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Living Copolymerization of Ethylene with Styrene Catalyzed by (Cyclopentadienyl)(ketimide)titanium(IV) Complex−MAO Catalyst System: Effect of Anionic Ancillary Donor Ligand

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ABSTRACT: The ethylene/styrene copolymerization by $\mathrm{Cp^*TiCl_2(N{=}C^tBu_2)}$ ($\mathrm{Cp^* = C_5Me_5}$, **1**) −methylaluminoxane (MAO) catalyst proceeded in a living manner, and the living nature maintained under various conditions (Al/Ti molar ratios, ethylene pressure, styrene concentrations, temperature). Poly(ethylene-*co*-styrene)s were obtained exclusively in the polymerization using **1**, $\mathrm{Cp^*TiX_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)}$ [X = Cl (**3**), Me(**5**)] −MAO, and **5**−$\mathrm{[PhN(H)Me_2][B(C_6F_5)_4]}$ catalysts under the same conditions, and both the styrene incorporation and the microstructures were highly influenced by the anionic donor ligand employed. The resultant polymers prepared by $\mathrm{Cp^*TiX_3}$ [X = Cl (**4**), Me (**6**)] −MAO catalysts were a mixture of polyethylene and syndiotactic polystyrene (SPS), whereas the resultant polymer did not contain SPS in the polymerization by **6**−$\mathrm{[PhN(H)Me_2][B(C_6F_5)_4]}$ catalyst. These facts clearly indicate that the anionic donor ligand strongly affects the styrene incorporation and the polymerization behavior and that catalytically active species for the syndiospecific styrene polymerization and the copolymerization are apparently different.

Introduction

Precise control over macromolecular structure is a central goal in synthetic polymer chemistry, and copolymerization is an important method that usually allows the alteration of the (physical, mechanical, and electronic) properties by varying the ratio of individual components. Considerable attention has thus been paid to establish the new synthetic strategy for precise placement of the chemical functionality, and transition metal catalyzed living polymerization[1] is one of the best methods to control monomer repeating units in the desired polymers.[1−3] Although many reports for the living polymerization of ethylene, α-olefin, and others[1−7] are known, examples for the living copolymerization with the exception of block copolymerization are limited.[2b,c,3f,h,6,7]

Ethylene/styrene copolymers,[8−10] which cannot be prepared by free radical or ordinary Ziegler−Natta processes,[11] attract considerable attention due to their promising properties,[12] but no examples were known for living copolymerization. We recently reported as the preliminary communication that the efficient living copolymerization of ethylene with styrene could be achieved by using a half-titanocene containing a ketimide ligand,[13] $\mathrm{Cp^*TiCl_2(N{=}C^tBu_2)}$ (**1**, $\mathrm{Cp^* = C_5Me_5}$) −MAO (methylaluminoxane) catalyst (Scheme 1). We also communicated that the nature of both cyclopentadienyl and anionic donor ligands affects the styrene incorporation and the polymerization behavior.[13]

Half-titanocenes such as $\mathrm{Cp^*TiF_3}$, $\mathrm{Cp^*Ti(OMe)_3}$, and $\mathrm{IndTiCl_3}$ are efficient catalyst precursor for syndiospecific styrene polymerization;[14] however, these catalyst precursors showed low catalytic activities and the resultant polymers in the ethylene/styrene copolymerization afforded a mixture of polyethylene, syndiotactic polystyrene, and the copolymer.[8] In contrast, *nonbridged* half-titanocenes of the type $\mathrm{Cp'Ti(L)X_2}$ (Cp′ = cyclopentadienyl group; L = anionic ligand such as $\mathrm{O\text{-}2,6\text{-}{}^iPr_2C_6H_3}$, $\mathrm{N{=}C^tBu_2}$, $\mathrm{N{=}PR_3}$, X = halogen, alkyl) have been known to exhibit unique characteristics as olefin polymerization catalysts,[15−34] and we recently reported that $\mathrm{Cp'TiCl_2(OAr)}$ (OAr = $\mathrm{O\text{-}2,6\text{-}{}^iPr_2C_6H_3}$) showed not only high catalytic activities for ethylene polymerization[16,17] but also displayed unique characteristics for copolymerization of ethylene with α-olefin,[17,35] styrene,[36,37] norbornene,[38,39] cyclohexene,[40] and 2-methyl-1-pentene[41] and with vinylcyclohexane[42] in the presence of MAO. It turned out recently that both cyclopentadienyl ligand and anionic donor ligand affect the comonomer incorporation as well as the catalytic activity in these copolymerizations.[13,30,35−42] Moreover, it was also revealed that both the cyclopentadienyl and the anionic ancillary donor ligand directly affect the catalytic activity and molecular weight for styrene polymerization by using $\mathrm{Cp'TiCl_2(L)}$ (L = aryloxo, amide, anilide, and ketimide).[36,43] Although it has been postulated that cationic titanium(III) complex, $\mathrm{Cp'Ti(R')(styrene)^+}$, plays an essential role as the catalytically active species for syndiospecific styrene polymerization,[44] the above results indicate the possibility of another catalytically active species.[43] This would also be a very important question to consider the catalytically active species for both styrene polymerization and ethylene/styrene copolymerization especially by half-titanocene catalysts. Taking into account the above facts, we thus focused on effect of anionic donor ligand in ethylene/styrene copolymerization by half-

Scheme 1. Ethylene/Styrene Copolymerization by Half-Titanocenes (1-6) −Methylaluminoxane (MAO) Catalyst Systems [Ethylene 4 or 6 atm, Styrene 5−15 mL (Styrene + Toluene Total 30 mL), 25 or 40 °C]

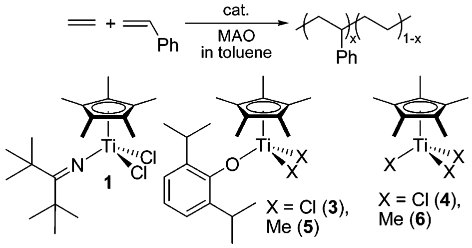

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Table 1. Living Copolymerization of Ethylene with Styrene by $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp* (1), Cp (2)] −Methylaluminoxane (MAO) Catalyst System at 25 °C[a]

run	Cp′	ethylene/atm	styrene/mL	time/min	polymer yield[b]/mg	activity[c]	styrene content[d]/mol %	M_n[e] × 10^{-4}	M_w/M_n[e]
1	Cp*	4	10	10	68	204	11.2	5.3	1.14
2	Cp*	4	10	15	100	200		7.61	1.21
3	Cp*	4	10	20	108	162	11.1	8.57	1.28
4	Cp*	4	10	25	154	185		10.9	1.24
5	Cp*	4	10	30	173	173	10.9	11.7	1.34
6	Cp*	4	10	35	236	202		15.1	1.30
7	Cp*	6	10	5	53	318		5.28	1.19
8	Cp*	6	10	10	132	396	7.4	9.5	1.18
9	Cp*	6	10	20	270	405	7.2	17.3	1.36
10	Cp*	4+6[f]	10	10 + 10	199	300	8.1	12.3	1.31
11	Cp*	- -	10	10	21	63	100	7.84	2.34
12	Cp*[g]	6		2	51	30 600		58.3	74.4
13	Cp*[g]	6		10	156	18 700		insoluble[h]	
14	Cp*[i]	4		10	552	16 600		47.3	2.2
15	Cp[i]	4		10	445	13 400		50.8	1.9
16	Cp	4	10	30	<5	<1			
17	Cp	6	10	30	<5	<1			

[a] Conditions: complex 2.0 μmol (Cp′ = Cp*) or 10.0 μmol (Cp′ = Cp), MAO (prepared by removing $AlMe_3$ and toluene from PMAO) 3.0 mmol, styrene + toluene total 30 mL, 100 mL scale autoclave. [b] Polymer yield based on acetone insoluble and THF soluble fractions (for detailed explanations, see ref 46). [c] Activity in kg of polymer/mol of Ti•h. [d] Styrene content (mol %) estimated by ^1H NMR. [e] GPC (gel permeation chromatography) data in *o*-dichlorobenzene vs polystyrene standards. M_n: number-average molecular weight. M_w: weight-average molecular weight. M_w/M_n: molecular weight distribution (polydispersity index, PDI). [f] First ethylene 4 atm (10 min) and then 6 atm (10 min), estimated yield = 200 mg (obtained 199 mg), M_n value = 14.8 × 10^4 (obtained 12.3 × 10^4), styrene content = 8.4 mol % (obtained 8.1 mol %). [g] Complex **1**, 0.05 μmol. [h] Insoluble for GPC measurement. [i] Complex, 0.20 μmol at 40 °C.[32]

titanocenes. In this report, we wish to introduce our results for ethylene/styrene copolymerization by $Cp'TiCl_2(N{=}C^tBu_2)$ [Cp′ = Cp* (**1**), Cp (**2**)], $Cp^*TiCl_2(OAr)$ (**3**), Cp^*TiCl_3 (**4**) in the presence of MAO under various conditions including the detailed results for living copolymerization by a **1**−MAO catalyst system (Scheme 1).[45] Moreover, we present our explored results by using $Cp^*TiMe_2(OAr)$−MAO (**5**−MAO), Cp^*TiMe_3−MAO (**6**−MAO), or $[PhN(H)Me_2][B(C_6F_5)_4]$ catalyst systems.

Results and Discussion

1. Living Copolymerization of Ethylene with Styrene by $Cp^*TiCl_2(N{=}C^tBu_2)$—MAO (1—MAO) Catalyst System. Table 1 summarizes the results for the ethylene/styrene copolymerization by **1** at 25 °C in toluene. The reaction proceeded efficiently without decrease in the activity (runs 1−9), and the activity increased at higher ethylene pressure. Poly(ethylene-*co*-styrene)s were obtained exclusively as the acetone insoluble fraction (and THF soluble fraction) and the resultant polymers possessed low PDI values [M_w/M_n = 1.14−1.36, M_n: number-average molecular weight, M_w: weight-average molecular weight, M_w/M_n: molecular weight distribution (polydispersity index, PDI)], and the styrene distributions were uniform confirmed by GPC/FT-IR spectra (GPC: gel permeation chromatography).[13,46] Time-course plots of the number-average molecular weights (M_n) and the M_w/M_n values (ethylene 4 and 6 atm, 25 °C) are shown in Figure 1,[47] and the first order relationship between the M_n values and the polymer yields with consistently low PDI values was observed under these conditions. No significant differences in the styrene contents in the copolymer (estimated by ^1H NMR spectra) over time course were observed under these conditions.[47] Moreover, the two step copolymerization under ethylene pressure of 4 and then 6 atm (run 10) afforded the copolymer with a low PDI value, and the polymer yield, the styrene content, and the M_n value were identical to the estimated values, based on the independent experimental runs (runs 1,8). These results clearly indicate that the present copolymerization took place in a living manner.

1 exhibited a low catalytic activity for styrene polymerization, affording syndiotactic polymer with a large PDI value (run 11).[31]

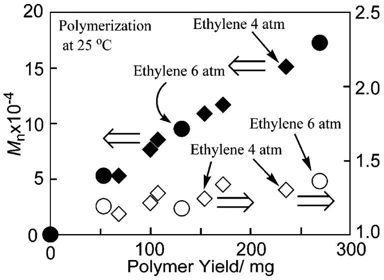


Figure 1. Time course plots of M_n, M_w/M_n vs polymer yields in ethylene/styrene copolymerization by the **1**−methylaluminoxane (MAO) catalyst system at 25 °C [**1** 2.0 μmol, styrene 10 mL, ethylene 4 atm (◆, ◇, runs 1−6) or 6 atm (●, ○ runs 7−9). M_n: number-average molecular weight. M_w: weight-average molecular weight. M_w/M_n: molecular weight distribution (polydispersity index, PDI)].

In contrast, remarkable activities were observed for the ethylene polymerization (runs 12−13), and the resultant polymer possessed a high molecular weight with a large PDI value, and the distribution became unimodal if the reaction was performed at 40 °C (M_w/M_n = 2.20, run 14)[32] probably due to improved solubility for resultant polyethylene. Negligible catalytic activities were observed if $CpTiCl_2(N{=}C^tBu_2)$ (**2**) was used in place of **1** under the same conditions (runs 16−17), whereas notable catalytic activity was observed in ethylene polymerization by **2** (run 15).[32] Since **2** showed especially high catalytic activities and 1-hexene incorporation in ethylene/1-hexene copolymerization, these results indicate that the comonomer incorporation by **2** was strongly influenced not only by the steric but also by the electronic nature of comonomer employed.

Table 2 summarizes the copolymerization results by **1**−MAO catalyst system at 25 °C under various ethylene pressures and styrene concentrations.[46] These copolymerizations also took place efficiently, and the resultant polymers were poly(ethylene-*co*-styrene)s exclusively as the acetone insoluble fraction (and THF soluble fraction) and the resultant polymers possessed relatively low PDI values (M_w/M_n = 1.20−1.61). The styrene contents increased upon increasing the amount of styrene charged and the content also decreased upon increasing the ethylene pressure (from 4 to 6 atm). The observed catalytic

Table 2. Living Copolymerization of Ethylene with Styrene by $Cp^*TiCl_2(N{=}C^tBu_2)$ (1) −MAO Catalyst System at 25 °C[a]

run	**1**/μmol	ethylene/atm	styrene/mL	time/min	polymer yield[b]/mg	activity[c]	styrene content[d]/mol %	$M_n \times 10^{-4}$ [e]	M_w/M_n[e]
18	2.0	4	5	10	118	354		5.90	1.44
19	2.0	4	5	20	241	362	5.4	8.45	1.55
20	2.0	4	5	30	373	373		13.6	1.54
21	2.0	4	15	10	41	123		1.09	1.51
22	2.0	4	15	20	90	135	17.2	2.46	1.61
23	2.0	4	15	30	125	125		4.64	1.33
24	2.0	6	5	10	220	660		11.7	1.39
25	2.0	6	5	20	422	633	3.6	16.4	1.53
26	2.0	6	5	30	614	614		20.2	1.60
27	1.0	6	5	10	113	678		11.4	1.44
28	1.0	6	5	20	220	660	3.6	20.8	1.45
29	1.0	6	5	30	313	626		28.8	1.45
30	2.0	6	15	10	89	267		7.32	1.24
31	2.0	6	15	20	176	264	11.3	10.2	1.20
32	2.0	6	15	30	235	235		13.7	1.26

[a] Conditions: complex, 2.0 μmol, MAO (prepared by removing $AlMe_3$ and toluene from PMAO) 3.0 mmol, styrene + toluene total 30 mL. [b] Polymer yield based on acetone insoluble and THF soluble fractions (for detailed explanations, see ref 46). [c] Activity in kg of polymer/mol of Ti•h. [d] Styrene content (mol %) estimated by ^1H NMR. [e] GPC (gel permeation chromatography) data in *o*-dichlorobenzene vs polystyrene standards. [f] Complex, 1.0 μmol.

Table 3. Effect of Al/Ti Molar Ratio in Living Copolymerization of Ethylene with Styrene by $Cp^*TiCl_2(N{=}C^tBu_2)$ (1) −MAO Catalyst System at 25 °C[a]

run	Al/Ti[b]	ethylene/atm	time/min	polymer yield[c]/mg	activity[d]	styrene content[e]/mol %	M_n[f] $\times 10^{-4}$	M_w/M_n[f]
33	500	6	20	104	156	7.2	8.36	1.55
34	750	6	20	162	243	7.2	11.6	1.48
9	1500	6	20	270	405	7.2	17.3	1.36
35	1000	4	10	62	186	11.0	5.86	1.18
1	1500	4	10	68	204	11.2	5.30	1.14
36	3000	4	10	77	231	11.4	5.35	1.24
37	3000	4	20	137	206	11.3	8.15	1.33
38	3000	4	30	212	212	11.0	11.8	1.36

[a] Conditions: complex **1**, 2.0 μmol; MAO (prepared by removing $AlMe_3$ and toluene from PMAO); styrene, 10 mL; toluene, 20 mL. [b] Molar ratio of Al/Ti. [c] Polymer yield based on acetone insoluble and THF soluble fractions (for detailed explanations, see ref 46). [d] Activity in kg of polymer/mol of Ti•h. [e] Styrene content (mol %) estimated by ^1H NMR. [f] GPC (gel permeation chromatography) data in *o*-dichlorobenzene vs polystyrene standards.

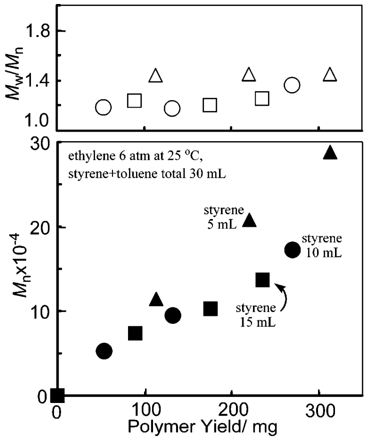


Figure 2. Time course plots of M_n, M_w/M_n vs polymer yields in ethylene/styrene copolymerization by the **1**−methylaluminoxane (MAO) catalyst system under various styrene concentrations at 25 °C [ethylene 6 atm, styrene 5 mL (▲, △, runs 27−29), 10 mL (●, ●, runs 7−9), or 15 mL (■, □, runs 30−32), Table 2].

activities decreased upon increasing the styrene concentration, and the results may be related to the low catalytic activity for the syndiospecific styrene polymerization as well as to the remarkable catalytic activity for the ethylene polymerization. The observed activities seemed increasing if the polymerization was performed under lower catalyst concentration, and the PDI values became somewhat low (runs 24−29). Time-course plots of the number-average molecular weights (M_n) and the M_w/M_n values (ethylene 6 atm, 25 °C) are shown in Figure 2,[46] and the first order relationships between the M_n values and the polymer yields with consistently low PDI values were observed in all cases under these conditions. These results also clearly indicate that the present copolymerization proceeded in a living manner.

As summarized in Table 3, the catalytic activities were affected by the Al/Ti molar ratios, and both M_n values and the polymer yields for resultant copolymers increased at high Al/Ti molar ratios with low PDI values. No distinct differences in the styrene contents for resultant copolymers were observed under these conditions (^{13}C NMR spectra are shown in the Supporting Information), suggesting that the styrene incorporation was dependent upon the catalyst precursor (**1** in this case) employed. A certain excess amount of MAO was required for exhibiting high catalytic activity (runs 9, 33, and 34), and the activity did not decrease upon increasing the amount (runs 1, 35, and 36). The first order relationship between the M_n values and the polymer yields with low PDI values was observed in the copolymerization even in the presence of large excess amount of MAO (runs 36−38), the results thus clearly indicate that the degree of chain transfer from Ti−alkyl to Al−alkyl was negligible even upon increasing the amount of MAO.

To explore the utility of this living polymerization system, the copolymerizations at 40 °C were employed (Table 4), because the living polymerization system at high temperature should be promising but limited reports are known as the successful examples.[2c,3h] As summarized in Table 4, relatively low PDI values were also observed for the copolymers prepared at 40 °C, and both the activities and styrene contents increased at higher temperature (25 → 40 °C). As also shown in Figure 3 (results at ethylene 4 atm at 40 °C, runs 39−44), the M_n values increased upon increasing the polymer yields with consistently low PDI values, and the first order relationships between the M_n values and the polymer yields were observed in all cases. These results also indicate that the present copolymerization proceeded in a living manner. These results clearly introduce the utility of this living polymerization system even at higher temperature of 40 °C.

Table 4. Living Copolymerization of Ethylene with Styrene by Cp*TiCl$_2$(N=C^{t}Bu$_2$) (1) −MAO Catalyst System at 40 °C[a]

run	catalyst **1**/μmol	ethylene/atm	time/min	polymer yield[b]/mg	activity[c]	styrene content[d]/mol %	M_n[e] × 10^{-4}	M_w/M_n[e]
39	2.0	4	10	121	363		6.35	1.42
40	2.0	4	15	151	302		7.55	1.40
41	2.0	4	20	183	275	15.5	8.76	1.34
42	2.0	4	25	224	269		11.5	1.44
43	2.0	4	30	284	284	14.9	12.7	1.50
44	2.0	4	35	328	281		14.5	1.44
45	2.0	6	10	282	846		11.1	1.53
46	2.0	6	15	417	834		14.2	1.65
47	2.0	6	20	551	827	9.1	15.9	1.62
48	1.0	6	10	137	822	9.0	10.4	1.34
49	1.0	6	15	204	816		14.1	1.34
50	1.0	6	20	270	810	9.0	18.2	1.43
51	1.0	6	25	343	823		23.6	1.47
52	1.0	6	30	411	822		28.1	1.45

[a] Conditions: complex **1**, 2.0 μmol; MAO (prepared by removing AlMe$_3$ and toluene from PMAO), 3.0 mmol; styrene, 10 mL; toluene, 20 mL. [b] Polymer yield based on acetone insoluble and THF soluble fractions (for detailed explanations, see ref 46). [c] Activity in kg of polymer/mol of Ti•h. [d] Styrene content (mol %) estimated by ^{1}H NMR. [e] GPC (gel permeation chromatography) data in *o*-dichlorobenzene vs polystyrene standards.

Table 5. Copolymerization of Ethylene with Styrene by Cp*TiCl$_2$(L) (1, 3, 4) [L = N=C^{t}Bu$_2$ (1), O-2,6-^{i}Pr$_2$C$_6$H$_3$ (3), Cl (4)] −MAO Catalyst Systems[a]

run	catalyst	temp/°C	[S]/[E][b]	composition (%)[c] E−S	PE	SPS	activity[d]	styrene content[e]/mol %	M_n[f] × 10^{-4}	M_w/M_n[f]
8	**1**	25	4.0	>99	trace	trace	396	7.4	9.5	1.18
48	**1**	40	4.75	>99	trace	trace	820	9.0	10.4	1.34
53	**1**	40	4.75	>99	trace	trace	790	9.3	14.4	1.28
54	**1**	55	5.56	>99	trace	trace	1110	10.4	19.7	1.31
55	**1**	70	6.41	>99	trace	trace	1260	12.2	16.3	1.57
56	**3**	25	4.0	>99	trace	trace	504	31.9	9.28	1.62
57	**3**	40	4.75	>98	trace	trace	660	34.3	9.79	1.5
58	**4**	25	4.0	trace	86.8	13.2	250	>99[g]	5.85 0.29	1.26 2.69
59	**4**	40	4.75	trace	81.6	18.4	280	>99[g]	5.07 0.31	1.31 1.75
60	**4**	55	5.56	trace	69.8	30.2	260	>99[g]	3.56 0.21	1.48 1.77

[a] Conditions: catalyst, 2.0 μmol (run 48 1.0 μmol); MAO (prepared by removing AlMe$_3$ and toluene from PMAO), 3.0 mmol; ethylene, 6 atm; styrene, 10 mL; styrene + toluene total, 30 mL; 10 min. [b] Initial molar ratio of styrene/ethylene in the reaction mixture [c] On the basis of a mixture of PE, SPS, and copolymer. (acetone insoluble fraction). [d] Activity in kg of polymer/mol of Ti•h. [e] Styrene content (mol %) estimated by ^{1}H NMR [f] GPC (gel permeation chromatography) data in *o*-dichlorobenzene vs polystyrene standards [g] Confirmed by GPC/FT-IR, ^{13}C NMR spectra, and DSC thermograms.

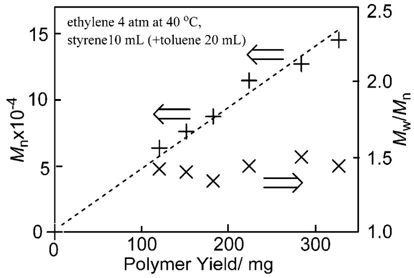


Figure 3. Time course plots of M_n, M_w/M_n vs polymer yields in ethylene/styrene copolymerization by **1**−methylaluminoxane (MAO) catalyst system at 40 °C (**1** 2.0 μmol, ethylene 4 atm at 40 °C, styrene10 mL, runs 39−44, Table 4).

2. Effect of Anionic Donor Ligand in Ethylene/Styrene Copolymerization by Cp*TiCl$_2$(L)—MAO Catalyst Systems [L = N=C^{t}Bu$_2$ (1), O-2,6-^{i}Pr$_2$C$_6$H$_3$ (3), Cl (4)]. Three-half-titanocene complexes containing Cp* ligand of type, Cp*TiCl$_2$(L) [L = N=C^{t}Bu$_2$ (**1**), O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**3**), Cl (**4**)], were chosen in this study to explore the effect of anionic donor ligand in the ethylene/styrene copolymerization at various temperature, and the results are summarized in Table 5.

The observed catalytic activities by the ketimide analogue **1** increased at higher temperature, and resultant polymers (as acetone insoluble fraction) were poly(ethylene-*co*-styrene)s with uniform styrene distributions confirmed by ^{13}C NMR spectra, differential scanning calorimetric (DSC) thermograms and by GPC/FT-IR.[13] The styrene content increased at higher temperature due to the increase in the [S]$_0$/[E]$_0$ molar ratios ([S]$_0$ and [E]$_0$ are the initial concentrations,[48] respectively). Relatively low PDI values were also observed for the copolymers prepared by **1** even at 55 and 70 °C, suggesting the possibility of a living polymerization.[49]

In contrast, the polymerizations by the aryloxide analogue **3** under the same conditions afforded the copolymers with high styrene contents (31.9−34.3 mol %), and significant increase in the catalytic activity was not observed at higher temperature. The resultant polymers were poly(ethylene-*co*-styrene)s exclusively as suggested in the previous report,[36,37] and the copolymers prepared by **3** possessed relatively lower M_n values with a unimodal, rather large PDI values (M_w/M_n = 1.50−1.62, runs 56,57), strongly suggesting that some extents of chain transfer reaction occurred.[36,37] Note that the resultant polymer prepared by the chloride analogue **4** under the same conditions possessed bimodal molecular weight distributions with different polarity in the GPC trace, and the ^{13}C NMR spectra and DSC thermograms strongly suggested the formation of a mixture of polyethylene and syndiotactic polystyrene (runs 58−60). In addition, the ratio in the high molecular weight portion increased upon increasing the polymerization temperature, and the fact was consistent with that the catalytic activity in syndiospecific styrene polymerization by **4** increased at higher temperature.[43] These results clearly indicate that nature of anionic donor ligands *directly affect* the polymerization behavior.

Figure 4 shows the selected ^{13}C NMR spectra for the resultant polymers (acetone insoluble fraction) prepared by **1**, **3**, **4**, and possible monomer sequences in the poly(ethylene-*co*-styrene)s are summarized in Scheme 2. Figure 5 shows DSC thermograms for the resultant polymers prepared by **1**−MAO, **3**−MAO, and

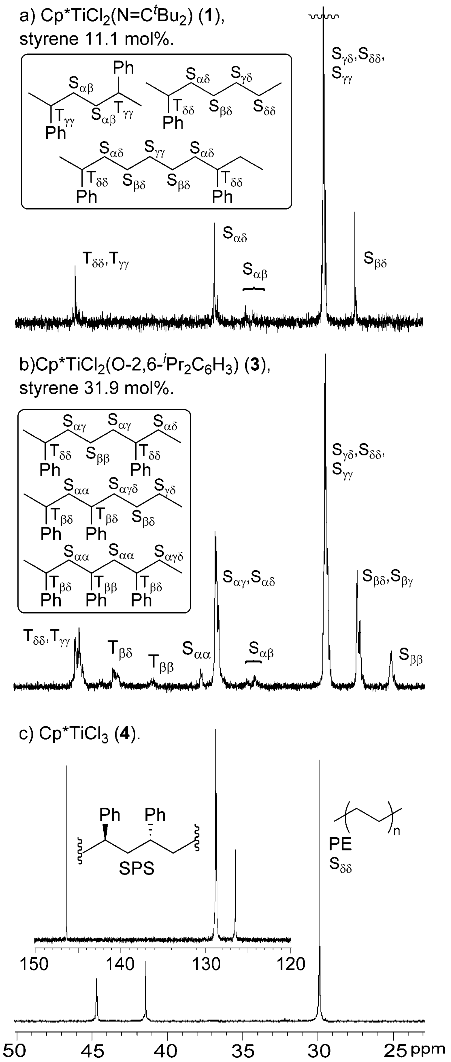
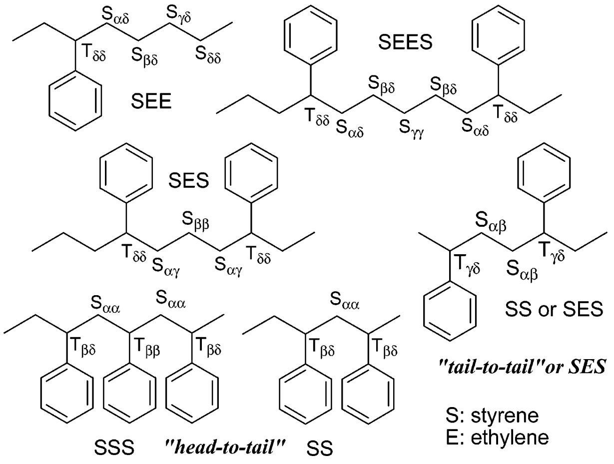


Figure 4. ^{13}C NMR spectra (in 1,1,2,2,-tetrachloroethane-d_2 at 110 °C) for the resultant polymers (acetone insoluble fraction) prepared by a) Cp*TiCl$_2$(N=C^{t}Bu$_2$) (**1**, ethylene 4 atm, 25 °C, run 3), (b) Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**, ethylene 6 atm, 25 °C, run 56), and (c) Cp*TiCl$_3$ (**4**, ethylene 6 atm, 55 °C, run 60).

Scheme 2. Possible Monomer Sequences in Poly(ethylene-*co*-styrene)



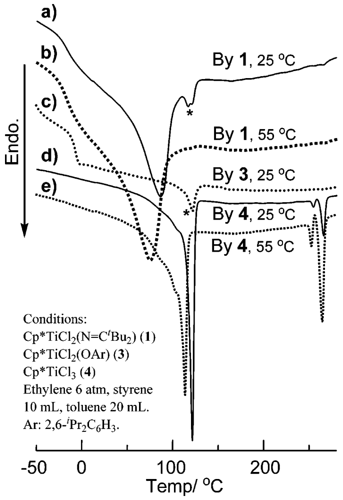


Figure 5. Differential scanning calorimetric (DSC) thermograms for resultant polymers (acetone insoluble fraction) prepared by (a, b) Cp*TiCl$_2$(N=C^{t}Bu$_2$) (**1**), (c) Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**), and (d, e) Cp*TiCl$_3$ (**4**). Conditions: ethylene 6 atm, styrene 10 mL, toluene 20 mL, 25 °C (a, c, d) or 55 °C (b, e). The peak observed at 120 °C (marked with an asterisk) is due to the remaining polyethylene being contaminated.

4−MAO catalysts. DSC thermograms for the resultant polymers prepared by both **1** and **3** showed single glass transition temperatures (T_g) (Figure 5a-c) in addition to melting temperatures (T_m) for copolymers with lower styrene contents (Figure 5a,b), and the increase in the T_g values (as well as decrease in the T_m values) was observed upon increasing the styrene content, suggesting that the resultant polymers were poly(ethylene-*co*-styrene)s with uniform styrene distribution, as also confirmed by GPC/FT-IR previsouly.[13]

A trace amount of resonances due to so-called pseudo random [S$_{\alpha\beta}$, SS by tail-to-tail and/or SES (S = styrene, E = ethylene), Scheme 2] sequences were observed in both ^{13}C NMR spectra. No resonances ascribed to (head-to-tail) styrene repeating unit (T$_{\beta\delta}$, T$_{\beta\beta}$, S$_{\alpha\alpha}$) were seen in the copolymer prepared by **1**, whereas the peaks due to two, three styrene repeating units were seen for the polymer prepared by **3**. Since styrene repeating units were not seen in the ^{13}C NMR spectra for the copolymers by **1**, also since **1** showed notable catalytic activity affording high molecular weight polyethylene with rather broad distributions, it is thus assumed that some degree of styrene insertion may inhibit the chain transfer in this catalysis. Both the ^{13}C NMR spectrum (Figure 4c) and the DSC thermograms (Figure 5d,e) for the resultant polymer prepared by the chloride analogue **4** showed a mixture of polyethylene and syndiotactic polystyrene (SPS) and the ratio of SPS increased at higher temperature. The formation of poly(ethylene-*co*-styrene)s seemed negligible under these conditions (in the presence of MAO white solid prepared by removing AlMe$_3$ and toluene from ordinary commercially available MAO). Taking into account the above facts, it is thus concluded that the nature of anionic donor ligand directly affects not only the polymerization behavior but also the monomer reactivity (styrene incorporation).

3. Copolymerization of Ethylene with Styrene by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (5) and Cp*TiMe$_3$ (6) —Cocatalyst Systems. To explore the reasons for observed difference in the copolymerization behavior especially between Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**), Cp*TiCl$_3$ (**4**) in the presence of MAO cocatalyst, we conducted the copolymerization of the methyl analogues, Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5**) and Cp*TiMe$_3$ (**6**), in the presence of MAO, [PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] (AFPB) at 25 °C.[50] Al^{i}Bu$_3$ was also added into the reaction mixture to remove impurities as well as to improve the catalyst efficiency by partial replacement of the methyl group in **5** into ^{i}Bu without reduction.[3k,51] The polymerization results are summarized in Table 6, and ^{13}C NMR spectra for the resultant polymers

Table 6. Copolymerization of Ethylene with Styrene by $Cp^*TiMe_2((O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (5), Cp^*TiMe_3 (6) −MAO or − $[PhN(H)Me_2][B(C_6F_5)_4]$ (AFPB) Catalyst Systems[a]

run	catalyst (amount/μmol)	time/min	composition (%)[b] E−S	PE	SPS	activity[c]	styrene content[d]/mol %	M_n[e] × 10^{-4}	M_w/M_n[e]
61	**5**/MAO (2.0)	10	99	trace	trace	519	30.5	5.34	2.05
62	**5**/AFPB (5.0)	20	99	trace	trace	79.2	46.7	2.81	2.16
63	**6**/MAO (2.0)	10	trace	68.6	31.4	366	>99	8.66	1.37
								0.81	2.33
64	**6**/AFPB (10.0)	20	trace	99	trace	43.8	trace	0.5	3.53

[a] Conditions: catalyst, 2.0 μmol; MAO (prepared by removing $AlMe_3$ and toluene from PMAO), 3.0 mmol (runs 61, 63), or Al^iBu_3, 1.0 mmol (runs 62, 64); $[C_6H_5NH(CH_3)_2][B(C_6F_5)_4]$ (AFPB), 2.0 μmol (runs 62, 64); styrene, 10.0 mL; toluene, 20 mL; 10 min. [b] On the basis of a mixture of PE, sPS, and copolymer (acetone insoluble fraction). [c] Activity in kg of polymer/mol of Ti•h. [d] Styrene content (mol %) estimated by ^1H NMR. [e] GPC (gel permeation chromatography) data in *o*-dichlorobenzene vs polystyrene standards.

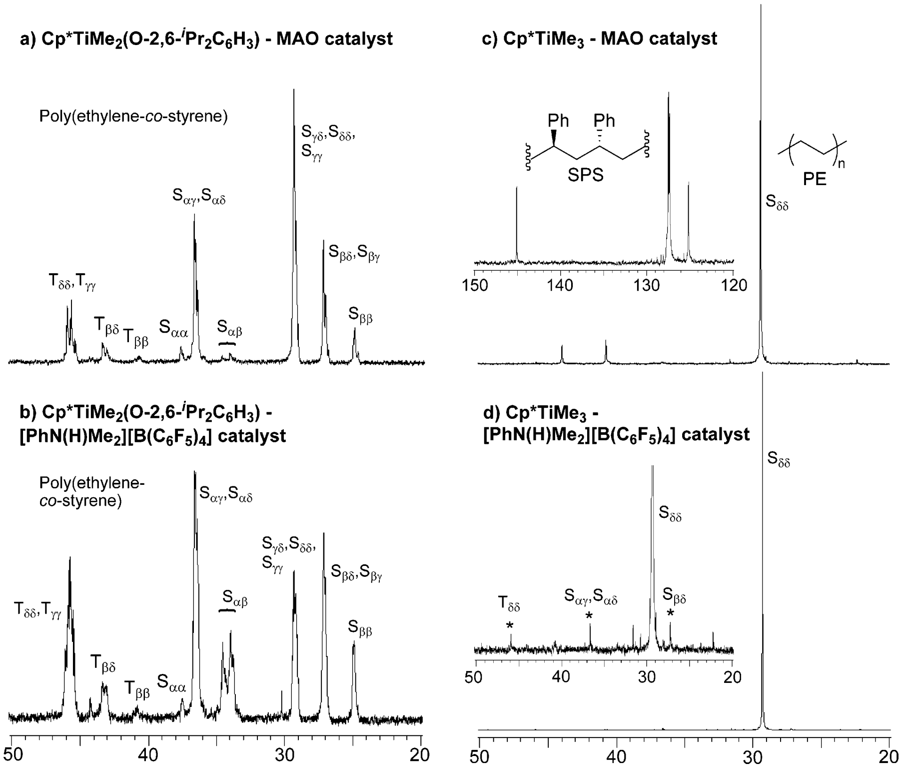


Figure 6. ^{13}C NMR spectra (in 1,1,2,2,-tetrachloroethane-d_2 at 110 °C) for the resultant polymers (acetone insoluble fraction) prepared by (a) $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$−methylaluminoxane (MAO) catalyst (run 61), (b) $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)-[PhN(H)Me_2][B(C_6F_5)_4]$ catalyst (run 62), (c) Cp^*TiMe_3−methylaluminoxane (MAO) catalyst (run 63), and (d) $Cp^*TiMe_3-[PhN(H)Me_2][B(C_6F_5)_4]$ catalyst (run 64). Conditions: ethylene 6 atm, styrene 10 mL, toluene 20 mL, 25 °C (Table 6).

(acetone insoluble fraction after removing atactic polystyrene prepared by MAO) are shown in Figure 6.

The aryloxo analogue (**5**) showed high catalytic activity in the presence of MAO, and the activity decreased if AFPB was used in place of MAO. The resultant polymers were high molecular weight poly(ethylene-*co*-styrene)s exclusively with relatively high styrene contents as well as with unimodal molecular weight distributions. The styrene content in the resultant copolymer (30.5 mol %, run 61) prepared by **5**−MAO catalyst was close to that prepared by **3**−MAO catalyst (31.9 mol %, run 56) under the same conditions and no significant differences were observed in the ^{13}C NMR spectrum (Figure 6a). The fact strongly suggests that the similar catalytically active species play a role in this copolymerization. Moreover, **5**−AFPB catalyst also afforded the copolymer as the sole Ti-catalyzed polymerization product, although the styrene content was somewhat higher than that prepared by **3**,**5**−MAO catalysts, probably due to the presence of a weak coordination/dissociation equilibrium between the cationic Ti metal center and $PhNMe_2$. The ^{13}C NMR spectrum for the copolymer prepared by **5**−AFPB catalyst showed no distinct differences in the monomer sequences with those for the copolymer prepared by **5**−MAO catalyst (Figure 6a,b). These results clearly suggest that the similar catalytically active species (seems likely to be cationic Ti(IV) species) play a key role in this copolymerization.

In contrast, the resultant polymers were a mixture of polyethylene and syndiotactic polystyrene (SPS) if the polymerization by the trimethyl analogue **6** was performed in the presence of MAO. The observed fact was analogous to that in the polymerization by the trichloride analogue **4** in the presence of MAO, and no significant differences were observed in the ratio of polyethylene/SPS as well as M_n values for these polymers, although the activity slightly increased by using the trimethyl analogue **6** under the same conditions. These results also suggest that the similar catalytically active species (two different species for producing polyethylene and SPS) play a role in this catalysis. Note that **6**−AFPB catalyst did not produce SPS under the same conditions confirmed by ^{13}C NMR spectra, and the spectrum also suggested that the resultant polymer was polyethylene containing trace amount of poly(ethylene-*co*-styrene) with low styrene content or poly(ethylene-*co*-styrene) with extremely low styrene content. The resultant polymer possessed relatively low molecular weight which was similar to that prepared by **6**−MAO catalyst with rather broad molecular weight distribution. The fact that no SPS was formed in this polymerization by **6**−AFPB catalyst seems analogous to that facts that the tribenzyl analogue, Cp*Ti(CH_2Ph)$_3$−AFPB catalyst did not afford SPS in an attempted styrene polymerization (under dark conditions) and only poly(propylene-*co*-styrene) oligomer was formed in the propylene/styrene copolymerization.[44b] On the basis of these facts, it is thus assumed that cationic Ti(IV) species, which will be generated by the reaction of **6** with AFPB, catalyzes ethylene polymerization as well as ethylene/styrene copolymerization. The fact also suggests that another catalytically active species (seems likely Ti(III) species) which catalyze syndiospecific styrene polymerization was formed upon the presence of MAO cocatalyst. Taking into account these results, it is thus strongly suggested that cationic Ti(IV) species play an important key role for ethylene polymerization as well as for ethylene/styrene copolymerization. The above facts also indicate that the anionic donor (OAr vs Me) strongly affect the styrene incorporation as well as the copolymerization behavior.

We have shown that a living ethylene/styrene copolymerization can be achieved by Cp*TiCl$_2$(N=C^{t}Bu$_2$)−MAO (**1**−MAO) catalyst, and the living nature maintained under various conditions (by varying Al/Ti molar ratios, ethylene pressure, styrene concentrations, temperature). Resonances corresponding to styrene repeating units were not observed in the resultant poly(ethylene-*co*-styrene)s, suggesting that a certain degree of the styrene insertion inhibited the chain transfer in this catalysis. The Cp analogue, CpTiCl$_2$(N=C^{t}Bu$_2$) (**2**) showed negligible catalytic activity under the same conditions although **2** showed notable catalytic activity for ethylene polymerization. Since the notable differences in the composition of resultant polymers, styrene incorporation and the microstructures were observed in the polymerization using half-titanocenes containing different anionic donor ligands (chloride, aryloxide, ketimide), it is thus concluded that the nature of the anionic donor ligands plays an essential key role in the copolymerization. The resultant polymers prepared by Cp*TiCl$_3$−MAO (**4**−MAO) and Cp*TiMe$_3$−MAO (**6**−MAO) were a mixture of polyethylene and syndiotactic polystyrene, whereas the resultant polymer was polyethylene containing trace amount of poly(ethylene-*co*-styrene) with low styrene content or poly(ethylene-*co*-styrene) with extremely low styrene content in the polymerization using **6**−[PhN(H)Me$_2$][B(C_6F_5)$_4$] catalyst. In contrast, poly(ethylene-*co*-styrene)s were obtained exclusively in the polymerization using **1** and Cp*TiX$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) [X = Cl (**3**), Me(**5**)] −MAO catalysts as well as **5**−[PhN(H)Me$_2$][B(C_6F_5)$_4$] catalyst under the same conditions. These facts also indicate that the anionic donor strongly affects both the styrene incorporation and the copolymerization behavior. The fact also suggests that another catalytically active species (seems likely Ti(III) species) which catalyze syndiospecific styrene polymerization was formed upon in the polymerization using **4**−MAO and **6**−MAO catalyst systems, and thus strongly suggested that cationic Ti(IV) species play an important key role for ethylene polymerization as well as for ethylene/styrene copolymerization. The next stage in the copolymerization is to clarify the origin of the observed difference, and we are expecting to explore the possibility to explain by the values in coordination energy using DFT calculations, as previously shown in ethylene/norbornene copolymerization using various half-titanocenes containing aryloxide ligand.[39] The synthesis of various unique (block, graft) copolymers by this living copolymerization technique using the present catalyst system can also be possible as the extension of this study and the project is also now underway.

Experimental Section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade toluene (Kanto Chemical Co., Inc.) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A $^1/_{16}$ and 13X) under nitrogen stream in the drybox, and was used without further purification. Styrene of reagent grade (Kanto Chemical Co., Inc.) was stored in a freezer after passing through an alumina short column under nitrogen flow in the drybox. Cp*TiCl$_2$(N=C^{t}Bu$_2$) (**1**),[27] and CpTiCl$_2$(N=C^{t}Bu$_2$) (**2**),[27] Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**),[17] and Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5**)[17] were prepared according to previous reports. Toluene and AlMe$_3$ in the commercially available methylaluminoxane [PMAO−S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were removed under reduced pressure (at ca. 50 °C for removing toluene and AlMe$_3$ and then heated at $>$100 °C for 1 h for completion) in the drybox to give white solids.

All ^{1}H (399.65 MHz) and ^{13}C (100.40 MHz) NMR spectra were recorded on a JEOL JNM-LA400 spectrometer (399.65 MHz, ^{1}H). All deuterated NMR solvents were stored over molecular sieves under a nitrogen atmosphere, and all chemical shifts are given in ppm and are referenced to Me$_4$Si. ^{13}C NMR spectra for polyethylene and poly(ethylene-*co*-styrene)s were recorded on a JEOL JNM-LA400 spectrometer (100.40 MHz, ^{13}C) with proton decoupling. The pulse interval was 5.2 s, the acquisition time was 0.8 s, the pulse angle was 90°, and the number of transients accumulated was ca. 6000. The copolymer samples for analysis were prepared by dissolving the polymers in 1,1,2,2,-tetrachloroethane-d_2 solution, and the spectra were measured at 110 °C.

Molecular weight and molecular weight distribution for the poly(ethylene-*co*-styrene)s were measured by gel permeation chromatography (GPC, Tosoh HLC-8121GPC/HT) using a RI-8022 detector (for high temperature, Tosoh Co.) with polystyrene gel column (TSK gel GMH$_{HR}$-H HT × 2, 30 cm × 7.8 mmϕ ID), ranging from $<10^2$ to $<2.8 \times 10^8$ MW) at 140 °C using *o*-dichlorobenzene containing 0.05 w/v % 2,6-di-*tert*-butyl-*p*-cresol as the solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Differential scanning calorimetric (DSC) data for the copolymer were recorded by means of DSC6100 (Seiko Instruments Co.) under nitrogen atmosphere [conditions: heating from 25 to 300 °C (20 °C/min); cooling from +300 to −100 °C (10 °C/min)].

Typical Reaction Procedure for Copolymerization of Ethylene with Styrene by Cp*TiCl$_2$(N=C^{t}Bu$_2$) (1). The typical reaction procedure for ethylene/styrene copolymerization (run 1, Table 1) is as follows. Toluene (19 mL), styrene (10 mL), and MAO solid (174 mg, 3.0 mmol) were added into the autoclave (100 mL scale stainless steel) in the drybox, and the reaction apparatus was then replaced and filled with ethylene (1 atm) at room temperature (25 °C). A toluene solution (1.0 mL) containing **1** (2.0 μmol) was then added into the autoclave, and the reaction apparatus was then immediately pressurized to 3 atm (total ethylene pressure 4 atm). The mixture was magnetically stirred for 10 min, the ethylene that remained was purged after the reaction, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH and was then dried in vacuo. Basic experimental procedure in the ethylene (or styrene) homopolymerization was the same as that in ethylene/styrene copolymerization except that toluene were added in place of various amounts of styrene (10 mL) partially (total 29 mL).

According to the previous report,[36,37] the resultant polymer mixture was separated into three fractions, and atactic polystyrene which was prepared only by MAO was extracted with acetone. Poly(ethylene-*co*-styrene) was extracted with tetrahydrofuran (THF), and polyethylene and/or syndiotactic polystyrene which were the byproduct in this reaction was separated as THF insoluble fraction. The basic experimental procedure is as follows:

The polymer sample obtained in the copolymerization experiment was added into a round-bottom flask containing acetone equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate acetone soluble and insoluble fraction. Then the acetone insoluble fraction was dried and added into a round-bottom flask containing THF equipped with a reflux condenser, and the mixture was refluxed for 6 h to separate THF soluble and insoluble fractions. Trace amount of polymers were isolated as THF insoluble fractions, clearly indicating that the polymerization afforded poly(ethylene-*co*-styrene)s exclusively.

The polymerization by varying the ethylene pressure (run 13 in the text) was performed by increasing the ethylene pressure (6 atm) after 10 min of first polymerization (as run 1, ethylene 4 atm), and the post polymerization was carried out for additional 10 min (under the conditions as the same as in run 8).

The microstructure analyses in the resultant copolymers were estimated by the ^{13}C NMR spectra of the copolymer, and each of the resonances were assigned by comparison with the previous report concerning poly(ethylene-*co*-styrene)s.[36,37] The styrene contents were estimated based on ratio of the total integration values of styrene vs ethylene at each resonances in the ^{1}H NMR spectra.[36]

Typical Procedure for Copolymerization of Ethylene with Styrene by Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (5) or Cp*TiMe$_3$ (6) — [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] Catalyst System. The typical reaction procedure for ethylene/styrene copolymerization (run 62, Table 6) is as follows. Toluene (19 mL), styrene (10 mL), and Al^{i}Bu$_3$ (0.95 mmol) were added into the autoclave in the drybox, and the reaction apparatus was then replaced, filled with ethylene (1 atm) at room temperature (25 °C). Then, 1.0 mL of a 5.0 μmol solution of Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**5**) in toluene was added into a 25 mL Schlenk tube, followed by Al^{i}Bu$_3$ compound (50.0 μmol), [PhNMe$_2$H][B(C$_6$F$_5$)$_4$] (AFPB, 5.0 μmol). This mixture was stirred for ca. 10 min and was then added into the autoclave. The reaction apparatus was then immediately pressurized to 5 atm (total ethylene pressure 6 atm), and the mixture was magnetically stirred for 20 min. After the reaction, ethylene remained was purged upon cooling in the ice bath, and the mixture was then poured into EtOH (50 mL) containing HCl (5 mL). The resultant polymer was collected on a filter paper by filtration, and was adequately washed with EtOH, and was then dried in vacuo.

According to the procedure described above, the resultant polymer mixture was separated into two fractions, and atactic polystyrene which was prepared only by MAO was extracted with acetone. The reaction product prepared by **5**−AFPB catalyst was poly(ethylene-*co*-styrene) exclusively as THF soluble fraction, and the major product by **6**−AFPB catalyst was polyethylene as THF insoluble fraction.

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Supporting Information Available: Figures showing selected ^{13}C NMR spectra for poly(ethylene-*co*-styrene)s prepared by Cp*TiCl$_2$(N═C^{t}Bu$_2$) (**1**), Cp*TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**3**), Cp*TiMe$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)−MAO (**5**−MAO), and **5**−[PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] catalysts and for polymers prepared by Cp*TiCl$_3$ (**4**), Cp*TiMe$_3$−MAO (**6**−MAO), and **6**−[PhN(H)Me$_2$][B(C$_6$F$_5$)$_4$] catalysts and differential scanning calorimetric (DSC) thermograms for poly(ethylene-*co*-styrene)s prepared by **1**−MAO catalysts, and for polymers prepared by **4**−MAO catalyst. This material is available free of charge via the Internet at http://pubs.acs.org.

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(46) The resultant polymer consisted of poly(ethylene-*co*-styrene) and (acetone soluble) atactic polystyrene produced by MAO. The copolymer was isolated as the acetone insoluble and THF soluble fraction,[36] and amounts of THF insoluble fraction (polyethylene, syndiotactic polystyrene) were negligible. The detailed results were shown in the Supporting Information in our preliminary communication.[13.]

(47) To obtain the copolymer with uniform compositions, the polymerization should be terminated at the initial stage. MAO white solid was prepared by removing toluene and $AlMe_3$ from the commercially available MAO (PMAO−S, Tosoh Finechem. Co.), and a certain excess amount of MAO was required for exhibiting high catalytic activity.

(48) Ethylene concentrations under the reaction conditions were estimated by the equation quoted by Kissin (Kissin, Y. V. *Isospecific Polymerization of Olefin with Heterogeneous Ziegler−Natta Catalysts*; Springer-Verlag: NewYork, 1985; p 3), and the ethylene solubilities in the reaction mixture (1 atm) were used as those in toluene reported in the following article: Sahgal, A.; La, H. M.; Hayduk, W. *Can. J. Chem. Eng.* **1978**, *56*, 354−357.

(49) In our attempts for the copolymerization by **1** at 55 and 70 °C for longer hours (20 min) under rather high styrene concentrations (styrene 15.0 mL, [S]/[E] = 8.33, 9.62, respectively), the resultant copolymers possessed rather broad molecular weight distributions with the unimodal distributions and a first-order plots between M_n value and polymers yields were not seen. These results might suggest that a certain extent of chain transfer took place for the copolymerization at higher temperature, and the living nature at 55 or 70 °C may thus be observed only at the initial stage or under limited conditions.

(50) $[PhN(H)(Me)_2][B(C_6F_5)_4]$ (AFPB) was chosen as the borate cocatalyst, and this is because that $Ph_3CB(C_6F_5)_4$ explosively produces atactic polymer (APS) probably in a cationic manner[43] and that $(^tBuC_5H_4)$-$TiCl_2(O$-$2,6$-$^iPr_2C_6H_3)$ exhibited relatively high catalytic activity for syndiospecific styrene polymerization in the presence of AFPB and a mixture of $Al^iBu_3/Al(n$-$C_8H_{17})_3$.[43]

(51) Al^iBu_3 was added into the reaction mixture for the copolymerization in the presence of AFPB cocatalyst not only to remove impurities in the mixture but also to improve the catalyst efficiency by partial replacement of the methyl group into ^iBu, as seen in the living 1-hexene polymerization using **5** − $(Ph_3C)[B(C_6F_5)_4]$ catalyst system.[3k] The reaction of **5** with Al^iBu_3 did not afford any reduction products and only alkyl exchange was occuring.

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