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Effect of SiMe$_3$, SiEt$_3$ *Para*-Substituents for Exhibiting High Activity, Introduction of Hydroxy Group in Ethylene Copolymerization Catalyzed by Phenoxide-Modified Half-Titanocenes

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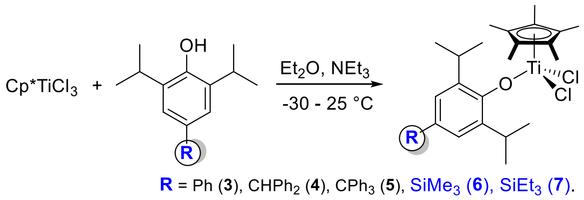
Abstract: Remarkable effects of SiMe$_3$, SiEt$_3$ *para*-substituent in the phenoxide-modified half-titanocenes, Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-R-C$_6$H$_2$) [R = SiMe$_3$ (**6**), SiEt$_3$ (**7**)], toward the catalytic activities in ethylene copolymerizations with 2-methyl-1-pentene, 1-decene, 1-dodecene and with 9-decen-1-ol (DC-OH) have been demonstrated. The activities by **6**, **7** at 50 ºC showed higher than those conducted at 25 ºC in all cases in the presence of MAO cocatalyst. Efficient synthesis of high molecular weight (HMW) ethylene copolymers incorporating DC-OH (or 5-hexen-1-ol, HX-OH) has been attained in the copolymerization by **7**, which showed better DC-OH (HX-OH) incorporation at 50 ºC to afford the HMW copolymers, poly(ethylene-*co*-DC-OH)s, with high activities (activity 1.21–3.81×10^5 kg-polymer/mol-Ti·h, M_n = 6.55-10.0×10^4, DC-OH 2.3-3.6 mol %).

Design of efficient molecular catalysts for precise olefin polymerization has been a long-term interest in the field of catalysis, organometallic chemistry, and of polymer chemistry.[1,2] In particular, development of the molecular catalysts, which enable synthesis of new copolymers (containing sterically encumbered monomers or cyclic olefins that are not incorporated by ordinary catalysts,[3,4] or by incorporation of polar functionalities[5-10]), have been considered as the fascinating goals. Efficient synthesis of high molecular weight ethylene (propylene) copolymers containing hydroxy group has been the attractive target in early transition metal catalysis,[7-9] because the polymerization generally proceeds with low catalytic activities affording (rather) low molecular weight polymers due to a strong interaction of oxygen with the centered metal,[7-9] even though the OH group in alken-1-ol was protected with trialkylsilyl group[7c,d] or Al^{i}Bu$_3$ etc. in advance.[7-9] The direct ethylene copolymerization using nickel, palladium catalysts generally afforded copolymers with certain branching.[2,5,6] We herein communicate the efficient synthesis of high molecular weight ethylene copolymers containing hydroxy group by adopting Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$) (**7**)–MAO catalyst, through remarkable effects of SiMe$_3$, SiEt$_3$ groups in the aryloxo *para*-substituent toward the activity, comonomer incorporation in the ethylene copolymerizations with long chain α-olefins [1-dodecene (DD), 1-decene (DC)], 2-methyl-1-pentene (2M1P), and with 9-decen-1-ol (DC-OH).[11]

Modified half-titanocenes have been focused in this study, because the catalysts enable synthesis of ethylene copolymers with disubstituted α-olefins,[12] branched α-olefins,[13] and with cyclic olefins[4] by adopting the ligand modification.[4] A series of the dichloride complexes containing various *para*-substituents on the 2,6-diisopropylphenoxy ligand, Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-R-C$_6$H$_2$) [R = Ph (**3**), CHPh$_2$ (**4**), CPh$_3$ (**5**), SiMe$_3$ (**6**), SiEt$_3$ (**7**)],[11] were prepared by treating Cp*TiCl$_3$ with the corresponding phenol in Et$_2$O in the presence of NEt$_3$ [Scheme 1, details are shown in the Supporting Information (SI)].[14] The prepared complexes were identified by NMR spectra and elemental analysis; structures of complexes **5**-**7** were determined by X-ray crystallography (Figure 1).[14] It turned out that the Ti–O–C bond angles in **6**, **7** [172.5(3), 174.62(19)º for **6**,**7**, respectively][14] are close to those by complexes **1**,[15] **2**[16a] [173.0(3), 174.0(3)º for **1**,**2**, respectively].[14-17] It has been considered that a large Ti–O–C bond angle affects the high activity due to increased stabilization of the active species by O→Ti π-donation.[4c,15,16a] In contrast, the angle in **5** is rather small [163.96(10)º]. The Ti–O bond distances in **5**-**7** [1.7919(11), 1.787(4), 1.7965(19) Å, respectively] are rather long compared to **1**, **2** [1.772(3), 1.777(4) Å, respectively],[15,16] whereas no apparent differences were observed in the other bond distances and angles (Table S7-2, SI).[14]



Scheme 1. Synthesis of Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-R-C$_6$H$_2$) [R = Ph (**3**), CHPh$_2$ (**4**), CPh$_3$ (**5**), SiMe$_3$ (**6**), SiEt$_3$ (**7**)].

Ethylene polymerizations by **1**-**7** were conducted in toluene in the presence of MAO [Ti 1.5×10^{-8} mmol (0.015 μmol), ethylene 4 atm, 25 ºC, 10 min, MAO 3.0 mmol, Table S2-1, SI].[18] It turned out that the activity increased in the order: **5** (R = CPh$_3$, activity

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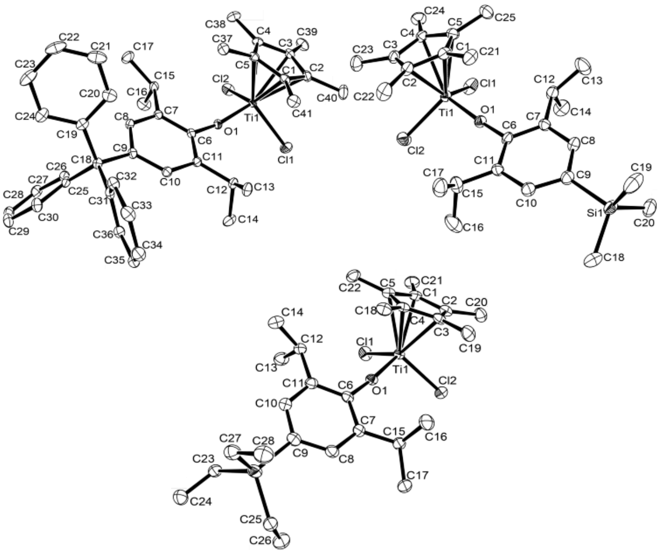
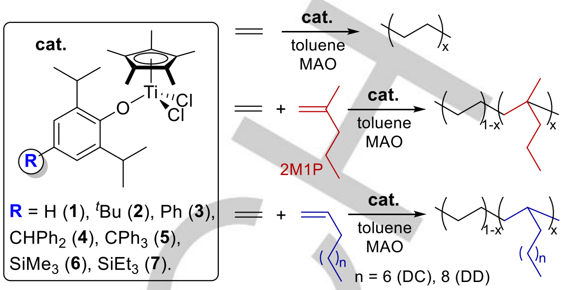


Figure 1. Structures of $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}RC_6H_2)$ [R = CPh_3 (**5**, top left), $SiMe_3$ (**6**, top right), $SiEt_3$ (**7**, bottom). Thermal ellipsoids are drawn at 30% probability level; H atoms are omitted for clarity.[14]

36800 kg-PE/mol-Ti·h) < **2** (^{t}Bu, 45600), **4** ($CHPh_2$, 46000), **1** (H, 47400) < **3** (Ph, 50700) < **6** ($SiMe_3$, 54300), **7** ($SiEt_3$, 56800).[18]The activities at 25 ºC by **6** and **7** further increased upon increasing the Al/Ti molar ratios [Ti 5.0×10^{-9} mmol (0.005 μmol), activity = 131000, 157000 kg-PE/mol-Ti·h, for **6**, **7** respectively, Table S2-1], whereas the activity by **1** decreased under these conditions. It was also revealed that the activities by **7** increased at 60 ºC, whereas decrease in the activity was observed by **1**.[18] These results thus suggest that the $SiMe_3$ (**6**) and the $SiEt_3$ (**7**) analogues exhibited better catalyst performances in the ethylene polymerization at high temperature.[18] The resultant polymers by **7** possessed high molecular weights with unimodal molecular weight distributions (Table S2-1).[18]

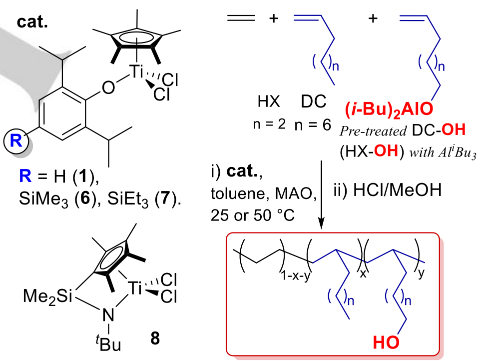
Selected results in the ethylene copolymerizations with 1-decene (DC), 1-dodecene (DD), and with 2-methyl-1-pentene (2M1P) are summarized in Table 1 (Scheme 2).[18] It was revealed that complexes **6** and **7** showed the higher catalytic activities than the others (runs 7,9 vs runs 1,3-6) in the ethylene/DD copolymerization at 25 ºC. Note that the activities by **6** and **7** increased at 50 ºC, whereas decrease in the activity was observed by **1**; the similar trend was observed in the ethylene/DC copolymerization (runs 12-17). The activities in the copolymerization with DD by **3**-**5** were lower than that by **1**, whereas improvements in the activities by **2**-**4** were seen at 50 ºC (Table S3-1, SI).[18] The resultant polymers were high molecular weight copolymers with unimodal molecular weight distributions; no apparent differences in the M_n values and the DD or DC contents were seen in the copolymers prepared by **1** and **6**, **7**.[18,19]

As reported previously,[12] **1** afforded poly(ethylene-*co*-2M1P)s with uniform compositions, whereas reported examples for synthesis of ethylene copolymers containing disubstituted 1-alkenes still have been limited.[3,4,12] It was revealed that the $SiMe_3$ (**6**) and $SiEt_3$ (**7**) analogues showed the higher activities than **1**, although the activity by **1** slightly increased at 50 ºC. Magnitude in the increases in the activities by **6**, **7** at 50 ºC were high compared to **1**, whereas no apparent differences in the M_n values and the 2M1P contents (estimated by DSC thermograms) were observed.[18,19] The activity by **7** further increased at 80 ºC, whereas the activities were slightly decreased upon increasing 2M1P concentration charged (Table S3-2, SI).[18]



Scheme 2. Ethylene polymerization and the copolymerizations with 1-decene (DC), 1-dodecene (DD), 2-methyl-1-pentene (2M1P) by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$–MAO catalysts.

Table 2 summarizes results in ethylene copolymerization with DC in the presence of 9-decen-1-ol (DC-OH) by **1**, **6**, **7**–MAO catalysts (Scheme 3), and the results conducted by the linked half-titanocene, $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**8**, constrained geometry type),[1e,13] are also placed for comparison.[18] The hydroxy group in DC-OH was pretreated with Al^iBu_3 for the protection according to the previous reports.[8,9,14]



Scheme 3. Ethylene copolymerization with 1-decene (DC) and 9-decen-1-ol (DC-OH) [1-hexene (HX) and 5-hexen-1-ol (HX-OH)], protected with Al^iBu_3 *in situ*, by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$ [R = H (**1**), $SiMe_3$ (**6**), $SiEt_3$ (**7**)], $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**8**)–MAO catalysts.

It should be noted that both **6** and **7** showed higher catalytic activities than **1**, and the activity increased at 50 ºC (runs 24-27, 29,30). The $SiMe_3$ analogue (**6**) showed the notable increase in the activity at 50 ºC (run 27), and the further increase at 80 ºC was observed by **7** (Table S4-1, SI).[18] In contrast, the activity by **1** and **8** decreased at 50 ºC (runs 25, 40). Noteworthy, *the activity by **7** at 50 ºC increased upon increasing the DC-OH concentration* (run 31), whereas decreases in the activities were observed by **6** and **8** under the same conditions (runs 28,41); the polymer yield by **8** became negligible. Importantly, *apparent decrease in the M_n value was not observed with increasing the DC-OH content* (2.5 mol%, run 31). The increase in the activity by **7** was also observed in the ethylene/1-hexene copolymerization upon co-presence of 5-hexen-1-ol (HX-OH) at 50 ºC (runs 35,36); the resultant polymers also possessed high molecular weights irrespective of the HX-OH content.[19]

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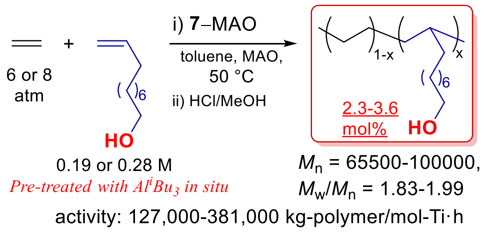
Table 1. Ethylene Copolymerization with 1-Decene (DC), 1-Dodecene, and with 2-Methyl-1-pentene (2M1P) by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-RC$_6$H$_2$) [R = H (**1**), ^{t}Bu (**2**), Ph (**3**), CHPh$_2$ (**4**), CPh$_3$ (**5**), SiMe$_3$ (**6**), SiEt$_3$ (**7**)]–MAO Catalysts[a]

run	catalyst (μmol)	comonomer (M)[b]	ethylene / atm	temp. / ºC	yield / mg	activity / kg-polymer/mol-Ti·h	M_n[c]×10^{-4}	M_w/M_n[c]	cont.[d] / mol%
1	**1** (0.0025)	DD (0.75)	6	25	161	644000	18.9	1.79	17.6
2	**1** (0.0025)	DD (0.75)	6	50	151	604000	16.5	1.85	
3	**2** (0.001)	DD (0.75)	6	25	73.9	739000	18.4	1.60	18.3
4	**3** (0.005)	DD (0.75)	6	25	99.8	200000	16.7	1.59	
5	**4** (0.005)	DD (0.75)	6	25	176	352000	16.7	1.57	
6	**5** (0.005)	DD (0.75)	6	25	108	216000	16.9	1.52	
7	**6** (0.001)	DD (0.75)	6	25	91.1	911000	15.0	1.62	
8	**6** (0.001)	DD (0.75)	6	50	188	1880000	15.3	1.54	16.3
9	**7** (0.001)	DD (0.75)	6	25	104	1040000	16.7	1.62	15.3
10	**7** (0.001)	DD (0.75)	6	50	161	1610000	16.2	1.60	16.7
11	Cp$_2$ZrCl$_2$ (0.01)[e]	DD (0.75)	6	25	301	1810000	56.2	1.99	2.0
12	**1** (0.005)	DC (0.88)	6	25	173	346000	19.7	1.61	21.4
13	**1** (0.005)	DC (0.88)	6	50	121	242000	16.0	1.73	
14	**6** (0.0025)	DC (0.88)	6	25	191	764000	18.4	1.67	20.1
15	**6** (0.001)	DC (0.88)	6	50	144	1440000	16.2	1.74	21.3
16	**7** (0.0025)	DC (0.88)	6	25	168	672000	15.4	1.55	
17	**7** (0.001)	DC (0.88)	6	50	81.1	811000	15.0	1.57	21.4
18	**1** (0.05)	2M1P (1.35)	4	25	41.7	5000	10.7	1.64	3.9
19	**1** (0.025)	2M1P (1.35)	4	50	68.0	16300	7.21	1.54	
20	**6** (0.05)	2M1P (1.35)	4	25	164	19700	6.69	1.62	
21	**6** (0.025)	2M1P (1.35)	4	50	183	43900	5.29	1.60	3.3
22	**7** (0.05)	2M1P (1.35)	4	25	75.6	9070	5.91	1.55	
23	**7** (0.025)	2M1P (1.35)	4	50	168	40300	6.19	1.58	2.9

[a] Conditions: toluene and 1-decene (DC) 1-dodecene (DD) or 2-methyl-1-pentene (2M1P) 5.0 mL total 30.0 mL, MAO 2.0 mmol for 6 min (DC, DD) or 3.0 mmol 10 min (2M1P). [b] Initial monomer concentration. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer content estimated by ^{13}C NMR spectra.[19] [e] Cited from reference 13.

Note that the ethylene copolymerization with DC-OH by **7**–MAO catalyst proceeded with high activity (381000 kg-polymer/mol-Ti·h) affording high molecular weight copolymer with unimodal molecular weight distribution (M_n = 65500, M_w/M_n = 1.83), uniform composition [confirmed by DSC thermograms as observed sole melting temperature (T_m) at 94.1 ºC (run 32, Scheme 4, Figure S6-2, SI)].[19] The activity was higher than that in the co-presence of DC (run 31) without change in the DC-OH content and the M_n value. Moreover, the high activity was preserved upon increasing the DC-OH concentration; *surprisingly, the M_n value did not change with increasing the DC-OH content* (run 33). The similar trend was observed in the copolymerization with HX-OH, affording high molecular weight copolymers with uniform compositions (runs 37,38, Figures S6-3, SI).[19]



Scheme 4. Ethylene copolymerization with 9-decen-1-ol (DC-OH) by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-SiEt$_3$-C$_6$H$_2$) (**7**)–MAO catalyst.

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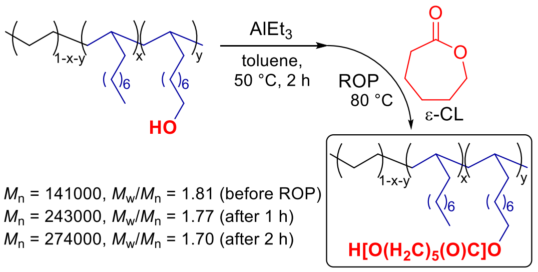
Table 2. Copolymerization of ethylene (E) with 1-Decene (DC) and 9-Decen-1-ol (DC-OH) by Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-RC$_6$H$_2$) [R = H (**1**), SiMe$_3$ (**6**), SiEt$_3$ (**7**)], [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**8**)–MAO Catalysts[a]

run	catalyst (μmol)	E / atm	DC (M)[b]	DC-OH (M)[b]	temp / ºC	yield / mg	activity / kg-polymer/mol-Ti·h	M_n[c]×10^{-4}	M_w/M_n[c]	DC-OH[d] / mol%	DC[d] / mol%	T_m[e] / ºC
24	**1** (0.025)	6	0.79	0.093	25	154	37000	13.8	1.83	0.8	15.2	
25	**1** (0.01)	6	0.79	0.093	50	53.0	31800	7.29	1.81	1.2	17.8	
26	**6** (0.025)	6	0.79	0.093	25	266	63800	13.0 (14.1)[f]	1.72 (1.81)[f]	1.2	14.6	
27	**6** (0.01)	6	0.79	0.093	50	305	183000	7.58	1.68	1.5	15.0	
28	**6** (0.01)	6	0.70	0.19	50	89.0	53300	7.10	1.67	1.8	13.7	
29	**7** (0.025)	6	0.79	0.093	25	189	45400	11.7	1.81	1.3	15.2	
30	**7** (0.01)	6	0.79	0.093	50	79.9	47900	6.82	1.70	1.5	16.7	
31	**7** (0.01)	6	0.70	0.19	50	122	73200	6.70	1.69	2.5	14.1	
32	**7** (0.01)	6	---	0.19	50	635	381000	6.55	1.83	2.6	--	94.1
33	**7** (0.01)	6	---	0.28	50	212	127000	7.16	1.84	3.6	--	93.2
34	**7** (0.01)	8	---	0.28	50	223	134000	10.0	1.99	2.3	--	97.6
35	**7** (0.01)	6	1.13[g]	0.14[g]	50	39.4	23600	5.32	1.51	0.3[h]	16.0[h]	
36	**7** (0.01)	6	1.00[g]	0.28[g]	50	101	60600	6.80	1.69	0.9[h]	15.2[h]	
37	**7** (0.01)	6	---	0.28[g]	50	120	72000	10.1	2.01	2.4[h]	--	110
38	**7** (0.01)	8	---	0.28[g]	50	185	111000	10.5	2.08	0.7[h]	--	115
39	**8** (0.025)	6	0.79	0.093	25	61.0	14600	8.97	1.79	0.9	14.0	
40	**8** (0.01)	6	0.79	0.093	50	11.1	6660	--	--			
41	**8** (0.01)	6	0.70	0.19	50	5.0	3060	--	--			

[a] Conditions: toluene and 1-decene (DC) 4.0 (0.70M) or 4.5 mL (0.79 M) and 9-decen-1-ol (DC-OH) 0.5 (0.093 M) or 1.0 mL (0.19 M) total 30.0 mL, ethylene 6 atm, MAO 3.0 mmol, Al^{i}Bu$_3$ 3.0 (DC-OH 0.5 mL) or 6.0 mmol (DC-OH 1.0 mL), 10 min. [b] Initial monomer concentration. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] DC-OH, DC content (mol%) estimated by ^{1}H NMR spectra.[19] [e] By DSC thermograms.[19] [f] GPC data in THF. [g] 1-Hexene and/or 5-hexen-1-ol were used. [h] 1-Hexene and/or 5-hexen-1-ol contents estimated by ^{1}H NMR spectra.[19]

As demonstrated previously in poly(1-octene-*co*-7-octen-1-ol)s,[20] the hydroxy group in the resultant polymer in poly{ethylene-*co*-DC-*co*-(DC-OH)} was treated with AlEt$_3$ and subsequent addition of ε-caprolactone (CL) at 80 ºC gave the amphiphilic graft copolymers, poly{ethylene-*co*-DC-*co*-(DC-OH)-*gr*-poly(CL)}, via Al-alkoxide initiated ring-opening polymerization (ROP, Scheme 5, detailed procedures are shown in Table S4-3, SI).[14,18,19] The M_n values increased over time course consistent with unimodal molecular weight distributions due to a living nature in this ROP;[20] the resultant amphiphilic polymers were identified by NMR spectra. Precise grafting by the living ROP has thus been demonstrated.



Scheme 5. Synthesis of amphiphilic block/graft copolymers by post-modification from the OH group (run 26) by Al-alkoxide initiated ring-opening polymerization (ROP) of ε-caprolactone (CL). Both M_n and M_w/M_n data are GPC data in THF versus polystyrene standards (Table S4-3, SI).

We have demonstrated efficient ethylene copolymerizations with 2-methyl-1-pentene, 1-dodecene especially by phenoxide-modified half-titanocenes containing SiMe$_3$ (**6**) or SiEt$_3$ (**7**) group in the phenoxy *para*-substituent. In particular, these catalysts (**6**, **7**) exhibited high activities for ethylene copolymerization with 1-decene (DC) and 9-decen-1-ol (DC-OH), affording high molecular weight copolymers containing hydroxy group with unimodal molecular weight distributions. The activities by **6**, **7** at 50 ºC showed higher than those conducted at 25 ºC. In particular, **7** showed better DC-OH (HX-OH) incorporation at 50 ºC, and the copolymerizations with DC-OH (HX-OH) afforded high molecular weight copolymers with high catalytic activities. As far as we know, this is the first successful demonstration of the efficient synthesis of high molecular weight ethylene copolymers containing hydroxy group by (at least) group 4 transition metal catalysts. We speculate that an introduction of SiMe$_3$, SiEt$_3$ group could contribute to a stabilization of the active species at this moment.[11] Further studies concerning copolymerization with various monomers containing polar functionalities (including the scope and limitation) will be introduced in the near future.

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Keywords: titanium catalyst • ligand effect • half-titanocenes • ethylene copolymerization • polyolefin containing polar group

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[18] Additional polymerization data are shown in the Supporting Information. In the ethylene polymerization , the activity by **7** at 80 ºC under the optimized Al/Ti ratio (116000 kg-PE/mol-Ti·h) was close to that at conducted 60 ºC (123000 kg-PE/mol-Ti·h) but the rapid catalyst deactivation after 5 min was observed at 100 ºC (Table S2-1, SI).

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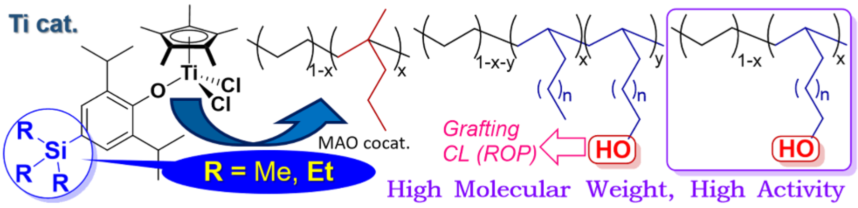
Entry for the Table of Contents



Remarkable effect of $SiMe_3$, $SiEt_3$ phenoxy *para*-substituent in $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}R\text{-}C_6H_2)$ toward the activity in the ethylene copolymerizations with 2-methyl-1-pentene, 1-dodecene and with 9-decen-1-ol have been demonstrated; efficient synthesis of high molecular weight ethylene copolymers containing 9-decen-1-ol (5-hexen-1-ol) has been attained by $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}SiEt_3\text{-}C_6H_2)$–MAO catalyst.