

Review

Half-Titanocenes Containing Anionic Ancillary Donor Ligands: Effective Catalyst Precursors for Ethylene/Styrene Copolymerization

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Abstract: This review summarizes recent results for ethylene/styrene copolymerization using half-titanocenes containing anionic donor ligands, $\text{Cp}^*\text{TiX}_2(\text{Y})$ (X = halogen, alkyl; Y = aryloxo, ketimide *etc.*)–cocatalyst systems. The product composition, the styrene incorporation and microstructures in the resultant copolymers are highly influenced by the anionic donor employed. A methodology for an exclusive synthesis of the copolymers even under high temperature and high styrene concentrations has been introduced on the basis of a proposed catalytically-active species in this catalysis.

Keywords: polymerization; ethylene; styrene; copolymerization; titanium; catalyst; polymerization mechanism; homogeneous catalysis

1. Introduction

Precise control over macromolecular structure is a central goal in synthetic polymer chemistry, and copolymerization is an important method that usually modifies physical, mechanical and electronic properties by varying the ratio of the individual components. Considerable effort has been devoted to establishing a new synthetic strategy for precise placement of a chemical functionality, and the design and synthesis of efficient transition metal complex catalysts for precise olefin polymerization have been a subject of extensive studies [1–18]. Ethylene/styrene copolymers, which cannot be prepared by free radical or ordinary Ziegler-Natta processes [19–22], are promising due to their unique properties [23–25]. The introduction of styrene into the PE backbone results in drastic changes in both the viscoelastic behavior and thermo-mechanical properties of the polymeric material [24], since the

crystallizability of PE chains is gradually inhibited by the incorporation of styrene. The copolymers range from semi-crystalline to amorphous materials, depending on the styrene content [23]. Therefore, these copolymers can become effective blend compatibilizers for PS/PE blends and also have potential in foam, film and sheet applications.

Half-titanocenes, such as Cp^*TiF_3 , $\text{Cp}^*\text{Ti}(\text{OMe})_3$ and $(\text{indenyl})\text{TiCl}_3$, are efficient catalyst precursors for syndiospecific styrene polymerization [26–40]; however, these catalyst precursors showed low activities in the copolymerization, and the resultant polymers were a mixture of polyethylene (PE), syndiotactic polystyrene (SPS) and the copolymer (E-S) [41–45]. As related examples, Cp^*TiMe_3 exhibited catalytic activities for both ethylene polymerization and styrene polymerization in the presence of MAO or $\text{B}(\text{C}_6\text{F}_5)_3$, and the resultant polystyrene possessed both atactic (via a cationic mechanism) and syndiotactic (via a coordination insertion mechanism) stereoregularity; the ratios were dependent upon the polymerization temperature [46–51]. This catalyst also polymerizes isobutene via a carbocationic mechanism rather than a coordination insertion mechanism [51].

In contrast, it has been known that modified half-titanocenes, $\text{Cp}'\text{TiX}_2(\text{Y})$ (Cp' = cyclopentadienyl group; Y = anionic ligand, such as O -2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$, $\text{N}=\text{C}'\text{Bu}_2$, $\text{N}=\text{PR}_3$ etc.; X = halogen, alkyl), are effective not only for syndiospecific styrene polymerization, but also for ethylene/styrene copolymerization to exclusively give poly(ethylene-*co*-styrene)s [15,17,52–63]. Linked half-titanocenes (so-called “constrained geometry type”) are also effective for copolymerization [5,64–77], although these complexes exhibited extremely low catalytic activities for styrene polymerization [64,73]. In this reviewing article, I wish to summarize reported examples for copolymerization, especially using modified half-titanocene catalysts [78,79].

2. Ethylene/Styrene Copolymers: Microstructures, Thermal Properties and Composition Analyses

Poly(ethylene-*co*-styrene)s are generally obtained by the copolymerization of ethylene with styrene in the presence of catalysts composed of a transition metal complex and cocatalyst [methylaluminoxane (MAO), methyl isobutyl aluminoxane (modified MAO, MMAO), borate, such as $\text{B}(\text{C}_6\text{F}_5)_3$, $\text{Ph}_3\text{CB}(\text{C}_6\text{F}_5)_4$, $\text{PhN}(\text{H})\text{MeB}(\text{C}_6\text{F}_5)_4$] [78,79]. In most cases, the resultant copolymer (E-S copolymer) should be isolated from a mixture of atactic polystyrene (APS, prepared by the cocatalyst itself), polyethylene (PE) and syndiotactic polystyrene (SPS).

Typical ^{13}C NMR spectra (methylene and methine regions) of the copolymers, including assignment of the monomer sequences, are shown in Figure 1 [53]. As described below, the microstructures for the resultant poly(ethylene-*co*-styrene)s depend on the catalysts used. The glass transition temperature (T_g), as measured by differential scanning calorimetry (DSC) increased with an increase in the styrene content (−8.1–58.3 °C), because the crystallizability of PE chains is gradually inhibited by the incorporation of styrene [23].

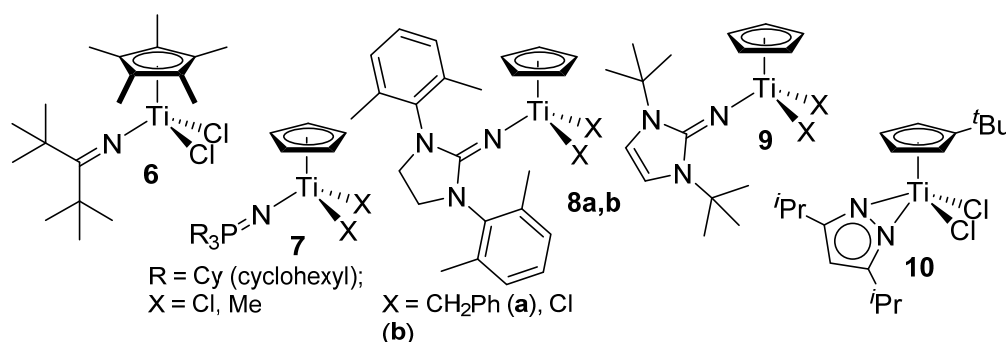
As summarized in Table 1, Cp'TiCl₂(OAr) (Cp' = 1,2,3-Me₃C₅H₂ (**1**), 1,3-Me₂C₅H₃ (**2**), ^tBuC₅H₄ (**3**) *etc.*; Ar = 2,6-ⁱPr₂C₆H₃) exhibited remarkable activities for ethylene/styrene copolymerization in the presence of MAO [52,53], whereas the Cp* analogue (**4**), which exhibited remarkable activities and comonomer incorporations in ethylene/ α -olefin copolymerization [80–83], exhibited lower activities than **1–3** (Table 1) [52–56]. The resultant polymers are poly(ethylene-*co*-styrene)s exclusively without by-producing polyethylene and/or syndiotactic polystyrene [52,53]. The resultant copolymers possessed not only relatively high molecular weights with unimodal molecular weight distributions, but also a single composition, as confirmed by DSC thermograms, CFC and GPC/FT-IR [53]. The activities by **1–3** decreased slightly with an increase in the styrene concentration, whereas the styrene contents in the copolymers increased upon increasing the styrene concentration. Styrene incorporations with aryloxo analogues is more efficient than that with [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**5**). An analysis of the microstructure of the resultant poly(ethylene-*co*-styrene)s by ¹³C NMR spectroscopy (Figure 1) indicated that the resultant copolymer prepared by **1** possesses resonances ascribed to two and three styrene units connected via head-to-tail coupling [at δ = 40.7–41.0 ppm (T _{$\beta\beta$}), 43.1–45 ppm (S _{$\alpha\alpha$} and T _{$\beta\delta$}), respectively], in addition to the resonances ascribed to tail-to-tail coupling of a styrene unit or head-to-head bridged by an intervening ethylene unit (S _{$\alpha\beta$} , at δ = 34.3 and 35.1 ppm). This is especially interesting in contrast to the results with the linked half-titanocene (**5**).

Copolymerization with the other modified half-titanocenes has also been reported (Scheme 2). Ethylene/styrene copolymerization by Cp*TiCl₂(N=C^tBu₂) (**6**) took place in a living manner in the presence of MAO cocatalyst, although the homopolymerization of ethylene and styrene did not proceed in a living manner [57]. No styrene repeating units were observed in the resultant copolymers, which suggest that a certain degree of styrene insertion inhibits chain transfer in this catalysis. The living nature was maintained under various conditions (Al/Ti molar ratios, ethylene pressure, styrene concentrations, temperature) [58].

Table 1. Ethylene/styrene copolymerization by Cp'TiCl₂(OAr) [Cp' = 1,2,3-Me₃C₅H₂ (**1**), 1,3-Me₂C₅H₃ (**2**), ^tBuC₅H₄ (**3**); OAr = O-2,6-ⁱPr₂C₆H₃] or [Me₂Si(C₅Me₄)(N^tBu)]TiCl₂ (**5**)–MAO catalyst systems [52,53].^a

Complexes	Styrene /mL	Activity ^b	THF soluble (E/S copolymer)			
			Content ^c /wt. %	M _w ^d ×10 ^{−4}	M _w /M _n ^d	Styrene /mol% ^e
(1,2,3-Me ₃ C ₅ H ₂)TiCl ₂ (OAr) (1)	3	4100	99.1	17.0	1.6	26.0
(1,2,3-Me ₃ C ₅ H ₂)TiCl ₂ (OAr) (1)	5	3070	98.3	11.0	1.7	38.8
(1,2,3-Me ₃ C ₅ H ₂)TiCl ₂ (OAr) (1)	10	2720	97.8	6.6	1.6	51.2
(1,3-Me ₂ C ₅ H ₃)TiCl ₂ (OAr) (2)	3	3670	97.1	6.4	1.8	32.3
(1,3-Me ₂ C ₅ H ₃)TiCl ₂ (OAr) (2)	5	4280	98.2	6.0	2.1	38.5
(1,3-Me ₂ C ₅ H ₃)TiCl ₂ (OAr) (2)	10	4140	98.2	3.7	1.6	49.0
(^t BuC ₅ H ₄)TiCl ₂ (OAr) (3)	5	2180	99.6	5.9	1.7	37.6
(^t BuC ₅ H ₄)TiCl ₂ (OAr) (3)	10	1840	98.7	3.5	2.2	51.2
[Me ₂ Si(C ₅ Me ₄)(N ^t Bu)]TiCl ₂ (5)	10	5630	99.6	18.0	1.8	32.7

^a Reaction conditions: catalyst 1.0 μ mol (2 μ mol/mL-toluene), ethylene 4 atm, total volume of toluene and styrene = 30 mL, MAO white solid (Al/Ti = 2000, molar ratio), 25 °C, 10 min. ^b Activity (kg-polymer/mol-Ti·h), polymer yield in acetone insoluble fraction. ^c Percentage of content in copolymer based on polymer obtained. ^d GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^e Styrene content (mol%) in copolymer estimated by ¹H NMR (1,1,2,2-C₂D₂Cl₄).

Scheme 2. Other half-titanocenes employed for ethylene/styrene copolymerization [48–51].

Copolymerization with $\text{CpTiX}_2(\text{N}=\text{PCy}_3)$ (**7**, $X = \text{Cl, Me}$)–cocatalyst (MAO, borates) systems proceeded with remarkable catalytic activities [at 60–90 °C, ethylene 70 psi (4.76 atm)], however, styrene incorporation seemed less efficient than with either aryloxo analogues (**1–3**) or linked half-titanocene (**5**) [styrene content: 33.4–61.4 wt% (<27.6 mol%)] [60,84]. Half-titanocene-containing imidazolidin-2-iminato ligand (**8a**) also exhibited remarkable catalytic activity under certain conditions, but the styrene content in the resultant copolymer was low [ethylene 5 bar, styrene/toluene = 20/210 mL, 80 °C; activity = 1960 kg-polymer/mol-Ti·h, $M_w = 1.79 \times 10^5$, $M_w/M_n = 2.1$, styrene 10 wt% (2.9 mol%)] [59]. However, the copolymerization using the dichloro- analogue (**8b**) afforded a mixture of PE and the copolymer confirmed by DSC thermograms [61]. The imidazolin-2-iminato analogue (**9**) showed moderate catalytic activities and afforded the copolymers exclusively under the optimized conditions: the copolymerization proceeded in a quasi living manner, as observed in the copolymerization by **6** [63]. The pyrazolato analogue (**10**) also showed the similar copolymerization behavior to those observed by **6,9**, although the activities were low [62]. Microstructure analysis results indicate that the resultant poly(ethylene-*co*-styrene)s prepared by **9,10** possessed resonances ascribed to isolated and alternating styrene inserted units. On the basis of these experiments, it seems likely that an isolated (and/or alternating) insertion of styrene plays a role for the (quasi) living polymerization to disturb the propagated chain from β -H elimination [57,58,62,63].

On the basis of the above results, modified half-titanocenes, $\text{Cp}^*\text{TiX}_2(\text{Y})$, especially the aryloxo modified half-titanocenes, are better catalyst precursors for the synthesis of ethylene/styrene copolymers, and both the activity and the styrene incorporation are highly affected by the kind of ligands used (both cyclopentadienyl and anionic donor).

2.1.2. Role of Anionic Donor Ligand (Y) and Mechanistic Considerations

Three half-titanocene complexes containing Cp^* ligand of type, $\text{Cp}^*\text{TiX}_2(\text{Y})$ [$X = \text{Cl}$, $\text{Y} = \text{N}=\text{C}^t\text{Bu}_2$ (**6**), O -2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (**4**), Cl (**11**); $X = \text{Me}$, $\text{Y} = O$ -2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (**12**), Me (**13**)]–cocatalyst systems were used for the copolymerization to explore the effect of anionic donor ligands under the same conditions (Tables 2,3) [58,85,86]. The ketimide analogue (**6**)–MAO catalyst showed moderate catalytic activities, and the styrene content increased at higher temperature. The resultant copolymers prepared with **6** even at 55 and 70 °C still possessed relatively low PDI values, suggesting that the living nature was maintained under these conditions (Table 2). In contrast, the polymerizations by the aryloxo analogue (**4**) gave copolymers with high styrene contents (31.9–34.3 mol%), and a

significant increase in the activity was not observed at high temperature. The resultant copolymers possessed lower M_n values with unimodal, rather large PDI values ($M_w/M_n = 1.50$ – 1.62), which strongly suggests that a chain transfer reaction occurred to some degree. Note that the polymers prepared with the trichloride analogue (**11**) showed bimodal molecular weight distributions consisting of a mixture of PE and SPS, and the proportion of SPS increased at high temperature, due to an increase in the activity for syndiospecific styrene polymerization [58,87,88].

Table 2. Copolymerization of ethylene with styrene by $\text{Cp}^*\text{TiCl}_2(\text{Y})$ [$\text{Y} = \text{N} = \text{C}^t\text{Bu}_2$ (**6**), O -2,6- $i\text{Pr}_2\text{C}_6\text{H}_3$ (OAr, **4**), Cl (**11**)]–MAO catalyst systems [58]^a.

Catalysts Y	Temp. /°C	Composition (%) ^c			Activity ^d	Styrene cont. ^e /mol%	M_n^f $\times 10^{-4}$	M_w/M_n^f
		E-S	PE	SPS				
$\text{N}=\text{C}^t\text{Bu}_2$ (6)	25	>99	trace	trace	396	7.4	9.5	1.18
$\text{N}=\text{C}^t\text{Bu}_2$ (6)	40	>99	trace	trace	790	9.3	14.4	1.28
$\text{N}=\text{C}^t\text{Bu}_2$ (6)	55	>99	trace	trace	1110	10.4	19.7	1.31
$\text{N}=\text{C}^t\text{Bu}_2$ (6)	70	>99	trace	trace	1260	12.2	16.3	1.57
OAr (4)	25	>99	trace	trace	504	31.9	9.28	1.62
OAr (4)	40	>98	trace	trace	660	34.3	9.79	1.5
Cl (11)	25	trace	86.8	13.2	250	>99 ^g	5.85	1.26
						-	0.29	2.69
Cl (11)	40	trace	81.6	18.4	280	>99 ^g	5.07	1.31
						-	0.31	1.75
Cl (11)	55	trace	69.8	30.2	260	>99 ^g	3.56	1.48
						-	0.21	1.77

^aConditions: catalyst 2.0 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. ^bInitial molar ratio of styrene/ethylene in the reaction mixture.

^cBased on a mixture of PE, SPS and copolymer. (acetone insoluble fraction). ^dActivity in kg-polymer/mol-Ti-h. ^eStyrene content (mol%) estimated by ^1H NMR. ^fGPC data in *o*-dichlorobenzene vs. polystyrene standards. ^gConfirmed by GPC/FT-IR, ^{13}C NMR spectra, DSC thermograms.

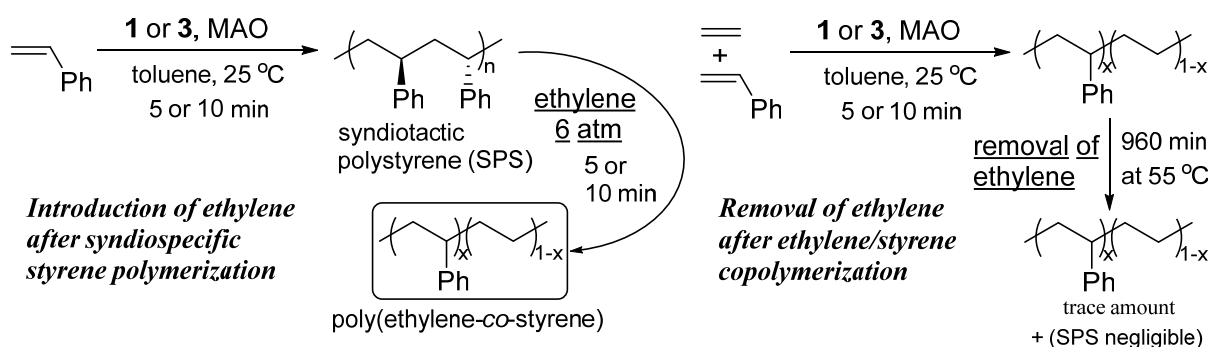
Copolymerization using the aryloxo-dimethyl analogue (**12**)–MAO or $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (AFPB) catalyst system afforded the copolymer (Table 3); no distinct differences in the microstructures were seen between MAO and AFPB in the ^{13}C NMR spectra. In contrast, note that the polymer prepared with the Cp^*TiMe_3 (**13**)–AFPB catalyst was PE (containing a trace amount of the copolymer with low styrene content) or the copolymer with an extremely low styrene content, whereas the copolymerization in the presence of MAO afforded a mixture of PE and SPS, as seen with the trichloride analogue (**11**). The fact that no SPS was formed in polymerization with **13**–AFPB catalyst was analogous to the fact that $\text{Cp}^*\text{Ti}(\text{CH}_2\text{Ph})_3$ –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 [89]. These results strongly suggest that cationic Ti(IV) species play an important key role in ethylene polymerization, as well as ethylene/styrene copolymerization. These results also suggest that another catalytically-active species [likely Ti(III)] for syndiospecific styrene polymerization is formed in the presence of MAO [58].

Table 3. Ethylene/styrene copolymerization by $\text{Cp}^*\text{TiMe}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (**12**), Cp^*TiMe_3 (**13**)–MAO or $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (AFPB)–catalyst systems [58]^a.

Cat. (μmol)	Time /min	Composition (%) ^b			Activity ^c	styrene cont. ^d /mol%	M_n^e $\times 10^{-4}$	M_w/M_n^e
		E-S	PE	SPS				
12 /MAO (2.0)	10	99	trace	trace	519	30.5	5.34	2.05
12 /AFPB (5.0)	20	99	trace	trace	79.2	46.7	2.81	2.16
13 /MAO (2.0)	10	trace	68.6	31.4	366	>99	8.66	1.37
						-	0.81	2.33
13 /AFPB (10.0)	20	trace	99	trace	43.8	trace	0.5	3.53

^aConditions: catalyst 2.0 μmol , MAO 3.0 mmol or Al^iBu_3 1.0 mmol (borate system), $[\text{C}_6\text{H}_5\text{NH}(\text{CH}_3)_2][\text{B}(\text{C}_6\text{F}_5)_4]$ (AFPB) 2.0 μmol , styrene 10.0 mL, toluene 20 mL, 10 min. ^bBased on a mixture of PE, SPS and copolymer. (acetone insoluble fraction). ^cActivity in kg-polymer/mol-Ti·h. ^dStyrene content (mol%) estimated by ^1H NMR. ^eGPC data in *O*-dichlorobenzene vs. polystyrene standards.

The exclusive formation of copolymers without formation of SPS as a by-product was observed with the introduction of ethylene into a solution of syndiospecific styrene polymerization using $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ –MAO catalysts (Scheme 3) [90]. Moreover, the activities and the M_w values, as well as the styrene contents in the latter copolymerizations, were identical to those in independent runs (Table 4), clearly indicating that the catalytically active species for the syndiospecific styrene polymerization can be tuned to the active species for copolymerization by exposure of ethylene.

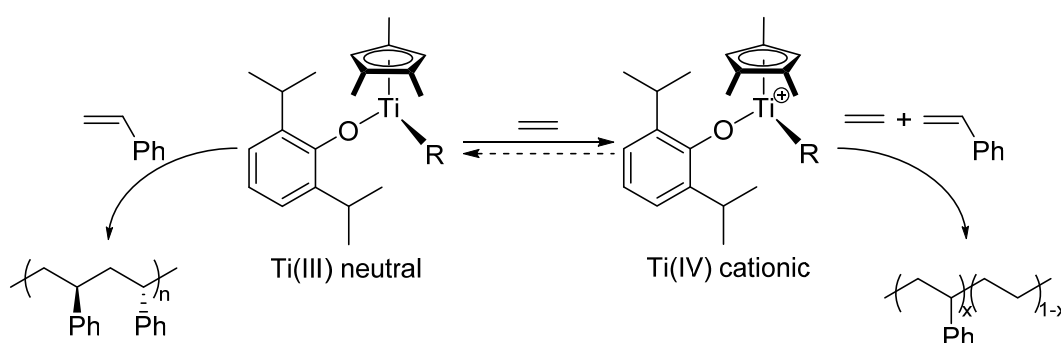
Scheme 3. Step (co)polymerization of ethylene with styrene [90].

Taking into account these findings [58,87,88,91], it is thus highly assumed that the cationic $\text{Ti}(\text{IV})$ species, $[\text{Cp}^*\text{TiR}(\text{Y})]^+$, likely play a role in copolymerization, and the active species containing an anionic ancillary donor ligand [assumed to be neutral $\text{Ti}(\text{III})$, $\text{Cp}^*\text{TiR}(\text{Y})$] proposed by Tomotsu *et al.* [37,38] plays a role in syndiospecific styrene polymerization (Scheme 4) [90]. These results should also explain the reported finding that the catalytic activities and molecular weight of the resultant syndiotactic polystyrene in styrene polymerization using $\text{Cp}^*\text{TiX}_2(\text{Y})$ –cocatalyst systems were highly dependent upon the anionic donor ligand (Y), regardless of the kind of the cocatalyst used [90]. These proposals are in contrast to the hypothesis that cationic $\text{Ti}(\text{III})$ species, $[\text{Cp}^*\text{Ti}(\text{R})(\text{styrene})]^+$, play a role as the catalytically-active species for the styrene polymerization using Cp^*TiX_3 [89,92]. This hypothesis should help to explain why polystyrene structures in the resultant copolymers prepared with $\text{Cp}^*\text{TiCl}_2(\text{Y})$ –MAO catalysts are atactic [52–63].

Table 4. Two step ethylene/styrene (co)polymerization by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ [$\text{Cp}^* = 1,2,4\text{-Me}_3\text{C}_5\text{H}_2$ (**1**), $t\text{-BuC}_5\text{H}_4$ (**3**)]–MAO catalysts [90]^a.

catalysts Cp^*	Ethylene ^b 1 st +2 nd /atm.	Time. 1 st +2 nd /min	Copolymers ^c				SPS ^d		
			Yield /mg	M_w^e $\times 10^{-4}$	M_w/M_n^e	Styrene ^f /mol%	Yield /mg	M_w^e $\times 10^{-4}$	M_w/M_n^e
1,2,4-Me ₃ C ₅ H ₂ (1)	0	5	-				45	24.1	1.82
1,2,4-Me ₃ C ₅ H ₂ (1)	0	10	-				175	24.6	2.07
1,2,4-Me ₃ C ₅ H ₂ (1)	6	5	440	12.4	1.80	48.3	trace		
1,2,4-Me ₃ C ₅ H ₂ (1)	6	10	593	11.5	1.54	50.4	trace		
$t\text{-BuC}_5\text{H}_4$ (3)	0	5	-				242	17.2	2.70
$t\text{-BuC}_5\text{H}_4$ (3)	6	5	574	12.7	1.85	44.7	trace		
1,2,4-Me ₃ C ₅ H ₂ (1)	0+6	10+5	340	10.7	2.54	48.3	140	21.9	2.53
1,2,4-Me ₃ C ₅ H ₂ (1)	0+6	10+10	577	10.8	1.92	49.8	157	25.7	2.07
$t\text{-BuC}_5\text{H}_4$ (3)	0+6	5+5	360	13.2	2.36	45.3	221	16.8	2.51

^a Conditions: Ti cat. 1.0 μmol , styrene 10 mL, toluene 20 mL, MAO 3.0 mmol, 25 °C. ^b 1st styrene 10 mL (5 or 10 min, ethylene 0 atm) and then ethylene 6 atm (5 or 10 min). ^c Isolated as acetone insoluble and THF soluble fraction. ^d Isolated as acetone insoluble and THF insoluble fraction. ^e GPC data in *O*-dichlorobenzene vs. polystyrene standards. ^f Styrene content (mol%) estimated by ¹H NMR spectra.

Scheme 4. Proposed active species in two polymerization using half-titanocenes [90].

2.2. Effect of Cocatalyst in Ethylene/Styrene Copolymerization by Aryloxo-Modified Half-Titanocene Catalysts for Exclusive Synthesis of Copolymers under High Styrene Concentration Conditions

Although ethylene/styrene copolymerizations using the aryloxo-modified half-titanocenes, $\text{Cp}^*\text{TiCl}_2(\text{OAr})$ [$\text{Cp}^* = 1,2,3\text{-Me}_3\text{C}_5\text{H}_2$, $1,3\text{-Me}_2\text{C}_5\text{H}_3$, $t\text{-BuC}_5\text{H}_4$, C_5Me_5 (Cp^* , **4**); $\text{OAr} = \text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3$], in the presence of MAO generally affords copolymers [52,53,58,90], it was revealed that syndiotactic polystyrene (SPS) was a by-produced when the polymerization was performed especially at a rather high temperature under high styrene concentrations [54,55]: the ratio of the copolymer/SPS was affected by the polymerization temperature and the [styrene]/[ethylene] feed molar ratio in the reaction mixture [54]. For example, the resultant polymers were poly(ethylene-*co*-styrene)s when the copolymerization was conducted at 25 °C or 40 °C under ethylene 6 atm. (Table 5, runs 1,4), whereas SPS was by-produced when the reactions were conducted at 40 °C or 55 °C under ethylene 4 atm (runs 2-3,5) [55]. As shown in Figure 2a, resonances ascribed to two (head-to-tail) styrene repeating units ($T_{\beta\delta}$, $S_{\alpha\alpha}$) in addition to resonances due to so-called pseudo random [$S_{\alpha\beta}$, SS by tail-to-tail and/or SES (S = styrene,

E = ethylene)] were observed in the NMR spectrum. However, resonances ascribed to carbons in SPS (marked as * *ca.* 40.8 and 44.1 ppm) also increased upon increasing the polymerization temperature (runs 2,3 in Figures 2b,c) [55].

Since the reports concerning the efficient synthesis of the copolymers with high styrene contents have been limited so far, we explored a possibility for the exclusive synthesis of copolymers under high temperature conditions. Development of the catalyst systems for the exclusive synthesis should be thus considered as potentially important in terms of not only polymer synthesis, but also better understanding of polymerization mechanism, although the copolymers with high styrene contents can be easily prepared when the polymerizations were conducted at 25 °C under high styrene concentrations [52,53].

Table 5. Copolymerization of ethylene with styrene by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (4)–MAO catalyst system [55]^a.

Run	Ethylene /atm.	Tem p /°C	[S] ₀ /[E] ₀ ^b	Activity ^c	Comp. ^d /wt.%		<i>M</i> _w ^e ×10 ^{−4}	<i>M</i> _w / <i>M</i> _n ^e	Styrene ^f /mol%
					E-S	SPS			
1	4	25	6.01	525	>99	-	8.4	2.25	34
2	4	40	7.13	384	77	23	8.7	1.72	-
3	4	55	8.34	363	43	57	10.0	1.8	-
4	6	40	4.75	660	>99	-	9.8	1.5	34
5	6	55	5.56	600	69	31	4.2/9.20	1.64/2.32	-

^a Conditions: Ti 2.0 μmol, ethylene 4 atm, styrene 10 mL, toluene 20 mL, MAO (white solid prepared by removing AlMe₃ and toluene from commercially available PMAO-S, Tosoh Finechem Co.) 3.0 mmol, (Al/Ti = 1500, molar ratio), 10 min. ^b Initial molar ratio of styrene/ethylene in the reaction mixture. ^c Activity in kg-polymer/mol-Ti·h, polymer yields were based on a mixture of SPS (syndiotactic polystyrene) and E-S (copolymer) as acetone insoluble fraction. ^d Composition estimated by ¹³C NMR spectra (and confirmed by ¹H NMR spectra). ^e GPC data in *o*-dichlorobenzene vs. polystyrene standards. ^f Styrene content in mol% estimated by ¹H NMR spectra.

Figure 2. ¹³C NMR spectra (in 1,1,2,2-tetrachloroethane-*d*₂ at 110 °C) for the resultant polymers (acetone insoluble fraction) prepared by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{Pr}_2\text{C}_6\text{H}_3)$ (4)–MAO catalyst system [55]. Conditions: 4 2.0 μmol, ethylene 4 atm., styrene 10 mL, toluene 20 mL, 10 min., temperature at (a) 25 °C (run 1), (b) 40 °C (run 2), (c) 55 °C (run 3).

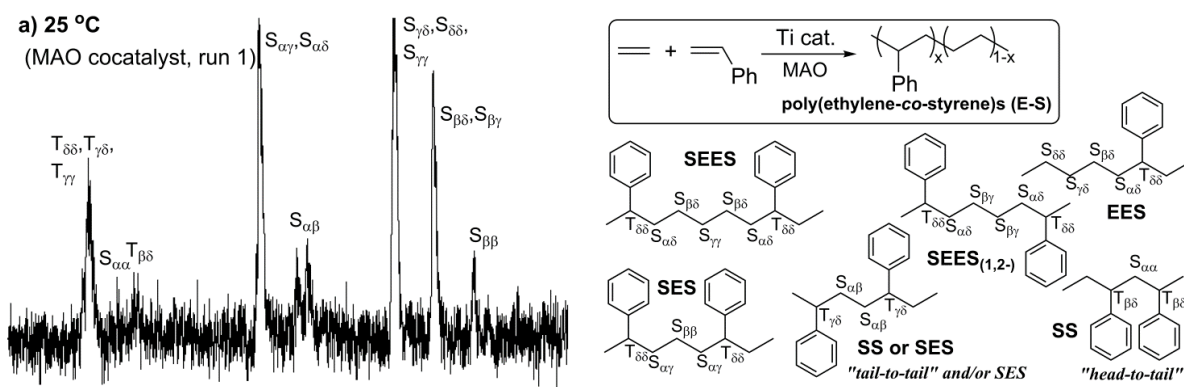
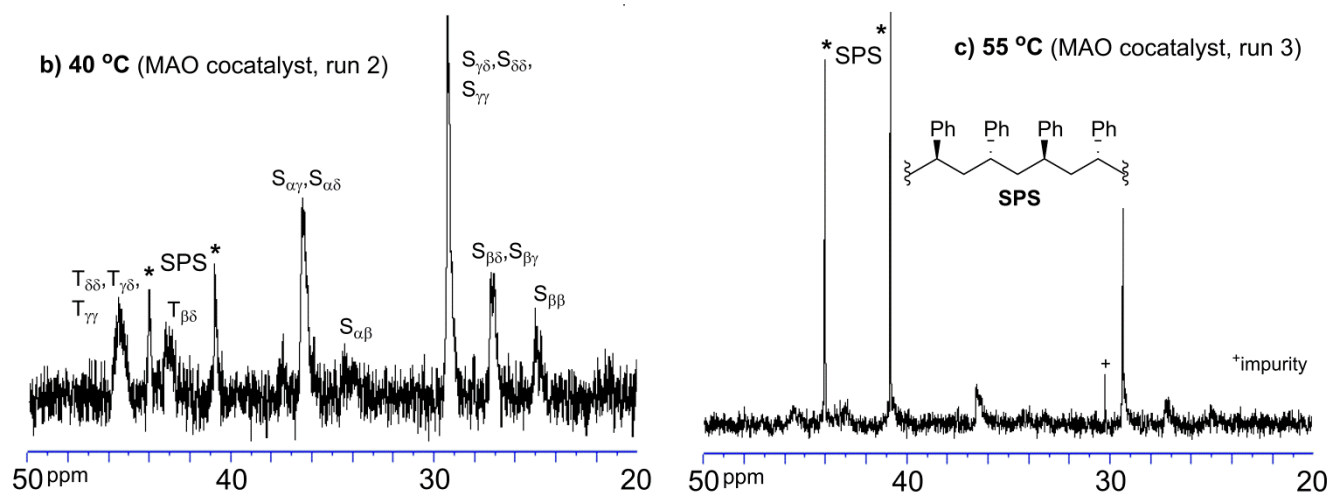


Figure 2. Cont.



On the basis of our proposed assumption shown in Scheme 4 that two catalytically active species (for the syndiospecific styrene polymerization and ethylene/styrene copolymerization) are present in the reaction mixture, we chose an approach in the presence of borate (in place of MAO) as the cocatalyst in combination with Al alkyls to generate the cationic species preferentially. $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ was chosen, because the cationic polymerization of styrene (probable accompanying reaction in the mixture) by this borate did not proceed rapidly as that by $[\text{Ph}_3\text{C}][\text{B}(\text{C}_6\text{F}_5)_4]$ in the presence of Al alkyls [93]. Although the observed catalytic activities were lower than those in the presence of MAO, poly(ethylene-*co*-styrene)s became the sole reaction product by **4** when the polymerizations were conducted in the presence of $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ and $\text{Al}^i\text{Bu}_3/\text{Al}(n\text{-octyl})_3$ (Table 6) [55]. The exclusive synthesis has been achieved even at 70 °C (run 13), and the styrene content exceeded 50 mol% under high styrene concentration conditions (run 12). An optimization of Al/Ti molar ratios was a prerequisite for the exclusive synthesis (runs 8–10, Figure 3), and the observed activities were affected by the Al/Ti molar ratios. Moreover, the observed catalytic activity could be improved when partially fluorinated $\text{Cp}^*\text{TiCl}[\text{OCH}(\text{CF}_3)_2](\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**14**) was employed as the catalyst precursor [56]. The high activity, as well as the high selectivity, could be thus maintained even at 70 °C (Table 7).

Table 6. Ethylene/styrene copolymerization by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}^i\text{Pr}_2\text{C}_6\text{H}_3)$ (**4**)– $[\text{PhN}(\text{H})\text{Me}_2][\text{B}(\text{C}_6\text{F}_5)_4]$ – $\text{Al}^i\text{Bu}_3/\text{Al}(n\text{-octyl})_3$ systems [55]^a.

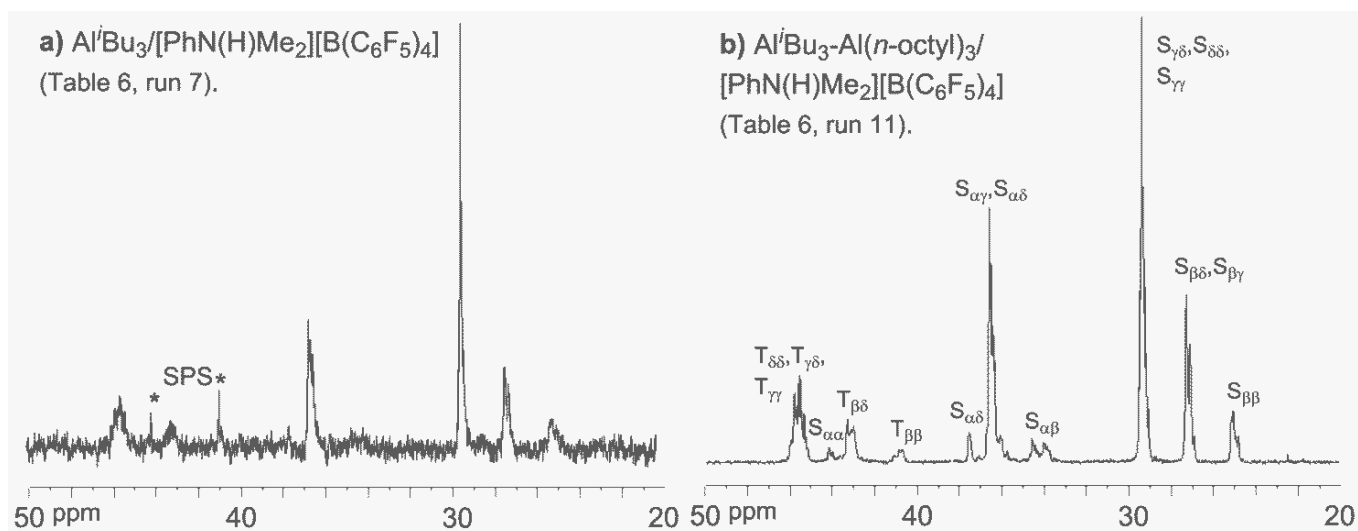
Run	Al cocat. (molar ratio, Al/Ti) ^b	Temp /°C	Activity ^c	Comp. (wt.%) ^d		M_w^e ×10 ^{−4}	M_w/M_n^e	Styrene ^f /mol%
				E-S	SPS			
1	MAO (1500)	25	525	>99	–	8.4	2.25	34
6	Al^iBu_3 (100)	25	256	>99	–	18	1.81	37
2	MAO (1500)	40	384	77	23	8.7	1.72	
3	MAO (1500)	55	363	43	57	10.0	1.8	
7	Al^iBu_3 (100)	55	56	83	17			
8	Al^iBu_3 (20)/ $\text{Al}(n\text{-octyl})_3$ (80)	40	224	94	6			
9	Al^iBu_3 (20)/ $\text{Al}(n\text{-octyl})_3$ (20)	40	53	>99	---	7.6	1.72	38

Table 6. Cont.

10	Al ⁱ Bu ₃ (5)/Al(<i>n</i> -octyl) ₃ (35)	40	100	>99	-	12	1.56	37
11	Al ⁱ Bu ₃ (5)/Al(<i>n</i> -octyl) ₃ (35)	55	104	>99	-	8.2	1.74	40
12 ^g	Al ⁱ Bu ₃ (5)/Al(<i>n</i> -octyl) ₃ (35)	55	17	>99	-	9.5	1.79	51
13	Al ⁱ Bu ₃ (5)/Al(<i>n</i> -octyl) ₃ (35)	70	51	>99	-	5.8	1.60	44

^a Conditions: Ti 5.0 μmol, [PhN(H)Me₂][B(C₆F₅)₄] 5.0 μmol, ethylene 4 atm, styrene 10 mL, toluene 20 mL, 10 min. ^b Initial molar ratio of Al/Ti. ^c Activity in kg-polymer/mol-Ti·h, polymer yields were based on a mixture of SPS (syndiotactic polystyrene) and E-S (copolymer) as acetone insoluble fraction. ^d Composition estimated by ¹³C NMR spectra (and confirmed by ¹H NMR spectra). ^e GPC data in *O*-dichlorobenzene vs. polystyrene standards. ^f Styrene content in mol% estimated by ¹H NMR spectra. ^g Styrene 15 mL, toluene 15 mL.

Figure 3. ¹³C NMR spectra for the resultant polymers (acetone insoluble fraction) prepared by Cp*TiCl₂(*O*-2,6-^{*i*}Pr₂C₆H₃) (**4**)–[PhN(H)Me₂][B(C₆F₅)₄]–Al alkyls systems (in 1,1,2,2,-tetrachloroethane-*d*₂ at 110 °C) [55].



We have shown that an exclusive synthesis of ethylene/styrene copolymers has been achieved by using modified half-titanocene, Cp*TiCl₂(*O*-2,6-^{*i*}Pr₂C₆H₃), in the presence of [PhN(H)Me₂][B(C₆F₅)₄] and Al^{*i*}Bu₃/Al(*n*-octyl)₃. The fact presented here should be promising not only from academic, but also from practical, viewpoints. We are exploring a possibility for synthesis of new styrene copolymers by efficient copolymerization. An exclusive synthesis of the copolymers at high temperature should be important in terms of better process application (viscosity, mass transport), especially from the practical viewpoint. The exclusive synthesis of copolymers with high styrene contents by adopting the borate cocatalyst should also be important. This is because the fact may suggest a presence of two catalytically active species [for the syndiospecific styrene polymerization and ethylene/styrene copolymerization, neutral Ti(III) and cationic Ti(IV)], as well as preferred formation of the cationic species *in situ*.

Table 7. Ethylene/styrene copolymerization by $\text{Cp}^*\text{TiCl}_2(\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$ (**4**), $\text{Cp}^*\text{TiCl}[\text{OCH}(\text{CF}_3)_2](\text{O}-2,6\text{-}i\text{-Pr}_2\text{C}_6\text{H}_3)$ (**14**)– $\text{Al}^i\text{Bu}_3/\text{Al}(n\text{-octyl})_3/[\text{PhN}(\text{Me})\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]$ catalyst systems [55,56] ^a.

Run	Complex	Temp. / °C	Activity ^b	Comp. (wt.%) ^c		M_w^d ×10 ^{−4}	M_w/M_n^d	Styrene ^e / mol%
				E-S	SPS			
11	1	55	104	>99	-	8.2	1.74	40
13	1	70	51	>99	-	5.8	1.60	44
14	14	55	130	>99	-	5.7	1.98	42
15	14	70	106	>99	-	5.8	1.85	44

^a Conditions: Ti 5.0 μmol, ethylene 4 atm, styrene 10 mL, toluene 20 mL, 10 min, $\text{Al}^i\text{Bu}_3/\text{Al}(n\text{-octyl})_3/[\text{PhN}(\text{Me})\text{H}][\text{B}(\text{C}_6\text{F}_5)_4]/\text{Ti} = 5.0/35/1.0/1.0$ (molar ratio). ^b Activity in kg-polymer/mol-Ti·h, polymer yields were based on a mixture of SPS (syndiotactic polystyrene) and E-S (copolymer) as acetone insoluble fraction. ^c Compositions estimated by ¹H NMR spectra. ^d GPC data in *O*-dichlorobenzene vs. polystyrene standards. ^e Styrene content in mol% estimated by ¹H NMR spectra.

3. Summary and Outlook

Promising results have been reported regarding copolymerization using modified half-titanocenes [$\text{Cp}^*\text{TiX}_2(\text{Y})$, Y = anionic ancillary donor ligands], affording a random copolymer with various styrene contents, and both the catalytic activities and the styrene incorporation are highly affected by both the cyclopentadienyl fragments and anionic donor ligands employed. The efficient synthesis of random copolymers could be achieved by using half-titanocene-containing aryloxo ligands. Cationic Ti(IV) species play an important role as catalytically active species in copolymerization, whereas (neutral and/or cationic) Ti(III) species play roles in syndiospecific styrene polymerization, and these findings may suggest why the polystyrene structure in random copolymer prepared with half-titanocenes was atactic. Various copolymers, which differ with regard to their compositions, microstructures and properties, and these unique characteristics are dependent upon the nature of the complex catalysts used. I hope that the development of other new polyolefin materials would follow the use of this synthetic technique, which can be applied not only to styrene, but also to styrene-containing reactive functionalities (in combination with other polymerization techniques, such as ATRP, RAFT, ROP *etc.*).

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Conflict of Interest

The authors declare no competing financial interest.

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