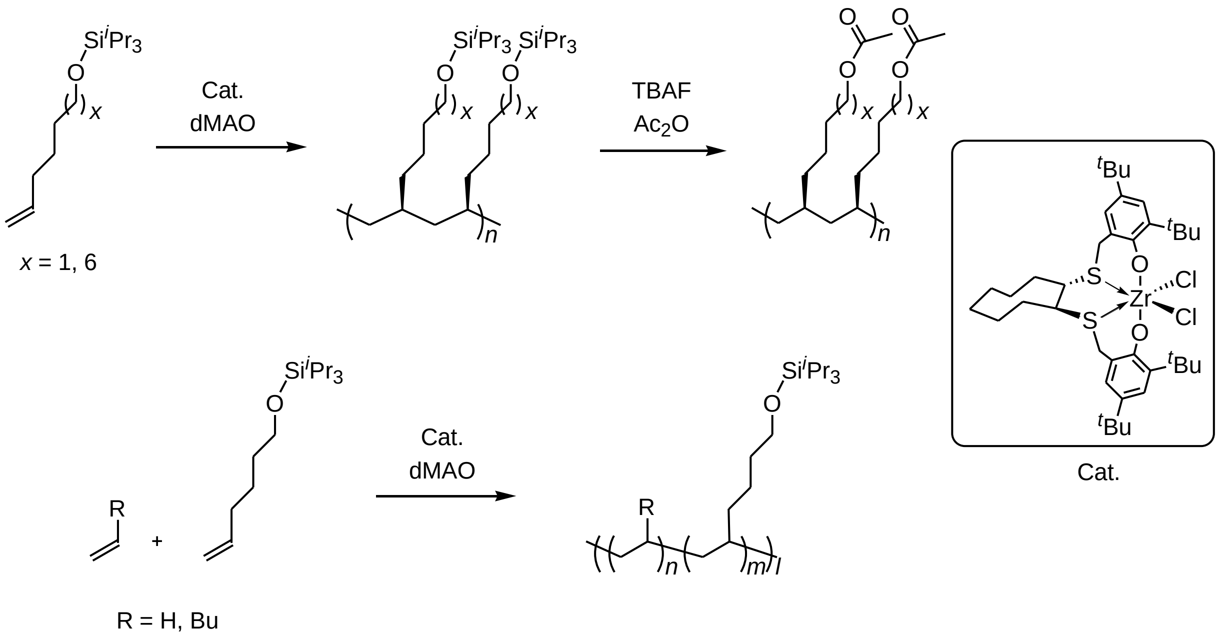
Chapter 5

Conclusion and Outlook

The author achieved the first isospecific polymerization of the terminal functionalized α-olefins by focusing on the treatment with the zirconium complex bearing an [OSSO]-type ligand, performing the perfect stereo-controlled polymerization, where the hydroxyl group was protected with silyl groups to prevent the deactivation of the central metal. In particular, the 10-undecen-1-oxytriisopropylsilane was polymerized isospecifically and efficiently by using the catalytic system of the dichloro zirconium complex and the dMAO as an activator with high activities. In addition, the obtained polymer was transformed into the polymer having acetoxy substituents. Additionally, the combination of the zirconium complex and dMAO showed good copolymerization ability for the terminal siloxy-substituted α-olefin and non-polar α-olefins. Notably, the polar monomer contents in the copolymer synthesized by the system exhibited up to 21.4 mol % for the ethylene/5-hexene-1-oxytriisopropylsilane and 52.8 mol % for the 1-hexene/5-hexen-1-oxytriisopropylsilane.



In this study, the author summarizes that the zirconium complex is an extremely high-potential polymerization precatalyst for α-olefins including ethylene, propylene, styrene, and polar monomers to produce the corresponding highly isotactic poly(α-olefin)s with considerably high activities.

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Professor *Akihiko Ishii*

Assistant Professor *Norio Nakata*

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Mrs. *Hitomi Toda*, Ms. *Eriko Toyoda*, Mr. *Yuichiro Nemoto*, Mr. *Yoshiyuki Furukawa*

Ms. *Suzuka Yamamoto*, Ms. *Chizuru Komatsubara*, Mr. *Keita Ikuma*

Mr. *Fumihiko Kawauchi*, Ms. *Tsuiman Kao*, Mr. *Shota Kobayashi*, Mr. *Yutaro Aoki*

Ms. *Jing An*, Mr. *Izuru Suzuki*, Ms. Noriko Sekizawa, Mr. *Hiroki Mikami*, Mr. *Hiroki Abe*

Mr. *Hiroki Kobayashi*, Mr. *Yukihiro Makishima*, Ms. *Hanako Yamamoto*

Mr. *Laurent Bacque*, Mr. *Tasuku Ogasawara*, Ms. *Chika Shibata*, Ms. *Mari Shibata*

Ms. *Narimi Hosoda*, Mr. *Takanori Watanabe*, Ms. *Estefania da Costa Baptista*

Mr. *Yusuke Oshima*, Ms. *Sawako Shoda*, Ms. *Miki Toyoda*, Ms. *Yuri Hirai*

Mr. *Andreas Meißner*, Ms. *Natalia del Rio Garcia*, Ms. *Shoko Ikeda*

Ms. *Chiharu Kikushima*, Mr. *Shintaro Takahashi*, Mr. *Kazuaki Nakamura*

Mr. *Jérémy Saouli*

Yusuke Saito

Saitama University

March, 2016

List of Publications

Publications for this thesis

1) Norio Nakata, Yusuke Saito, Takahiro Watanabe, and Akihiko Ishii.「Completely Isospecific Polymerization of 1-Hexene Catalyzed by Hafnium(IV) Dichloro Complex Incorporating with an [OSSO]-type Bis(phenolate) Ligand」, *Topic in Catalysis*, *57*, pp918–922, **2014**.
2) Norio Nakata, Yusuke Saito, and Akihiko Ishii,「Neutral Methyl and Cationic Aluminum Complexes Supported by a *trans*-1,2-Cyclooctanediyl-bridged [OSSO]-type Ligand: Synthesis, Structures, and Use in Catalysis for Propylene Oxide Polymerization」, *Organometallics 33*(7), pp1840–1844, **2014**.
3) Yusuke Saito, Norio Nakata, and Akihiko Ishii.「Highly Isospecific Polymerization of Silyl-protected ω-Alkenols using an [OSSO]-Type Bis(phenolato) Dichloro Zirconium(IV) Precatalyst」, Submitted.
4) Yusuke Saito, Norio Nakata, and Akihiko Ishii.「Copolymerization of Ethylene with $^{i}\mathrm{Pr}_3\mathrm{Si}$-protected 5-Hexen-1-ol with an [OSSO]-type Bis(phenolato) Dichloro Zirconium(IV) Complex」, Submitted.

Other publications

1) Norio Nakata, Tomoyuki Toda, Yusuke Saito, Takahiro Watanabe, and Akihiko Ishii.「Highly Active and Isospecific Styrene Polymerization Catalyzed by Zirconium Complexes Bearing Aryl-substituted [OSSO]-Type Bis(phenolate) Ligands」, *Polymers*, *8*(2), pp31–41, **2015**.