Ligand effect in olefin polymerization catalyzed by (cyclopentadienyl)(aryloxy) titanium(IV) complexes, Cp′TiCl₂(OAr)–MAO system.
Ethylene/1-hexene copolymerization by (1,3-ᵗBu₂C₅H₃)TiCl₂(O-2,6-ⁱPr₂C₆H₃)–MAO catalyst system

Kotohiro Nomura[*], Takashi Komatsu, Yukio Imanishi

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

Abstract

Effect of substituents on cyclopentadienyl group for catalytic activity in 1-hexene and 1-octene polymerization with the series of $Cp′TiCl_2(O-2,6-{}^iPr_2C_6H_3)$ [$Cp′ = Cp$ (**1a**), $^tBuC_5H_4$ (**2a**), $1,3-Me_2C_5H_3$ (**3a**), $1,3-{}^tBu_2C_5H_3$ (**4a**), and C_5Me_5 (**5a**)]–methylaluminoxane (MAO) catalysts have been explored, and the activity increased in the order: **4a** (26 kg polymer/mol Ti · h) < **1a** (63) < **2a** (89) < **3a** (184) < **5a** (728). The catalytic activity in 1-hexene polymerization with the series of $Cp^*TiCl_2(OAr)$ [$OAr = 2,6-{}^iPr_2C_6H_3$ (**5a**), $2,4,6-Me_3C_6H_2$ (**5b**), $2,6-Me_2C_6H_3$ (**5c**), $2-{}^tBu-4,6-Me_2C_6H_2$ (**5d**), $4-MeC_6H_4$ (**5e**)]–MAO catalysts increased in the order: **5a** (728 kg polymer/mol Ti · h) > **5d** (694) > **5c** (76) > **5e** (48) > **5b** (39). These orders are somewhat different from those in ethylene polymerization, and these differences observed here would be due to the steric bulk of monomer used as well as of substituents on both cyclopentadienyl and aryloxy groups. Although $(1,3-{}^tBu_2C_5H_3)TiCl_2(O-2,6-{}^iPr_2C_6H_3)$ (**4a**) showed the lowest catalytic activity for polymerization of both 1-hexene and 1-octene, **4a** exhibited the significant activity for copolymerization of ethylene with 1-hexene, resulting in obtaining copolymer with relatively high 1-hexene contents (20.2–36.5 mol%) with relatively narrow molecular weight distributions. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: Olefin polymerization; Titanium; Ligand effect

1. Introduction

Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the field of both organometallic chemistry and catalysis [1–4].[1] There are thus a lot of reports concerning this subject to find the efficient catalyst precursor, however, only a few

---

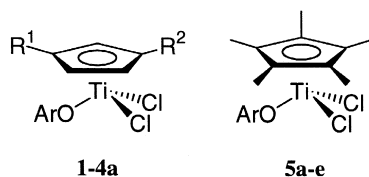[*] Corresponding author. Tel.: +81-743-72-6041; fax: +81-743-72-6049.

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

[1] For examples concerning olefin polymerization with metallocene catalysts, see Ref. [1]. For examples concerning olefin polymerization with hybrid half-metallocene type catalysts, review Ref. [2]. For a review concerning the so-called non-metallocene type olefin polymerization catalyst, see Ref. [3]. Our recent report concerning olefin polymerization with bis(amide)–titanium(IV) catalyst is seen in Ref. [4].

reports have been known concerning olefin polymerization with non-bridged half-metallocene type group 4B transition metal complex catalysts [5–8].

We have recently reported that $Cp^*TiCl_2(O-2,6-{}^iPr_2C_6H_3)$ (**5a**) showed an exceptionally higher catalytic activity than those previously reported for ethylene polymerization in the presence of methylaluminoxane (MAO) or $Al^iBu_3/Ph_3CB(C_6F_5)_4$ [9]. We assumed that the reason for high activity would be due to a unique bond angle (173°) of Ti−O−C (phenyl group) in **5a** that was determined by X-ray crystallography. We also reported that **5a** was an efficient catalyst precursor for ethylene/1-butene copolymerization, and that the $r_E r_B$ values for the resultant poly(ethylene-*co*-1-butene)s were very small ($r_E r_B = 0.25$–0.27: r_E and r_B are monomer reactive ratios of ethylene and 1-butene, respectively), indicating that the copolymerization did not proceed in a random manner [10].

In this paper, we wish to summarize the effect of ligands in 1-hexene and 1-octene polymerization with various (cyclopentadienyl)(aryloxy) titanium(IV) complex, $Cp'TiCl_2(OAr)$ [$Cp' = Cp$ (**1a**), ${}^tBuC_5H_4$ (**2a**), $1,3-Me_2C_5H_3$ (**3a**), $1,3-{}^tBu_2C_5H_3$ (**4a**), and C_5Me_5 (**5a**), OAr $= O-2,6-{}^iPr_2C_6H_3$; $Cp' = C_5Me_5$, and OAr $= O-2,6-{}^iPr_2C_6H_3$ (**5a**), $2,4,6-Me_3C_6H_2$ (**5b**), $2,6-Me_2C_6H_3$ (**5c**), $2-{}^tBu-4,6-Me_2C_6H_2$ (**5d**), $4-MeC_6H_4$ (**5e**) (Chart 1)],– MAO catalyst systems. We also wish to report our explored results for copolymerization of ethylene with 1-hexene by **4a**–MAO catalyst [11].

2. Experimental section

2.1. General procedure

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox or using standard Schlenk techniques unless otherwise specified. All chemicals used were reagent grade and were purified by the standard purification procedures. Toluene for the polymerization was distilled over sodium and benzophenone under nitrogen atmosphere, and was stored in a Schlenk tube in the drybox in the presence of molecular sieves (mixture of 3A and 4A 1/16, and 13X). Reagent grade of 1-hexene, 1-octene, and 1-decene were also stored in the drybox in the presence of molecular sieves. Ethylene for polymerization was of polymerization grade (purity > 99.9%, Sumitomo Seika) and was used as received. Syntheses of various (cyclopentadienyl)(aryloxy)–titanium(IV) complexes, $Cp'TiCl_2(OAr)$ were according to our previous report [10]. Toluene and $AlMe_3$ in the commercially available methylaluminoxane (PMAO-S, 9.5 wt.% (Al) toluene solution, Tosoh Akzo) were removed and dried in vacuo in the drybox, and used as a white solid [12–14].[2]

All ^{1}H NMR and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H; 100.40 MHz, ^{13}C). All chemical shifts are given in ppm and are referenced to tetramethylsilane. Obvious multiplicities and routine coupling constants are usually not listed, and all spectra were obtained in the solvent indicated at 25°C unless otherwise noted. All deuterated NMR solvents were stored over molecular sieves. ^{13}C NMR spectra for the poly(ethylene-*co*-1-hexene)s were performed by using JEOL LA400 spectrometer (*o*-dichlorobe-

1-4a   **5a-e**

R^1, $R^2 = H, H$ (**1**); ${}^tBu, H$ (**2**); Me, Me (**3**); ${}^tBu, {}^tBu$ (**4**)
Ar = $2,6-{}^iPr_2C_6H_3$ (**a**); $2,4,6-Me_3C_6H_2$ (**b**); $2,6-Me_2C_6H_3$ (**c**); $2-{}^tBu-4,6-Me_2C_6H_2$ (**d**); $4-MeC_6H_4$ (**e**)

nzene-d_4) with proton decoupling at 50°C or 120°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. 8000. The polymer solutions were prepared by dissolving polymers in o-dichlorobenzene-d_4 up to 10% by weight. ^{13}C NMR spectra of poly(1-hexene) were also measured in the same manner (solvent $CDCl_3$) at room temperature.

2.2. Typical procedure for polymerization of 1-hexene.

1-Hexene (5 ml) and prescribed amount of MAO were added to a round bottom flask (25 ml) connected to three-way valves under N_2, and the polymerization was started by the addition of a toluene solution (2.5 ml) containing the catalyst (5.0 μmol). The reaction mixture was stirred for 30 min at room temperature, and the polymerization was terminated with the addition of EtOH. The reaction product was extracted with $CHCl_3$ which was washed with HCl aqueous solution and then rinsed with water. The chloroform extract was dried over Na_2SO_4, and chloroform and 1-hexene remained was then removed in vacuo.

Molecular weights and the molecular weight distributions of poly(1-hexene) and poly(1-octene), and poly(1-decene) were measured by means of gel-permeation chromatography (GPC). HPLC grade THF was used for GPC and were degassed prior to use. GPC were performed at 40°C on a Shimazu SCL-10A using a RID-10A detector (Shimazu) in THF (containing 0.03 wt.% 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 ml/min). GPC columns (Shim-PAC GPC-806, 804 and 802, 30 cm × 8.0 mmφ) were calibrated vs. polystyrene standard samples.

2.3. Typical reaction procedure for copolymerization of ethylene with 1-hexene by (1,3-$^tBu_2C_5H_3$)TiCl_2(O-2,6-$^iPr_2C_6H_3$) (4a)–MAO catalyst

Toluene (30 ml), 1-hexene (3, 5, or 10 ml) and MAO were added into the autoclave (100 ml, stainless steel) in the drybox, and the reaction apparatus was then replaced with ethylene. The reaction mixture was then pressurized to the prescribed ethylene pressure soon after the addition of a toluene solution containing **4a**. The mixture was stirred for 10 min, and the

Table 1
Polymerization of 1-hexene by Cp[*]TiCl_2(O-2,6-$^iPr_2C_6H_3$) **(5a)**–MAO catalyst[a]

Run no.	**5a** (μmol)	Al/Ti[b]	Temperature (°C)	Time (min)	Polymer yield (mg)	Activity[c]	TON[d]	M_w[e]	M_w/M_n[e]
1	2.0	500	25	10	100	300	594	17.4	1.74
2	2.0	500	25	30	219	219	1300	41.0	1.71
3	2.0	1000	25	10	336	1010	2000	45.5	1.71
4	2.0	1000	25	30	625	625	3710	48.9	1.85
5	1.0	500	25	30	157	314	1870	48.3	1.76
6	1.0	1000	25	30	268	536	3180	66.5	1.81
7	1.0	2000	25	10	243	1460	2890	45.1	1.81
8	1.0	2000	25	30	364	728	4330	69.4	1.62
9	1.0	2000	25	60	410	410	4870	74.2	1.79
10	1.0	2000	0	30	46	92	547	57.6	1.51
8	1.0	2000	25	30	364	728	4330	69.4	1.62
11	1.0	2000	40	30	410	820	4870	86.8	2.12

[a] Reaction conditions: 1-hexene 5 ml, catalyst 2 μmol/ml toluene, MAO white solid, 25°C.

[b] Molar ratio of Al/Ti.

[c] Polymerization activity (kg polymer/mol Ti · h).

[d] TON (turnover number = molar amount of 1-hexene reacted/ mol Ti).

[e] GPC data in THF vs. polystyrene standard.

polymerization was terminated with the addition of EtOH (15 ml). The solution was then poured into EtOH (50 ml), and the resultant polymer was adequately washed with EtOH and then dried in vacuo for several hours.

Molecular weights and the molecular weight distributions of the resultant polymers were measured at 145°C by means of GPC [Tosoh 8121GPC/HT (with polystyrene gel column, TSK gel GMHHR-H(20)HT × 3)] using *o*-dichlorobenzene containing 0.05 w/v% 2,6-di-*tert*-butyl-*p*-cresol as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

3. Results and discussion

3.1. Polymerization of 1-hexene, 1-octene, and 1-decene by $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$–MAO catalyst

1-Hexene polymerization proceeded at significant rate in the presence of **5a**–MAO catalyst even at room temperature. The use of MAO white solid plays an essential role for this catalysis not only to proceed at remarkable rate, but also to obtain high molecular weight polymers with relatively narrow molecular weight distributions (ex. $M_w = 69.4 \times 10^4$, $M_w/M_n = 1.62$, run 8) [10]. These are probably due to the fact
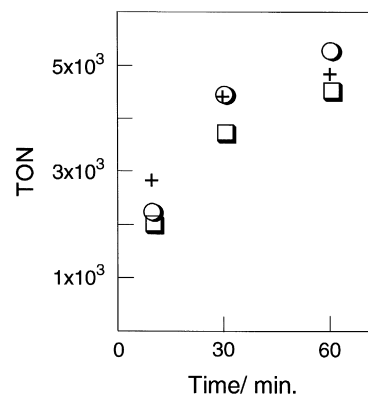

Fig. 1. Time course for polymerization of 1-hexene (○), 1-octene (+), and 1-decene (□) catalyzed by the **5a**–MAO system (1-hexene 5 ml, **5a** 1.0 μmol, 25°C, Al/Ti = 2000 (molar ratio), Tables 1 and 2).

that the deactivation by AlMe₃, which contains in the MAO toluene solution, and which would attack the aryloxy group to give another low-active species, can be inhibited, and is also due to the fact that the degree of chain-transfer reaction can be decreased by removing AlMe₃ from the ordinary MAO solution (ex. 9.5 wt.% (Al) toluene solution).

As shown in Table 1, the observed catalytic activity increased upon the addition of MAO [activity: 314 kg polymer/mol Ti · h (run 5, Al/Ti = 500) < 536 (run 6, Al/Ti = 1000) < 728 (run 8, Al/Ti = 2000)], and the Al/Ti molar ratio of 2000 seemed to be more suited in this catalysis. The polymer yields increased for

Table 2
Polymerization of 1-octene, 1-decene by $Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**5a**)–MAO catalyst[a]

Run no.	Olefin	**5a** (μmol)	Al/Ti[b]	Time (min)	Polymer yield (mg)	Activity[c]	TON[d]
12	1-octene	2.0	500	30	323	323	1440
13	1-octene	2.0	1000	60	636	318	2830
14	1-octene	1.0	2000	10	243	1460	2170
15	1-octene	1.0	2000	30	485	970	4320
16	1-octene	1.0	2000	60	590	590	5260
17	1-decene	2.0	1000	30	797	797	2840
18	1-decene	1.0	2000	10	270	1620	1930
19	1-decene	1.0	2000	30	518	1040	3690
20	1-decene	1.0	2000	60	620	620	4420

[a]Reaction conditions: 1-octene or 1-decene 5 ml, catalyst 2 μmol/ml toluene, MAO white solid, 25°C.
[b]Molar ratio of Al/Ti.
[c]Polymerization activity (kg polymer/mol Ti · h).
[d]TON (turnover number = molar amount of α-olefin reacted/mol Ti).

longer reaction hours, but the rate gradually decreased (Fig. 1) probably due to the deactivation of the catalytically active species or to the increased viscosity in the reaction mixture. On the other hand, the molecular weight for the resultant poly(1-hexene) was low if the reaction was terminated only at 10 min. The catalytic activity increased at higher reaction temperature (92 kg polymer/mol Ti · h, 0°C < 728, 25°C < 982, 40°C) with the increase of the molecular weight for the resultant polymer (57.6×10^4, 0°C < 69.4×10^4, 25°C < 86.8×10^4, 40°C). This might be explained by an assumption that the propagation rate increased at higher reaction temperature whereas the chain-transfer rate was not so enhanced due to the use of MAO solid removed $AlMe_3$ in advance.

Results for polymerization of 1-octene and 1-decene by the same catalyst under the well-performed reaction conditions (Al/Ti = 2000) are summarized in Table 2. The similar facts were also observed in polymerization of both 1-octene and 1-decene (Fig. 1). Note that the observed turnover numbers in both 1-hexene and 1-octene polymerizations were very similar under the same conditions [ex. TON 4330 (1-hexene, run 8) vs. 4320 (1-octene, run 15); 1300 (1-hexene, run 2) vs. 1440 (1-octene, run 12)]. But the observed turnover numbers in 1-decene polymerization were lower than those for 1-hexene and 1-octene under the same conditions. We assume that this would be probably be due to the fact that a rather bulky 1-decene (*n*-octyl group as the side chain) than 1-hexene (*n*-butyl group as the side chain) disturbs the olefin coordination or insertion.

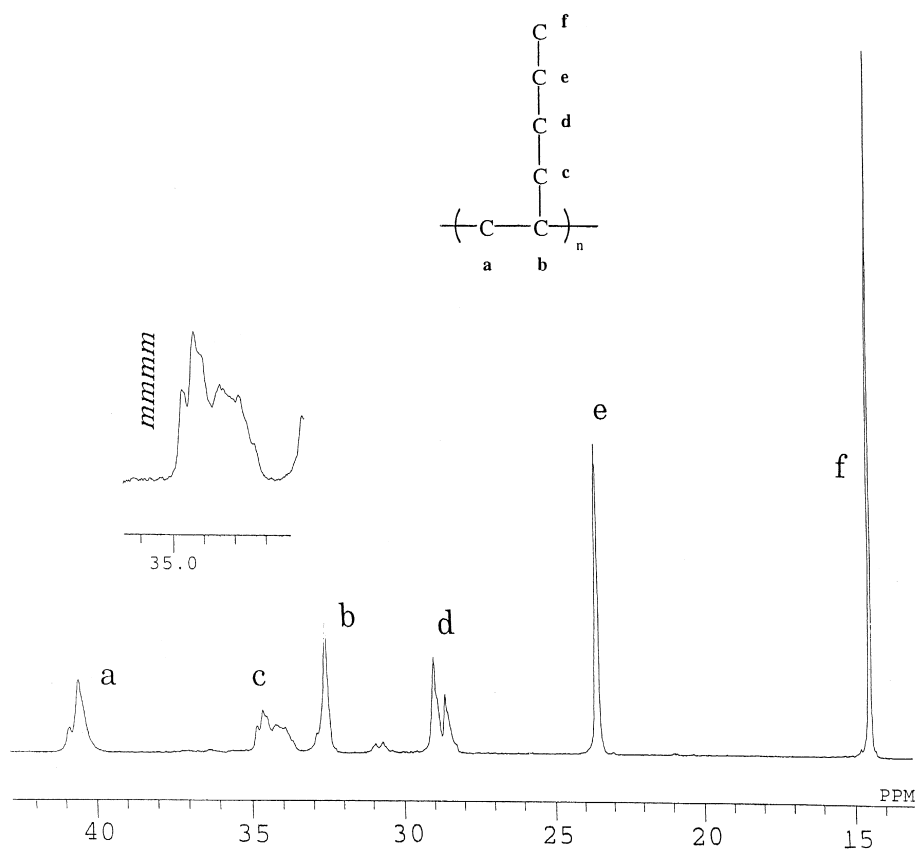Fig. 2 shows the typical ^{13}C NMR spectrum for poly(1-hexene) prepared by **5a**–MAO cata-

Fig. 2. Typical ^{13}C NMR spectrum for poly(1-hexene) prepared by **5a**–MAO catalyst system.

Table 3
Effect of substituents on cyclopentadienyl group. Polymerization of 1-hexene, 1-octene, and 1-decene by $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$–MAO catalyst[a]

Run no.	Catalysis (μmol)	α-Olefin	Al/Ti[b]	Polymer yield (mg)	Activity[c]	TON[d]	$M_w^e \times 10^{-4}$	M_w^e/M_n^e
21	**1a** (5.0)	1-hexene	1000	156	62	370	0.68	
22	**1a** (5.0)	1-octene	1000	200	80	356	0.63	
23	**2a** (5.0)	1-hexene	1000	224	90	532	8.04	1.64
24	**2a** (5.0)	1-octene	1000	313	125	558	8.25	1.85
25	**3a** (5.0)	1-hexene	1000	460	184	1090	8.73	1.85
26	**3a** (5.0)	1-octene	1000	550	220	980	6.73	1.84
27	**4a** (5.0)	1-hexene	1000	64	26	152	2.16	1.62
28	**4a** (5.0)	1-octene	1000	94	38	168	1.75	1.49
8	**5a** (1.0)	1-hexene	2000	364	728	4330	69.4	1.62
15	**5a** (1.0)	1-octene	2000	485	970	4320	49.5	1.84
19	**5a** (1.0)	1-decene	2000	518	1036	3690	41.7	1.65

[a] Reaction conditions: α-olefin 5 ml, catalyst 2 μmol/ml toluene, MAO white solid, 25°C, 30 min.

[b] Molar ratio of Al/Ti.

[c] Polymerization activity (kg polymer/mol Ti · h).

[d] TON (turnover number = molar amount of α-olefin reacted/mol Ti).

[e] GPC data in THF vs. polystyrene standard.

lyst. The resultant polymer does not have stereoregularity [15], even though the reaction was performed at 0°C. These calculations were made on the basis of the following paper using ^{13}C NMR spectra [15].[3] This would be due to the basic structure of **5a**, and suggests that **5a** would not be suited for stereospecific polymerization of α-olefin.

3.2. Effect of substituents on cyclopentadienyl group for polymerization of 1-hexene, 1-octene and 1-decene with the series of $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$– MAO catalyst

The results for 1-hexene and 1-octene polymerizations with a series of $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$–MAO catalysts are summarized in Table 3. It was revealed that the catalytic activity for the 1-hexene polymerization increased in the order: **4a** (26 kg polymer/mol Ti · h) < **1a** (63) < **2a** (89) < **3a** (184) ≪ **5a** (728). **5a** was found to exhibit the highest catalytic activity among these complexes, which was the same as that for ethylene polymerization. On the other hand, the order by **4a** was quite different from that observed on ethylene polymerization [**5a** (2220 kg PE/mol Ti · h) > **4a** (653) > **3a** (215), **2a** (258) ≫ **1a** (77); $Al^iBu_3/Ph_3CB(C_6F_5)_4$ cocatalyst] [10]. We assume that this is due to the steric hindrance of bulky two *tert*-butyl groups on cyclopentadienyl ring, and is also due to a rather bulky monomer of 1-hexene (1-octene) than ethylene. Both electronic and steric factors of substituents on cyclopentadienyl group thus play an essential role for the catalytic activity [16–20].[4]

It is also important to note that the same turnover numbers could be obtained in both 1-hexene and 1-octene polymerizations by these catalysts. This result suggests that effect of monomer bulkiness is negligible for the activity in between 1-hexene and 1-octene polymerization. This result also thus suggests that monomer insertion or coordination is not rate-determining in these catalytic reactions.

---

[3] In addition, the spectrum shown here [15] is almost the same which we showed in the supporting information [10] previously, except that the pattern of carbon region was somewhat different. The both spectra certainly indicate that the resultant poly(1-hexene) does not have stereoregularity

---

[4] The similar ligand effect was reported for styrene polymerization with a series of $Cp'Ti(OMe)_3$ complexes–MAO system [16]

Table 4
Effect of substituents on cyclopentadienyl group for olefin polymerization by Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)-cocatalyst[a]

Run no.	Catalyst	Olefin	Activity[b]	TON[c]
	CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1a**)	ethylene[d]	77	2750
21	CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1a**)	1-hexene	62	370
22	CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1a**)	1-octene	80	356
	(^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2a**)	ethylene[d]	258	9200
23	(^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2a**)	1-hexene	90	532
24	(^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2a**)	1-octene	125	558
	(1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3a**)	ethylene[d]	215	7660
25	(1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3a**)	1-hexene	184	1090
26	(1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3a**)	1-octene	220	980
	(1,3-^{t}Bu$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**4a**)	ethylene[d]	653	23,300
27	(1,3-^{t}Bu$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**4a**)	1-hexene	26	152
28	(1,3-^{t}Bu$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**4a**)	1-octene	38	168
	Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5a**)	ethylene[d]	2220	79,100
8	Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5a**)	1-hexene	728	4330
15	Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5a**)	1-octene	970	4320
19	Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5a**)	1-decene	1036	3690

[a]Reaction conditions: See Table 3 (1-hexene, 1-octene, and 1-decene).
[b]Polymerization activity (kg polymer/mol Ti · h).
[c]TON (turnover number) = (molar amount of olefin reacted)/mol Ti.
[d]Conditions, see Ref. [10] (A^{i}Bu$_3$–Ph$_3$CB(C$_6$F$_5$)$_4$ cocatalyst).

The M_w value for the resultant poly(1-hexene) increased in the order: **5a** (69.4×10^4) > **3a** (8.73×10^4), **2a** (8.04×10^4) > **4a** (2.16×10^4) > **1a** (0.68×10^4). This is probably due to that the introduction of an electron donating group into the cyclopentadienyl ring stabilizes the catalytically active species [16–20][4] and the propagation rate in this catalysis can be thus increased, although the lower Mw value by **4a** would be due to the extremely low catalytic activity. In addition, molecular weight for the resultant polymers by **5a** decreased in the order: poly(1-hexene), 69.4×10^4 > poly(1-octene), 49.5×10^4 > poly(1-decene), 41.7×10^4. The

Table 5
Effect of aryloxy group. Polymerization of 1-hexene and 1-octene by Cp*TiCl$_2$(OAr)–MAO catalyst[a]

Run no.	Catalysis (μmol)	α-Olefin	Al/Ti[b]	Polymer yield (mg)	Activity[c]	TON[d]	$M_w^e(\times 10^{-4})$	M_w/M_n^e
8	**5a** (1.0)	1-hexene	2000	364	728	4330	69.4	1.62
15	**5a** (1.0)	1-octene	2000	485	970	4320	49.5	1.84
29	**5b** (5.0)	1-hexene	1000	90	39	202	1.73	3.05
30	**5b** (5.0)	1-octene	1000	91	39	156	2.05	2.84
31	**5c** (5.0)	1-hexene	1000	191	76	438	13.0	1.80
32	**5c** (5.0)	1-octene	1000	194	78	346	9.50	1.75
33	**5d** (1.0)	1-hexene	1000	347	694	3980	36.6	1.84
34	**5d** (1.0)	1-octene	1000	340	680	3030	34.8	2.44
35	**5e** (5.0)	1-hexene	1000	117	48	269	0.10	
36	**5e** (5.0)	1-octene	1000	138	55	246	0.13	

[a]Reaction conditions: α-olefin 5 ml, catalyst 2 μmol/ml toluene, MAO white solid, 25°C, 30 min.
[b]Molar ratio of Al/Ti.
[c]Polymerization activity (kg polymer/mol Ti · h).
[d]TON (turnover number) = (molar amount of olefin reacted)/mol Ti.
[e]GPC data in THF vs. polystyrene standard.

Table 6
Effect of substituents on aryloxy group for olefin polymerization by $Cp^*TiCl_2(OAr)$–MAO catalyst[a]

Run no.	Catalyst	Olefin	Activity[b]	TON[c]
	$Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**5a**)	ethylene[d]	1240	44,200
8	$Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**5a**)	1-hexene	728	4330
15	$Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**5a**)	1-octene	970	4320
16	$Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**5a**)	1-decene	1036	3690
	$Cp^*TiCl_2(O\text{-}2,4,6\text{-}Me_3C_6H_2)$ (**5b**)	ethylene[d]	369	13,200
29	$Cp^*TiCl_2(O\text{-}2,4,6\text{-}Me_3C_6H_2)$ (**5b**)	1-hexene	39	202
30	$Cp^*TiCl_2(O\text{-}2,4,6\text{-}Me_3C_6H_2)$ (**5b**)	1-octene	39	156
	$Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**5c**)	ethylene[d]	1000	35,700
31	$Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**5c**)	1-hexene	76	438
32	$Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**5c**)	1-octene	78	346
	$Cp^*TiCl_2(O\text{-}2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2)$ (**5d**)	ethylene[d]	446	15,900
33	$Cp^*TiCl_2(O\text{-}2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2)$ (**5d**)	1-hexene	694	3980
34	$Cp^*TiCl_2(O\text{-}2\text{-}^tBu\text{-}4,6\text{-}Me_2C_6H_2)$ (**5d**)	1-octene	680	3030
	$Cp^*TiCl_2(O\text{-}4\text{-}MeC_6H_4)$ (**5e**)	ethylene[d]	25	890
35	$Cp^*TiCl_2(O\text{-}4\text{-}MeC_6H_4)$ (**5e**)	1-hexene	48	269
36	$Cp^*TiCl_2(O\text{-}4\text{-}MeC_6H_4)$ (**5e**)	1-octene	55	246

[a] Reaction conditions: See Table 5 (1-hexene, and 1-octene).
[b] Polymerization activity (kg polymer/mol Ti · h).
[c] TON (turnover number) = (molar amount of olefin reacted)/mol Ti.
[d] Conditions, see Ref. [10].

same tendency could also be observed for the polymers prepared by both **4a** and **3a**. These might be due to that the steric bulk of side chain group (n-butyl, n-hexyl, and n-octyl, respectively) would disturb the coordination or insertion, or would enhance the degree of chain-transfer reaction.

Table 4 summarizes the catalytic activities and turnover numbers for olefin polymerization with the series of $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ catalysts. The activities for the ethylene polymerization were higher than those for 1-hexene and 1-octene, and this might be due to a steric factor of monomer used. The difference of TONs between ethylene and 1-hexene polymerization by **4a** seemed notable (turnover numbers: 23,300 for ethylene, and 152 for 1-hexene). We thus expected that synthesis of ethylene/1-hexene copolymer with precise monomer sequence might be able to be attained by utilizing this difference, if the monomer sequence would be only influenced by their homopolymerization activity.

3.3. Effect of substituents on aryloxy group for polymerization of 1-hexene, and 1-octene with the series of $Cp^*TiCl_2(OAr)$–MAO catalyst

The results for 1-hexene and 1-octene polymerization with a series of $Cp^*TiCl_2(OAr)$ (**5a–e**)–MAO catalysts are summarized in Table 5. The catalytic activity for 1-hexene polymerization increased in the order: **5a** (728 kg polymer/mol Ti · h) > **5d** (694) > **5c** (76) > **5e** (48) > **5b** (39). It is clear that substituents in 2,6-position should be necessary for the high catalytic activity [21].[5] The order observed here is somewhat different from that observed for ethylene polymerization (especially **5d**, Table 6). On the other hand, the M_w value for poly(1-hexene) increased in the order: **5a** (69.4

---

[5] It was reported by J.A.M. Canich that $(2,6\text{-}^tBu_2C_6H_3O)_3ZrCl$ was an efficient catalyst precursor for ethylene polymerization in the presence of MAO. It was suggested that the high activity by this complex was due to the effect of the steric bulk of aryloxy group especially having substituents in the 2,6-position.

$\times 10^4) >$ **5d** $(36.6 \times 10^4) >$ **5c** $(13.0 \times 10^4) >$ **5b** $(1.73 \times 10^4) >$ **5e** (0.10×10^4). These results clearly indicate that substituents in the *ortho* position inhibit the chain-transfer reaction by Al species which would lead to afford the the resultant polymers with higher molecular weight. The steric bulk of *ortho* substituents on aryloxy group would be thus an important factor for controlling the molecular weight in this type of catalyst.

Note that the turnover numbers calculated by **5b**, **5c**, **5d** were not the same between 1-hexene and 1-octene polymerizations. This was an interesting contrast with those shown in Table 3 with the series of Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)–MAO catalyst. The reason for high activity of **5d** on 1-hexene polymerization is thus probably due to the promotion of the chain-transfer reaction, because **5d** has both a rather smaller methyl group than isopropyl group which would facilitate the chain-transfer reaction, and a rather bulky *tert*-butyl group than isopropyl group which would facilitate elimination to afford poly(1-hexene) efficiently.

Table 6 also summarizes the effect of aryloxy group for observed catalytic activities in both ethylene and 1-hexene polymerizations. It is clear that the steric factor in 2,6-position is very important for the high activity, and the activity

with a catalyst without any substituents in 2,6-positions gave lower catalytic activity. In addition, the electronic factor of the *para*-position also seems important for the activity (**5b** and **5c**), and this might be due to an electronic factor of Ti−O−C (phenyl) bond. The *para*-substituents with electron-withdrawing group might improve the activity.

3.4. Copolymerization of ethylene with 1-hexene, 1-octene catalyzed by (1,3-^{t}Bu$_2$C$_5$H$_3$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)–MAO system

Particular attention should be paid regarding the remarkable catalytic activity for copolymerization of ethylene with 1-hexene by **4a**–MAO catalyst system [ex. 26 kg polymer/mol Ti · h (run 27) < 9900 (run 39), Table 7]. The observed polymerization activities were higher than that for homopolymerization of ethylene in most case (ex. runs 38–40), and the polymer yields increased at higher ethylene pressures. The low catalytic activities were observed if the reactions were emplyed at low temperature (0°C and 25°C, runs 42–46), and the low activity was also observed if a large amount of 1-hexene was charged into the reaction mixture (run 41).

The resultant poly(ethylene-*co*-1-hexene)s were high 1-hexene contents (20.2–36.5 mol%,

Table 7
Copolymerization of ethylene with 1-hexene by **4a**–MAO catalyst[a]

Run no.	**4a** (μmol)	Ethylene (atm)	1-Hexene (ml)	Al/Ti[b]	Temperature (°C)	Polymer yield (mg)	Activity[c]	$M_w^d (\times 10^{-4})$	M_w/M_n^d
27	5.0	none	5	1000	25	64	26	2.16	1.62
37	0.5	5	none	4000	40	653	7840	99.7	2.97
38	0.5	7	3	4000	40	1231	14,770	20.5	1.97
39	0.5	5	5	4000	40	825	9900	11.1	1.95
40	0.5	7	5	4000	40	1023	12,280	15.4	1.86
41	0.5	7	10	4000	40	554	6650	10.0	1.93
42	0.5	5	5	4000	0	129	1550	21.3	1.59
43	0.5	7	5	4000	0	221	2650	34.1	1.68
44	0.5	5	5	4000	25	587	7040	15.7	1.61
45	0.5	5	10	4000	0	151	1812	10.6	1.69
46	0.5	7	10	4000	0	227	2724	22.7	1.72

[a] Reaction conditions (runs 37–46): catalyst 2 μmol/ml toluene, toluene 30 ml, MAO white solid, 10 min, 100 ml autoclave.
[b] Molar ratio of Al/Ti.
[c] Polymerization activity (kg polymer/mol Ti · h).
[d] GPC data in *o*-dichlorobenzene vs. polystyrene standard (runs 37–46).

Table 8
Monomer sequence distribution of poly(ethylene-co-1-hexene) prepared by **4a**–MAO catalyst[a]

Run no.	[1-Hexene][b] (mol%)	Triad sequence distribution[c] (%)						$r_E r_H^d$
		EEE	HEE + EEH	HEH	EHE	EHH + HHE	HHH	
38	20.2	48.6	27.8	3.4	16.0	4.2	–	0.42
39	36.5	25.7	31.9	5.9	21.2	15.0	0.3	0.51
40	33.5	31.4	27.7	7.4	20.7	12.5	0.3	0.51

[a] Polymerization conditions, see Table 7.

[b] Molar amount of 1-hexene in copolymer determined by ^{13}C NMR spectra.

[c] Determined by ^{13}C NMR spectra.

[d] $r_E r_H = 4[EE][HH]/[EH]^2$, $[EE] = [EEE] + [HEE + EEH]/2$, $[EH] = [HEE + EEH]/2 + [HEH] + [EHE] + [EHH + HHE]/2$, $[HH] = [HHH] + [EHH + HHE]/2$.

Table 8) with narrow M_w/M_n values (1.59–1.97). One possible explanation for the high activity is due to the fact that a steric hindrance affected by the repeated coordination or insertion of 1-hexene can be reduced by incorporating ethylene, which would lead the high activity. These results are, we believe, very interesting, because the significant increase in the catalytic activity cannot be expected only from the 1-hexene homopolymerization result.

The monomer sequence distributions of poly(ethylene-co-1-hexene)s prepared by **4a** were studied by ^{13}C NMR, and the results are listed in Table 8. Note that the amount of observed HHH sequence was very small, and that the resultant $r_E r_H$ values (r_E and r_H are monomer reactive ratios of ethylene and 1-hexene) for the copolymers were low (0.42–0.51) [22]. These values were relatively similar to those observed for poly(ethylene-co-1-butene)s by the **5a**–MAO system, and this is an interesting contrast with copolymers prepared by $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**6**), in which the copolymerization proceeds in a random manner ($r_E r_B = $ ca. 1.0) [3].

The low $r_E r_H$ value by **4a** would also support our previous assumption [10] that a rather flexible structure of **4a** than **6** would give low $r_E r_H$. We also assume that the differnce of $r_E r_H$ value by these catalysts would also be due to the rather wide bond angle of Cp–Ti–O (**5a**: 120.5°; **4a**: 119.3°) than **6** (107.6°), which would

be able to control the monomer coordination with bulky substituents in both cyclopentadienyl and aryloxy groups (Chart 2) [23]. This information is, we believe, potentially important for the design of a suitable olefin polymerization catalyst. We are currently exploring more details concerning a relationship between the basic catalyst structure and their monomer sequence. These results will be introduced in the future.
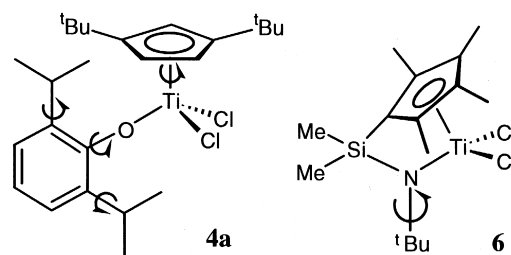
Acknowledgements

References

[1] K.H. Brintzinger, D. Fischer, R. Mülhaupt, B. Rieger, R.M. Waymouth, Angew. Chem., Int. Ed. Engl. 34 (1995) 1143.

[2] A.L. McKnight, R.M. Waymouth, Chem. Rev. 98 (1998) 2587.

[3] G.J.P. Britovsek, V.C. Gibson, D.F. Wass, Angew. Chem., Int. Ed. Engl. 38 (1999) 429.

[4] K. Nomura, N. Naga, K. Takaoki, Macromolecules 31 (1998) 8009, References concerning this topic are also cited therein.

[5] J.C. Stevens, D.R. Neithamer, UP Patent 5,064,-802, 1991.

[6] Q. Wang, R. Quyoum, D.J. Gills, M.-J. Tudoret, D. Jeremic, B.K. Hunter, M.C. Baird, Organometallics 15 (1996) 693.

[7] S.A.A. Shah, H. Dorn, A. Voigt, H.W. Roesky, E. Parisini, H.-G. Schmidt, M. Noltemeyer, Organometallics 15 (1996) 3176.

[8] D.W. Stephan, J.C. Stewart, F. Guérin, R.E.v.H. Spence, W. Xu, D.G. Harrison, Organometallics 18 (1999) 1116.

[9] K. Nomura, N. Naga, M. Miki, K. Yanagi, A. Imai, Organometallics 17 (1998) 2152.

[10] K. Nomura, N. Naga, M. Miki, K. Yanagi, Macromolecules 31 (1998) 7588.

[11] Our preceeding letter concerning effect of substituent on cyclopentadienyl group, and copolymerization of ethylene with 1-hexene by $(1,3\text{-}^tBu_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$– MAO catalyst, K. Nomura et al. J. Mol. Catal. A. 152 (2000) 249.

[12] N. Ishihara, Y. Takakura, T. Miura, JP Kokai, H6-329714, 1994, examples for the preparation of MAO solid.

[13] C. Sishta, R. Hathorn, T.J. Marks, J. Am. Chem. Soc. 114 (1992) 1112, examples for the preparation of MAO solid.

[14] L. Resconi, S. Bossi, L. Abis, Macromolocules 23 (1990) 4489, examples for the preparation of MAO solid.

[15] T. Asakura, M. Demura, Y. Nishiyama, Macromolecules 24 (1991) 2334.

[16] T.H. Newman, R.E. Campbell, M.T. Malanga, Metcon '93 (1993) 315.

[17] N. Tomotsu, H. Shouzaki, M. Takeuchi, Polymer Preprints, Japan, 47 (1998) 1597.

[18] N. Tomotsu, N. Ishihara, Catal. Surv. Jpn 1 (1997) 97.

[19] N. Tomotsu, N. Ishihara, T.H. Newman, M.T. Malanga, J. Mol. Catal. A. 128 (1998) 167.

[20] For review concerning the influence of cyclopentadienyl-ring substituents, P.C. Möhring, and N.J. Coville, J. Organomet. Chem., 479 (1994) 1.

[21] J.A.M. Canich, US Patent 5,079,205 (1992).

[22] J.C. Randall, JMS Rev. Macromol. Chem. Phys. C29 (2–3) (1989) 201.

[23] B. Tsuie, D.C. Swenson, R.F. Jordan, Organometallics 16 (1997) 1392, Example for a comparison of key structual data for L_2TiX_2 type complexes.