

Letter

Polymerization of 1-hexene, 1-octene catalyzed by
 $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{-MAO}$ system. Unexpected
increase of the catalytic activity for ethylene/1-hexene
copolymerization by
 $(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{-MAO}$ catalyst system

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Abstract

Although $(1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3)\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**4**) showed the lowest catalytic activity for polymerization of 1-hexene, 1-octene with the series of $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}' = \text{Cp}, ^t\text{BuC}_5\text{H}_4, 1,3\text{-Me}_2\text{C}_5\text{H}_3, 1,3\text{-}^t\text{Bu}_2\text{C}_5\text{H}_3,$ and C_5Me_5]-methylaluminoxane (MAO) catalysts, **4** exhibited the significant catalytic activity for copolymerization of ethylene with 1-hexene, resulting in obtaining a copolymer with relatively high 1-hexene content (20.2–36.5 mol%) with relatively narrow molecular weight distribution. © 2000 Elsevier Science B.V. All rights reserved.

Keywords: 1-Hexene; 1-Octene; $\text{Cp}'\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)\text{-MAO}$ system

Olefin polymerization by homogeneous catalysis has been one of the most attractive subjects in the field of both organometallic chemistry and catalysis [1–3]. We reported recently that $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**5**) showed an exceptionally high catalytic activity for ethylene polymerization in the presence of MAO (meth-

ylaluminoxane) or $\text{Al}^i\text{Bu}_3/\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$ [4]. We assumed that the reason for high activity would be due to a unique bond angle (173°) of Ti–O–C (phenyl group) in **5** that was observed by X-ray crystallography [4]. We also reported that **5** was an efficient catalyst precursor for ethylene/1-butene copolymerization and the $r_E r_B$ values for the resultant poly(ethylene-co-1-butene)s were very small (r_E and r_B are monomer reactivity ratios of ethylene and 1-butene) [5]. In this paper, we wish to present a ligand effect for polymerization of 1-hexene and 1-octene with a series of $\text{Cp}'\text{TiCl}_2(\text{OAr})\text{-MAO}$

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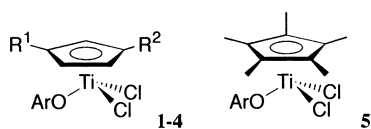


Fig. 1. R^1 , R^2 = H, H (1); t Bu, H (2); Me, Me (3); Bu, Bu (4); Ar = 2,6- t Pr₂C₆H₃.

catalysts [Cp' = Cp (1), (t BuC₅H₄) (2), 1,3-Me₂C₅H₃ (3), 1,3- t Bu₂C₅H₃ (4), and C5Me5 (5): OAr = O-2,6- t Pr₂C₆H₃ (Fig. 1). We also wish to report an efficient ethylene/ α -olefin copolymerization by 4–MAO catalyst.

Syntheses of various Cp'TiCl₂(O-2,6- t Pr₂C₆H₃) complexes were prepared according to our previous reports [4,5]. MAO was used as white solid after removing toluene and excess amount of AlMe₃ in vacuo [5–8]. Catalytic polymerizations of 1-hexene and 1-octene were performed in a round bottom flask connected to a three-way valves,² and the catalytic copolymerizations were conducted in a 100 ml stainless steel autoclave.³ ¹H and ¹³C NMR spectra of poly(ethylene-*co*-1-hexene)s were recorded at 50°C or 120°C on JEOL JNM-LA400 spectrometer (100.40 MHz ¹³C; 399.65 MHz, ¹H), and the sample solutions were prepared in *o*-dichlorobenzene-*d*₄ up to 10% by weight. Molecular weight and molecular weight distributions of

copolymers were determined by gel permeation chromatography.⁴

The results for 1-hexene and 1-octene polymerizations with a series of Cp'TiCl₂(O-2,6- t Pr₂C₆H₃)–MAO catalysts are summarized in Table 1. The use of the MAO white solid, prepared by removing toluene and excess amount of AlMe₃, is very important in order for this catalysis to obtain high molecular weight polymers with narrower molecular weight distributions, as we previously reported [5]. It was revealed that 1-hexene polymerization activity increased in the order: Cp* (5, 728 kg polymer/(mol-Ti) h) \gg 1,3-Me₂C₅H₃ (3, 184) > t BuC₅H₄ (2, 89) > Cp (1, 63) > 1,3- t Bu₂C₅H₃ (4, 26). The order on 4 was quite different from that observed in ethylene polymerization (Al t Bu₃/Ph₃CB(C₆F₅)₄ cocatalyst) [5 (2220 kg polymer/(mol-Ti) h) > 4 (653) > 3 (215), 2 (258) \gg 1 (77)]. We assume that this is due to the steric hindrance of bulky two *tert*-butyl groups in cyclopentadienyl ring, and is also due to rather bulky monomer of 1-hexene (1-octene) than ethylene [9]. Both electronic and steric factors thus play a role for the high activity.

It is important to note that turnover numbers (TON) obtained for both 1-hexene and 1-octene polymerizations by these catalyses were the same. This result clearly indicates that effect of monomer bulkiness is negligible for the activity during this series of catalysts. In addition, the molecular weight for the resultant poly(1-hexene) increased in the order: 1 ($M_n = 0.63 \times 10^4$) < 4 (2.16×10^4) < 2 (8.0×10^4), 3 (8.73×10^4) < 5 (69.4×10^4). The order (1 < 2,3 < 5) might be due to that the electron-donating

² Typical reaction procedure: 1-hexene (5 ml) and prescribed amount of MAO were added to a round bottom flask (25 ml) connected to three-way valves under N₂, and the polymerization was started by the addition of a toluene solution (2.5 ml) containing the catalyst (5.0 μ mol). 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 CHCl₃, which was washed with HCl aqueous solution and then dried in vacuo.

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

⁴ Molecular weights and the molecular weight distributions of the poly(ethylene-*co*-1-hexene)s were measured by means of gel permeation chromatography (Tosoh HLC-8121GPC/HT) with polystyrene gel columns (TSK gel GMHHR-H(20)HT \times 3) at 145°C using *o*-dichlorobenzene as solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples.

Table 1

Polymerization of 1-hexene, 1-octene, and 1-decene by Cp'TiCl₂(O-2,6-ⁱPr₂C₆H₃)-MAO catalyst^a

Run no.	Cat. (μmol)	α-Olefin	Al/Ti ^b	Polymer yield/mg	Activity ^c	TON ^d	$M_n^e \times 10^{-4}$	M_w/M_n^e
1	1 (5.0)	1-hexene	1000	156	62	370	0.68	
2	1 (5.0)	1-octene	1000	200	80	356	0.63	
3	2 (5.0)	1-hexene	1000	224	90	532	8.04	1.64
4	2 (5.0)	1-octene	1000	313	125	558	8.25	1.85
5	3 (5.0)	1-hexene	1000	460	184	1093	8.73	1.85
6	3 (5.0)	1-octene	1000	550	220	980	6.73	1.84
7	4 (5.0)	1-hexene	1000	64	26	152	2.16	1.62
8	4 (5.0)	1-octene	1000	94	38	168	1.75	1.49
9	5 (1.0)	1-hexene	2000	364	728	4330	69.4	1.62
10	5 (1.0)	1-octene	2000	485	970	4320	49.5	1.84
11	5 (1.0)	1-decene	2000	518	1036	3690	41.7	1.65

^aReaction conditions: α-olefin 5 ml, catalyst 2 μmol/(ml toluene), MAO white solid, 25°C.^bMolar ratio of Al/Ti.^cPolymerization activity (kg polymer/(mol-Ti) h).^dTON (turnover number = molar amount of α-olefin reacted/mol-Ti).^eGPC data in THF vs polystyrene standard.

substituents on cyclopentadienyl group enhance the propagation, although the lower M_n value by **4** would be due to the extremely low catalytic activity. The resultant poly(1-hexene) was atactic polymer, while the amounts of 2,1- or other insertion units were very small.

Particular attention should be paid regarding the unexpected remarkable increase of the catalytic activity for copolymerization of ethylene with 1-hexene by **4**-MAO catalyst system [26 kg polymer/(mol-Ti)h (run 8) → 9900 (run

13), Table 2]. The observed polymerization activities (runs 13–15) were higher than that for homopolymerization of ethylene (run 12), and the activity increased at higher ethylene pressures. In addition, the resultant poly(ethylene-co-1-hexene)s were high 1-hexene contents (20.2–36.5 mol%, Table 3) with narrow M_w/M_n values (1.86–1.97). One possible explanation for the high activity is due to that a steric hindrance, caused by between the repeated coordination or insertion by 1-hexene and bulky

Table 2

Copolymerization of Ethylene with 1-hexene by **4**-MAO catalyst^a

Run no.	Catalyst	Amount/μmol	α-Olefin (ml)	Ethylene/atm	Al/Ti ^b	Polymer yield/mg	Activity ^c	$M_w^d \times 10^{-4}$	M_w/M_n^d
8	4	5.0	1-hexene (5)	–	1000	64	26	2.16	1.62
12	4	0.5	–	5	4000	653	7840	99.7	2.97
13	4	0.5	1-hexene (5)	5	4000	825	9900	11.1	1.95
14	4	0.5	1-hexene (5)	7	4000	1023	12280	15.4	1.86
15	4	0.5	1-hexene (3)	7	4000	1231	14770	20.5	1.97

^aReaction conditions (runs 12–15): catalyst 2 μmol/ml toluene, toluene 30 ml, MAO white solid, 40°C, 10 min, 100 ml autoclave.^bMolar ratio of Al/Ti.^cPolymerization activity (kg polymer/(mol-Ti) h).^dGPC data in *o*-dichlorobenzene vs. polystyrene standard (runs 12–15).

Table 3

Monomer sequence distribution of Poly(ethylene-co-1-hexene)s prepared by 4-MAO catalyst^a

Run no.	[1-Hexene] ^b	Triad sequence distribution ^c (%)					$r_E r_H^d$	
		EEE	HEE + EEH	HEH	EHE	EHH + HHE		HHH
13	36.5	25.7	31.9	5.9	21.2	15.0	0.3	0.51
14	33.5	31.4	27.7	7.4	20.7	12.5	0.3	0.51
15	20.2	48.6	27.8	3.4	16.0	4.2	–	0.42

^a Polymerization conditions, see Table 2.^b Molar amount of 1-hexene in copolymer determined by ¹³C-NMR spectra.^c Determined by ¹³C-NMR spectra.^d $r_E r_H = 4[EE][HH]/[EH]^2$, $[EE] = [EEE] + [HEE + EEH]/2$, $[EH] = [HEE + EEH]/2 + [HEH] + [EHE] + [EHH + HHE]/2$, $[HH] = [HHH] + [EHH + HHE]/2$.

two *tert*-butyl group in **4**, can be reduced by incorporating ethylene, which thus leads 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 polymerization result.

The monomer sequence distributions of poly(ethylene-co-1-hexene)s prepared by **4** were studied by ¹³C NMR [10], and the results are listed in Table 3. Note that the amount of observed HHH sequence was very small, and that the obtained $r_E r_H$ values (r_E and r_H are monomer reactive ratios of ethylene and 1-hexene) for the copolymers were thus low (0.42–0.51) [10]. These values were very similar to those observed for poly(ethylene-co-1-butene)s by the 5-MAO system, and this is an interesting contrast with copolymers prepared by [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**6**), in which the polymerization proceeds in a random manner ($r_E r_B = \text{ca.} 1$) [3, 5]. The low $r_E r_H$ value by **4** would also suggest our previous speculation [5] that a rather flexible structure of **4** than **6** would give low $r_E r_H$.

We are currently exploring more detail concerning a relationship between the basic catalyst structure and $r_E r_X$ (X = H, O etc.) values, including a relationship between the monomer sequence and the substituents on cyclopentadienyl group in this catalysis. These results will be reported in the future.

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