

Ethylene/ α -olefin copolymerization by various nonbridged (cyclopentadienyl)(aryloxy)titanium(IV) complexes — MAO catalyst system

Kotohiro Nomura*, Keima Oya, Yukio Imanishi

Graduate School of Materials Science, Nara Institute of Science and Technology (NAIST), 8916-5 Takayama, Ikoma, Nara 630-0101, Japan

Received 31 January 2001; accepted 12 April 2001

Abstract

Effect of ligand in copolymerization of ethylene with 1-hexene by (cyclopentadienyl)(aryloxy)titanium(IV) complexes of the type, $\text{Cp}'\text{TiCl}_2(\text{OAr})$ [$\text{OAr} = \text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3$ and $\text{Cp}' = \text{C}_5\text{Me}_5$ (**1**), $1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3$ (**2**), $^t\text{Bu}_2\text{C}_5\text{H}_4$ (**3**), $1,3\text{-Me}_2\text{C}_5\text{H}_3$ (**5**), Cp (**6**); $\text{OAr} = \text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3$ and $\text{Cp}' = \text{C}_5\text{Me}_5$ (**7**), $1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3$ (**8**)], has been explored in the presence of MAO, and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^t\text{Bu})]\text{TiCl}_2$ (**4**) was chosen as the reference. It was revealed that **1** exhibited the highest catalytic activity, and the resultant poly(ethylene-*co*-1-hexene)s possessed relatively high molecular weights with narrow molecular weight distributions ($M_w = 29.5 \times 10^4$ to 34.5×10^4 , $M_w/M_n = 1.74\text{--}1.88$), and contained 1-hexene in relatively high extents (36.6–43.5 mol%). Effect of both cyclopentadienyl and aryloxy groups plays an essential key role in the copolymerization not only to exhibit high catalytic activity but also to afford relatively high molecular weight copolymer with narrow polydispersity.

It also turned out that α -olefin incorporation into the copolymer is highly affected by the substituents on the cyclopentadienyl group. The monomer reactivity ratios were not affected by both the polymerization temperature and Al/Ti molar ratios, but the monomer sequence distributions and the monomer reactivity ratios depended upon cyclopentadienyl fragment used. In spite of the rather wide bond angle of Cp-Ti-O (ca. 120.5°) in **1–3** than that of Cp-Ti-N in **4** (107.6°), a high level of 1-hexene incorporation and smaller $r_E r_H$ value by **1–3** than those by **4** were attained, which would be due to the flexible internal rotation of both cyclopentadienyl and aryloxy groups. © 2001 Elsevier Science B.V. All rights reserved.

Keywords: Olefin polymerization; Titanium(IV); Ethylene

1. Introduction

Olefin polymerization by homogeneous transition metal complex catalysts attracts particular attention in the field of organometallic chemistry, catalysis, and polymer chemistry. Many reports have been reported concerning this topic especially using early transition metal complexes [1–6].

Among them, we focused nonbridged half-metallocene type group 4B transition metal complexes of the type, $\text{Cp}'\text{M}(\text{L})\text{X}_2$ (Cp' : cyclopentadienyl group; M : Ti, Zr; L : anionic ligand, such as OAr ; X : halogen, alkyl, etc.) [7–21], because this type of complexes might exhibit unique characteristics as olefin polymerization catalysts which would be different from ordinary metallocene type and/or so-called ‘constrained geometry’ (hybrid ‘half-metallocene’) type catalysts [22–31]. Another reason why we focused to this type is that the synthesis is not so complicated (shorter synthetic steps with relatively high yield), and that

* Corresponding author. Tel.: +81-743-72-6041;

fax: +81-743-72-6049.

E-mail address: nomurak@ms.aist-nara.ac.jp (K. Nomura).

Table 1

Copolymerization of ethylene with 1-hexene by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1**) — MAO catalyst system^a

Run no.	Temperature (°C)	Al/Ti ^b	Activity ^c ($\times 10^{-3}$)	1-Hexene ^d (mol%)	M_w^e ($\times 10^{-4}$)	M_w/M_n^e
1	0	30000	5.06			
2	0	30000	6.32 ^f		37.2	1.83
3	15	30000	69.4	36.6	29.8	1.75
4	25	30000	181	37.3	29.5	1.82
5	40	30000	179	42.6	31.7	1.77
6 ^g	40	30000	176	43.4	33.2	1.79
7	50	30000	176	43.6	25.9	1.81
8	40	20000	139		33.4	1.74
5	40	30000	179	42.6	33.2	1.79
9	40	35000	171		32.3	1.83
10	40	50000	189	43.5	32.1	1.88

^a Effect of temperature and Al/Ti molar ratio. Reaction conditions: complex **1** 0.07 mmol; toluene + 1-hexene total 55 ml; MAO white solid prepared by removing toluene and AlMe_3 ; 1-hexene 1.45 mmol/ml; ethylene 5 atm; 6 min; 100 ml scale autoclave.

^b Molar ratio of Al/Ti.

^c Activity in kg polymer/mol Ti h.

^d 1-Hexene content in copolymer determined by ^{13}C NMR spectra [40].

^e GPC data in *o*-dichlorobenzene vs. polystyrene standards.

^f Time 60 min.

^g Repeated experiment of run 5.

the modification of ligand moiety, L, sterically and/or electronically should be easier especially than the ordinary bridged-type complexes.

We have recently shown that (cyclopentadienyl)(aryloxy)titanium(IV) complex of the type, $\text{Cp}^*\text{Ti}(\text{OAr})\text{X}_2$ (OAr: aryloxy group), exhibited remarkable catalytic activities for ethylene, 1-hexene, and 1-octene polymerization in the presence of methylaluminoxane (MAO) [7–10]. We have also shown that $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ exhibited exceptionally high catalytic activity for ethylene/ α -olefin copolymerization [8,11] and that the monomer reactivities as well as monomer sequence distributions were affected by the substituents in cyclopentadienyl group [11]. Moreover, we have also reported that the catalyst of this type could be tuned to the efficient catalyst precursor for both styrene homopolymerization and ethylene/styrene copolymerization by the simple ligand modification [12]. These are, we believe, very attractive characteristics of the nonbridged half-metallocene type catalyst especially for precise ethylene-based copolymerization.

Since, we introduced our preliminary results for effect of cyclopentadienyl fragment for monomer reactivities and monomer sequence distributions in ethylene/ α -olefin copolymerization [11], we wish to

report the more details concerning the polymerization using various complexes in the present paper [32–39].¹

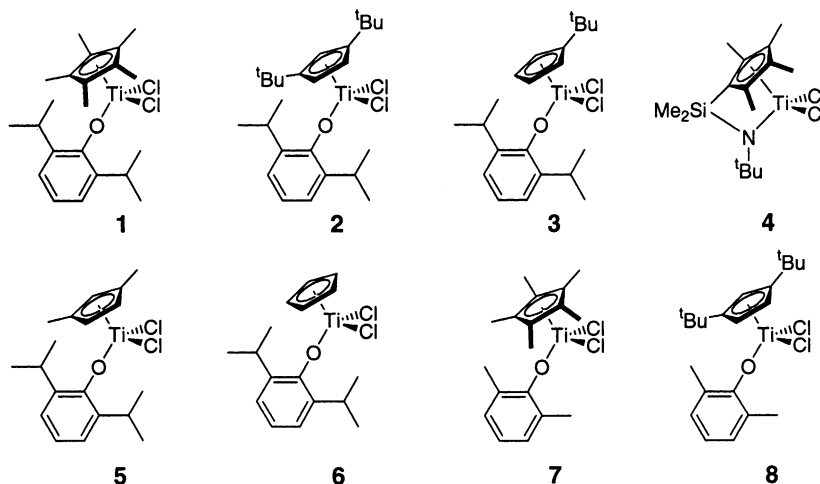
2. Results and discussion

2.1. Copolymerization of ethylene with 1-hexene and 1-octene by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**1**), and $[\text{Me}_2\text{Si}(\text{C}_5\text{Me}_4)(\text{N}^i\text{Bu})]\text{TiCl}_2$ (**4**) — MAO catalyst systems

Table 1 summarizes the results for ethylene/1-hexene copolymerization by **1** — MAO catalyst systems. In order to control the 1-hexene conversions less than 10%, which would affect the monomer reactivity ratios and monomer sequence distributions, these copolymerizations were terminated at 5–6 min (Scheme 1).

It was revealed that **1** exhibited the remarkable catalytic activity in the presence of MAO which was prepared from commercially available MAO (PMAO-S) by removing toluene and the excess amount of AlMe_3

¹ Under peculiar copolymerization conditions at 0°C, *meso*- $[\text{Me}_2\text{Si}(2\text{-Me-1-Ind})_2]\text{ZrCl}_2$ — MAO catalyst gave alternating ethylene/1-octene copolymer [34].



Scheme 1.

in vacuo. The activity did not change between 6 and 60 min at 0°C (runs 1 and 2). The resultant copolymers possessed relatively high molecular weights with unimodal molecular weight distributions ($M_w = 25.9 \times 10^4$ to 33.4×10^4 , $M_w/M_n = 1.75$ – 1.88), and contained 1-hexene in relatively high contents (36.6–43.5 mol%) [40]. The observed catalytic activity was somewhat low when the polymerization was performed at 15°C, but the rate did not change between 25 and 50°C (69.4×10^3 , 181×10^3 , 179×10^3 , and 176×10^3 kg polymer/mol Ti h at 15, 25, 40, and 50°C, respectively). The observed catalytic activity also decreased at low Al/Ti molar ratio, but the value did not change after the molar ratio of 30,000. It might be interesting to note that the M_w values of the resultant copolymers did not change under different Al/Ti molar ratios (activity = 139×10^3 , 179×10^3 , and 189×10^3 kg polymer/mol Ti h; $M_w = 33.4 \times 10^4$, 33.2×10^4 , and 32.1×10^4 at Al/Ti = 20,000, 30,000 and 50,000, respectively), which might suggest the major chain-transfer reaction in this catalysis would not be due to the transfer to aluminum. The results presented here were reproducible as shown in run 6.

Table 2 summarizes the effect of ethylene pressure in the copolymerization. The catalytic activity, which is calculated from the total polymer yield based on molar amount of titanium charged, increased at higher ethylene pressure, and 1-hexene content in the resultant copolymer decreased at higher ethylene pressures.

The molecular weight for the resultant copolymer decreased at lower ethylene pressure probably due to the increase of α -olefin content that would increase the extent of chain-transfer reaction, although the polydispersities did not change under these conditions. Initial turnover frequencies for both ethylene and 1-hexene (1-octene) in the copolymerization increased at higher ethylene pressures, although we do not analyze the more details at this moment.

Table 3 summarizes the results under various 1-hexene concentrations. These copolymerizations by **1** — MAO catalyst system proceeded at remarkable rates affording copolymer with relatively high molecular weights as well as with narrow molecular weight distributions. The observed catalytic activity did not change drastically between 2 and 8 min, but the rate gradually decreased after 20 min probably due to the partial deactivation of the catalytically-active species and/or accumulation of copolymers formed in the reaction mixture.

It was also revealed that **4** — MAO catalyst system showed lower catalytic activity than **1** — MAO catalyst system under these conditions (Table 3). On the other hand, the M_w value for the resultant copolymer prepared by **4** was higher than that by **1** under these conditions (e.g. run 19 versus run 29 and run 20 versus run 28).

It should be noted that the catalytic activity by **1** increased significantly upon the increase of 1-hexene

Table 2

Copolymerization of ethylene with 1-hexene and 1-octene by **1** — MAO catalyst system^a

Run no.	α -Olefin	Ethylene (atm)	Activity ^b ($\times 10^{-3}$)	1-Hexene ^c (mol%)	M_w^d ($\times 10^{-4}$)	M_w/M_n^d	TOF ^e ($\times 10^{-4}$)		
							Ethylene	1-Hexene	Total
11	1-Hexene	3	81.4		30.5	1.76			
12	1-Hexene	4	133		31.3	1.75			
5	1-Hexene	5	179	42.6	31.7	1.77	198	147	345
13	1-Hexene	6	237		34.5	1.77			
14	1-Hexene	7	263	38.1	33.7	1.87	329	203	532
15	1-Octene	3	78.2		23.8	1.76			
16	1-Octene	4	133		25.7	1.90			
17	1-Octene	5	198	36.6 ^f	33.8	1.83	258	149 ^g	407
18	1-Octene	6	213	34.0 ^f	34.0	1.85	298	154 ^g	452

^a Effect of ethylene pressure. Reaction conditions: complex **1** 0.07 mmol; toluene + α -olefin total 55 ml; α -olefin 10 ml (1-hexene 1.45 mmol/ml); MAO white solid prepared by removing toluene and AlMe₃; Al/Ti = 30,000 (molar ratio); 40°C; 6 min; 100 ml scale autoclave.

^b Activity in kg polymer/mol Ti h.

^c 1-Hexene content in copolymer determined by ¹³C NMR spectra.

^d GPC data in *o*-dichlorobenzene vs. polystyrene standards.

^e TOF (turnover frequency = molar amount of ethylene and/or 1-hexene consumed) (mol Ti h).

^f 1-Octene content in copolymer.

^g TOF of 1-octene in place of 1-hexene.

Table 3

Copolymerization of ethylene with 1-hexene by Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) (**1**), and [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**4**) — MAO catalyst system^a

Run no.	Complex (μ mol)	Al/Ti ^b	Ethylene (atm)	1-Hexene concentration (mmol/ml)	Time (min)	Activity ^c ($\times 10^{-3}$)	1-Hexene ^d (mol%)	M_w^e ($\times 10^{-4}$)	M_w/M_n^e
5	1 (0.07)	30000	5	1.45	6	179	42.6	31.7	1.77
19	1 (0.10)	30000	5	1.09	6	79.5	40.3	32.0	1.88
20	1 (0.08)	25000	5	0.73	6	83.2	28.7	38.2	1.80
14	1 (0.07)	30000	7	1.45	6	263	38.1	33.7	1.87
21	1 (0.10)	30000	7	1.09	6	120	36.0	33.4	1.73
22	1 (0.08)	25000	7	0.73	6	103	24.6	45.5	1.98
23	1 (0.10)	25000	7	0.44	2	59.8		44.2	1.98
24	1 (0.10)	25000	7	0.44	4	65.2		45.0	1.93
25	1 (0.10)	25000	7	0.44	8	71.3		46.5	1.95
26	1 (0.10)	25000	7	0.44	20	33.0		47.9	2.18
27	4 (0.65)	5000	5	1.45	6	5.01	60.0	40.5	1.77
28	4 (0.60)	5000	5	0.73	6	9.49	30.0	74.5	2.05
29	4 (0.65)	5000	7	1.45	6	6.96	39.4	88.0	2.21
30	4 (0.60)	5000	7	0.73	4	14.6	23.7	119	2.30
31	4 (0.55)	5000	7	0.44	3	30.2		132	2.15

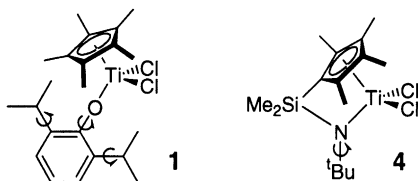
^a Effect of ethylene pressure and 1-hexene concentration. Reaction conditions: toluene + 1-hexene total 55 ml; MAO white solid prepared by removing toluene and AlMe₃; 40°C; 100 ml scale autoclave.

^b Molar ratio of Al/Ti.

^c Activity in kg polymer/mol Ti h.

^d 1-Hexene content in copolymer determined by ¹³C NMR spectra.

^e GPC data in *o*-dichlorobenzene vs. polystyrene standards.



Scheme 2.

concentrations, although the opposite tendency was observed if **4** was employed as the catalyst. This would be an interesting contrast among these complexes.

Table 4 summarizes triad and dyad sequence distributions in the resultant poly(ethylene-*co*-1-hexene) prepared by **1** and **4** — MAO catalyst systems under various ethylene, 1-hexene concentrations [40]. As reported in our preliminary communication [11], the resultant copolymer prepared by **1** possessed relatively higher percentage of EHE and HEH, and EH+HE sequences than those by **4**, and the $r_{E}r_{H}$ values by **1** calculated from the dyads were small (0.29–0.32). On the other hand, $r_{E}r_{H}$ values by **4** were ca. 1.0, which demonstrates that the copolymerization proceeds in a random manner. In addition, **4** seemed to be more suited as the efficient catalyst to prepare the copolymer containing 1-hexene higher than ca. 50 mol%. We assumed that the difference observed here might be due to the different structure or different electronic nature of these catalytically-active species. One possible explanation for a high level of 1-hexene incorporation by **1** would be due to the flexible internal rotation of both cyclopentadienyl and aryloxy groups (Scheme 2). This would be an important key role to offer relatively wide coordination sphere in spite of wide bond angle of Cp'-Ti-O (120.5°) in **1** compared to that of Cp-Ti-N (107.6°) in **4** [30]. Moreover, the reason for small $r_{E}r_{H}$ values by **1** might also be assumed to be due to the result of internal rotation especially of aryloxy group which would form high percentage of favored conformation in equilibrium among the catalytically-active species as shown in Scheme 3.²

² We speculated that the reason for small $r_{E}r_{H}$ value might be due to the flexible rotation of aryloxy group. This is due to that the monomer sequence distributions also obey the simple first-order Markov model, and that there should have a difference in relative coordination and/or insertion rate into two alkyl cationic species shown in Scheme 3 because there should have equilibrium due to the rotation of aryloxy group.

Generally, structural features of the catalyst, in particular the steric bulk of ligand, bite angle, configuration and conformation, do influence the coordination and/or insertion of monomers in transition metal catalyzed coordination polymerization reactions, and this is a distinct difference from conventional radical and ionic polymerization reactions [41]. In most cases of ethylene/ α -olefin copolymerization, especially by metallocene-type catalyst, the copolymerization proceeds in a random manner and the monomer sequences obey the first-order Markov model. Table 5 summarizes the analyses results for triad sequence distributions that are calculated from the dyads based on either the Bernoullian or the simple first-order Markov model.³ It turned out that the distributions in the copolymerization by **1** — MAO system are good agreements with those by the first-order Markov model rather than those by the Bernoullian model. Although this tendency is the general characteristic feature in transition metal catalyzed olefin copolymerization, we would at least say that the last inserted monomer unit should give a great influence to insert and/or coordinate next monomer unit by choosing favored conformation. This would

³ These calculations were made based on dyad distributions according to the following assumption: (a) calculation of triad sequence distribution according to the simple first-order Markov model, $P_1(E) = P_{HE}/(P_{HE} + P_{EH})$, $P_1(H) = P_{EH}/(P_{EH} + P_{HE})$, $P_{EH} = 1 - P_{EE} = [EH]/([EE] + [EH]) = (1/2)[HE + EH]/([EE] + (1/2)[HE + EH])$, $P_{HE} = 1 - P_{HH} = [HE]/([EE] + [HE]) = (1/2)[HE + EH]/([EE] + (1/2)[HE + EH])$; $[EE] = P_2(EE) = P_1(E)P_{EE} = P_{HE}(1 - P_{EH})/(P_{HE} + P_{EH})$, $[EH + HE] = P_2(EH) + P_2(HE) = P_1(E)P_{EH} + P_1(H)P_{HE} = 2P_{EH}P_{HE}/(P_{EH} + P_{HE})$, $[HH] = P_2(HH) = P_1(H)P_{HH} = P_{EH}(1 - P_{HE})/(P_{EH} + P_{HE})$; $[EEE] = P_3(EEE) = P_1(E)P_{EE}P_{EE} = P_{HE}(1 - P_{EH})(1 - P_{EH})/(P_{HE} + P_{EH})$, $[EEH + HEE] = P_3(HEE) + P_3(EEH) = P_1(H)P_{HE}P_{EE} + P_1(E)P_{EE}P_{EH} = 2P_{EH}P_{HE}(1 - P_{EH})/(P_{EH} + P_{HE})$, $[HEH] = P_3(HEH) = P_1(H)P_{HE}P_{EH} = P_{HE}P_{HE}P_{EH}/(P_{HE} + P_{EH})$, $[EHE] = P_3(EHE) = P_{HE}P_{EH}P_{EH}/(P_{HE} + P_{EH})$, $[HHE + EHH] = P_3(HHE) + P_3(EHH) = 2P_{EH}P_{HE}(1 - P_{HE})/(P_{EH} + P_{HE})$, $[HHH] = P_3(HHH) = P_{EH}(1 - P_{HE})(1 - P_{HE})/(P_{HE} + P_{EH})$. (b) Calculation of triad sequence distribution according to the Bernoullian model, $P_1(E) = P_E = 1 - P_H = ([EE] + (1/2)[EH + HE])/([EE] + (1/2)[EH + HE] + [HH])$; $[EE] = P_2(EE) = P_E P_E$, $[EH + HE] = P_2(EH) + P_2(HE) = 2P_E P_H$, $[HH] = P_2(HH) = P_H P_H$, $[EEE] = P_3(EEE) = P_E P_E P_E$, $[EEH + HEE] = P_3(HEE) + P_3(EEH) = P_H P_E P_E + P_E P_E P_H = 2P_H P_E P_E$, $[HEH] = P_3(HEH) = P_H P_E P_H$, $[EHE] = P_3(EHE) = P_E P_H P_E$, $[HHE + EHH] = P_3(HHE) + P_3(EHH) = 2P_H P_H P_E$, $[HHH] = P_3(HHH) = P_H P_H P_H$.

Table 4
Monomer sequence distribution of poly(ethylene-co-1-hexene)^a

Run no.	Complex	Ethylene (atm)	1-Hexene concentration ^b	1-Hexene ^c (mol%)	Triad sequence distribution ^d (%)						Dyads ^e			$r_{E^*H}^f$
					EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH	
12	1	5	1.45	43.5	12.5	26.6	17.4	22.6	18.0	2.9	25.8	62.3	11.9	0.32
5	1	4	1.45	42.6	12.2	26.0	19.2	22.2	16.8	3.6	25.2	62.8	12.0	0.31
19	1	5	1.09	40.3	14.7	28.6	16.4	21.4	17.7	1.2	29.0	60.9	10.1	0.31
14	1	7	1.45	38.0	17.3	30.4	14.3	22.5	14.0	1.5	32.4	59.0	8.5	0.31
20	1	7	1.09	36.0	19.9	31.1	13.0	22.0	13.2	0.8	35.4	57.2	7.4	0.32
21	1	5	0.73	28.7	31.1	31.3	8.9	21.5	6.8	0.4	46.8	49.5	3.7	0.29
22	1	7	0.73	24.6	40.0	29.6	5.8	19.4	4.6	0.6	55.1	42.5	2.4	0.29
27	4	5	1.45	60.0	9.6	15.8	14.6	8.8	32.8	18.4	17.5	47.7	34.8	1.07
29	4	7	1.45	39.4	23.3	28.6	8.7	14.3	20.0	5.1	37.6	47.4	15.0	1.01
28	4	5	0.73	30.0	35.5	28.6	5.9	14.2	14.4	1.4	49.8	41.6	8.6	0.99
30	4	7	0.73	23.7	45.3	27.2	3.8	13.8	9.4	0.5	58.9	35.9	5.2	0.96

^a Detailed polymerization conditions, see Tables 1–3.

^b Initial 1-hexene concentration (mmol/ml).

^c 1-Hexene content in copolymer determined by ¹³C NMR spectra.

^d Calculated by ¹³C NMR spectra.

^e [EE] = [EEE] + (1/2)[EEH + HEE], [EH] = [HEH] + [EHE] + (1/2){[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + (1/2)[HHE + EHH].

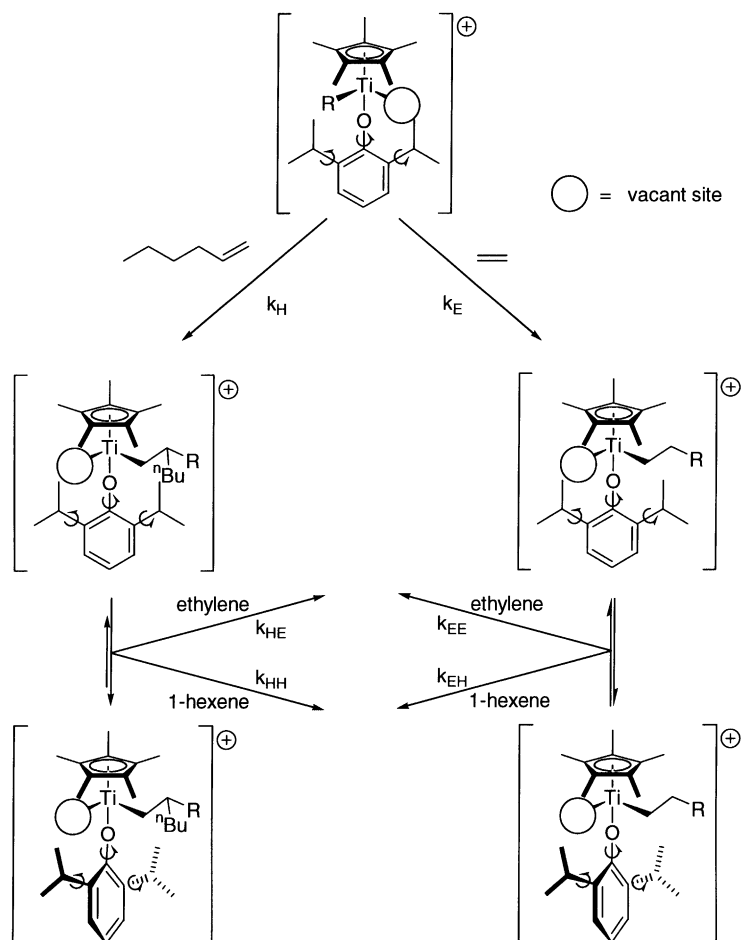
^f $r_{E^*H} = 4[EE][HH]/[EH + HE]^2$.

Table 5
Calculated and observed monomer sequence distribution of poly(ethylene-co-1-hexene)s prepared by 1^a

Run no.	Method ^b	1-Hexene (mol%)	Dyads (%)			Triad sequence distribution (%)					
			EE	EH + HE	HH	EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH
5	Exp.	42.6	25.2	62.8	12.0	12.2	26.0	19.2	22.2	16.8	3.6
	B					18.2	27.8	10.7	13.9	21.3	8.2
	M1					11.2	28.0	17.4	22.7	17.3	3.3
19	Exp.	40.3	29.0	60.9	10.1	14.7	28.6	16.4	21.4	17.7	1.2
	B					21.0	28.7	6.0	11.1	19.5	6.7
	M1					14.1	29.7	15.6	22.9	15.1	2.5
14	Exp.	38.0	32.4	59.0	8.5	17.3	30.4	14.3	22.5	14.0	1.5
	B					23.8	29.2	9.0	14.6	17.9	5.5
	M1					17.3	30.4	14.3	22.5	14.0	1.5
20	Exp.	36.0	35.4	57.2	7.4	19.9	31.1	13.0	22.0	13.2	0.8
	B					26.2	29.5	8.3	14.7	16.6	4.7
	M1					19.6	31.6	12.8	22.7	11.8	1.5
21	1	28.7	46.8	49.5	3.7	31.1	31.3	8.9	21.5	6.8	0.4
	B					36.6	29.1	5.8	14.6	11.6	2.3
	M1					30.6	32.4	8.5	21.5	6.5	0.5
22	1	24.6	55.1	42.5	2.4	40.0	29.6	5.8	19.4	4.6	0.6
	B					44.5	27.6	4.3	13.8	8.5	1.3
	M1					39.7	30.7	5.9	19.1	4.3	0.2

^a Detailed polymerization conditions, see Table 3.

^b Exp.: experimental value; B: calculated value from dyads based on the Bernoullian model; M1: calculated value from dyads based on the simple first-order Markov model (see footnote 3).



Scheme 3.

be one plausible, probable support for our speculative scheme (Scheme 3) to explain the reason for small $r_E r_H$ value by **1**.

Table 6 summarizes effect of polymerization temperature and Al/Ti molar ratios on monomer reactivities and monomer sequence distributions in the poly(ethylene-*co*-1-hexene)s prepared by **1** — MAO catalyst system.⁴ It was revealed that Al/Ti molar ratio gave no strong influence to these parameters, as we

described that the effect to the molecular weight and the 1-hexene contents were negligible. The resultant both r_E and r_H values were smaller than those by **4**, which thus affords small $r_E r_H$ values.

It should be noted that the resultant r_E and r_H values were not influenced by the polymerization temperature between 15 and 50°C (runs 3–5 and 7). This is an interesting contrast to the ordinary metallocene-type complex catalysts, which both r_E and r_H values are strongly influenced by the polymerization temperature, although we do not have any clear elucidation for explaining this difference [44–46]. The r_E and r_H values drastically changed if the polymerization was performed at 0°C, and this might give us a plausible idea to explain the above difference among these

⁴ The calculation of r_E and r_H values are based on dyads and the initial monomer concentrations. Ethylene concentrations under the reaction conditions were estimated by the equation quoted by Kissin [42], and the ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported [43].

Table 6

Monomer sequence distribution of poly(ethylene-co-1-hexene)s prepared by **1** — MAO catalyst system^a

Run no.	α -Olefin	Temperature (°C)	Al/Ti ^b	α -Olefin ^c (mol%)	Triad sequence distribution ^d (%)						Dyads ^e (%)			r_E^f	r_H^f	$r_E r_H^f$
					EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH			
2	1-Hexene	0	30000	60.2	16.0	27.0	20.2	17.2	27.0	16.0	11.2	59.3	29.5	0.66	0.58	0.38
3	1-Hexene	15	30000	36.6	18.7	30.7	14.0	22.9	13.1	0.6	34.0	58.8	7.2	2.45	0.12	0.28
4	1-Hexene	25	30000	37.4	18.9	29.1	14.6	23.9	11.8	1.7	33.5	58.9	7.6	2.70	0.11	0.29
5	1-Hexene	40	30000	42.6	12.2	26.0	19.2	22.2	16.8	3.6	25.2	62.8	12.0	2.29	0.13	0.31
7	1-Hexene	50	30000	43.6	10.9	27.9	17.6	23.9	15.0	4.7	24.9	63.0	12.1	2.51	0.12	0.31
17	1-Octene	40	30000	36.6	17.3	32.4	13.8	24.5	12.0	0.1	33.4	60.4	6.1	2.65	0.09	0.23
5	1-Hexene	40	30000	42.6	12.2	26.0	19.2	22.2	16.8	3.6	25.2	62.8	12.0	2.29	0.13	0.31
10	1-Hexene	40	50000	43.5	12.5	26.6	17.4	22.6	18.0	2.9	25.8	62.3	11.9	2.36	0.13	0.32

^a Effect of polymerization temperature on monomer reactivities and on monomer sequence distributions. Detailed polymerization conditions, see Tables 1 and 2.

^b Molar ratio of Al/Ti.

^c α -Olefin content in copolymer determined by ¹³C NMR spectra.

^d Calculated by ¹³C NMR spectra.

^e [EE] = [EEE] + (1/2)[EEH + HEE], [EH] = [HEH] + [EHE] + (1/2){[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + (1/2)[HHE + EHH].

^f $r_E r_H = 4[EE][HH]/[EH + HE]^2$, $r_E = [H]_0/[E]_0 \times 2[EE]/[EH + HE]$, $r_H = [E]_0/[H]_0 \times 2[HH]/[EH + HE]$, $[E]_0$ and $[H]_0$ are the initial monomer concentrations.

Table 7

Copolymerization of ethylene with 1-hexene by (1,3-^tBu₂C₅H₃)TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**2**), and (^tBu₂C₅H₃)TiCl₂(O-2,6-ⁱPr₂C₆H₃) (**3**) — MAO catalysts^a

Run no.	Complex (μ mol)	Temperature (°C)	Al/Ti ^b	Ethylene (atm)	1-Hexene concentration ^c	Time (min)	Activity ^d ($\times 10^{-3}$)	1-Hexene ^e (mol%)	M_w^f ($\times 10^{-4}$)	M_w/M_n^f
32	2 (0.45)	40	6500	5	1.45	8	4.70	37.5	10.3	1.84
33	2 (0.45)	40	6500	7	1.45	8	6.85	33.9	12.4	1.78
34	2 (0.30)	40	9000	5	0.73	6	11.3	27.0	19.7	1.82
35	2 (0.30)	40	9000	7	0.73	6	17.5	23.5	24.8	1.71
36	2 (0.60)	40	6500	3	2.54	30	1.42	54.0	7.63	1.89
37	3 (0.75)	40	4000	5	1.45	5	8.79	58.7	10.4	1.58
38	3 (0.75)	40	4000	7	1.45	5	15.0	41.4	13.0	1.60
39	3 (0.60)	40	5000	5	0.73	8	6.41	32.0	11.4	1.99
40	3 (0.60)	40	3300	7	0.73	6	14.2	26.9	12.7	1.60
41	3 (0.75)	40	4000	5	1.09	5	8.86	52.6	10.3	1.70
42	3 (0.60)	40	3300	7	0.44	4	5.29		11.3	2.02
43	3 (0.75)	40	4000	3	2.54	6	3.76		6.11	1.68

^a Reaction conditions: toluene + 1-hexene total 55 ml; MAO white solid prepared by removing toluene and AlMe₃; 100 ml scale autoclave.

^b Molar ratio of Al/Ti.

^c 1-Hexene concentration measured in mmol/ml.

^d Activity measured in kg polymer/mol Ti h.

^e 1-Hexene content in copolymer determined by ¹³C NMR spectra.

^f GPC data in *o*-dichlorobenzene vs. polystyrene standards.

complexes, although we do not have clear reason concerning the temperature dependence.

2.2. Copolymerization of ethylene with 1-hexene by various $Cp^*TiCl_2(OAr)$ — MAO catalyst systems

Table 7 summarizes results for ethylene/1-hexene copolymerization using $(1,3-^tBu_2C_5H_3)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (**2**) and $(^tBu_2C_5H_4)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (**3**) complexes in the presence of MAO cocatalyst under various conditions. Although the polymerization conditions, especially Al/Ti molar ratio, could be optimized, the observed catalytic activities were somewhat lower than those by **1**, suggesting that the effect of substituent on cyclopentadienyl group plays an essential key role for the activity. On the other hand, **3** exhibited higher levels of 1-hexene incorporations than **1** and/or **2** under the same conditions (e.g. 1-hexene content in poly(ethylene-co-1-hexene)s: 42.6, 37.5, and 58.7 mol% by **1** (run 5), **2** (run 32), and **3** (run 37), respectively, ethylene 5 atm, 1-hexene 1.45 mmol/ml). The molecular weights for the resultant copolymers by both **2** and **3** were lower than those by **1**, although these copolymers possessed narrow polydispersities. These results also suggest that the ligand effect also plays a role for the molecular weight of the resultant polymer.

Table 8 summarizes the results for ethylene/1-hexene copolymerization by $(1,3-Me_2C_5H_3)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (**5**) and $CpTiCl_2(O-2,6-^iPr_2C_6H_3)$ (**6**) — MAO catalyst^a

Table 8

Copolymerization of ethylene with 1-hexene by $(1,3-Me_2C_5H_3)TiCl_2(O-2,6-^iPr_2C_6H_3)$ (**5**), and $CpTiCl_2(O-2,6-^iPr_2C_6H_3)$ (**6**) — MAO catalyst^a

Run no.	Complex (μmol)	Temperature ($^{\circ}\text{C}$)	Al/Ti ^b	Ethylene (atm)	1-Hexene concentration ^c	Time (min)	Activity ^d	M_w^e ($\times 10^{-4}$)	M_w/M_n^e
44	5 (0.55)	40	5000	7	0.73	6	10020	10.9	3.07
45	5 (0.55)	40	5000	5	0.73	6	9390	9.7	2.76
46	5 (0.60)	40	5000	7	1.45	8	8170	7.8	2.79
47	5 (0.60)	40	5000	5	1.45	8	6520	7.9	2.33
48	5 (0.65)	25	5000	5	0.73	6	9650	10.2	2.15
49	6 (15.0)	40	200	7	0.73	60	11.9	14.6	10.8
50	6 (15.0)	40	200	5	0.73	60	9.2	3.7	5.16
51	6 (15.0)	40	200	7	1.45	60	10.0	3.2	4.07
52	6 (15.0)	40	200	5	1.45	60	6.6	3.1	4.46

^a Reaction conditions: toluene + 1-hexene total 55 ml; MAO white solid prepared by removing toluene and $AlMe_3$; 100 ml scale autoclave.

^b Molar ratio of Al/Ti.

^c 1-Hexene concentration measured in mmol/ml.

^d Activity is in kg polymer/mol Ti h.

^e GPC data in *o*-dichlorobenzene vs. polystyrene standards.

$Pr_2C_6H_3)$ (**5**) and $CpTiCl_2(O-2,6-^iPr_2C_6H_3)$ (**6**) complexes in the presence of MAO cocatalyst. The observed catalytic activities were at the same level as that by **2** and/or **3** when **5** was employed as the catalyst precursor. The resultant polymers have relatively high molecular weights, but the molecular weight distributions were rather broad due to the contamination of low molecular weight polymers. These results suggest that the catalytically-active species would be decomposed partially, and the copolymerization thus did not proceed with a single-site nature. Compound **6** showed the lowest catalytic activity among the series of $Cp^*TiCl_2(O-2,6-^iPr_2C_6H_3)$ complexes, and the resultant polymer possessed low molecular weight and broad polydispersity.

In order to explore the effect of aryloxy group not only for the catalytic activity but also for both monomer reactivities and monomer sequence distributions in ethylene/1-hexene copolymerization catalyzed by the series of (cyclopentadienyl)(aryloxy)titanium(IV) complexes — MAO systems, we performed the polymerization with $Cp^*-TiCl_2(O-2,6-Me_2C_6H_3)$ (**7**) and $(1,3-^tBu_2C_5H_3)TiCl_2(O-2,6-Me_2C_6H_3)$ (**8**) complexes. These results are summarized in Table 9.

It was revealed that the observed catalytic activities by **7** were lower than those by **1** under the same conditions (e.g. 484 kg polymer/mol Ti h by **7** (run 55) versus 83,200 kg polymer/mol Ti h (run 20), ethylene

Table 9

Copolymerization of ethylene with 1-hexene by Cp*TiCl₂(O-2,6-Me₂C₆H₃) (**7**), and (1,3-^tBu₂C₅H₃)TiCl₂(O-2,6-Me₂C₆H₃) (**8**) — MAO catalyst^a

Run no.	Complex (μmol)	Temperature (°C)	Al/Ti ^b	Time (min)	Activity ^c	M _w ^d (×10 ⁻⁴)	M _w /M _n ^d
53	7 (1.0)	40	1500	15	582	32.5	4.33
54	7 (1.0)	40	3000	15	550	25.6	4.80
55	7 (1.0)	40	4500	15	484	21.4	5.21
56	7 (1.0)	0	4500	15	1230	67.2	5.37
57	7 (1.0)	25	4500	15	4840	37.6	8.91
58	7 (1.0)	25	3000	5	7020	47.7	6.07
59	7 (1.0)	25	3000	7	7020	49.1	6.40
60	7 (1.0)	25	3000	15	6000	41.7	8.67
61	7 (1.0)	25	3000	30	3610	44.0	8.44
62	7 (1.0)	25	3000	60	1870	46.3	10.25
63	8 (3.0)	0	500	15	312	36.0	1.67 ^e
64	8 (3.0)	0	1000	15	1550	48.8	2.89
65	8 (3.0)	0	3000	15	56	9.09	2.21
66	8 (3.0)	25	500	15	1230	24.0	1.92 ^e
67	8 (3.0)	25	1000	15	1250	32.8	2.03 ^e
68	8 (3.0)	25	3000	15	345	16.0	1.81 ^e
69	8 (3.0)	40	500	15	407	9.09	2.21
70	8 (3.0)	40	3000	15	110	10.4	2.54

^a Reaction conditions: toluene 50 ml; 1-hexene 5 ml; ethylene 5 atm; MAO white solid prepared by removing toluene and AlMe₃; 100 ml scale autoclave.

^b Molar ratio of Al/Ti.

^c Activity is in kg polymer/mol Ti h.

^d GPC data in *o*-dichlorobenzene vs. polystyrene standards.

^e Small peak of low molecular weight polymer was also observed (run 63: M_w = 8670, M_w/M_n = 1.16; run 66: M_w = 7160, M_w/M_n = 1.58; run 67: M_w = 6920, M_w/M_n = 1.34; run 68: M_w = 9700, M_w/M_n = 1.28).

5 atm, 1-hexene 0.73 mmol/ml, in toluene). The observed catalytic activities by **8** were also lower than those by **2** (407 kg polymer/mol Ti h (run 69) versus 11,300 kg polymer/mol Ti h (run 34), ethylene 5 atm, 1-hexene 0.73 mmol/ml, in toluene). These results strongly suggest that the effect of aryloxy ligand also plays an important key role to exhibit high catalytic activity.

The observed catalytic activities by **7** and **8** were found to be dependent upon Al/Ti molar ratios and polymerization temperature. For instance, the low catalytic activities were observed when the polymerization was performed at 40°C and/or rather high Al/Ti molar ratios. In addition, in the case by **7**, the extent of low molecular weight polymer increased with the increase in Al/Ti molar ratios as shown in Fig. 1. These results suggest that the catalytically-active species would decompose partially to convert another active species, and thus the copolymerization did not proceed in a single-site nature.

Taking into account the above results, effect of substituent in both cyclopentadienyl and aryloxy groups plays an essential key role in order for the copolymerization not only to exhibit remarkably high catalytic activity but also to proceed with single catalytically-active species.

2.3. Effect of cyclopentadienyl group on monomer reactivities and monomer sequence distributions

Although a lot of attempts have been made to explore the effect of substituents in both cyclopentadienyl and aryloxy groups for monomer reactivities and monomer sequence distributions in ethylene/1-hexene copolymerization, results by **1–3** could only be chosen, because the resultant poly(ethylene-*co*-1-hexene)s prepared by the other complexes had broad (and/or bimodal) molecular weight distributions that should not be suited for this discussion. Selected data are summarized in Table 10.

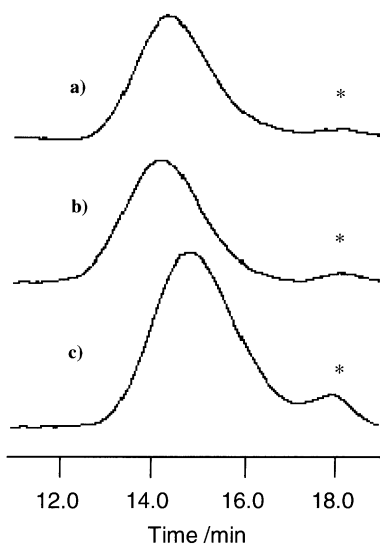


Fig. 1. GPC traces for poly(ethylene-co-1-hexene)s prepared by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-Me}_2\text{C}_6\text{H}_3)$ (**7**) — MAO catalyst system with various Al/Ti molar ratios (Conditions: Al/Ti = 1500 (a, run 53), 3000 (b, run 54), and 4500 (c, run 55), respectively). (*) Peak displays the low molecular weight shoulder. In case of (c), bimodal molecular weight distribution consisted of $M_w = 25.5 \times 10^4$, $M_w/M_n = 1.94$, and $M_w = 1.44 \times 10^4$, $M_w/M_n = 1.53$.

The sequence distributions of copolymers reveal that the contents of EHE and HHE + EHH sequences and the resultant $r_{\text{E}r_{\text{H}}}$ values (r_{E} and r_{H} are the monomer reactivity ratios of ethylene and 1-hexene, respectively) by **1–3** are significantly different from that by **4** under the same conditions. The monomer reactivity ratios in the copolymerization with **4** are consistent with those reported previously [4,6,32,33], and a little larger than those obtained by **1–3**. The difference might reflect the different structure or different

electronic structure either of the catalytically-active species.

Noteworthy is that the sequence distributions as well as their r_{E} , r_{H} , and $r_{\text{E}r_{\text{H}}}$ values in the copolymerizations by **1–3** were strongly affected by the substituent on cyclopentadienyl group. This result should be very interesting for the first example of that the substituents in cyclopentadienyl group directly control the monomer reactivity ratios and the sequence distributions in ethylene/1-hexene copolymerization.

As assumed above, we believe that the high extent of α -olefin incorporation by **1–3**, in spite of the rather wide bond angles of Cp–Ti–O in **1** (120.5°) and **2** (119.3°) than that of Cp–Ti–N in **4** (107.6°), would be due to the rotational flexibility of these complexes. We assume that effect of substituent on cyclopentadienyl group which would directly affect both the monomer reactivity ratios and the sequence distributions would be due to its easy internal rotation, which facilitates to choose favored conformation after the insertion of last monomer unit (Scheme 4). The observed difference in both the monomer reactivities and the monomer sequence distributions among the series of $\text{Cp}'\text{TiCl}_2(\text{OAr})$ catalysts (**1–3**) would thus assumed to be the consequence of the different equilibrium for favorable conformations for coordinating and/or inserting ethylene and/or 1-hexene in the catalysis cycle (Scheme 5).

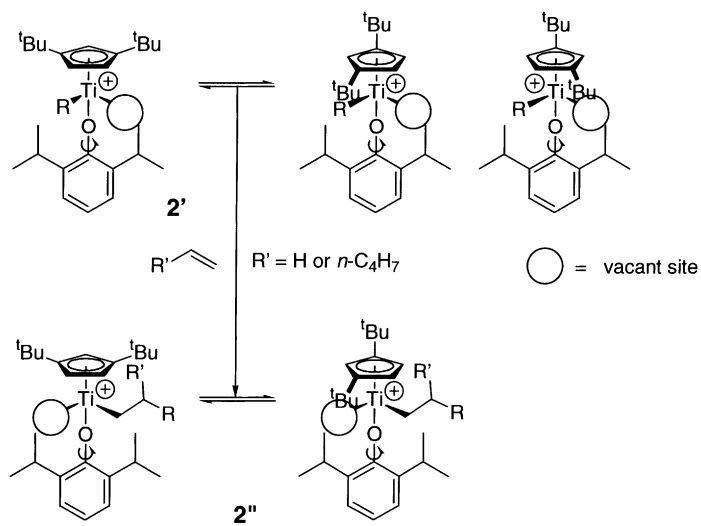
3. Experimental section

3.1. General procedure

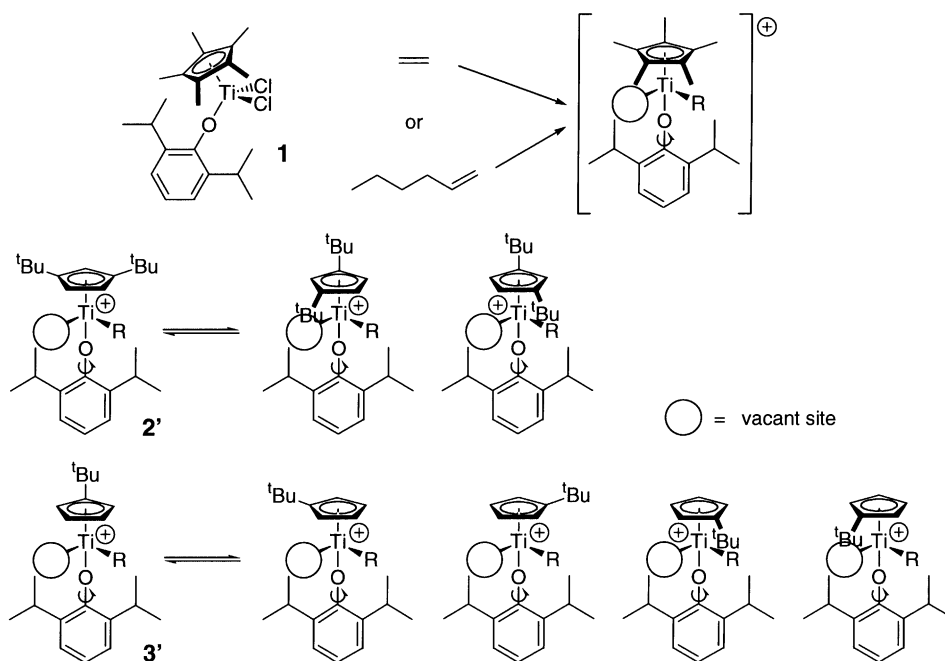
All experiments were carried out under nitrogen atmosphere in a vacuum atmospheres drybox

Table 10
Selected data for monomer sequence distribution of poly(ethylene-co-1-hexene)s

Run no.	Complex	1-Hexene (mol%)	Triad sequence distribution (%)						Dyads (%)			$r_{\text{E}r_{\text{H}}}$	r_{E}	r_{H}
			EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH+ HE	HH			
20	1	28.7	31.1	31.3	8.9	21.5	6.8	0.4	46.8	49.5	3.7	0.28	2.70	0.10
22	1	24.6	40.0	29.6	5.8	19.4	4.6	0.6	55.1	42.5	2.4	0.29	2.64	0.11
33	2	33.9	26.0	29.7	10.4	20.5	12.0	1.4	40.9	51.7	7.4	0.45	3.23	0.14
34	2	27.1	34.6	31.2	7.1	18.4	7.8	0.9	50.3	45.0	4.8	0.48	3.19	0.15
39	3	32.0	27.6	31.4	9.0	20.1	10.9	1.0	43.3	50.2	6.5	0.45	2.46	0.18
40	3	26.9	35.9	31.1	6.2	19.2	7.3	0.4	51.4	44.6	4.0	0.41	2.35	0.18
28	4	30.0	35.5	28.6	5.9	14.2	14.4	1.4	49.8	41.6	8.6	0.99	3.42	0.29



Scheme 4.



Scheme 5.

or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene for polymerization was distilled in the presence of Na and benzophenone under nitrogen atmosphere, and was stored in a Schlenk tube in the drybox. Ethylene for polymerization was of polymerization grade (purity > 99.9%, Sumitomo Seika Co. Ltd.) and was used as received. 1-Hexene and 1-octene of reagent grade were stored in the drybox in the presence of molecular sieves, and were used without further purification. Series of (cyclopentadienyl)(aryloxy)titanium(IV) complexes, such as Cp'TiCl₂(O-^tPr₂C₆H₃) [Cp': C₅Me₅ (**1**), 1,3-^tBu₂C₅H₃ (**2**), ^tBuC₅H₄ (**3**)], were prepared according to our previous report [8]. [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ was purchased from Kanto Chemical Co. Ltd.

Molecular weight and molecular weight distribution of the resultant polymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel column (TSK gel GMH_{HR}-H HT × 2) at 140°C using *o*-dichlorobenzene containing 0.05% (w/v) 2,6-di-^tbutyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

All ¹H and ¹³C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ¹H). All deuterated NMR solvents were stored over molecular sieves under nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me₄Si. All spectra were obtained in the solvent indicated at 25°C unless otherwise noted. ¹³C NMR spectra for poly(ethylene-*co*-1-hexene)s were recorded on JEOL JNM-LA400 spectrometer (100.40 MHz, ¹³C) with proton decoupling at 130°C. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 10,000. The polymer solutions were prepared by dissolving polymers in a mixed solution of 1,3,5-trichlorobenzene/benzene-*d*₆ (90/10 wt.%).

The 1-hexene contents and the monomer sequence distributions in the resultant poly(ethylene-*co*-1-hexene)s were estimated by the previous report using ¹³C NMR spectra of copolymer. The calculation of *r*_E and *r*_H values are based on dyads by the following

equations ([H]₀ and [E]₀ are the initial monomer concentrations, respectively):

$$r_E = \frac{[H]_0}{[E]_0} \frac{2[EE]}{[EH + HE]}, \quad r_H = \frac{[E]_0}{[H]_0} \frac{2[HH]}{[EH + HE]}$$

The initial monomer concentrations, especially for ethylene were estimated by using the equation quoted by Kissin, and ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported previously (see footnote 4) [42].

3.2. Polymerization procedures

Ethylene/1-hexene copolymerizations were conducted in a 100 ml scale stainless steel autoclave. The typical reaction procedure (run 5, Table 1) is as follows. Toluene (44.5 ml), 1-hexene (10 ml), and MAO solid (122 mg, prepared from ordinary MAO (Tosoh Finechem Co. PMAO-S) by removing toluene and AlMe₃) were added into the autoclave in the drybox. The reaction apparatus was then filled with ethylene (1 atm), and the autoclave was then placed into an oil bath preheated at 40°C. Compound **1** (0.07 mmol) in toluene (0.5 ml) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 5 atm, and the mixture was magnetically stirred for 6 min. After the above procedure, ethylene remained was purged, and the mixture was then poured into EtOH (50 ml) containing HCl (5 ml). The resultant polymer (white precipitate) was collected on a filter paper by filtration, and was adequately washed with EtOH and water, then dried in vacuo for several hours. Typical ¹³C NMR spectra, and the general reproducibility in this polymerization as well as NMR analysis procedure were introduced in the Supporting Information in our preliminary communication [11].

Acknowledgements

The part of this research is supported by Grant-in-Aid for encouragement of young scientists from the Ministry of Education, Science, Sports and Culture of Japan (No. 11750677). K. Nomura would like to express his heartfelt thanks to Tosoh Finechem Co. for donating MAO (PMAO-S).

References

- [1] H.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, *Angew. Chem., Int. Ed. Engl.* 34 (1995) 1143.
- [2] W. Kaminsky, *Macromol. Chem. Phys.* 197 (1996) 3903.
- [3] W. Kaminsky, M. Arndt, *Adv. Polym. Sci.* 127 (1997) 143.
- [4] J. Suhm, J. Heinemann, C. Wörner, P. Müller, F. Stricker, J. Kressler, J. Okuda, R. Mülhaupt, *Macromol. Symp.* 129 (1998) 1.
- [5] A.L. McKnight, R.M. Waymouth, *Chem. Rev.* 98 (1998) 2587.
- [6] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, *Angew. Chem., Int. Ed. Engl.* 38 (1999) 429.
- [7] K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, *Organometallics* 17 (1998) 2152.
- [8] K. Nomura, N. Naga, M. Miki, K. Yanagi, *Macromolecules* 31 (1998) 7588.
- [9] K. Nomura, T. Komatsu, Y. Imanishi, *J. Mol. Catal. A* 152 (2000) 249.
- [10] K. Nomura, T. Komatsu, Y. Imanishi, *J. Mol. Catal. A* 159 (2000) 127.
- [11] K. Nomura, K. Oya, T. Komatsu, Y. Imanishi, *Macromolecules* 33 (2000) 3187.
- [12] K. Nomura, T. Komatsu, Y. Imanishi, *Macromolecules* 33 (2000) 8122.
- [13] A. Antiñolo, F. Carrillo-Hermosilla, A. Corrochano, J. Fernández-Baeza, A. Lara-Sanchez, M.R. Ribeiro, M. Lanfranchi, A. Otero, M.A. Pellinghelli, M.F. Portela, J.V. Santos, Report concerning synthesis and ethylene polymerization with (cyclopentadienyl)-(aryloxy)-zirconium(IV) complexes, *Organometallics* 19 (2000) 2837.
- [14] S.A.A. Shah, H. Dorn, A. Voigt, H.W. Roesky, E. Parisini, H.-G. Schmidt, M. Noltemeyer, *Organometallics* 15 (1996) 3176.
- [15] S. Doherty, R.J. Errington, A.P. Jarvis, S. Collins, W. Clegg, M.R.J. Elsegood, *Organometallics* 17 (1998) 3408.
- [16] D.W. Stephan, J.C. Stewart, F. Guérin, R.E.V.H. Spence, W. Xu, D.G. Harrison, *Organometallics* 18 (1999) 1116.
- [17] D.W. Stephan, F. Guérin, R.E.V.H. Spence, L. Koch, X. Gao, S.J. Brown, J.W. Swabey, Q. Wang, W. Xu, P. Zoricak, D.G. Harrison, *Organometallics* 18 (1999) 2046.
- [18] J. Richter, F.T. Edelman, M. Noltemeyer, H.-G. Schmidt, M. Schmulinson, M.S. Eisen, *J. Mol. Catal. A* 130 (1998) 149.
- [19] R. Vollmerhaus, P. Shao, N.J. Taylor, S. Collins, *Organometallics* 18 (1999) 2731.
- [20] K.C. Jayaratne, L.R. Sita, *J. Am. Chem. Soc.* 122 (2000) 958.
- [21] L.R. Sita, J.R. Babcock, *Organometallics* 17 (1998) 5228.
- [22] J.A.M. Canich, G.G. Hlatky, H.W. Turner, US Patent 542,236 (1990).
- [23] J.A.M. Canich, US Patent 5,026,798 (1991) to Exxon.
- [24] J.A.M. Canich, European Patent Application 420,436 (1991) to Exxon.
- [25] J.C. Stevens, F.J. Timmers, D.R. Wilson, G.F. Schmidt, P.N. Nickias, R.K. Rosen, G.W. Knight, S.-Y. Lai, European Patent Application 416,815 (1991) to Dow.
- [26] J.C. Stevens, D.R. Neithamer, European Patent Application 418,022 (1991) to Dow.
- [27] J. Okuda, F.J. Schattenmann, S. Wocadlo, W. Massa, *Organometallics* 14 (1995) 789.
- [28] D.D. Devore, F.J. Timmers, D.L. Hasha, R.K. Rosen, T.J. Marks, P.A. Deck, C.L. Stern, *Organometallics* 14 (1995) 3132.
- [29] K.L. du Plooy, U. Moll, S. Wocadlo, W. Massa, J. Okuda, *Organometallics* 14 (1995) 3129.
- [30] D.W. Carpenetti, L. Kloppenburg, J.T. Kupec, J.L. Petersen, *Organometallics* 15 (1996) 1572.
- [31] A.L. McKnight, M.A. Masood, R.M. Waymouth, *Organometallics* 16 (1997) 2879.
- [32] J. Suhm, M.J. Schneider, R. Mülhaupt, *R. J. Mol. Catal. A* 128 (1998) 215.
- [33] K. Soga, T. Uozumi, S. Nakamura, T. Toneri, T. Teranishi, T. Sano, T. Arai, *Macromol. Chem. Phys.* 197 (1996) 4237.
- [34] T. Uozumi, K. Miyazawa, T. Sano, K. Soga, Report concerning the synthesis of alternating ethylene/propylene and ethylene/1-octene copolymers by bridged metallocene type catalysts, *Macromol. Rapid. Commun.* 18 (1997) 883.
- [35] J. Jin, T. Uozumi, T. Sano, K. Soga, T. Shiono, Report concerning the synthesis of alternating ethylene/propylene and ethylene/1-octene copolymers by bridged metallocene type catalysts, *Macromol. Rapid. Commun.* 19 (1998) 337.
- [36] M. Arndt, W. Kaminsky, A.M. SchauWienold, U. Weingarten, Report concerning the synthesis of alternating ethylene/propylene and ethylene/1-octene copolymers by bridged metallocene type catalysts, *Macromol. Chem. Phys.* 199 (1998) 1135.
- [37] M.K. Leclerc, R.M. Waymouth, Report concerning the synthesis of alternating ethylene/propylene and ethylene/1-octene copolymers by bridged metallocene type catalysts, *Angew. Chem., Int. Ed. Engl.* 67 (1998) 922.
- [38] B.A. Harrington, D.J. Crowther, Synthesis of stereoregular alternating ethylene/norbornene copolymers by metallocene and linked Cp'-amide type catalysts, *J. Mol. Catal. A* 128 (1998) 79.
- [39] A.L. McKnight, R.M. Waymouth, Report concerning the effect of the cyclopentadienyl fragment on monomer reactivity ratios and copolymer microstructure in ethylene/norbornene copolymerization, *Macromolecules* 32 (1999) 2816.
- [40] J.C. Randall, These calculations were made by the following paper using ¹³C NMR spectra of copolymers, *JMS Rev. Macromol. Chem. Phys.* C29 (2/3) (1989) 201.
- [41] G. Fink, W.J. Richter, in: J. Briandrup, E.H. Immergut, E.A. Grulle (Eds.), *Polymer Handbook*, 4th Edition, Wiley, New York, 1999, p. II/329.
- [42] Y.V. Kissin, *Isospecific Polymerization of Olefin with Heterogeneous Ziegler-Natta Catalysts*, Springer, New York, 1985, p. 3.
- [43] A. Sahgal, H.M. La, W. Hayduk, *Can. J. Chem. Eng.* 56 (1978) 354.
- [44] J.C.W. Chien, P. He, *J. Polym. Sci., Polym. Chem. Ed.* 29 (1991) 1395.
- [45] K. Heiland, W. Kaminsky, *W. Makromol. Chem.* 193 (1992) 601.
- [46] J. Suhm, M.J. Schneider, R. Mülhaupt, *J. Polym. Sci.: A, Polym. Chem.* 35 (1997) 735.