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Effect of the Cyclopentadienyl Fragment on Monomer Reactivities and Monomer Sequence Distributions in Ethylene/α-Olefin Copolymerization by a Nonbridged (Cyclopentadienyl)(aryloxy)titanium(IV) Complex−MAO Catalyst System

Kotohiro Nomura,* Keima Oya, Takashi Komatsu, and Yukio Imanishi

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

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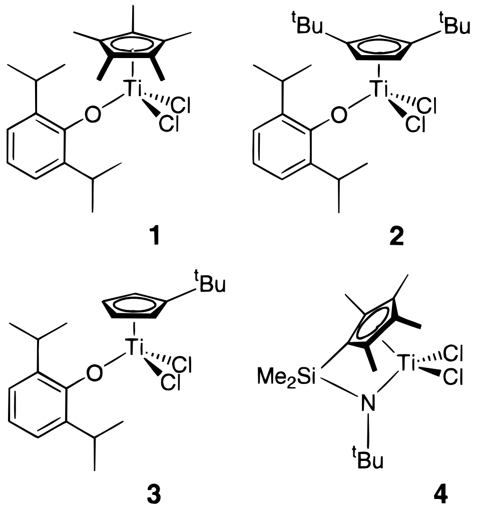
Introduction. Olefin polymerization by homogeneous transition metal catalysis has been one of the most attractive subjects in the fields of both organometallic chemistry and polymer chemistry. There have thus been many reports concerning this topic especially using group 4B transition metal complexes.[1] We have recently reported that $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ ($Cp^* = C_5Me_5$ **1**) exhibited remarkable catalytic activity for ethylene homopolymerization as well as for ethylene/1-butene copolymerization in the presence of MAO (methylaluminoxane)[2] and that the copolymerization did not proceed in a random manner. The latter feature is completely different from that observed by hybrid "half-metallocene" type $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**) as well as by an ordinary metallocene-type catalyst.[1a−f,3] Since the control of the monomer sequence in ethylene/α-olefin copolymers, which are widely used commercially, has been an unsolved problem in this research field,[4,5] we thus began to investigate the different behaviors in more detail. In this paper, we wish to introduce our examined results concerning the effect of the cyclopentadienyl fragment on monomer reactivity ratios and the microstructure of poly(ethylene-*co*-1-hexene)s in these polymerizations.[6]

Results and Discussion. On the basis of the preliminary results concerning the effects of substituent of the cyclopentadienyl group on ethylene, 1-hexene, and 1-octene homopolymerizations,[7] we chose three different catalysts, $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**), $(1,3\text{-}{}^tBu_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**2**), and $({}^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**3**) (Chart 1), because these complexes, especially **2**, showed different catalytic activities in these homopolymerizations. **4** was chosen as the reference. The results are summarized in Table 1.[8]

Chart 1



1

2

3

4

It was revealed that **1** exhibited a remarkable catalytic activity under optimal conditions and that the activity was much higher than **4** in the presence of MAO which was prepared from commercially available MAO (PMAO-S) by removing toluene and the excess $AlMe_3$ in vacuo. The resultant copolymers possessed relatively high molecular weights, unimodal molecular weight distributions ($M_w = (31.7-45.5) \times 10^4$; $M_w/M_n = 1.77-1.98$), and relatively high 1-hexene contents (24.2−42.5 mol %) which were of the same level as those obtained by **4**.[9] The observed catalytic activity decreased when the polymerization was performed at 15 °C, but the rate was unchanged between 25 and 50 °C (69.4, 181, 179, and 176 × 10^3 kg of polymer/(mol of Ti h) at 15, 25, 40, and 50 °C, respectively).[10] The observed catalytic activity also decreased at a low Al/Ti molar ratio, but the M_w values of the resultant copolymers were unchanged under different Al/Ti molar ratios (139, 179, and 189 × 10^3 kg of polymer/(mol of Ti h); $M_w = 33.4$, 33.2, and 32.1 × 10^4 at Al/Ti = 20 000, 30 000, and 50 000, respectively).[10]

It is important to note that the 1-hexene content in the resultant copolymer depends strongly upon the substituent of Cp′ group under the same conditions. The complex **3** exhibited the highest level of 1-hexene incorporation among these complexes (example: 42.5, 37.5, and 59.0 mol % by **1**, **2**, and **3**, respectively, at ethylene 5 atm and 1-hexene 1.45 mmol/mL), indicating that the nature of cyclopentadienyl fragment affects the relative rate of monomer coordination or insertion.

Triad sequence distributions in the resultant poly(ethylene-*co*-1-hexene)s determined by ^{13}C NMR spectra[11] and the monomer reactivity ratios[12] are summarized in Table 2. The sequence distributions of copolymers shows that the contents of EHE and HHE + EHH sequences and the resultant r_Er_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 copolymerimerization with **4** are consistent with those reported previously[1d,e,3] 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. In addition, r_E, r_H, and r_Er_H values were not strongly affected either by the reaction temperature or by the Al/Ti molar ratio under the present conditions.[13] These are in contrast with those in copolymerizations by ordinary metallocene catalysts.[14]

Noteworthy is that the sequence distributions as well as their r_E, r_H, and r_Er_H values in the copolymerizations by **1**−**3** were strongly affected by the nature of the cyclopentadienyl group. This result should be very interesting for the first example of that the substitutents in cyclopentadienyl group *directly* control the monomer reactivity ratios and sequence distributions in ethylene/1-hexene copolymerization.

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* Corresponding author. Telephone: +81-743-72-6041. Fax: +81-743-72-6049. E-mail: nomurak@ms.aist-nara.ac.jp.

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Scheme 1

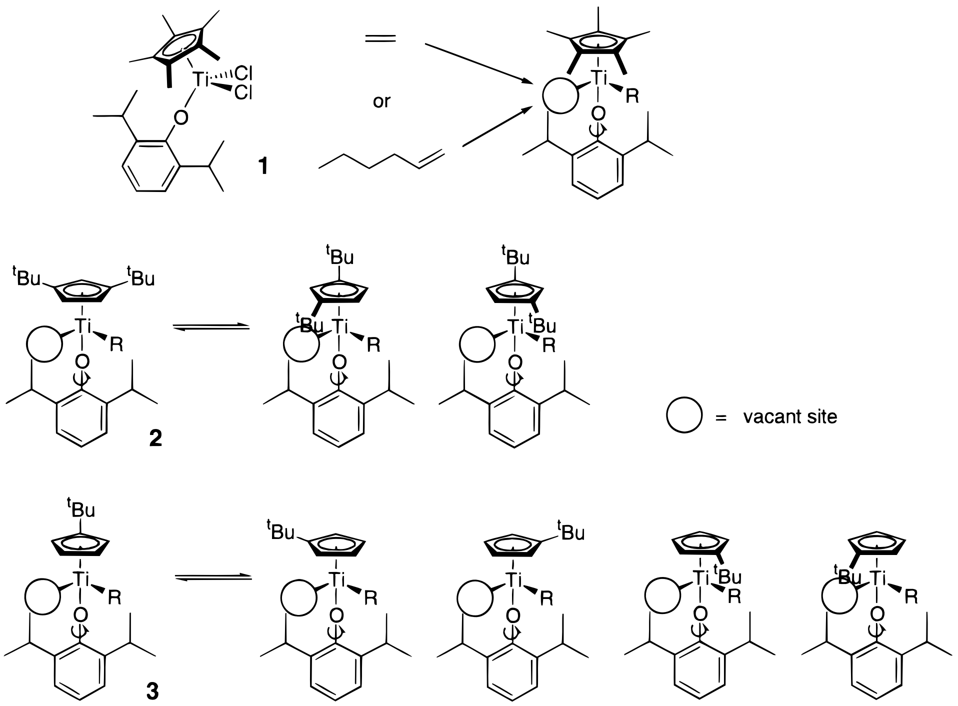

Table 1. Copolymerization of Ethylene with 1-Hexene by a Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)−MAO Catalyst System [Cp′ = Cp* (1), 1,3-^{t}Bu$_2$C$_5$H$_3$ (2), and ^{t}BuC$_5$H$_4$ (3)][a]

run no.	complex (concn/μmol)	temp/°C	Al/Ti[b]	ethylene/atm	1-hexene concn[c]	activity[d]/×10^{-3}	1-hexene[e]/mol %	M_w /×10^{-4} [f]	M_w/M_n [f]
1	**1** (0.07)	40	30 000	5	1.45	179	42.5	31.7	1.77
2	**1** (0.07)	40	30 000	5	1.45	176	43.4	33.2	1.79
3	**1** (0.07)	40	30 000	5	1.22[g]	198	36.6	33.8	1.83
4	**1** (0.07)	40	30 000	7	1.45	263	38.1	33.7	1.87
5	**1** (0.10)	40	30 000	5	1.09	79.5	40.3	32.0	1.88
6	**1** (0.10)	40	30 000	7	1.09	120	36.0	33.4	1.73
7	**1** (0.08)	40	25 000	5	0.73	83.2	28.6	38.2	1.80
8	**1** (0.08)	40	25 000	7	0.73	103	24.2	45.5	1.98
9	**4**[h] (0.60)	40	5000	5	0.73	9.49	30.0	74.5	2.05
10	**2** (0.45)	40	6500	5	1.45	4.70	37.5	10.3	1.84
11	**2** (0.45)	40	6500	7	1.45	6.85	33.9	12.4	1.78
12	**2** (0.30)	40	9000	5	0.73	11.3	27.0	19.7	1.82
13	**2** (0.30)	40	9000	7	0.73	17.5	23.5	14.5	1.71
14	**3** (0.75)	40	4000	5	1.45	8.79	59.0	10.4	1.58
15	**3** (0.75)	40	4000	7	1.45	15.0	41.4	13.0	1.60
16	**3** (0.60)	40	5000	5	0.73	6.41	32.0	11.4	1.99
17	**3** (0.60)	40	3300	7	0.73	14.2	26.9	12.7	1.60

[a] Reaction conditions: toluene + 1-hexene, total 55 mL (runs 10−13, 66 mL); MAO white solid, prepared by removing toluene and AlMe$_3$; time, 6 min (runs 12, 13, and 17, 8 min; runs 15 and 16, 5 min); 100 mL scale autoclave. [b] Molar ratio of Al/Ti. [c] 1-Hexene concentration, mmol/mL. [d] kg of polymer/(mol of Ti h). [e] 1-Hexene content in copolymer determined by ^{13}C NMR spectra. [f] GPC in *o*-dichlorobenzene vs polystyrene standard. [g] 1-Octene used in place of 1-hexene. [h] [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ as catalyst.

Table 2. Monomer Sequence Distirbution of Poly(ethylene-*co*-1-hexene)s[a]

			triad sequence distribution[c]/%						diad[d]					
run no.	complex	1-hexene[b]/mol %	EEE	EEH + HEE	HEH	EHE	HHE + EHH	HHH	EE	EH + HE	HH	r_Er_H [e]	r_E [f]	r_H [f]
7	**1**	28.6	31.1	31.3	8.9	21.5	6.8	0.4	46.8	49.5	3.7	0.28	2.70	0.10
8	**1**	24.2	40.0	29.6	5.8	19.4	4.6	0.6	55.1	42.5	2.4	0.29	2.64	0.11
11	**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
12	**2**	27.0	34.6	31.2	7.1	18.4	7.8	0.9	50.3	45.0	4.8	0.48	3.19	0.15
15	**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
17	**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
9	**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

[a] For detailed polymerization conditions, see Table 1. [b] 1-Hexene content in copolymer determined by ^{13}C NMR spectra. [c] Determined by ^{13}C NMR spectra. [d] [EE] = [EEE] + $^1/_2$[EEH + HEE], [EH] = [HEH] + [EHE] + $^1/_2${[EEH + HEE] + [HHE + EHH]}, [HH] = [HHH] + $^1/_2$[HHE + EHH]. [e] r_Er_H = 4[EE][HH]/[EH + HE]^2. [f] r_e = [H]$_0$/[E]$_0$ × 2[EE]/[EH + HE], r_h = [E]$_0$/[H]$_0$ × 2[HH]/[EH + HE], [E]$_0$ and [H]$_0$ are the initial monomer concentrations.

We believe that the high extent of α-olefin incorporation by **1**−**3**, despite the rather wide bond angles[2b] of Cp−Ti−O in **1** (120.5°) and **2** (119.3°) than that of Cp−Ti−N in **4** (107.6°),[15] would be due to the rotational flexibility of these complexes. In addition, the influence of the substituted cyclopentadienyl group on the monomer reactivity ratios and the sequence distributions would also be due to its easy internal rotation, facilitating coordination or insertion of higher olefins (Scheme 1). We are currently studying the mechanism of polymerization in more detail.

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Supporting Information Available: Text giving experimental details of general polymerization procedures in the presence of MAO, figures showing ^{1}H and ^{13}C NMR spectra of poly(ethylene-*co*-1-hexene)s and poly(ethylene-*co*-1-octene) prepared by **1**−**3** or $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (shown in Table 2), and tables giving polymerization results concerning the effects of reaction temperature and the Al/Ti molar ratio (total 12 pages). This material is available free of charge via the Internet at http://pubs.acs.org.

References and Notes

(1) For example (review): (a) Brintzinger, K. H.; Fischer, D.; Mülhaupt, R.; Rieger, B.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1995**, *34*, 1143. (b) Kaminsky, W. *Macromol. Chem. Phys.* **1996**, *197*, 3903. (c) Kaminsky, W.; Arndt, M. *Adv. Polym. Sci.* **1997**, *127*, 143. (d) Suhm, J.; Heinemann, J.; Wörner, C.; Müller, P.; Stricker, F.; Kressler, J.; Okuda, J.; Mülhaupt, R. *Macromol. Symp.* **1998**, *129*, 1. (e) McKnight, A. L.; Waymouth, R. M. *Chem. Rev.* **1998**, *98*, 2587. (f) Britovsek, G. J. P.; Gibson, V. C.; Wass, D. F. *Angew. Chem., Int. Ed. Engl.* **1999**, *38*, 429.

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(4) Report concerning the synthesis of alternating ethylene/propylene and ethylene/1-octene copolymers by bridged metallocene type catalysts: (a) Uozumi, T.; Miyazawa, K.; Sano, T.; Soga, K. *Macromol. Rapid. Commun.* **1997**, *18*, 883. (b) Jin, J.; Uozumi, T.; Sano, T.; Soga, K.; Shiono, T. *Macromol. Rapid. Commun.* **1998**, *19*, 337. (c) Arndt, M.; Kaminsky, W.; SchauWienold, A. M.; Weingarten, U. *Macromol. Chem. Phys.* **1998**, *199*, 1135. (d) Leclerc, M. K.; Waymouth, R. M. *Angew. Chem., Int. Ed. Engl.* **1998**, *67*, 922. Under peculiar copolymerization conditions at 0 °C, *meso*-$[Me_2Si(2\text{-}Me\text{-}1\text{-}Ind)_2]ZrCl_2$−MAO catalyst gave an alternating ethylene/1-octene copolymer.[4a] This is probably due to the extremely low r_O value,[1a−e,3] and the $r_E r_O$ value also depended upon the reaction temperature.

(5) Synthesis of stereoregular alternating ethylene/norbornene copolymers by metallocene and linked Cp′−amide type catalysts: Harrington, B. A.; Crowther, D. J. *J. Mol. Catal. A* **1998**, *128*, 79.

(6) Report concerning the effect of the cyclopentadienyl fragment on monomer reactivity ratios and copolymer microstructure in ethylene/norbornene copolymerization: McKnight, A. L.; Waymouth, R. M. *Macromolecules* **1999**, *32*, 2816.

(7) (a) Nomura, K.; Komatsu, T.; Imanishi, Y. *J. Mol. Catal. A* **2000**, *152*, 249; (b) *J. Mol. Catal. A*, in press.

(8) To control the 1-hexene conversion less than 10%, these copolymerizations were terminated at 5−8 min. For more experimental details, see the Supporting Information.

(9) Molecular weight and molecular weight distribution of the resultant copolymers were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH_{HR}-H HT × 2) at 140 °C 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.

(10) These copolymerizations were performed under the same conditions as in run 1, except the reaction temparature or Al/Ti molar ratio. For details, see the Supporting Information.

(11) These calculations were made by the following paper using ^{13}C NMR spectra of copolymers, Randall, J. C. *J. Macromol. Sci. Rev.*−*Macromol. Chem. Phys.* **1989**, *C29* (2&3), 201.

(12) The caluculation 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 (Kissin, Y. V. *Isospecific Polymerization of Olefin with Heterogeneous Ziegler*−*Natta Catalysts*; Springer-Verlag: New York, 1985; p 3), and the ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported in the following article: Sahgal, A.; La, H. M.; Hayduk, W. *Can. J. Chem. Eng.* **1978**, *56*, 354.

(13) $r_E r_H = 0.28{-}0.32$, $r_E = 2.29{-}2.70$, $r_H = 0.11{-}0.13$, 15−50 °C, and Al/Ti = 30 000−50 000. For details, see the Supporting Information.

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