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Copolymerization of Ethylene with *tert*-Butylethylene Using *Nonbridged* Half-Titanocene-Cocatalyst Systems

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ABSTRACT: The copolymerization of ethylene with *tert*-butylethylene (TBE, 3,3-dimethyl-1-butene) using various half-titanocene [$Cp'TiCl_2X$ (X = O-2,6-$^iPr_2C_6H_3$, N=C$^tBu_2$)]-cocatalyst systems has been carried out. The aryloxo-containing half-titanocenes, $Cp'TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (Cp′ = Cp*, $^tBuC_5H_4$, 1,2,4-$Me_3C_5H_2$), displayed the capability to bring about TBE incorporation in the presence of MAO as a cocatalyst, while their ketimide analogues, $Cp'TiCl_2$(N=C$^tBu_2$) (Cp′ = Cp, Cp*, $^tBuC_5H_4$), could not accomplish TBE enchainment in ethylene/TBE copolymerization. Among aryloxo derivatives, those carrying *tert*-butyl and trimethyl substituents on the cyclopentadienyl moiety, $Cp'TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (Cp′ = $^tBuC_5H_4$, 1,2,4-$Me_3C_5H_2$), exhibited efficient TBE incorporation and moderate catalytic activity in the presence of MAO, affording ethylene/TBE copolymers with relatively high molecular weight and uniform molecular weight distribution. However, the copolymerization conducted by employing constrained geometry catalyst (linked half-titanocene), [$Me_2Si(C_5Me_4)(N^tBu)$]$TiCl_2$, and zirconocene [Cp_2ZrCl_2]−MAO catalyst systems resulted in polyethylene without TBE incorporation. Furthermore, the copolymerization of 1-hexene (1-Hex) with TBE and vinyltrimethylsilane (VTMS), by ($^tBuC_5H_4$)$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) and $CpTiCl_2$(N=C$^tBu_2$)−MAO catalyst systems, indicated a considerably higher reactivity of VTMS. The 1-Hex/VTMS copolymerization has been elucidated to proceed via 1,2-insertion as manifested by the remarkably efficient VTMS enchainment, hence revealing the difference in the reactivity of TBE and VTMS to arise from that in their electronic and/or steric nature.

Introduction

The potential applications of a polymer are determined by its physical and mechanical properties, which mainly depend on the polymer composition and architecture. The development of homogeneous single-site olefin polymerization catalysts has played a critically important role in the creation of new polymer materials with controlled microstructures and desired properties.[1,2]

During the past decade of our systematic studies regarding ethylene copolymerization with 1-hexene,[3] styrene,[4] cyclohexene,[5] norbornene,[6] and other nontraditional olefinic substrates, aryloxo- and ketimide-containing half-titanocenes have been witnessed to exhibit notable catalytic activity and/or efficient comonomer incorporation. For instance, Cp*$TiCl_2$(OAr) (Ar = 2,6-$^iPr_2C_6H_3$) (**1**), exhibited notable catalytic activity and efficient comonomer incorporation in ethylene/1-hexene[3] and ethylene/2-methyl-1-pentene (2M1P)[7] copolymerization, while its ^{t}BuCp analogue, **2,** was capable of bringing about even better comonomer incorporation in the copolymerization of ethylene with 1-hexene,[3] and with styrene[4a,b] and cyclohexene as well.[5] On the other hand, the Cp-ketimide derivative, $CpTiCl_2$(N=C$^tBu_2$) (**3**), has been revealed to show remarkable catalytic activity and excellent comonomer incorporation in ethylene/norbornene copolymerization,[6c] whereas its Cp* analogue, Cp*$TiCl_2$(N=C$^tBu_2$) (**7**), is known to mediate living ethylene/styrene copolymerization.[4c,d]

Synthesis of novel ethylene copolymers by enchainment of sterically encumbered comonomers using newly designed molecular catalysts has gained considerable prominence, and precise control in the copolymerization usually allows the alteration of physical, mechanical, and electronic properties by varying the ratio of the individual components/monomers. Although examples for the copolymerization of ethylene with γ-disubstituted monoolefins such as 3-methyl-1-pentene (3M1P)[8] and vinylcyclohexane,[9] especially by using half-titanocenes containing anionic ancillary donor ligands,[2j,8b,9d] are available, there are no reports regarding ethylene copolymerization with *tert*-butylethylene (CH_2=CH^{t}Bu, TBE, 3,3-dimethyl-1-butene) most probably due to the steric bulk in the close proximity of the olefinic double bond.

In a recent communication, we have reported efficient comonomer incorporation in the copolymerization of ethylene with vinyltrimethylsilane (VTMS) attained by Cp*$TiCl_2$(OAr) (Ar = 2,6-$^iPr_2C_6H_3$) (**1**) and $CpTiCl_2$(N=C$^tBu_2$) (**3**)-MAO catalyst systems, while the copolymerization with TBE afforded polyethylene with negligible TBE incorporation under the same conditions.[10] However, it is a well established fact that the structural features of the catalyst, in particular the steric bulk of the ligand, bite angle, configuration, and conformation, do influence the coordination and/or insertion of monomers in the transition-metal-catalyzed polymerization, an attribute distinctive from the conventional radical and ionic polymerization.[11] Our previous research efforts have demonstrated that switching from Cp*$TiCl_2$OAr (Cp* = C_5H_5, Ar = 2,6-$^iPr_2C_6H_3$) to its ^{t}BuCp ($^tBuC_5H_4$) analogue in ethylene/cyclohexene copolymerization resulted in a remarkably enhanced cyclohexene content in the resulting copolymers.[5] Therefore, we employed a series of half-titanocene [$Cp'TiCl_2X$ {X = O-2,6-$^iPr_2C_6H_3$ (**1**, **2**, **6**); N=C$^tBu_2$ (**3**, **7**, **8**)}] cocatalyst systems and tried to explore the most suitable catalyst precursor which can accomplish efficient TBE enchainment in ethylene/TBE copolymerization.

The present contribution presents the first example of appreciable TBE incorporation in the ethylene copolymerization achieved by using $Cp'TiCl_2$(OAr)-MAO catalyst systems (Scheme 1). The effect of varying the polymerization conditions such as comonomer conc., ethylene pressure, Al/Ti molar ratio, temperature, time, and the type of Al cocatalysts on the extent of TBE enchainment, catalytic activity, molecular weight, and molecular weight distribution has also been elucidated. More-

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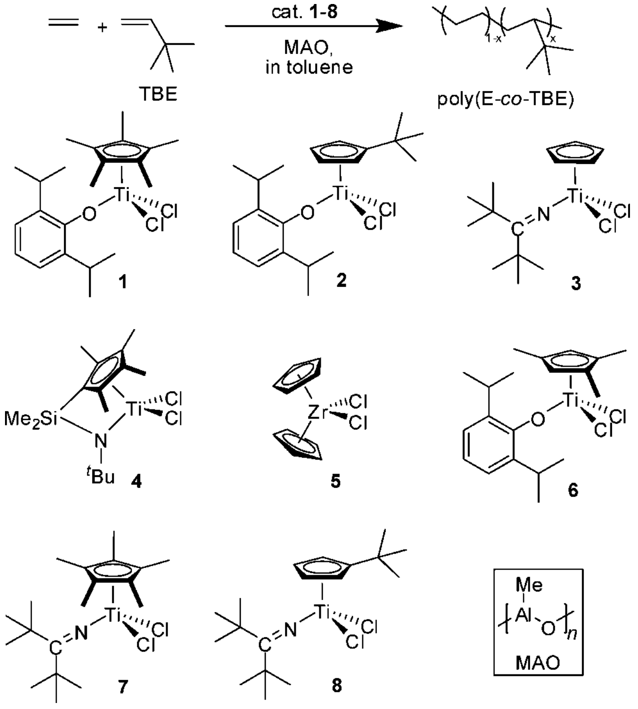
Scheme 1. Copolymerization of Ethylene with *tert*-Butylethylene (TBE) by $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp′ = Cp* (1), ${}^tBuC_5H_4$ (2), 1,2,4-$Me_3C_5H_2$ (6)], $Cp'TiCl_2(N{=}C{}^tBu_2)$ [Cp′ = Cp (3), Cp* (7), ${}^tBuC_5H_4$ (8)], $[Me_2Si(C_5Me_4)(N{}^tBu)]TiCl_2$ (4), and Cp_2ZrCl_2 (5) Catalyst Systems with MAO



over, the copolymerization of 1-hexene with VTMS has been carried out to discern the difference in TBE and VTMS reactivity, *i.e.*, whether the difference in the steric and/or electronic nature or in the mode of insertion endows VTMS with higher reactivity than that of TBE.

Results and Discussion

Table 1 summarizes the results for the copolymerization of ethylene with *tert*-butylethylene (TBE) and vinyltrimethylsilane (VTMS) using $Cp'TiCl_2(OAr)$ [Ar = 2,6-${}^iPr_2C_6H_3$; Cp′ = Cp* (**1**), ${}^tBuC_5H_4$ (**2**)], $CpTiCl_2(N{=}C{}^tBu_2)$ (**3**), $[Me_2Si(C_5Me_4)(N{}^tBu)]TiCl_2$ (**4**), and Cp_2ZrCl_2 (**5**)-MAO catalyst systems in toluene at 25 °C.[8b,10] It has been reported in a recent communication that **1**−**3** exhibited efficient VTMS incorporation in the copolymerization of ethylene with VTMS affording high molecular weight poly(ethylene-*co*-VTMS)s with unimodal molecular weight distribution.[10] The lowering of the ethylene pressure led to the increase in the VTMS content in the resulting copolymers accompanied by the decrease in activity (*c.f.* run 2, 3, 8, and 9 in Table 1). The constrained geometry catalyst (linked half-titanocene) (**4**) and zirconocene (**5**) have also been employed as catalyst precursors for comparison,[12] where zirconocene (**5**) showed low catalytic activity yielding low molecular weight polyethylene with negligible VTMS incorporation.[10] Quite interestingly, the linked half-titanocene (**4**) brought about an efficient VTMS incorporation (run 11) despite the fact that **4** affected negligible cyclohexene and 2M1P incorporation under the similar conditions.[5,7] These findings contradict the observation that VTMS did not coordinate to $(MeC_5H_4)_2Zr^+(O{}^tBu)(ClCD_2Cl)$.[13]

As far as ethylene/TBE copolymerization is concerned, the use of complexes **1**, **3**, and **4** as catalyst precursors did not result in any TBE enchainment under the same conditions (run 1, 6, 7, and 10).[10] Notwithstanding, the ^{t}BuCp-aryloxo complex, **2**, displayed the potential to copolymerize TBE with ethylene although the incorporated commoner content was quite low (run 4). Keeping in view the capability of **2** to mediate TBE incorporation, we envisioned that a careful selection of polymerization conditions can help us attain the synthesis of novel ethylene copolymers with sterically encumbered commoners like TBE. Therefore, a variety of half-titanocenes were employed to carry out ethylene/TBE copolymerization under a different set of polymerization conditions.

The results for the copolymerization of ethylene with TBE catalyzed by $Cp'TiCl_2(OAr)$ [Ar = 2,6-${}^iPr_2C_6H_3$; Cp′ = ${}^tBuC_5H_4$ (**2**), 1,2,4-$Me_3C_5H_2$ (**6**)]-MAO catalyst systems, at TBE concentration higher than those mentioned in Table 1, in toluene at 25 °C are listed in Table 2. Both of these catalyst systems mediated appreciable TBE incorporation, and these results comply well with those demonstrated previously that **2** and **6**-MAO catalyst systems showed rather efficient cyclohexene incorporation in the copolymerization of ethylene with cyclohexene.[5] The present series of experiments has revealed that **2** and **6** displayed moderate catalytic activity under these conditions affording high molecular weight copolymers with unimodal molecular weight distribution (run 13−18). The resulting polymers were poly(ethylene-*co*-TBE)s with uniform TBE incorporation as manifested by ^1H and ^{13}C NMR spectra, GPC profiles, and DSC thermograms.[14] The TBE content in the copolymers increased upon increasing the TBE concentration and/or upon decreasing the ethylene pressure (run 13−16), while the catalytic activity and M_n of the copolymers underwent the decrement. Furthermore, a linear relationship between melting temperature and TBE content of the resulting poly(ethylene-*co*-TBE)s, *i.e.* the decrease in the T_m value upon increasing the TBE content,[14] strongly suggests that the copolymerization proceeded with single catalytically active species thus giving rise to uniform copolymer composition (the TBE incorporation was uniform).[15]

The ^{13}C NMR (DEPT) spectra of poly(ethylene-*co*-TBE) in benzene-d_6/1,2,4-trichlorobenzene at 110 °C (run 14) are shown in Figure 1, and all resonances were identified by the DEPT analysis as well as by the comparison of the ^{13}C NMR spectra of the copolymers with different TBE content. The copolymer prepared by **2**-MAO catalyst system possessed isolated TBE units inserted among repeated ethylene units. Although the presence of alternating ethylene/TBE sequences cannot be ruled out exclusively, no resonance ascribable to the repeated TBE incorporation was witnessed. Moreover, the attempts to carry out homopolymerization of TBE by **2**-MAO catalyst system were unsuccessful, thus justifying the moderate TBE incorporation in poly(ethylene-*co*-TBE).[16] Our previous report has demonstrated similar tendency for 2M1P incorporation in poly(ethylene-*co*-2M1P).[7]

For the sake of elaborate understanding, the ethylene/TBE copolymerization by a **2**−MAO catalyst system was executed in toluene under 2 atm of ethylene pressure by varying the Al/Ti molar ratio, temperature, time, and the type of Al cocatalysts. The effect of varying the aforementioned factors on the catalytic activity, molecular weight, and the extent of TBE incorporation in poly(ethylene-*co*-TBE)s was discerned, and the results are summarized in Table 3. The catalytic activity of the **2**-MAO catalyst system displayed a clear dependence on the Al/Ti molar ratio and was observed to be the highest at 5.0×10^3 (*cf.* runs 14, 19−22, 25, and 26), whereas no large difference was observed in both the M_n values and the TBE content of the resulting copolymers. A closer look on the copolymerization results indicates that both the catalytic activity and the M_n values were prone to the changes in temperature, and underwent a considerable decrease when copolymerization was conducted at 40 °C (run 23); while the TBE content remained unaffected. The elongation of the copolymerization time (from 10 to 20 min.) did not result in a significant decrease in the catalytic

Table 1. Copolymerization of Ethylene with *tert*-Butylethylene (TBE) and Vinyltrimethylsilane (VTMS) Using Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp′ = Cp* (1), ^{t}BuC$_5$H$_4$ (2)], CpTiCl$_2$(N=C^{t}Bu$_2$) (3), [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (4), and Cp$_2$ZrCl$_2$ (5) Catalyst Systems with MAO[a]

run	complex (μmol)	ethylene (atm)	comonomer (M)	yield (mg)	activity[b]	M_n[c] × 10^{-4} (g mol^{-1})	M_w/M_n[c]	content[d] (mol %)
1[e]	**1** (0.20)	6	TBE (1.29)	471	14100	15.5	2.0	trace
2[f]	**1** (0.50)	6	VTMS (1.15)	156	1870	30.5	1.9	5.1
3[f]	**1** (2.00)	2	VTMS (1.15)	50	150	4.28	1.9	18.6
4	**2** (1.00)	6	TBE (2.58)	551	3310	11.7	2.5	1.3
5[f]	**2** (0.20)	6	VTMS (1.15)	77	92	1.41	2.8	13.6
6	**3** (0.20)	6	TBE (1.29)	261	7830	71.1	1.9	trace
7	**3** (0.20)	6	TBE (2.58)	200	6000	68.7	1.9	trace
8[f]	**3** (1.00)	6	VTMS (1.15)	622	3730	57.3	2.3	11.9
9[f]	**3** (1.00)	4	VTMS (1.15)	260	1560	42.2	2.3	18.7
10[e]	**4** (0.25)	6	TBE (1.29)	126	3020	32.0	2.0	none
11	**4** (0.25)	6	VTMS (1.15)	95 (92)[g]	2280	36.7	2.5	10.4
12[f]	**5** (10.0)	6	VTMS (1.15)	38	23	0.56	3.9	trace

[a] Conditions: comonomer, 5.0 mL (runs 4 and 7, 10.0 mL); toluene, 20 or 25 mL (total volume, 30.0 mL); dried MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 3.0 mmol; 25 °C; 10 min. [b] Activity = kg-polymer/mol-Ti•h. [c] Estimated by GPC in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer content estimated by ^{13}C NMR spectra. [e] Cited from ref 8b. [f] Cited from ref 10. [g] Independent polymerization result for reproducibility.

Table 2. Copolymerization of Ethylene with *tert*-Butylethylene (TBE) Using Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [Cp′ = ^{t}BuC$_5$H$_4$ (2), 1,2,4-Me$_3$C$_5$H$_2$ (6)] Catalyst Systems with MAO[a]

run	complex (μmol)	ethylene (atm)	TBE (M)	yield (mg)	activity[b]	M_n[c] × 10^{-4} (g mol^{-1})	M_w/M_n[c]	content[d] (mol %)	T_m (T_g)[e] (°C)
13	**2** (1.0)	2	1.6	153	918	7.27	2.1	4.4	101
14	**2** (1.0)	2	3.9	126	756	4.04	2.0	6.8	78 (−32)
15	**2** (1.0)	2	6.4	92	552	2.23	2.8	9.5	55 (−38)
16	**2** (1.0)	4	3.9	336	2020	8.17	2.4	3.3	104
17	**6** (1.0)	2	1.6	173	1040	9.12	2.2	2.3	-[f]
18	**6** (1.0)	2	3.9	115	690	4.93	2.3	7.8	76 (−33)

[a] Conditions: comonomer + toluene (total volume) = 10.0 mL; dried MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 3.0 mmol; 25 °C; 10 min. [b] Activity = kg-polymer/mol-Ti•h. [c] Estimated by GPC in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer content estimated by ^{13}C NMR spectra. [e] Determined by DSC analysis. [f] No measurement.

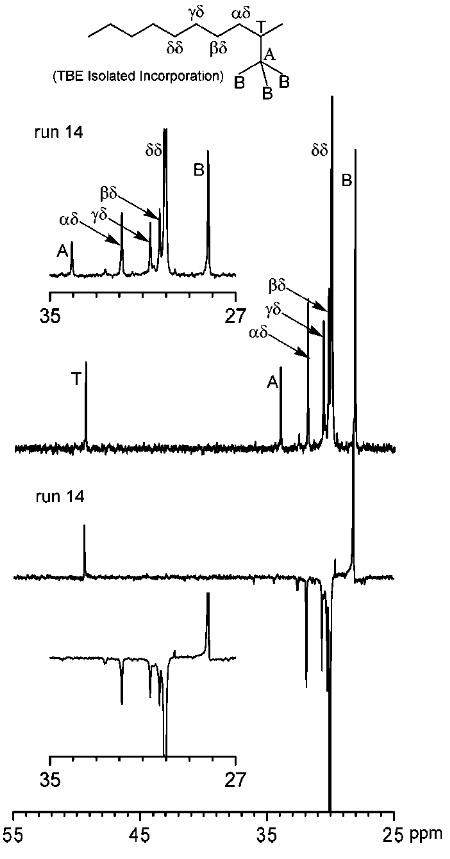


Figure 1. ^{13}C NMR and DEPT spectra, in benzene-d_6/1,2,4-trichlorobenzene at 110 °C, for poly(ethylene-*co*-*tert*-butylethylene) prepared by using a (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**) catalyst system with MAO (run 14, Table 2).

activity while the M_n and the TBE content of the formed copolymer were virtually unaltered (run 22 and 24).

As described above (*cf.* run 14, 19−22, 25, and 26), the M_n values of poly(ethylene-*co*-TBE)s were immune to the variation in the Al/Ti molar ratio, suggesting that the dominant chain transfer pathway in the ethylene/TBE copolymerization would be either β-hydrogen elimination or β-hydrogen transfer to monomer rather than the chain transfer to Al, as observed in the ethylene/2M1P copolymerization.[7b]

The type of Al cocatalyst selected to bring about ethylene/TBE copolymerization had a direct bearing on the catalytic activity of the system, and the use of modified MAO (MMAO) in place of MAO (Scheme 2) led to a vital lowering of the activity without influencing the TBE content of poly(ethylene-*co*-TBE)s (*c.f.* run 22 and 27−29). The catalytic activity decreased in the order **2**-MAO (1130 kg of polymer/(mol of Ti•h)) > **2**-MMAO-3AT (342, Me/^{i}Bu = 2.33) = **2**-MMAO-3AH (342, Me/^{i}Bu = 2.67) > **2**-MMAO-3BH (64, Me/^{i}Bu = 3.54). Nonetheless, the GPC profiles of all the copolymers prepared by **2**-MMAO catalyst systems were unimodal indicative of the fact that the copolymerization proceeded with a single catalytically active species. Although these trends are similar to those observed in the copolymerization of ethylene with 1-hexene and 2M1P catalyzed by the Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)-cocatalyst systems[3b,7b] as well as olefin copolymerization by ordinary metallocenes,[2a,e] these findings furnish an interesting contrast to those reported in the copolymerization of ethylene with isobutene or 1-octene mediated by the mononuclear/dinuclear constrained geometry catalyst (linked half-titanocene)-cocatalyst systems, in which both the activity and the comonomer content in the resulting copolymers were highly effected by the type of cocatalyst employed.[12d]

Since this paper constitutes the first detailed report concerning the synthesis and characterization of ethylene/TBE copolymers, attempts were made to explore the capability of various half-titanocene−MAO catalyst systems (under the optimized Al/Ti molar ratio as shown in Table 3) to accomplish copolymerization of ethylene with TBE, and results are given in Table 4. As discussed above, among Cp′−aryloxo-containing half-titanocenes,

Table 3. Copolymerization of Ethylene with *tert*-Butylethylene (TBE) Using $(^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (2) Catalyst Systems with MAO/MMAO[a]

run	complex (μmol)	Al[b]/mmol (Al/Ti × 10^{-3})	yield (mg)	activity[c]	M_n[d] × 10^{-4} (g mol^{-1})	M_w/M_n[d]	content[e] (mol %)
19	**2** (1.0)	MAO 1.0 (1.0)	52	312	3.18	2.0	6.6
20	**2** (1.0)	MAO 2.0 (2.0)	115	690	4.22	2.0	6.6
14	**2** (1.0)	MAO 3.0 (3.0)	126	756	4.04	2.0	6.8
21	**2** (1.0)	MAO 4.0 (4.0)	161	966	4.98	2.0	6.2
22	**2** (1.0)	MAO 5.0 (5.0)	189	1130	5.31	2.1	6.3
23[f]	**2** (1.0)	MAO 5.0 (5.0)	91	546	2.43	2.5	7.0
24[g]	**2** (1.0)	MAO 5.0 (5.0)	283	849	5.63	2.0	6.2
25	**2** (1.0)	MAO 6.0 (6.0)	169	1010	5.06	2.1	6.5
26	**2** (1.0)	MAO 7.0 (7.0)	161	966	4.82	2.1	6.4
27	**2** (1.0)	MMAO-3AT 5.0 (5.0)	57	342	2.98	2.0	7.1
28	**2** (1.0)	MMAO-3AH 5.0 (5.0)	57	342	2.78	2.2	6.1
29[h]	**2** (1.0)	MMAO-3BH 5.0 (5.0)	32	64	1.66	2.1	6.0

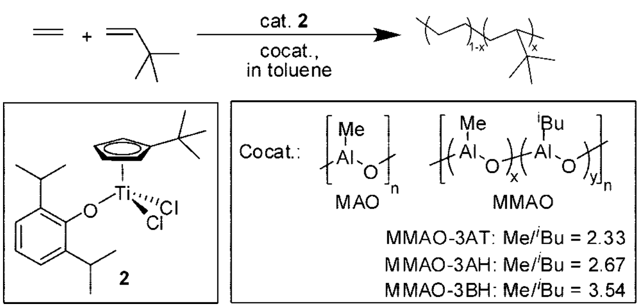
[a] Conditions: ethylene, 2 atm; TBE, 5.0 mL (3.9 M); toluene, 5.0 mL (total volume, 10.0 mL); 25 °C; 10 min. [b] Methylaluminoxane (MAO) or modified methylaluminoxane (MMAO, methyl isobutyl alumioxane) prepared by removing toluene and $AlMe_3$ (and/or $Al(^iBu)_3$) from ordinary MAO or MMAO, MMAO-3AT ($Me/^iBu$= 2.33), MMAO-3AH ($Me/^iBu$= 2.67), MMAO-3BH ($Me/^iBu$= 3.54). [c] Activity = kg-polymer/mol-Ti•h. [d] Estimated by GPC in *o*-dichlorobenzene vs polystyrene standards. [e] Comonomer content estimated by ^{13}C NMR spectra. [f] Polymerization at 40 °C. [g] Polymerization for 20 min. [h] Polymerization for 30 min.

Table 4. Copolymerization of Ethylene with *tert*-Butylethylene (TBE) Using $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ [Cp′ = Cp* (1), $^tBuC_5H_4$ (2), 1,2,4-$Me_3C_5H_2$ (6)], $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp (3), Cp* (7), $^tBuC_5H_4$ (8)], $[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (4), and Cp_2ZrCl_2 (5) Catalyst Systems with MAO[a]

run	complex (μmol)	yield (mg)	activity[b]	M_n[c] × 10^{-4} (g mol^{-1})	M_w/M_n[c]	content[d] (mol %)	T_m (T_g)[e] (°C)
30	$Cp^*TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**1**) (0.2)	96	2880	20.4	2.0	1.7	*f*
22	$(^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2**) (1.0)	189	1130	5.31	2.1	6.3	83 (−31)
31	$(1,2,4\text{-}Me_3C_5H_2)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**6**) (1.0)	153	918	5.76	2.1	8.0	74 (−34)
32	$CpTiCl_2(N{=}C^tBu_2)$ (**3**) (0.4)	125	1880	13.9	1.9	trace	*f*
33	$Cp^*TiCl_2(N{=}C^tBu_2)$ (**7**) (0.4)	142	2130	15.7	2.0	none	*f*
34	$(^tBuC_5H_4)TiCl_2(N{=}C^tBu_2)$ (**8**) (0.4)	188	2820	19.7	2.2	none	*f*
35	$[Me_2Si(C_5Me_4)(N^tBu)]TiCl_2$ (**4**) (1.0)	198	1190	11.9	2.1	none	*f*
36	Cp_2ZrCl_2 (**5**) (0.02)	81	24300	56.3	2.4	none	*f*

[a] Conditions: ethylene, 2 atm; TEB, 5.0 mL (3.9 M); toluene, 5.0 mL (total volume, 10.0 mL); dried MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 5.0 mmol; 25 °C; 10 min. [b] Activity = kg-polymer/mol-Ti•h. [c] Estimated by GPC in *o*-dichlorobenzene vs polystyrene standards. [d] Comonomer content estimated by ^{13}C NMR spectra. [e] Determined by DSC analysis. [f] No measurement.

Scheme 2. Copolymerization of Ethylene with *tert*-Butylethylene (TBE) by $(^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (2) in the Presence of Various Cocatalysts



the ^{t}Bu- and 1,2,4-Me_3-substituted derivatives (**2** and **6**) were discerned to be the best to bring about efficient TBE incorporation, affording high molecular weight poly(ethylene-*co*-TBE)s with unimodal molecular weight distribution. On the other hand, the TBE content of copolymers prepared by the Cp* aryloxo analogue (**1**), under the same conditions, was quite low (run 30), thus evincing the fact that the nature of cyclopentadienyl ligand strongly effects the catalytic activity as well as the comonomer enchainment in the ethylene/TBE copolymerization. However, no TBE incorporation was observed with the Cp′-ketimide-containing catalyst precursors (**3**, **7**, and **8**; run 32−34). These findings demonstrate the vital significance of anionic ancillary donor ligand (X) of $Cp'TiCl_2(X)$ (X = $O\text{-}2,6\text{-}^iPr_2C_6H_3$, $N{=}C^tBu_2$) for the efficient comonomer enchainment, and only the aryloxo-carrying half-titanocenes (**1**, **2**, and **6**) displayed the potential to incorporate TBE in the ethylene/TBE copolymerization as witnessed in the ethylene/cyclohexene copolymerization.[5] Moreover, the comparison with both the constrained geometry catalyst (**4**) and zirconocene (**5**) revealed no TBE incorporation under the same polymerization conditions (runs 35 and 36).

Copolymerization of 1-Hexene with *tert*-Butylethylene and Vinyltrimethylsilane. As indicated by the findings in the present contribution as well as in the previous communication,[10] the reactivity of TBE in ethylene copolymerization was rather low compared with that of VTMS (Table 1), and the difference in reactivity can be ascribed to the presence of Si atom in the latter or *vice versa*. There may be two plausible explanations for the observed difference: (i) steric and/or electronic factors ($CH_2{=}CHSiMe_3$ is relatively less crowded than $CH_2{=}CH^tBu$) leading to the difference in coordination energy, (ii) a possibility of 2,1- rather than 1,2-insertion of VTMS, as has been reported before.[17]

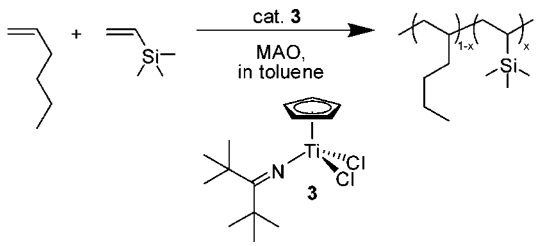
To gain a clear piece of information about the mode of insertion and hence to discern the difference in comonomer reactivity, attempts were made to execute copolymerization of 1-hexene (1-Hex) with TBE and VTMS by half-titanocene (**2**, **3**) catalyst systems with MAO, and results are shown in Table 5. The 1-Hex/TBE copolymerization by $(^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$ (**2**), the catalyst precursor revealed to bring about efficient TBE enchainment in ethylene/TBE copolymerization, proceeded with relatively low catalytic activity (29 kg of polymer/mol of Ti•h) and negligible TBE incorporation (run 37). The half-titanocene bearing aryloxo group as an anionic ancillary donor ligand (**2**) showed quite low catalytic activity in 1-Hex/VTMS copolymerization.[18] Nevertheless, the Cp−ketimide analogue (**3**), reported to exhibit high catalytic activity and notable comonomer incorporation in ethylene/VTMS copolymerization, displayed low catalytic activity (5.8 kg of polymer/mol of Ti•h) but very efficient VTMS enchainment (≈47 mol %). As shown in Scheme 3, the obtained polymer was poly(1-hexene-*co*-VTMS) with high VTMS content and uniform composition as confirmed by the NMR spectra and unimodal

Table 5. Copolymerization of 1-Hexene (1-Hex) with *tert*-Butylethylene (TBE) and Vinyltrimethylsilane (VTMS) and Homopolymerization of Vinyltrimethylsilane (VTMS) Using (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (2) and CpTiCl$_2$(*N*=C^{t}Bu$_2$) (3) Catalyst Systems with MAO[a]

run	complex (μmol)	monomer (mL)	comonomer (mL)	yield (mg)	activity[b]	M_n[c] × 10^{-4} (g mol^{-1})	M_w/M_n[c]	content[d] (mol %)
37	(**2**) (10.0)	1-Hex (1.0)	TBE (9.0)	144	29	5.45	1.86	none
38	(**3**) (10.0)	1-Hex (2.5)	VTMS (2.5)	29	5.8	0.46	1.40	47
39	(**3**) (10.0)	1-Hex (4.0)	VTMS (1.0)	100	20	1.03	1.62	8.5
40[e]	(**3**) (10.0)	VTMS (2.5)		26	2.6	0.34	1.44	

[a] Conditions: total volume = 11.0 mL (run 37), 6.0 mL (run 38), 6.0 mL (run 39) 3.5 mL (run 40); dried MAO (prepared by removing toluene and AlMe$_3$ from ordinary MAO), 3.0 mmol; 25 °C; 30 min. [b] Activity = kg-polymer/mol-Ti·h. [c] Estimated by GPC in THF vs polystyrene standards. [d] Comonomer content estimated by ^{13}C NMR spectra. [e] Polymerization for 60 min.

Scheme 3. Copolymerization of 1-Hexene (1-Hex) with Vinyltrimethylsilane (VTMS) by CpTiCl$_2$(N=C^{t}Bu$_2$) (3) Catalyst System with MAO



GPC profiles.[14] An appreciably high VTMS enchainment in 1-Hex/VTMS copolymerization suggests that VTMS incorporation proceeded via 1,2-insertion. The catalytic activity of **3**-MAO catalyst system and VTMS content of copolymers were dependent upon the 1-Hex/VTMS ratio in the copolymerization system (run 38 and 39). Moreover, homopolymerization of VTMS has been accomplished by **3**-MAO catalyst system yielding poly(VTMS) with uniform molecular weight distribution (M_n, 3400 g mol^{-1}; M_w/M_n, 1.44) in low yield (catalyst activity, 2.6 kg of polymer/mol of Ti·h), whereas low monomer reactivity and/or low catalytic activity did not allow the formation of poly(TBE) by using **2**-MAO catalyst system.[16]

As demonstrated above, the efficient VTMS incorporation in 1-Hex/VTMS copolymerization furnishes a clear evidence for 1,2-insertion of VTMS thus excluding the possibility of the latter speculation (2,1-insertion). Therefore, higher reactivity of VTMS than that of TBE in ethylene and 1-hexene copolymerization can be concluded to ensue from the difference in the electronic and/or steric nature of Si and C. In other words, higher coordination energy of VTMS [defined as the difference in energy between the optimized π-complex and the cationic complex and the monomer, namely $\Delta E_{\text{coord}} = (E_{\text{cation}} + E_{\text{monomer}}) - E_{\pi\text{-complex}}$], estimated on the basis of simple PM3 calculations, has most probably led to better VTMS incorporation than that of TBE.[19]

Concluding Remarks

The present study is concerned with the copolymerization of ethylene with an α-olefin carrying a bulky substituent in the vicinity of the double bond, and deciphers the ability of aryloxo-containing half-titanocenes to mediate efficient comonomer incorporation in the ethylene/TBE copolymerization. A series of half-titanocenes [Cp′TiCl$_2$X {X = O-2,6-^{i}Pr$_2$C$_6$H$_3$ (Cp′ = Cp*, **1**; ^{t}BuC$_5$H$_4$, **2**; 1,2,4-Me$_3$C$_5$H$_2$, **6**; N=C^{t}Bu$_2$ (Cp′ = Cp, **3**; Cp*, **7**; ^{t}BuCp, **8**)}], a constrained geometry catalyst (linked half-titanocene) [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**4**), and zirconocene [Cp$_2$ZrCl$_2$] (**5**) were used as catalyst precursors in the presence of MAO as a cocatalyst. The Cp*−aryloxo complex (**1**) exhibited low TBE incorporation, while employing its *tert*-butyl and trimethyl-substituted analogues (**2**, **6**) entailed a considerable enhancement in the enchained TBE content, demonstrating the significance of the structural attributes of the cyclopentadienyl moiety. The Cp−ketimide complex (**3**), which has been discerned to be the best catalyst precursor for the ethylene copolymerization of a structurally related comonomer (VTMS), could incorporate TBE in trace amount and the use of its Cp* (**7**) and ^{t}BuCp (**8**) derivatives led to virtually zero TBE content, thus revealing the crucial role played by the anionic ancillary donor ligand. Nonetheless, employing the constrained geometry catalyst (**4**) and zirconocene (**5**) under the same conditions could result in polyethylene formation without TBE enchainment. Moreover, the accomplishment of considerably high VTMS incorporation in 1-Hex/VTMS copolymerization by CpTiCl$_2$(N=C^{t}Bu$_2$)−MAO catalyst system has suggested VTMS insertion to be proceeding in a 1,2- rather than 2,1-mode. The higher reactivity of VTMS in ethylene as well as in 1-hexene copolymerization has been ascribed to the higher coordination energy of VTMS than that of TBE, most presumably attributable to the steric and/or electronic differences.

Experimental Section

Materials and General Procedure. All manipulations were performed under a dry and oxygen-free nitrogen atmosphere in a Vacuum Atmospheres drybox, unless otherwise specified. *tert*-Butylethylene (TBE, TCI), vinyltrimethylsilane (VTMS, Aldrich), and 1-hexene (1-Hex, Wako) of reagent grade, and anhydrous grade toluene (Kanto Chemical Co., Inc.) were passed through a short alumina column, and stored over molecular sieves (mixture of 3A 1/16, 4A 1/8, and 13X 1/16) in the drybox. The polymerization grade ethylene (purity >99.9%, Sumitomo Seika Co. Ltd.) was used as received without further purification. The commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] was purified by stripping the toluene and AlMe$_3$ under reduced pressure (at ca. 50 °C for removing toluene and AlMe$_3$, and then heated at >100 °C for 1 h for complete drying) in the drybox to afford white solid. Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**),[20] (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**2**),[20] CpTiCl$_2$(N=C^{t}Bu) (**3**),[21] [Me$_2$Si(C$_5$Me$_4$)(N^{t}Bu)]TiCl$_2$ (**4**),[22] (1,2,4-Me$_3$C$_5$H$_2$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**6**),[4b] Cp*TiCl$_2$(N=C^{t}Bu) (**7**),[21] and (^{t}BuC$_5$H$_4$)TiCl$_2$(N=C^{t}Bu) (**8**)[23] were synthesized according to the literature. The Cp$_2$ZrCl$_2$ (**5**) (Wako Pure Chemical. Ind., Ltd.) was used as received. The deuterated NMR solvents (CIL) were stored over molecular sieves under the nitrogen atmosphere.

The weight-average molecular weight (M_w), number-average molecular weight (M_n), and molecular weight distribution (M_w/M_n) of ethylene copolymers were measured by means of gel permeation chromatography on TOSOH HLC-8121GPC/HT using an RI-8022 detector with a polystyrene gel column (TSK gel GMH$_{HR}$-H HT × 2; 30 cm × 7.8 mm Φ ID; MW range from >10^2 to <2.8 × 10^8) at 140 °C using *o*-dichlorobenzene, containing 0.05% w/v 2,6-di-*tert*-butyl-*p*-cresol, as an eluent. On the other hand, the M_w, M_n, and M_w/M_n for 1-hexene copolymers (runs 37, 38) and poly(VTMS) were estimated by GPC on a Shimadzu SCL-10A using an RID-10A detector with the polystyrene gel columns (ShimPAC GPC-806, 804 and 802; 30 cm × 8.0 mm) at 40 °C in HPLC grade THF, containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, at a flow rate of 1.0 mL/min. The elution times were converted into molecular weights using the calibration curve based on polystyrene standards, in combination with the information obtained from the refractive index detector.

The ^{1}H and ^{13}C NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (^{1}H, 399.65 MHz and ^{13}C 100.40 MHz), and the residual proton or carbon signal of the deutrated solvent was used as an internal standard. The samples for the NMR measurements were prepared at the concentration of 15 mg/mL in a mixed solvent of 1,2,4-trichlorobenzene/benzene-d_6 (90/10 wt %), and chemical shifts are given in ppm. The spectra for ethylene copolymers were recorded at 110 °C, while those for 1-hexene copolymers and poly(VTMS) were measured at room temperature (~22 °C). For the ^{1}H NMR spectra of ethylene copolymers, the number of transients accumulated was ca. 64 (pulse delay, 10 s; acquisition time, 2.7 s; pulse angle, 90°), whereas for the ^{13}C NMR spectra ca. 6000 scans were accumulated with proton decoupling (pulse delay, 5.2 s; acquisition time, 1.3 s; pulse angle, 90°). However, for 1-hexene copolymers and poly(VTMS) the number of transients accumulated for the ^{1}H NMR spectra was ca. 8 (pulse delay, 10 s; acquisition time, 2.7 s; pulse angle, 90°), while ca.16 000 scans were accumulated with proton decoupling for the ^{13}C NMR spectra (pulse delay, 1.0 s; acquisition time, 1.3 s; pulse angle, 45°).

Differential scanning calorimetric (DSC) analyses were performed on a Seiko DSC6200/EXSTAR6000 apparatus, and measurements were carried out by using 3−6 mg samples, under N_2 atmosphere. The samples were first heated from ambient temperature (~25 °C) to 200 °C at the scanning rate of 20 °C min^{-1} (first heating scan) and then quenched to −150 °C at the rate of 20 °C min^{-1}. The second heating scans were run from −150 to +200 °C at the scanning rate of 20 °C min^{-1} to record stable thermograms. The data for glass transition temperature (T_g) were obtained from the second run and correspond to the midpoint of discontinuity in the heat flow.

Copolymerization of Ethylene with *tert*-Butylethylene. A typical procedure for ethylene/TBE copolymerization (Table 2, run 14) is as follows. d-MAO (174 mg, 3.0 mmol), TBE (5.0 mL), and toluene (4.0 mL) were charged into a stainless steel autoclave (100 mL scale) in the drybox. The apparatus was moved out of the drybox and purged with ethylene. The reaction mixture was then pressurized to 1 atm (total ethylene pressure 2 atm) immediately after the addition of toluene solution (1.0 mL) containing **2** (1.0 μmol), and was magnetically stirred for 10 min. The remaining ethylene was purged after the reaction along with cooling in the ice bath, and the mixture was poured into methanol (50 mL) containing HCl (5 mL). The resulting polymer was collected by filtration after being thoroughly washed with methanol, and was dried *in vacuo* at 60 °C for several hours. The copolymerization of ethylene with vinyltrimethylsilane (VTMS) was conducted in the same way as that for ethylene/TBE, except that VTMS was charged into the autoclave in place of TBE.[10]

The comonomer (TBE/VTMS) content and the monomer sequence distribution in the copolymers were estimated by the ^{13}C NMR spectra, and each resonance was assigned by the DEPT analysis. The TBE/VTMS contents were estimated on the basis of the integration ratio of the signals arising from TBE/VTMS to those ascribed to ethylene, in the ^{13}C NMR spectra.

Copolymerization of 1-Hexene with *tert*-Butylethylene. d-MAO (174 mg, 3.0 mmol), 1-Hex (1.0 mL), and TBE (9.0 mL) were charged into a Schlenk flask (100 mL) in the drybox, and the reaction mixture was magnetically stirred for 10 min. immediately following the addition of toluene solution (1.0 mL) containing **2** (10.0 μmol). The reaction mixture was poured into HCl (5 mL)-containing methanol (20 mL), and stirred for a few minutes. $CHCl_3$ (25 mL) was added and stirring was continued. The polymer was collected by solvent extraction after adding water (5 mL) into the mixture, and was dried *in vacuo* at 60 °C for several hours.

The copolymerization of 1-hexene (1-Hex) with vinyltrimethylsilane (VTMS) was carried out in the same way, but VTMS was charged into the Schlenk flask instead of TBE. The TBE/VTMS contents were estimated on the basis of the integration ratio of the signals arising from TBE/VTMS to those assignable to 1-Hex, in the ^{13}C NMR spectra. The homopolymerization of VTMS (run 40) was carried out by following the same procedure as described above, but without the addition of 1-Hex.

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Supporting Information Available: Figures showing selected ^{1}H and ^{13}C NMR spectra, GPC profiles, and DSC thermograms of poly(ethylene-*co*-TBE)s, and ^{13}C NMR spectra of the polymers resulting from the copolymerization of 1-Hex with TBE/VTMS and poly(VTMS). This material is available free of charge via the Internet at http://pubs.acs.org.

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(14) The ^1H and ^{13}C NMR spectra, GPC profiles, and DSC thermograms of selected poly(ethylene-*co*-TBE)s, and ^{13}C NMR spectra of the polymers resulting from the copolymerization of 1-hexene with TBE/VTMS are shown in the Supporting Information.

(15) The DSC thermograms of poly(ethylene-*co*-TBE)s prepared by **6**-MAO catalyst system exhibited two melting temperatures, first one corresponding to the copolymer (run 18, $T_m \approx 76$ °C; run 31, $T_m \approx 74$ °C) and the second indicating the presence of polyethylene (run 18, 31; $T_m \approx 125$ °C).[14] These observations suggest that the partial decomposition of the active species in the polymerization system might have led to the generation of two catalytically active species.

(16) The homopolymerization of TBE by **2**, used as a catalyst precursor, could not yield polymer most likely due to very low catalytic activity under quite high TBE concentration. [Conditions: TBE, 8.0 mL; **2**, 10 μmol; total volume, 10 mL; dried MAO (prepared by removing toluene and $AlMe_3$ from ordinary MAO), 3.0 mmol; 25 °C; 60 min.]

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