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Ethylene/Styrene Copolymerization by $(Me_3SiC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2\text{-}4\text{-}RC_6H_2)$ (R = H, $SiEt_3$)-MAO Catalysts: Effect of $SiMe_3$ Group on Cp for Efficient Styrene Incorporation

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Abstract: Synthesis and structural analysis of $(Me_3SiC_5H_4)TiCl_2(OAr)$ [OAr = O-2,6-${}^iPr_2$-4-RC_6H_2; R = H, $SiEt_3$] that exhibit higher catalytic activities than $({}^tBuC_5H_4)TiCl_2(OAr)$, $Cp^*TiCl_2(OAr)$ with efficient comonomer incorporation in the ethylene/styrene copolymerization in the presence of methylaluminoxane (MAO) cocatalyst. The catalytic activity in the copolymerization increased upon increasing the styrene concentration charged along with increase in the styrene content in the copolymers, whereas the activities by other catalysts showed the opposite trend. $(Me_3SiC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ displayed the most suitable catalyst performance in terms of the activity and the styrene incorporation to afford the amorphous copolymers with styrene contents higher than 50 mol% (up to 63.6 mol%) with random styrene incorporation confirmed by ^{13}C-NMR spectra.

Keywords: titanium; catalyst; homogeneous catalyst; copolymerization; half-titanocene; ethylene; styrene; ligand effect; cyclopentadienyl

1. Introduction

Olefin coordination polymerization using transition metal catalysts is the core technology for production of polyolefins, and development of new polymeric materials, especially copolymers consisting of ethylene or propylene with monomers which have never been used by the conventional catalysts (Ziegler-Natta, metallocene catalysts etc.) is a long-term interest in this research field. The catalyst development has been considered to play an important key role for the success [1–10]. Ethylene copolymers with aromatic vinyl monomers exemplified as ethylene/styrene copolymers are known to be interesting materials which can be modified their thermo-mechanical and viscoelastic properties by incorporation of the comonomer (styrene) [11]. Half-titanocene complexes [5–9,11–28] have been known as the efficient catalysts in terms of better capability of styrene incorporation than ordinary metallocene catalysts [11,29,30].

Linked (*ansa*) half-titanocenes (called "constrained geometry type") [5–7,12–19], certain *ansa*-metallocenes [29,30], and nonbridged modified half-titanocenes (exemplified in Scheme 1) [20–28] are known to be the effective transition metal catalysts in the copolymerization [11]. In particular, the bimetallic linked half-titanocene, $(CH_2CH_2)[Me_2Si(indenyl)(N{}^tBu)TiMe_2]_2$ [17,19], and the phenoxide-modified half-titanocenes, $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp' = ${}^tBuC_5H_4$ (**3**), 1,2,4-$Me_3C_5H_2$] [20,21], have been recognized as the effective catalysts in terms of synthesis of the copolymers with high styrene contents (>50 mol%) [17,19–21]. The resultant copolymers with high styrene contents (ca. >30 mol%) are amorphous and the glass transition temperature (T_g) increased upon increase in the styrene content (shown below).[21] However, as described above, the catalysts affording the copolymers with high styrene contents (especially >50 mol%) still have been limited. Moreover, these phenoxide modified catalysts (shown above) also exhibited remarkable catalytic activities for syndiospecific

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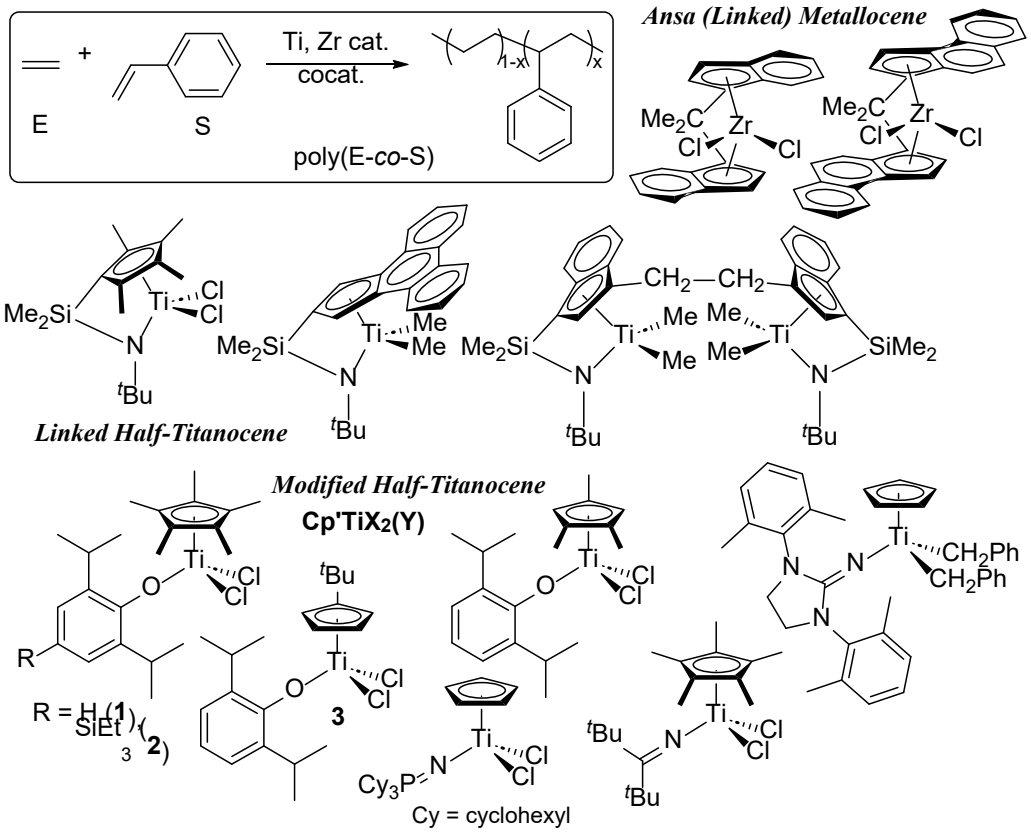
styrene polymerization [20,31], whereas the bimetallic linked half-titanocene gave the atactic polystyrene [17]. In contrast, the C_5Me_5 (Cp*) analogues, Cp*$TiCl_2$(O-2,6-^{i}Pr$_2$-4-RC_6H_2) [R = H (**1**), $SiEt_3$ (**2**), Scheme 1], exhibited remarkable catalytic activities for the ethylene copolymerization with α-olefins [3,8,9]; the $SiEt_3$ analogue (**2**) was effective for the ethylene copolymerization with alken-1-ol [32]. These results also suggest that the modification of the cyclopentadienyl fragment play a role to be the efficient catalysts for the desired ethylene copolymerization [3,8,9]; an introduction of $SiEt_3$ group would lead to the higher activity by better π-donation [32].



Scheme 1. Selected titanium, zirconium catalysts for ethylene/styrene copolymerization.

In this paper, we focused on the phenoxide modified half-titanocene catalysts for the ethylene/styrene copolymerization. We recently realized that the complexes containing trimethylsilyl-cyclopentadienyl ligand, ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$), showed better catalyst performance than the *tert*-BuC_5H_4 analogue (**3**) [20,21] in the copolymerization. We thus herein report our results concerning syntheses of ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr$_2$-4-RC_6H_2) [R = H (**5**), $SiEt_3$ (**6**)] and their uses as the catalysts for the ethylene/styrene copolymerization in the presence of methylaluminoxane (MAO) cocatalyst (Scheme 2).

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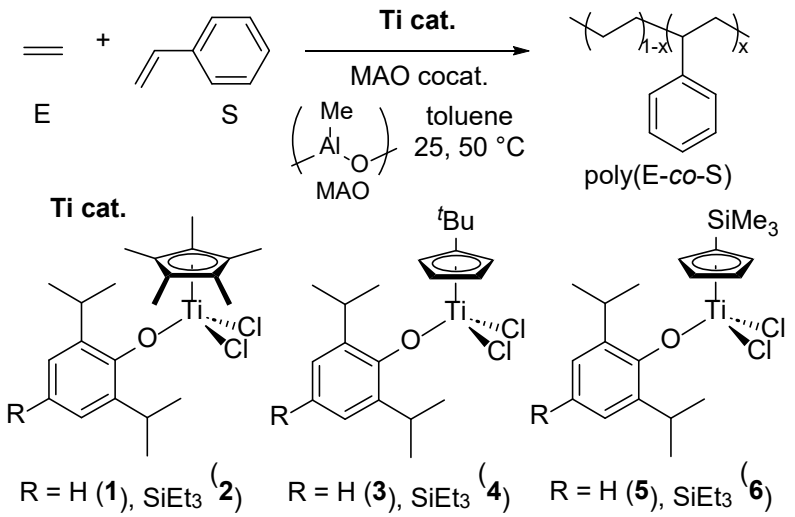

Scheme 2. Ethylene/styrene copolymerization by the phenoxide-modified half-titanocene catalysts.

2. Results and Discussion

2.1. Synthesis and Structural Analysis of (Me3SiC5H4)TiCl2(O-2,6-iPr2-4-RC6H2) (R = H, SiEt3).

The phenoxide modified half-titanocenes containing $Me_3SiC_5H_4$ ligand, $(Me_3SiC_5H_4)TiCl_2$(O-2,6-^{i}Pr$_2$-4-RC_6H_2) [R = H (**5**), $SiEt_3$ (**6**)] were prepared according to the previous report by treating $(Me_3SiC_5H_4)TiCl_3$ [33,34] with Li(O-2,6-^{i}Pr$_2$C$_6$H$_3$) or 2,6-^{i}Pr$_2$-4-$SiEt_3$-C_6H_2OH (in the presence of NEt_3) in diethyl ether. (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$-4-$SiEt_3$-C_6H_2) (**4**) was also prepared in the same manner (as described in Experimental section). These complexes were identified by NMR spectra and elemental analysis, and the structures for **5** and **6** were determined by X-ray crystallography (Figure 1, CCDC 2378274, 2378275, table for the crystal data and the collection parameters are shown in the Supplementary Material). Selected bond distances and the angles are summarized in Table 1. The data for Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$-4-RC_6H_2) [R = H (**1**) [35], $SiEt_3$ (**2**) [32]], and CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**7**) [35] are placed for comparison.

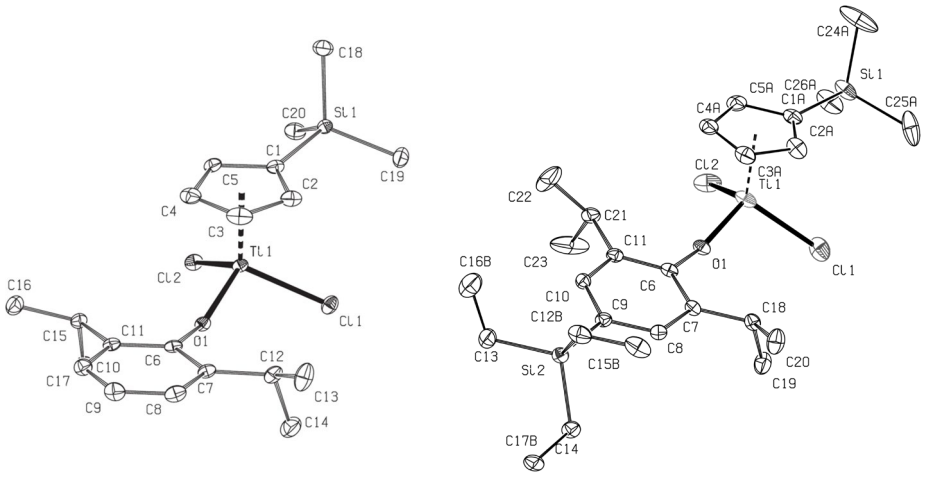

Figure 1. ORTEP drawings for $(Me_3SiC_5H_4)TiCl_2$(O-2,6-^{i}Pr$_2$-4-RC_6H_2) [R = H (**5**, left), $SiEt_3$ (**6**, right)]. Thermal ellipsoids are drawn at 30 % probability level, and the hydrogen atoms were omitted for clarity. Additional data including crystal data and collection parameters for structural analysis are shown in the Supplementary Material.

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Table 1. Selected bond distances (Å) and angles (º) in ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr_2-4-RC_6H_2) [R = H (**5**), $SiEt_3$ (**6**)],[a] and Cp*$TiCl_2$(O-2,6-^{i}Pr_2-4-RC_6H_2) [R = H (**1**) [35], $SiEt_3$ (**2**) [32]], Cp$TiCl_2$(O-2,6-^{i}$Pr_2C_6H_3$) (**7**) [35].[a]

	1[b]	**2**[c]	**5**	**6**	**7**[b]
			Bond Distances (Å)		
Ti(1)–Cl(1)	2.305(2)	2.2723(9)	2.2660(5)	2.2721(15)	2.262(1)
Ti(1)–Cl(2)	2.239(2)	2.2677(8)	2.2730(5)	2.2534(14)	2.262(1)
Ti(1)–O(1)	1.772(3)	1.7965(19)	1.7829(13)	1.773(2)	1.760(4)
Si(1)–C(1)	--	1.875(3)	1.876(2)	1.864(7)	--
O(1)–C(6)	1.367(5)	1.363(3)	1.373(2)	1.375(4)	1.368(4)
Ti(1)–C(1)	2.365(7)	2.403(3)	2.3678(17)	2.373(13)	2.282(8)
Ti(1)–C(2)	2.438(7)	2.411(3)	2.3854(19)	2.323(9)	2.299(5)
Ti(1)–C(3)	2.365(7)	2.359(3)	2.348(2)	2.325(8)	2.235(5)
Ti(1)–C(4)	2.311(7)	2.345(3)	2.335(2)	2.390(6)	2.235(5)
Ti(1)–C(5)	2.317(4)	2.357(3)	2.330(2)	2.398(8)	2.299(5)
			Bond Angles (º)		
Cl(1)–Ti(1)–Cl(2)	103.45(5)	102.33(3)	105.11(2)	103.74(5)	104.23(7)
Cl(1)–Ti(1)–O(1)	99.1(2)	100.97(7)	102.92(4)	102.31(10)	102.53(9)
Cl(2)–Ti(1)–O(1)	104.1(2)	103.24(7)	102.52(4)	103.04(9)	102.53(9)
Ti(1)–O(1)–C(6)	173.0(3)	174.62(19)	151.41(12)	157.0(2)	163.0(4)

[a] CCDC2378274 (complex **5**), CCDC2378275 (complex **6**) contain the supplementary crystallographic data in detail. [b] Cited from reference [35]. [c] Cited from reference [32].

The analyses revealed that these complexes fold a distorted tetrahedral geometry around titanium and no significant differences are observed in Ti–Cl, Ti–O, and O–C(phenyl) bond distances among these complexes. It seems that Ti–C(1) and Ti–C(2) in **5** [2.3678(17), 2.3854(19) Å] and Ti–C(4) and Ti–C(5) in **6** [2.390(6), 2.398(8) Å] are rather longer than the others in the cyclopentadienyl ligands, and these results might lead to an assumption that cyclopentadienyl group would be coordinated as η^3-fashion. However, these phenomena were also seen in complexes **1** [2.438(7) Å in Ti–C(2)] [35] and **2** [2.403(3), 2.411(3) Å in Ti–C(1) and Ti–C(2)] [32], even in **7** [2.299(5) Å in Ti–C(2) and Ti–C(5)] [35]. Therefore, it seems more likely that the observed fact could be probably due to the crystal packing in the crystallographic analysis. It was revealed that the Ti(1)–O(1)–C(6 in phenyl) angles in **5** [151.41(12)º] and **6** [157.0(2)º] are apparently smaller than those in **1** and **2** [173.0(3), 174.62(19)º, respectively] [32,35], and **7** [163.0(4)º] [35], suggesting that these complexes (**5**,**6**) showed inferior π-donation capability from the phenoxide ligand.

2.2. Ethylene/Styrene Copolymerization by Cp'$TiCl_2$(O-2,6-^{i}Pr_2-4-RC_6H_2) [Cp' = Cp, ^{t}BuC_5H_4, $Me_3SiC_5H_4$, R = H, $SiEt_3$]–MAO Catalyst Systems*

Table 2 summarizes the results in the ethylene/styrene copolymerization using a series of phenoxide modified half-titanocene catalysts, Cp'$TiCl_2$(O-2,6-^{i}Pr_2-4-RC_6H_2) [Cp' = Cp*, R = H (**1**), $SiEt_3$ (**2**); Cp' = ^{t}BuC_5H_4, R = H (**3**), $SiEt_3$ (**4**); Cp' = $Me_3SiC_5H_4$, R = H (**5**), $SiEt_3$ (**6**)], in the presence of MAO cocatalyst. MAO was used as the white solid (d-MAO) after removal of $AlMe_3$ and toluene from the commercially available samples [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.], because use of this MAO is quite effective for obtainment of high molar mass polymers efficiently as conducted in the previous reports [8,9,20,21,28,32,35]. The resultant polymers usually contained atactic polystyrene generated by MAO itself, and the polymer yields were described after removal of atactic polystyrene by extraction with acetone (see Experimental). As shown in Table 2, the contents (atactic polystyrene) were negligible in most cases (>99%), except when the copolymerization runs were conducted by the Cp* analogues (**1**,**2**) under high initial styrene concentrations (runs 2-6) due to low catalytic activities (low copolymer yields).

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Table 2. Ethylene copolymerization with styrene (St) by Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$-4-RC$_6$H$_2$) [Cp′ = Cp*, R = H (**1**), SiEt$_3$ (**2**); Cp′ = ^{t}BuC$_5$H$_4$, R = H (**3**), SiEt$_3$ (**4**); Cp′ = Me$_3$SiC$_5$H$_4$, R = H (**5**), SiEt$_3$ (**6**)]–MAO catalyst systems (ethylene 4atm, 20 ºC, 10 min). [a]

run	cat.	St / mL	yield[b] / mg	activity[b]	THF soluble fraction				
					cont.[c]/ wt.%	M_n[d]×10^{-4}	M_w/M_n[d]	T_g[e]/ ºC	St[f]/ mol%
1	**1**	3	60.0	720	97	16.7	1.66	-18.5	18.8
2	**1**	5	50.6	610	90	13.5	1.32	-6.6	27.5
3	**1**	10	39.5	470	86	6.86	1.26	15.0	42.6
4	**2**	3	32.4	390	96	9.23	1.65	-15.3	20.6
5	**2**	5	23.5	280	95	9.91	1.41	-10.8	25.4
6	**2**	10	19.2	230	93	7.38	1.14	10.7	40.3
7	**3**	3	429	5150	>99	4.65	1.51	6.6	32.3
8	**3**	5	406	4870	>99	3.98	1.48	27.6	40.5
9	**3**	10	371	4450	>99	3.34	1.87	31.0	51.1
10	**4**	3	197	2360	>99	14.7	1.81	11.4	32.3
11	**4**	5	180	2160	>99	6.76	1.51	22.2	38.1
12	**4**	10	154	1850	>99	5.28	2.05	29.5	46.8
13	**5**	3	323	3880	>99	5.18	1.58	14.2	35.0
14	**5**	5	450	5400	>99	4.65	1.76	23.2	41.3
15	**5**	10	723	8680	>99	3.82	1.70	38.9	54.2
16	**6**	3	361	4330	>99	10.9	1.80	15.3	36.6
17	**6**	5	411	4930	98	12.8	1.79	30.9	44.9
18	**6**	10	506	6070	96	8.78	1.71	41.3	55.6

[a] Reaction conditions: catalyst 0.50 μmol, toluene and styrene total 30.0 mL, d-MAO 3.0 mmol, 20 ℃, ethylene 4 atm, 10min. [b] Activity in kg-polymer/mol-Ti·h, polymer yield in acetone insoluble and THF soluble fraction. [c] Percentage (wt%) in acetone insoluble and THF soluble fraction (after removal of atactic polystyrene). [d] GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [e] Glass transition temperature (T_g) measured by DSC thermograms. [f] Styrene content in mol% estimated by ^{1}H NMR spectra in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC.

As reported previously [20,21], the *tert*-BuC$_5$H$_4$ analogue (**3**) showed higher catalytic activities than the Cp* analogue (**1**), and the activity based on the polymer yield decreased upon increase in the initial styrene concentration charged along with decrease in the M_n values (runs 1-3 vs runs 7-9). The resultant copolymers are amorphous and possessed uniform compositions confirmed by DSC thermograms [observed as a sole glass transition temperature (T_g)]; their uniform compositions were also confirmed previously by GPC–FT-IR and the cross fractionation (CFC) analyses [21]. The T_g value increased with increasing the styrene content (estimated by ^{1}H NMR spectra according to the reported procedure) [20,21]. It was revealed that an introduction of SiEt$_3$ group into the *para*-position in the phenoxide led to decrease in the catalytic activities. The activities by **2** and **4** were lower than those by **1**, **3**, respectively, whereas no remarkable differences were observed in the molecular weight and the styrene contents in the copolymers. This is an opposite trend in the ethylene copolymerization with α-olefin, 2-methyl-1-pentene reported previously by **1** and **2** [32], although we are not sure the reason at this moment.

It should be noted that the Me$_3$SiC$_5$H$_4$ analogue (**5**) showed higher catalytic activity than the others (**1**-**4**), and the styrene contents in the copolymers were close to those conducted by the *tert*-BuC$_5$H$_4$ analogue (**3**) under the same conditions. Note that the activity by **5** increased upon increasing the styrene charged along with increase in the styrene content in the resultant copolymers (runs 13-15); the M_n value in the resultant copolymer decreased upon increase in the styrene content. Similarly to the observed trend by **2** and **4**, an introduction of SiEt$_3$ group into the *para*-position in the phenoxide (**6**) led to decrease in the catalytic activities (runs 16-18). As observed in the copolymerization by **5**, the activity by **6** also increased upon increasing the styrene concentration charged along with increase in the styrene content in the copolymers. It seems that the M_n values in the copolymers by **6** were higher than those prepared by **5**.

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Table 3 summarizes results in the ethylene/styrene copolymerization by **5**, **6** under various conditions (temperature, ethylene pressure). The activity by **5** was affected by ethylene pressure employed (runs 13,19, and 28), and increased upon increasing the ethylene pressure along with decrease in the styrene content in the resultant copolymer. Decrease in the catalyst concentration (0.50 → 0.30 μmol) did not affect the activity, the M_n values and the styrene content in the copolymers (runs 13-15, 20-22). The styrene content in the copolymer reached to 63.6 mol% when the copolymerization was conducted under high styrene and low ethylene concentration conditions (run 29). Unfortunately, the activities conducted at 50 ºC (runs 23-27) were low compared to those conducted at 20 ºC (runs 13-15), and the resultant copolymers possessed low M_n values compared to those conducted at 20 ºC. The similar trend was also observed in the copolymerization using **6**–MAO catalyst system (runs 30-33 *vs* runs 16-18), whereas the M_n values in the copolymer possessed higher than those prepared by **5** under the same conditions. As shown in Figure 2, a linear correlation between the T_g values with the styrene contents in the copolymer was observed, as seen in the previous report [11].

Table 3. Ethylene (E) copolymerization with styrene (St) by ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr$_2$-4-RC_6H_2) [R = H (**5**), $SiEt_3$ (**6**)]–MAO catalyst systems: Effect of ethylene pressure, styrene concentration and temperature.[a]

run	cat. (μmol)	E / atm	St /mL	temp. / ºC	yield[b] /mg	activity[b]	THF soluble fraction cont.[c]/ wt.%	M_n[d]×10^{-4}	M_w/M_n[d]	T_g[e]/ ºC	St[f]/ mol%
19	**5** (0.50)	6	3	20	556	6670	97	9.12	1.88	2.0	29.9
13	**5** (0.50)	4	3	20	323	3880	99	5.18	1.58	14.2	35.0
14	**5** (0.50)	4	5	20	450	5400	99	4.65	1.76	23.2	46.6
15	**5** (0.50)	4	10	20	723	8680	>99	3.82	1.70	38.9	54.2
20	**5** (0.30)	4	3	20	192	3840	>99	5.35	1.76	11.4	34.7
19	**5** (0.50)	6	3	20	556	6670	97	9.12	1.88	2.0	29.9
21	**5** (0.30)	4	5	20	223	4460	99	4.78	1.68	25.7	41.0
22	**5** (0.30)	4	10	20	264	5280	>99	4.04	1.80	40.2	54.3
23	**5** (0.50)	4	3	50	162	1940	97	2.24	1.61	18.1	38.9
24[g]	**5** (0.50)	4	3	50	110	1320	95	1.96	1.43	14.7	39.4
25[h]	**5** (0.50)	4	3	50	185	2220	97	2.48	1.43	17.4	40.6
26	**5** (0.50)	4	5	50	199	2390	90	1.46	1.70	29.3	50.0
27	**5** (0.50)	4	10	50	229	2750	86	1.08	1.63	40.6	56.5
28	**5** (0.50)	2	3	20	177	2120	>99	4.45	1.47	33.0	52.6
29	**5** (0.50)	2	10	20	243	2920	98	1.17	1.90	48.5	63.6
30	**6** (0.50)	6	3	20	349	7000	99	20.2	1.99	2.6	27.2
16	**6** (0.50)	4	3	20	361	4330	>99	10.9	1.80	15.3	36.6
17	**6** (0.50)	4	5	20	411	4930	98	12.8	1.79	30.9	44.9
18	**6** (0.50)	4	10	20	506	6070	96	8.78	1.71	41.3	55.6
31	**6** (0.50)	4	3	50	217	2610	96	3.84	1.64	18.1	38.8
32	**6** (0.50)	4	5	50	291	3490	96	3.18	2.04	32.7	46.6
33	**6** (0.50)	4	10	50	359	4310	83	2.95	2.04	44.7	55.1

[a] Reaction conditions: toluene and styrene total 30.0 mL, d-MAO 3.0 mmol, 10min. [b] Activity in kg-polymer/mol-Ti·h, polymer yield in acetone insoluble and THF soluble fraction. [c] Percentage (wt%) in acetone insoluble and THF soluble fraction (after removal of atactic polystyrene). [d] GPC data in *o*-dichlorobenzene *vs* polystyrene standards. [e] Glass transition temperature (T_g) measured by DSC thermograms. [f] Styrene content in mol% estimated by ^{1}H NMR spectra in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC. [g] MAO 1.0 mmol. [h] MAO 2.0 mmol.

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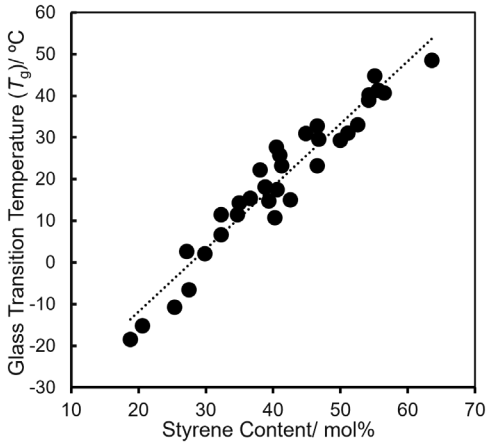

Figure 2. Plots of glass transition temperature (T_g/ ºC) versus styrene content (mol%) in the copolymer estimated by ^{1}H NMR spectra (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC).

Figure 3 shows typical ^{13}C NMR spectrum (in 1,1,2,2-tetrachloroethane-d_2 at 110 ºC) in the ethylene/styrene copolymer prepared by **5**–MAO catalyst system (run 13, styrene 35.0 mol%). As reported previously by catalysts **1** and **3** [11,20,21], the resonances corresponded to styrene head-to-tail incorporation in addition to SES or SS ($S_{\beta\beta}$, tail-to tail, called pseudo random) were observed in addition to resonances ascribed to isolated and alternating styrene incorporation (depicted in Figure 3). These results clearly suggest that the styrene incorporation was random in this catalysis. No significant differences in the spectra were observed in the resultant copolymers prepared by **6** (additional data are shown in the Supplementary Material).

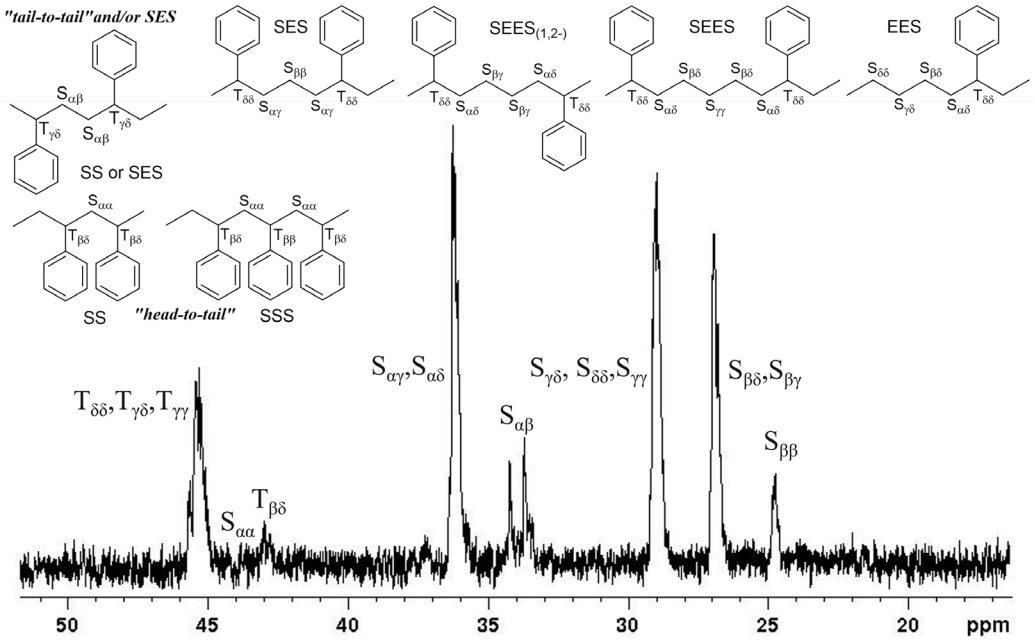

Figure 3. ^{13}C NMR spectrum (in $C_2D_2Cl_4$ at 110 ºC, methylene and methine region) of poly(ethylene-*co*-styrene) prepared by ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5**)–MAO catalyst system, styrene content 35.0 mol % (run 13).

3. Conclusions

We have demonstrated that newly prepared ($Me_3SiC_5H_4$)$TiCl_2$(OAr) [OAr = O-2,6-^{i}Pr$_2$-4-RC$_6$H$_2$; R = H (**5**), $SiEt_3$ (**6**)] exhibited the higher catalytic activities than (^{t}BuC$_5$H$_4$)$TiCl_2$(OAr), Cp*$TiCl_2$(OAr) with efficient comonomer incorporation in the ethylene/styrene copolymerization in the presence of

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MAO cocatalyst at 20 ºC. The catalytic activity in the copolymerization increased upon increasing the styrene concentration charged along with increase in the styrene content in the copolymers, whereas the activities by other catalysts showed the opposite trend. Catalyst **5** showed the most suitable catalyst performance in terms of the activity and the styrene incorporation to afford the amorphous copolymers containing styrene content higher than 50 mol% (up to 63.6 mol%) with random styrene incorporation. Unique characteristics observed in **5** should be helpful for further design of efficient molecular catalysts for synthesis of new polyolefins as well as should provide a new idea in the metal catalyzed polymerization of various monomers.

4. Materials and Methods

General. All experiments were conducted under a nitrogen atmosphere unless otherwise specified. Anhydrous grade toluene (Kanto Chemical Co., Inc.) containing a mixture of molecular sieves (3 Å 1/16 and 4 Å 1/8, and 13 × 1/16) was stored in a drybox, and styrene (Tokyo Chemical Industry Co., Ltd.) was stored under nitrogen in a freezer in the drybox and was passed an alumina short column before use. Ethylene (polymerization grade, purify >99.9%; Sumitomo Seika Co., Ltd.) was used as received. According to the previous reports [20,21,28,32,35], toluene and $AlMe_3$ in the commercially available MAO solution [TMAO-S, 9.5 wt% (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C and completion for 1 h at >100 °C) to afford $AlMe_3$-free MAO white solid (d-MAO) as the cocatalyst employed in this study. Cp′$TiCl_2$(O-2,6-^{i}Pr_2-C_6H_3) [Cp′=Cp* (**1**), ^{t}BuC_5H_4 (**3**)] [35], Cp*$TiCl_2$(O-2,6-^{i}Pr_2-4-$SiEt_3$-C_6H_2) (**2**) [32] were prepared according to previous reports.

All ^{1}H and ^{13}C NMR spectra were recorded on a Bruker AV500 spectrometer (500.13 MHz for ^{1}H, 125.77 MHz for ^{13}C), and chemical shifts are given in ppm and are referenced to $SiMe_4$. All spectra for analysis of titanium complexes were obtained in the solvent indicated at 25 ºC, and the resultant poly(ethylene-*co*-styrene)s were prepared by dissolving in 1,1,2,2-tetrachloroethane-d_2, and were measured at 110 °C. ^{13}C{^{1}H} NMR spectra (90° pulse angle) were measured with conditions of pulse interval, 5.2 s and acquisition time, 0.8 s; number of the transients in the analysis wase accumulated, ca. 6000. Gel-permeation chromatography (GPC) was performed to estimate the molecular weights (M_w, M_n) and their distributions, and the analysis was conducted by using Tosoh HLC-8321GPC/HT in *ortho*-dichlorobenzene (containing 0.05 wt% 2,6-di-*tert*-butyl-*p*-cresol) as eluent. The molecular weight was estimated with a calibration curve by using polystyrene standard samples. Thermal properties in the resultant poly(ethylene-*co*-styrene)s were analyzed by differential scanning calorimetric (DSC) thermograms (Hitachi DSC-7000X) under nitrogen atmosphere. The analysis of the copolymer sample was conducted upon heating from -100 to 250 °C at 20 °C/min, after preheating from 30 to 250 °C (20 °C/min) and cooling to -100°C (10 °C/min). In this heating scan, melting temperature (T_m) and glass transition temperature (T_g) were chosen from the middle of the phase transition.

Preparation of (^{t}BuC_5H_4)$TiCl_2$(O-2,6-^{i}Pr_2-4-$SiEt_3$-C_6H_2) (4). Et_2O solution (5.0 mL) containing 2,6-^{i}Pr_2-4-$SiEt_3$-C_6H_2OH (292 mg, 1.0 mmol) and Et_3N (152 mg, 1.5 mmol) was added into an Et_2O (20 mL) solution of (^{t}BuC_5H_4)$TiCl_3$ (233 mg, 0.85 mmol) in one portion at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et_2O. The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange oil. The resultant oil was then dissolved in a small amount of *n*-hexane. The chilled (−30 °C) solution in the freezer gave orange microcrystals (yield: 76%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (s, 2H, Ar-*H*), δ = 6.82 (t, 2H, *J* = 2.8 Hz, Cp-*H*), δ = 6.23 (t, 2H, *J* = 2.8 Hz, Cp-*H*), δ = 3.30-3.22 (m, 2H, Ar-C*H*(CH_3)$_2$), δ = 1.44 (s, 9H, Cp-C(C*H*$_3$)$_3$), δ = 1.23 (d, 12H, *J* = 6.9 Hz, Ar-CH(C*H*$_3$)$_2$), δ = 0.99 (t, 9H, *J* = 7.9 Hz, Ar-$SiCH_2$C*H*$_3$), δ = 0.78 (q, 6H, *J* = 7.9 Hz, Ar-Si*H*$_2$$CH_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 165.4, 151.4, 137.2, 133.3, 129.3, 119.3 (Aromatic group), δ = 34.2 (Cp-*C*(CH_3)$_3$), δ = 31.0 (Cp-C(*C*H$_3$)$_3$), δ = 27.0 (Ar-*C*H(CH_3)$_2$), δ = 23.9 (Ar-CH(*C*H$_3$)$_2$), δ = 7.66 (-$SiCH_2$*C*H$_3$), δ = 3.73 (-$SiCH_2$*C*H$_3$).

Preparation of ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr_2-C_6H_3) (5). Li(O-2,6-^{i}$Pr_2C_6H_3$) (221 mg, 1.2 mmol) was added in one portion to an Et_2O solution (30 mL) containing ($Me_3SiC_5H_4$)$TiCl_3$ (350 mg, 1.2 mmol) precooled at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred

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overnight. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et_2O. The combined filtrate and the wash were taken to dryness under reduced pressure to give orange solids. The resultant solids were then dissolved in a minimum amount of dichloromethane layered by a small amount of *n*-hexane. The chilled (−30 °C) solution in the freezer gave orange microcrystals (yield: 82%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = (d, 2H, *J* = 7.8 Hz, Ar-*H*), δ = (t, 1H, *J* = 7.2 Hz, Ar-*H*), δ = 7.04 (t, 2H, *J* = 1.9 Hz, Cp-*H*), δ = 6.40 (t, 2H, *J* = 2.2 Hz, Cp-*H*), δ = 3.27-3.19 (m, 2H, Ar-C*H*(CH_3)$_2$), δ = 1.23 (d, 12H, *J* = 6.8 Hz, Ar-CH(C*H*$_3$)$_2$), δ = 0.40 (s, 9H, Cp-Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 164.7, 138.3, 136.9, 127.9, 124.5, 123.5, 122.6 (Aromatic group), δ = 27.1 (Ar-CH(CH_3)$_2$), δ = 23.7 (Ar-CH(*C*H$_3$)$_2$), δ = -0.43 (-Si(*C*H$_3$)$_3$). EA: Found. C 55.52%, H 7.02%; Calcd. for $C_{20}H_{30}Cl_2OSiTi$: C 55.44%, H 6.98%.

Preparation of ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr_2-4-$SiEt_3C_6H_2$) (6). An Et_2O solution (5.0 mL) containing 2,6-^{i}Pr_2-4-$SiEt_3$-C_6H_2OH (292 mg, 1.0 mmol) and Et_3N (152 mg, 1.5 mmol) was added in one portion into an Et_2O solution (20 mL) containing ($Me_3SiC_5H_4$)$TiCl_3$ (262 mg, 0.9 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred overnight. The mixture was then filtered through a Celite pad, and the filter cake was washed with Et_2O. The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange oil. The oil was then dissolved in a small amount of *n*-hexane, and the chilled (−30 °C) solution in the freezer gave orange microcrystals (yield: 75%). ^{1}H NMR (500 MHz, $CDCl_3$): δ = 7.20 (s, 2H, Ar-*H*), δ = 7.04 (t, 2H, *J* = 2.3 Hz, Cp-*H*), δ = 6.43 (t, 2H, *J* = 2.3 Hz, Cp-*H*), δ = 3.27-3.19 (m, 2H, Ar-C*H*(CH_3)$_2$), δ = 1.23 (d, 12H, *J* = 6.8 Hz, Ar-CH(C*H*$_3$)$_2$), δ = 0.99 (t, 9H, *J* = 7.9 Hz, Ar-$SiCH_2C$*H*$_3$), δ = 0.78 (q, 6H, *J* = 7.9 Hz, Ar-Si*C*H$_2$CH$_3$), δ = 0.40 (s, 9H, Cp-Si(C*H*$_3$)$_3$). ^{13}C{^{1}H} NMR (125 MHz, $CDCl_3$): δ = 165.5, 137.1, 136.8, 133.4, 129.3, 127.9, 122.5 (Aromatic group), δ = 27.0 (Ar-*C*H(CH_3)$_2$), δ = 23.8 (Ar-CH(*C*H$_3$)$_2$), δ = 7.66 (-$SiCH_2CH_3$), δ = 3.74 (-$SiCH_2CH_3$), δ = -0.43 (-Si(*C*H$_3$)$_3$). EA: Found. C 57.18%, H 8.005%; Calcd. for $C_{26}H_{44}Cl_2OSi_2Ti$: C 57.03%, H 8.100%.

Typical Reaction Procedure for Ethylene Copolymerization with Styrene. A typical reaction procedure for copolymerization of ethylene with styrene by ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}$Pr_2C_6H_3$) (**5**)-MAO catalyst (**Table 2**, run 13) is as follows: toluene (26.0 mL) and d-MAO (white solid, 174 mg, 3.0 mmol) were added into the autoclave (100 mL, stainless steel) in the drybox, and the reaction apparatus was then filled with ethylene in the fume hood. A toluene solution (1.0 mL) containing **1** was then added into the autoclave after addition of styrene (3.0 mL), and the reaction apparatus was then immediately pressurized into the prescribed pressure employed. The mixture was stirred for 10 min, and the polymerization was terminated with the addition of MeOH. The solution was then poured into MeOH (100 mL), and the resultant polymer was adequately washed with MeOH and then dried *in vacuo* for several hours.

According to the previous reports [20,21], the resultant polymer mixture was separated into three fractions. Atactic polystyrene prepared by MAO itself (in a cationic manner) was extracted with acetone. Poly(ethylene-*co*-styrene)s were then extracted with THF from the acetone-insoluble portion, and polyethylene and syndiotactic polystyrene by-produced were separated as the THF-insoluble fraction. The basic experimental procedure is as follows. The resultant polymer solids (after precipitation with MeOH and dried *in vacuo*) was added acetone (15.0 mL) into a centrifugal sedimentation tube (50 mL, glass), and the copolymer was separated [with the removal of atactic polystyrene formed by MAO] as precipitates by a centrifuge. The procedure repeated three times. The acetone-insoluble fraction and added into a centrifugal sedimentation tube containing tetrahydrofuran (THF, 15.0 mL), and the THF-soluble and THF-insoluble fractions was separated; the procedure was repeated three times. As reported previously [20,21], the resultant copolymers were soluble in THF and amount of THF insoluble fractions were negligible in all cases. These fractions were analyzed by ^{1}H-, ^{13}C-NMR spectra, GPC analysis and DSC thermograms.

Supplementary Materials: The following supporting information can be downloaded at: www.mdpi.com/xxx/s1, crystal data and the collection parameters for analysis of ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-^{i}Pr_2-4-RC_6H_2) [R = H (**5**), $SiEt_3$ (**6**)], selected NMR spectra of poly(ethylene-*co*-styrene)s and selected DSC thermograms in the resultant poly(ethylene-*co*-styrene)s.

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Data Availability Statement: Data is contained within the article and the Supplementary Material. Crystallographic analysis data for ($Me_3SiC_5H_4$)$TiCl_2$(O-2,6-$^iPr_2$-4-RC_6H_2) [R = H (**5**), $SiEt_3$ (**6**)] are available as CCDC 2378274, 2378275, respectively from The Cambridge Crystallographic Data Centre (CCDC).

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Conflicts of Interest: The authors declare no conflicts of interest.

References

1. For example (selected books, and reviews in early transition metal catalysts), see references 1-4: Organometallic Reactions and Polymerization; Osakada, K., Ed.; The Lecture Notes in Chemistry 85; Springer-Verlag: Berlin, Germany, 2014.
2. Handbook of Transition Metal Polymerization Catalysts, 2nd ed.; Hoff, R., Ed.; Wiley: Hoboken, NJ, 2018.
3. Nomura, K.; Kitphaitun, S. In Catalysis for a Sustainable Environment: Reactions, Processes and Applied Technologies, Pombeiro, A. J. L.; Sutradhar, M.; Alegria, E. C. B. A., Eds.; John Wiley & Sons, Ltd.: Chichester, West Sussex, UK, pp. 323-338 (2024).
4. Baier, M.S.M.C.; Zuideveld, M.A.; Mecking, S. Post-Metallocenes in the Industrial Production of Polyolefins. *Angew. Chem. Int. Ed.* **2014**, *53*, 9722–9744, https://doi.org/10.1002/anie.201400799.
5. Selected reviews, accounts in bimetallic catalyst systems, see references 5-7: Li H.; Marks, T. J. Nuclearity and cooperativity effects in binuclear catalysts and cocatalysts for olefin polymerization. Proc. Nat. Acad. Sci. USA, 2006, 103, 15295-15302.
6. Delferro, M.; Marks, T.J. Multinuclear Olefin Polymerization Catalysts. *Chem. Rev.* **2011**, *111*, 2450–2485, https://doi.org/10.1021/cr1003634.
7. McInnis, J.P.; Delferro, M.; Marks, T.J. Multinuclear Group 4 Catalysis: Olefin Polymerization Pathways Modified by Strong Metal–Metal Cooperative Effects. *Accounts Chem. Res.* **2014**, *47*, 2545–2557, https://doi.org/10.1021/ar5001633.
8. Selected reviews in half-titanocenes, see references 8-10: Nomura, K. Half-titanocenes containing anionic ancillary donor ligands as promising new catalysts for precise olefin polymerization. Dalton Trans. 2009, 8811-8823.
9. Nomura, K.; Liu, J. Half-titanocenes for precise olefin polymerisation: effects of ligand substituents and some mechanistic aspects. *Dalton Trans.* **2011**, *40*, 7666–7682, https://doi.org/10.1039/c1dt10086f.
10. van Doremaele, G.; van Duin, M.; Valla, M.; Berthoud, A. On the development of titanium κ1-amidinate complexes, commercialized as Keltan ACETM technology, enabling the production of an unprecedented large variety of EPDM polymer structures. J. Poly. Sci. Part A: Polym. Chem. 2017, 55, 2877-2891.
11. Nomura, K. In Syndiotactic Polystyrene - Synthesis, Characterization, Processing, and Applications; Schellenberg, J., Ed.; John Wiley & Sons, Inc.: Hoboken, NJ, 2010; pp 60-91. References are cited therein.
12. Selected reports in ethylene/styrene copolymerization using linked half-titanocenes (constrained geometry type) [5-7,11],see references 12-19: Stevens, J. C.; Timmers, F. J.; Wilson, D. R.; Schmidt, G. F.; Nickias, P. N.; Rosen, R. K.; Knight, G. W.; Lai, S. Y. Dow Chemical Co. EP 0416815 A2, 1991. Constrained geometry addition polymerization catalysts, processes for their preparation, precursors therefor, methods of use, and novel polymers formed therewith.
13. Sernetz, F. G.; Mülhaupt, R.; Waymouth, R. M. Influence of polymerization conditions on the copolymerization of styrene with ethylene using Me2Si(Me4Cp)(N-tert-butyl)TiCl2/methylaluminoxane Ziegler-Natta catalysts. Macromol. Chem. Phys. 1996, 197, 1071-1083.
14. Sernetz, F.G.; Mülhaupt, R.; Amor, F.; Eberle, T.; Okuda, J. Copolymerization of ethene with styrene using different methylalumoxane activated half-sandwich complexes. *J. Polym. Sci. Part A: Polym. Chem.* **1997**, *35*, 1571–1578, https://doi.org/10.1002/(sici)1099-0518(199706)35:8<1571::aid-pola26>3.0.co;2-3.
15. Timmers, F. J. Dow Chemical Co. US 6670432 B1, 2003. Olefin polymers formed by use of constrained geometry addition polymerization catalysts.
16. Nomura, K.; Okumura, H.; Komatsu, T.; Naga, N.; Imanishi, Y. Effect of ligand in ethylene/styrene copolymerization by [Me2Si(C5Me4)(NR)]TiCl2 (R = tert-Bu, cyclohexyl) and (1,3-Me2C5H3)TiCl2(O-2,6-

 doi:10.20944/preprints202408.1826.v1

Pr2C6H3)-MAO catalyst system. *J. Mol. Catal. A: Chem.* **2002**, *190*, 225–234, https://doi.org/10.1016/s1381-1169(02)00223-6.

17. Guo, N.; Li, L.; Marks, T. J. Bimetallic catalysis for styrene homopolymerization and ethylene-styrene copolymerization. Exceptional comonomer selectivity and insertion regiochemistry. J. Am. Chem. Soc. 2004, 126, 6542-6543.
18. Arriola, D. J.; Bokota, M.; Campbell Jr., R. E.; Klosin, J.; LaPointe, R. E.; Redwine, O. D.; Shankar, R. B.; Timmers, F. J.; Abboud, K. A. Penultimate effect in ethylene-styrene copolymerization and the discovery of highly active Ethylene-styrene catalysts with increased styrene reactivity. J. Am. Chem. Soc. 2007, 129, 7065-7076.
19. Guo, N.; Stern, C. L.; Marks, T. J. Bimetallic effects in homopolymerization of styrene and copolymerization of ethylene and styrenic comonomers: Scope, kinetics, and mechanism. J. Am. Chem. Soc. 2008, 130, 2246-2261.
20. Selected reports in ethylene/styrene copolymerization using half-titanocenes [8,9,11], see references 20-29: Nomura, K.; Komatsu, T.; Imanishi, Y. Syndiospecific styrene polymerization and efficient ethylene/styrene copolymerization catalyzed by (cyclopentadienyl)(aryloxy)titanium(IV) complexes – MAO system. *Macromolecules* **2000**, *33*, 8122-8124.
21. Nomura, K.; Okumura, H.; Komatsu, T.; Naga, N. Ethylene/Styrene Copolymerization by Various (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−MAO Catalyst Systems. *Macromolecules* **2002**, *35*, 5388–5395, https://doi.org/10.1021/ma0200773.
22. Kretschmer, W. P., Dijkhuis, C., Meetsma, A., Hessen, B., Teuben, J. H. A highly efficient titanium-based olefin polymerisation catalyst with a monoanionic iminoimidazolidide π-donor ancillary ligand. Chem. Commun. 2002, 608-609.
23. Wang, Q.; Lam, P.; Zhang, Z.; Yamashita, G.; Fan, L. Ethylene styrene interpolymers with double reverse styrene incorporation. US 6579961 B1, 2003.
24. Zhang, H.; Nomura, K. Living Copolymerization of Ethylene with Styrene Catalyzed by (Cyclopentadienyl)(ketimide)titanium(IV) Complex−MAO Catalyst System. *J. Am. Chem. Soc.* **2005**, *127*, 9364–9365, https://doi.org/10.1021/ja052198z.
25. Zhang, H.; Nomura, K. Living Copolymerization of Ethylene with Styrene Catalyzed by (Cyclopentadienyl)(ketimide)titanium(IV) Complex−MAO Catalyst System: Effect of Anionic Ancillary Donor Ligand. *Macromolecules* **2006**, *39*, 5266–5274, https://doi.org/10.1021/ma060503a.
26. Nomura, K.; Pracha, S.; Phomphrai, K.; Katao, S.; Kim, D.-H.; Kim, H.J.; Suzuki, N. Synthesis and structural analysis of phenoxy-substituted half-titanocenes with different anionic ligands, Cp*TiX(Y)(O-2,6-iPr2C6H3): Effect of anionic ligands (X,Y) in ethylene/styrene copolymerization. *J. Mol. Catal. A: Chem.* **2012**, *365*, 136–145, https://doi.org/10.1016/j.molcata.2012.08.022.
27. Son, K.-S.; Waymouth, R.M. Stereospecific styrene polymerization and ethylene-styrene copolymerization with titanocenes containing a pendant amine donor. *J. Polym. Sci. Part A: Polym. Chem.* **2010**, *48*, 1579–1585, https://doi.org/10.1002/pola.23912.
28. Aoki, H.; Nomura, K. Synthesis of Amorphous Ethylene Copolymers with 2-Vinylnaphthalene, 4-Vinylbiphenyl and 1-(4-Vinylphenyl)naphthalene. *Macromolecules* **2020**, *54*, 83–93, https://doi.org/10.1021/acs.macromol.0c02224.
29. Selected reports in ethylene/styrene copolymerization using metallocenes,11 see references 25-2629,30: Arai, T.; Ohtsu, T.; Suzuki, S. Stereoregular and Bernoullian copolymerization of styrene and ethylene by bridged metallocene catalysts. Macromol. Rapid Commun. 1998, 19, 327-331.
30. Arai, T.; Suzuki, S.; Ohtsu, T. In: Olefin Polymerization: Emerging Frontiers; Arjunan, P., Ed.; ACS Symposium Series 749, American Chemical Society: Washington, D. C., 2000; pp 66-80.
31. Byun, D.J.; Fudo, A.; Tanaka, A.; Fujiki, M.; Nomura, K. Effect of Cyclopentadienyl and Anionic Ancillary Ligand in Syndiospecific Styrene Polymerization Catalyzed by Nonbridged Half-Titanocenes Containing Aryloxo, Amide, and Anilide Ligands: Cocatalyst Systems. *Macromolecules* **2004**, *37*, 5520–5530, https://doi.org/10.1021/ma049549z.
32. Kitphaitun, S.; Yan, Q.; Nomura, K. Effect of SiMe3, SiEt3 para-substituents for exhibiting high activity, introduction of hydroxy group in ethylene copolymerization catalyzed by phenoxide-modified half-titanocenes. Angew. Chem. Int. Ed. 2020, 59, 23072-23076.
33. Miyazawa, A.; Kase, T.; Soga, K. Cis-Specific Living Polymerization of 1,3-Butadiene Catalyzed by Alkyl and Alkylsilyl Substituted Cyclopentadienyltitanium Trichlorides with MAO. *Macromolecules* **2000**, *33*, 2796–2800, https://doi.org/10.1021/ma991489n.
34. Losio, S.; Bertini, F.; Vignali, A.; Fujioka, T.; Nomura, K.; Tritto, I. Amorphous Elastomeric Ultra-High Molar Mass Polypropylene in High Yield by Half-Titanocene Catalysts. *Polymers* **2024**, *16*, 512, https://doi.org/10.3390/polym16040512.
35. Nomura, K.; Naga, N.; Miki, M.; Yanagi, K. Olefin Polymerization by (Cyclopentadienyl)(aryloxy)titanium(IV) Complexes−Cocatalyst Systems. *Macromolecules* **1998**, *31*, 7588–7597, https://doi.org/10.1021/ma980690f.

 doi:10.20944/preprints202408.1826.v1