Effect of Cyclopentadienyl and Anionic Ancillary Ligand in Syndiospecific Styrene Polymerization Catalyzed by Nonbridged Half-Titanocenes Containing Aryloxo, Amide, and Anilide Ligands: Cocatalyst Systems

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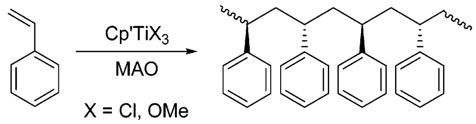
ABSTRACT: Styrene polymerizations with a series of nonbridged half-titanocenes of the type $Cp'TiCl_2(L)$ [L = O-2,6-$^iPr_2C_6H_3$, Cp′ = Cp (**1**), 1,3-$Me_2C_5H_3$ (**2**), 1,2,4-$Me_3C_5H_2$ (**3**), C_5Me_5 (Cp*, **4**); Cp′ = Cp*, L = OPh (**5**), O-4-MeC_6H_4 (**6**), O-2,6-$Me_2C_6H_3$ (**7**), O-2,6-$^tBu_2C_6H_3$ (**8**); Cp′ = 1,3-$Me_2C_5H_3$, L = NMeCy (**9**, Cy = cyclohexyl), N(2,6-$Me_2C_6H_3$)($SiMe_3$) (**10**); L = Cl, Cp′ = Cp (**1′**), 1,3-$Me_2C_5H_3$ (**2′**), 1,2,4-$Me_3C_5H_2$ (**3′**), C_5Me_5 (Cp*, **4′**)] have been explored in the presence of MAO cocatalyst under various conditions. The catalytic activities for syndiospecific styrene polymerization with a series of half-titanocenes containing an aryloxo ligand, $Cp'TiCl_2(O\text{-}2,6\text{-}^iPr_2C_6H_3)$, were higher than those with the trichloro analogues, $Cp'TiCl_3$, and the activity with a series of Cp* analogues (**4**, **4′**, **5**−**8**) and 1,3-$Me_2C_5H_3$ analogues (**2**, **2′**, **9**, **10**) were highly dependent upon the anionic donor ligand used. ($^tBuC_5H_4$)$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (**11**) exhibited a relatively high catalytic activity for syndiospecific styrene polymerization at 25 °C when both $[PhMe_2NH]B(C_6F_5)_4$ and a mixture of $Al^iBu_3/Al(n\text{-}C_8H_{17})_3$ were used as the cocatalyst, and the activity with a series of (1,3-$Me_2C_5H_3$)$TiCl_2$(OAr) depended on the aryloxide ligand used. The role of the anionic donor ligand, like the aryloxide ligand, toward both the catalytic activity and the M_w values of polystyrene has thus been observed irrespective of the kind of cocatalyst employed.

Introduction

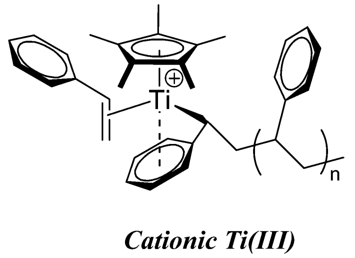
The design and synthesis of efficient transition metal complex catalysts directed for precise olefin polymerization have attracted considerable attention.[1] The ordinary half-titanocenes such as Cp^*TiCl_3, $Cp^*Ti(OMe)_3$, and (indenyl)$TiCl_3$ are efficient catalyst precursors for syndiospecific styrene polymerization (Scheme 1) in the presence of a cocatalyst,[2−5] and syndiotactic polystyrene (SPS) is a unique new polymeric material due to its high melting point (T_m = 270 °C), high crystallinity, low density, low dielectric constant, and high chemical resistance toward organic solvents.[2−4] These complexes were also effective as catalyst precursors for ethylene/styrene copolymerization[6] although some difficulties may be encountered in obtaining the copolymer exclusively. On the basis of the results, the oxidation state of the catalytically active species for the syndiospecific styrene polymerization has been invoked as cationic Ti(III) (Scheme 2),[2−5] whereas the cationic Ti(IV) species would play a role for the ethylene/styrene copolymerization.[6]

In contrast, Miyashita presented in 1994 that bridged titanoneces possessing small bite angles such as $[H_2C(Cp)_2]TiCl_2$ and $[Me_2Si(Cp)_2]TiCl_2$ showed catalytic activities for syndiospecific styrene polymerization although ordinary nonbridged metallocenes such as Cp_2TiCl_2 and Cp_2ZrCl_2 showed extremely low activities.[4a,b,7] This suggested that the bite angle plays an essential role for exhibiting the catalytic activity especially for repeated styrene insertion.[7]

Scheme 1



Scheme 2



Oliva and Zambelli reported that the regiospecificity of styrene insertion into the Zr−$^{13}CH_3$ bonds is prevailingly secondary in ethylene/styrene copolymerization using the $[Me(Ph)C(fluorenyl)(Cp)]ZrCl_2$−MAO catalyst system,[8] and Oliva later presented that some styrene units can be introduced in an isotactic polypropylene sequence (by 1,2-insertion mode) by using a small amount of ethylene to reactivate the catalyst after the styrene insertion (by 2,1-insertion mode) in the propylene/styrene copolymerization using a *rac*-[Et(indenyl)$_2$]$ZrCl_2$−MAO catalyst system.[9] Arai reported that isopropylidene-bridged zirconocenes such as $[Me_2C(indenyl)_2]ZrCl_2$, $[Me_2C(benzindenyl)_2]ZrCl_2$, and [$Me_2C$(3-cyclopenta[*c*]phenanthryl)]$ZrCl_2$ exhibited unique characteristics for ethylene/styrene copolymerization,[10] affording the copolymer with isotactic stereoregularity; these complexes also afforded isotactic polystyrene although the activity was somewhat low.[10b] Not only the small bite angle but also the C_2 symmetry of the catalyst structure has been proposed to be a prerequisite for both

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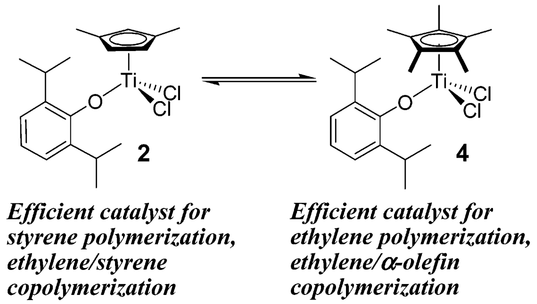
Scheme 3

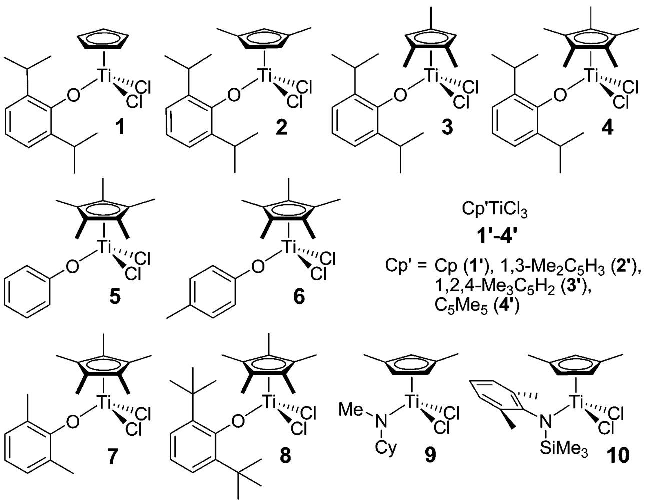


high activity and efficient styrene incorporation because complexes that possess a C_s symmetry like [Ph_2C-(fluorenyl)(Cp)]$ZrCl_2$ exhibited both extremely low activity and inefficient styrene incorporation in the ethylene/styrene copolymerization. Oliva recently presented that regiochemistry for styrene insertion by the *rac*-[H_2C(3-R-1-indenyl)$_2$]$ZrCl_2$−MAO catalyst changed from secondary to primary with increasing steric bulk in R: $H < CH_3 < CH_2CH_3 < CH(CH_3)_2 < C(CH_3)_3$.[11] High isospecificity was observed with *rac*-[H_2C(3-*tert*-Bu-1-indenyl)$_2$]$ZrCl_2$, whereas unsubstituted or ethyl-substituted analogues showed some syndiospecificity.[11] On the basis of these results, the oxidation state for the catalytically active species for styrene polymerization with this series of catalyst precursor is proposed to be cationic Zr(IV), which is somewhat different from that proposed for the polymerization using half-titanocene complex catalysts.[2−4]

We have recently reported that nonbridged half-titanocenes containing an anionic ancillary ligand such as aryloxo,[12−15] amide,[16] and anilide[17] displayed unique characteristics for olefin polymerization, especially (aryloxo)(cyclopentadienyl)titanium complexes which showed unique characteristics for the copolymerization of ethylene with α-olefin,[12] styrene,[13,14] and norbornene.[15] In addition, we have communicated that an efficient catalyst for ethylene polymerization can be modified for efficient catalysis for syndiospecific styrene polymerization (at 25 °C) only by ligand modification of the cyclopentadienyl fragment [Cp* analogue (**4**) ↔ 1,3-$Me_2C_5H_3$ analogue (**2**), Scheme 3].[13] The observed trend was similar in a series of half-titanocenes containing amide and anilide ligands,[16b,17] and we proposed that this should be one of the unique characteristics for using this type of complex as the catalyst precursor for olefin polymerization. However, no results concerning temperature dependences and effect of anionic donor ligands, especially for styrene polymerization, were shown. Moreover, **2** incorporates styrene efficiently in the ethylene/styrene copolymerization,[13,14] affording the copolymer exclusively even with high styrene content (>50−80 mol %),[14] although we do not have a clear reason why the polystyrene structure in the copolymer was atactic. On the basis of these facts, it is thus assumed that the catalytically active species for styrene polymerization and ethylene/styrene copolymerization, especially using half-titanocene catalysts, may be different.

Although the role of the anionic ancillary ligand (aryloxo, amide, anilide) should be negligible according to the assumption that cationic Ti(III), [Cp′Ti(R)(styrene)]$^+$ (R = polymer, alkyl chain), plays an essential role for the syndiospecific styrene polymerization,[2−4] we still believe that the electronic and/or steric nature of the anionic ancillary donor ligand should affect the catalytic activity. This is not only because bridged titanocenes and zirconocenes are active catalyst for styrene polymerization but also because Tomotsu insisted the possibility that neutral Ti(III) species,[2m] [Cp′Ti(L)(R)(styrene)] (L = anionic donor ligand), plays an important role as the catalytically active species.[4a,b] In this paper, we thus wish to introduce our results concerning the effect of both the cyclopentadienyl and the anionic donor ligands in syndiospecific styrene polymerization with a series of nonbridged half-titanocenes of the type Cp′$TiCl_2$(L) [L = O-2,6-$^iPr_2C_6H_3$, Cp′ = Cp (**1**), 1,3-$Me_2C_5H_3$ (**2**), 1,2,4-$Me_3C_5H_2$ (**3**), C_5Me_5 (Cp*, **4**); Cp′ = Cp*, L = OPh (**5**), O-4-MeC_6H_4 (**6**), O-2,6-$Me_2C_6H_3$ (**7**), O-2,6-$^tBu_2C_6H_3$ (**8**); Cp′ = 1,3-$Me_2C_5H_3$, L = NMeCy (**9**), N(2,6-$Me_2C_6H_3$)($SiMe_3$) (**10**), Chart 1] in the presence of methylaluminoxane (MAO).[18−21] Since we recently communicated that (*tert*-BuC_5H_4)$TiMe_2$(OAr) (**11**, OAr = O-2,6-$^iPr_2C_6H_3$) was effective for syndiospecific polymerization of styrene in the presence of a mixture of Al(n-C_8H_{17})/Al^iBu_3 and $Ph_3CB(C_6F_5)_4$,[22] we explored the role of both the cyclopentadienyl and the aryloxide ligands in this catalysis.

Chart 1



Results and Discussion

1. Syndiospecific Styrene Polymerization in the Presence of MAO Cocatalyst. 1.1. Styrene Polymerization with Cp′$TiCl_2$(O-2,6-$^iPr_2C_6H_3$)− and Cp′$TiCl_3$−MAO Catalyst Systems. Table 1 summarizes the results for styrene polymerization with a series of Cp′$TiCl_2$(O-2,6-$^iPr_2C_6H_3$) (**1**−**4**) and Cp′$TiCl_3$ [Cp′ = Cp (**1′**), 1,3-$Me_2C_5H_3$ (**2′**), 1,2,4-$Me_3C_5H_2$ (**3′**), C_5Me_5 (**4′**)] complexes in the presence of MAO at various temperatures. MAO was prepared as a white solid by removing toluene and $AlMe_3$ from commercially available MAO (PMAO, Tosoh Finechem Co.) and was chosen as the cocatalyst (optimized Al/Ti molar ratio was 1500 as described below) because it was quite effective in the preparation of ethylene/α-olefin copolymers with narrow molecular weight distributions as well as with relatively high molecular weights when **4** and [Me_2Si-(C_5Me_4)(N^tBu)]$TiCl_2$ were employed as the catalyst precursors.[12a] This is also because the catalytic activity for syndiospecific styrene polymerization with Cp′Ti-(OMe)$_3$ decreased upon the addition of $AlMe_3$.[4a,b,23] The polymerization products were syndiotactic polystyrenes (SPS) exclusively confirmed by DSC analysis as the acetone-insoluble fraction in all cases,[13] and a trace

Table 1. Syndiospecific Styrene Polymerization by $Cp'TiCl_2((O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (1−4)− and $Cp'TiCl_3$ (1′−4′)−MAO Catalyst Systems:[a] Temperature Dependence

Cp′	temp/°C	activity[b]	M_w[c] × 10^{-4}	M_w/M_n[c]
Cp (**1**)	40	1000	5.7	2.1
Cp (**1**)	55	4130	5.8	2.0
Cp (**1**)	70	15300	4.0	2.5
Cp (**1**)	85	16000	2.2	2.4
1,3-$Me_2C_5H_3$(**2**)	40	8460	35.2	2.3
1,3-$Me_2C_5H_3$(**2**)	55	11500	18.2	2.0
1,3-$Me_2C_5H_3$(**2**)	70	13700	8.6	1.9
1,3-$Me_2C_5H_3$(**2**)	85	13200	5.5	2.6
1,2,4-$Me_3C_5H_3$(**3**)	40	3680	35.4	2.1
1,2,4-$Me_3C_5H_3$(**3**)	55	5310	20.0	2.1
1,2,4-$Me_3C_5H_3$(**3**)	70	6900	12.5	1.7
1,2,4-$Me_3C_5H_3$(**3**)	85	7540	7.1	1.9
Cp* (**4**)	40	285	26.8	2.6
Cp* (**4**)	55	1640	53.1	2.5
Cp* (**4**)	70	3600	49.0	2.2
Cp* (**4**)	85	4290	32.3	2.2
Cp (**1′**)	40	15800	6.7	2.8
Cp (**1′**)	55	17500	4.8	2.7
Cp (**1′**)	70	15300	3.3	2.4
Cp (**1′**)	85	13300	2.2	2.2
1,3-$Me_2C_5H_3$ (**2′**)	40	6110	34.3	2.2
1,3-$Me_2C_5H_3$ (**2′**)	55	9510	17.6	2.0
1,3-$Me_2C_5H_3$ (**2′**)	70	7270	10.3	2.1
1,3-$Me_2C_5H_3$ (**2′**)	85	6950	6.3	2.1
1,2,4-$Me_3C_5H_3$ (**3′**)	40	1650	16.1	1.7
1,2,4-$Me_3C_5H_3$ (**3′**)	55	3690	13.5	2.0
1,2,4-$Me_3C_5H_3$ (**3′**)	70	3730	9.7	2.0
1,2,4-$Me_3C_5H_3$ (**3′**)	85	4120	6.6	2.2
Cp* (**4′**)	40	320	36.2	2.3
Cp* (**4′**)	55	666	33.2	2.3
Cp* (**4′**)	70	1970	24.8	2.5
Cp* (**4′**)	85	3280	17.5	2.2

[a] Conditions: complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min. [b] Activity in kg of SPS/(mol of Ti h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standards.

amount of atactic polymer (APS) produced by MAO itself was also collected as the acetone soluble fraction.[24]

The observed catalytic activities by $Cp'TiCl_2(OAr)$ (**1**−**4**)−MAO catalyst systems increased at higher temperature, and the activity with 16 000 kg of SPS/(mol of Ti h) could thus be attained with **1** at 85 °C (Table 1 and Figure 1). The observed catalytic activities by the aryloxy systems (**1**−**4**) at high temperatures (70 and 85 °C) were higher than those by the trichloride systems (**1′**−**4′**) in all cases, and the activity at 85 °C increased in the order Cp (**1**) > 1,3-$Me_2C_5H_3$ (**2**) ≫ 1,2,4-$Me_3C_5H_2$ (**3**) > C_5Me_5 (**4**). The trend observed for the aryloxy systems was the same as that by the trichloride systems, which suggests that the activity was strongly influenced by the nature of cyclopentadienyl fragment. The observed trend was similar to that reported by Kaminsky[2j] in which **1′** showed higher catalytic activity than **4′**, but was different from that reported by Tomotsu et al.[4] Moreover, as shown in Figure 2, M_w values for resultant SPS prepared by (**1**−**4**)−MAO catalyst systems increased in the order C_5Me_5 (**4**) > 1,2,4-$Me_3C_5H_2$ (**3**), 1,3-$Me_2C_5H_3$ (**2**) > Cp (**1**). The order in the M_w values was almost similar to that by the trichloride systems with the exception of (1,2,4-$Me_3C_5H_2$)$TiCl_3$, and it seems that the introduction of an electron-donating substituent on the cyclopentadienyl group was effective in obtaining high molecular weight SPS under these conditions (probably due to the enhanced propagation rate by introducing an electron-donating group on the Cp′ or as a result of the difference in the chain-transfer step by introducing steric bulk on Cp′). Since some M_w values by the aryloxy systems (**3**, **4**) were also different from those by the trichloride systems (**3′**, **4′**) under the same conditions, these results suggest that effect of the aryloxo ligand for both the catalytic activity and the M_w value was present regardless of the kind of cyclopentadienyl fragment.

1.2. Styrene Polymerization with $Cp^*TiCl_2(OAr)$−MAO Catalyst Systems.

The effect of the substituent on the aryloxo ligand with a series of Cp* analogues toward both the activity and the M_w value for resultant SPS was examined at various polymerization temperatures. The polymerization results are summarized in Table 2 and Figure 3.

$Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (**7**) showed exceptionally high catalytic activities which increased at higher temperature. The activity by $Cp^*TiCl_2(OAr)$−MAO catalyst systems (at 70 °C) increased in the order OAr = O-2,6-$Me_2C_6H_3$ (**7**) ≫ OPh (**5**), O-4-MeC_6H_4 (**6**), O-2,6-${}^iPr_2C_6H_3$ (**4**) > Cl (**4′**), O-2,6-${}^tBu_2C_6H_3$ (**8**). These results clearly indicate that the substituent on the aryloxy ligand *directly affects* the catalytic activity. It seems likely that one probable reason why methyl-substituted **7** showed a higher catalytic activity than those by **4** and **8** would be due to the steric bulk for styrene insertion with 2,1 manner rather than the electronic effect. Moreover, the M_w value for resultant SPS was also dependent upon the anionic donor ligand employed, and the value at 70 °C increased in the order **5** > **4** > **7**, **6**,

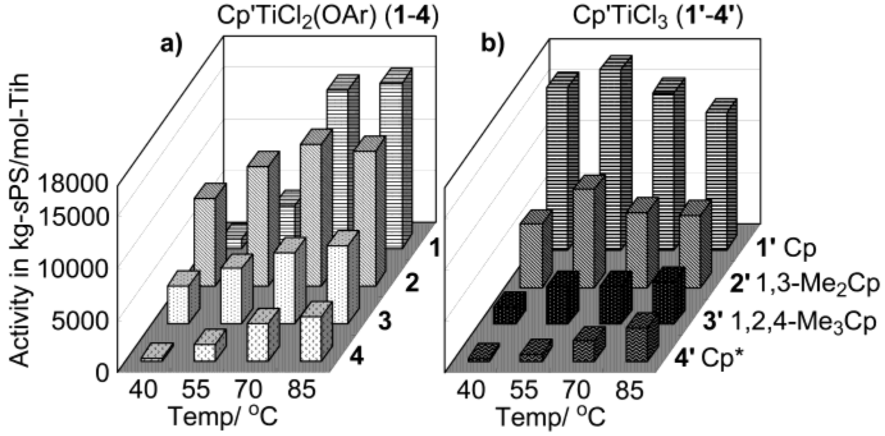


Figure 1. Temperature dependence toward the catalytic activity in syndiospecific styrene polymerization by (a) $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**1**−**4**) and (b) $Cp'TiCl_3$ (**1′**−**4′**)−MAO catalyst systems. Cp′ = Cp (**1**), 1,3-$Me_2C_5H_3$ (**2**), 1,2,4-$Me_3C_5H_2$ (**3**), and Cp* (**4**). Conditions: complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO 3.0 mmol (Al/Ti = 1500, molar ratio), 10 min.

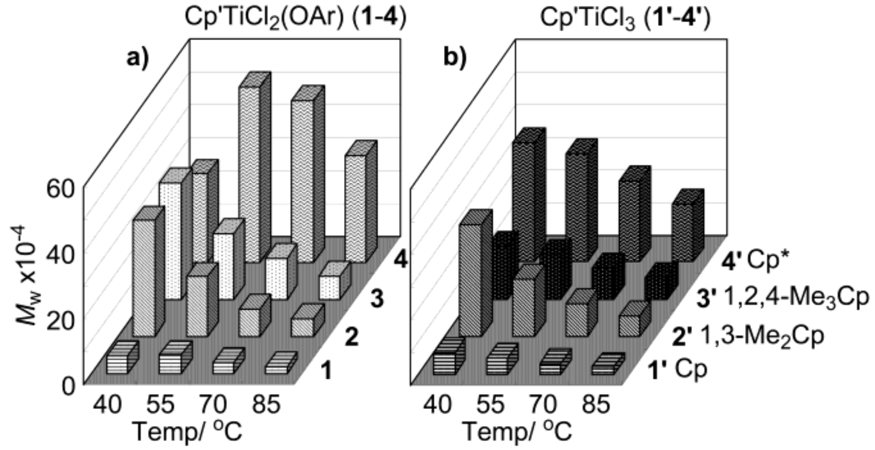


Figure 2. Temperature dependence toward the molecular weight for resultant SPS in syndiospecific styrene polymerization by (a) Cp′TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**−**4**) and (b) Cp′TiCl$_3$ (**1′**−**4′**)−MAO catalyst systems. Conditions: complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO 3.0 mmol (Al/Ti = 1500, molar ratio), 10 min.

Table 2. Effect of Aryloxide Ligand in Styrene Polymerization by Cp*TiCl$_2$(X)−MAO Catalyst Systems[a]

X	temp/°C	activity[b]	M_w[c] × 10^{-4}	M_w/M_n[c]
Cl (**4′**)	40	320	36.2	2.3
Cl (**4′**)	55	1640	33.2	2.3
Cl (**4′**)	70	1970	24.8	2.5
Cl (**4′**)	85	3280	17.5	2.2
O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**4**)	40	285	26.8	2.6
O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**4**)	55	1640	53.1	2.5
O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**4**)	70	3600	49.0	2.2
O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**4**)	85	4290	32.3	2.2
OC$_6$H$_5$ (**5**)	40	733	55.1	2.2
OC$_6$H$_5$ (**5**)	55	1600	55.1	2.0
OC$_6$H$_5$ (**5**)	70	4170	54.3	2.0
OC$_6$H$_5$ (**5**)	85	6390	47.8	2.1
O-4-MeC$_6$H$_4$ (**6**)	40	757	30.4	2.8
O-4-MeC$_6$H$_4$ (**6**)	55	1560	28.7	2.3
O-4-MeC$_6$H$_4$ (**6**)	70	3750	26.7	2.4
O-4-MeC$_6$H$_4$ (**6**)	85	6020	24.2	2.3
O-2,6-Me$_2$C$_6$H$_3$ (**7**)	40	1020	30.1	2.3
O-2,6-Me$_2$C$_6$H$_3$ (**7**)	55	4090	29.6	2.0
O-2,6-Me$_2$C$_6$H$_3$ (**7**)	70	9200	28.0	2.1
O-2,6-Me$_2$C$_6$H$_3$ (**7**)	85	12400	20.7	2.1
O-2,6-^{t}Bu$_2$C$_6$H$_3$ (**8**)	40	75	11.0	1.9
O-2,6-^{t}Bu$_2$C$_6$H$_3$ (**8**)	55	279	11.4	2.1
O-2,6-^{t}Bu$_2$C$_6$H$_3$ (**8**)	70	1780	20.5	2.3
O-2,6-^{t}Bu$_2$C$_6$H$_3$ (**8**)	85	5690	23.1	2.2

[a] Conditions: catalyst 2.0 μmol styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 1500, molar ratio), 10 min. [b] Activity in kg of SPS/(mol of Ti h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standard.

4′ > **8**. These results suggest that the aryloxo ligand plays an important role toward both the catalytic activity and the M_w value.[25] As the synthesis of high molecular weight polymer with high catalytic activity especially at high temperature could be attained when **7** was chosen as the catalyst precursor (activity at 85 °C = 12 400 kg of SPS/(mol of Ti h), M_w = 20.7 × 10^4, M_w/M_n = 2.1), and it is thus suggested that the catalytic activity and the M_w value can be tuned by a simple ligand modification.

Tomotsu et al. reported[2m] that the percentage of the catalytically active species for stopped flow styrene polymerization using the Cp*Ti(OMe)$_3$−MAO catalyst system became perfect in the presence of hydrogen, and they assumed that the addition of hydrogen activates a dormant site formed by irregular styrene coordination or change in the direction of monomer coordination during polymerization especially at the initial stage.[2m] If we accept this assumption (based on the proposed experimental results and DFT calculations),[26] a role that the aryloxide ligand increases the percentage of the catalytically active species generated in situ by varying the steric bulk (leading to improve the apparent catalytic activity calculated on the basis of polymer yield and the amount of Ti charged) can be thus assumed. On the other hand, however, since the M_w values for the resultant SPS depended upon the anionic ligand used, whereas the dominant chain-transfer step for the polymerization with Cp* analogues was transfer to alkylaluminum as described below, an electronic in addition to a steric effect of the aryloxide ligand to the catalytically active species should thus be considered. Since the role of anionic donor ligand toward both the activity and the molecular weight is present, it is possible that neutral Ti(III) or cationic Ti(IV) species plays a role for this polymerization, especially with this unique catalyst system, although it has been generally invoked that cationic Ti(III) plays an essential role for the syndiospecific styrene polymerization.

Table 3 summarizes styrene polymerizations by the Cp and the Cp* analogues (**1**, **1′**, **4′**, and **7**)−MAO catalyst systems at various Al/Ti molar ratios. The activities initially increased at higher Al/Ti molar ratios in all cases, and the optimized molar ratio of 1500 chosen for this study was thus shown to be appropriate. The M_w value for resultant SPS decreased upon increasing Al/Ti molar ratios when the Cp* analogues (**4′** and **7**) were employed as the catalyst precursors, and the M_w values were not affected by the Al/Ti molar ratios when the Cp analogues (**1** and **1′**) were employed as the catalyst precursors (Figure 4). These are, we believe, an interesting contrast in that the dominant chain transfer reaction was strongly influenced by the substitutent on the cyclopentadienyl group: chain transfer by β-hydrogen elimination was dominant when the Cp analogues were employed whereas chain transfer to Al was dominant when the Cp* analogues were used as the catalyst precursors. To confirm the observed difference between the Cp and the Cp* analogues, the effect of AlMe$_3$ addition toward both the activity and the M_w values were explored under lower monomer concentration conditions (Table 4). Although the results that both the activity and the M_w value decreased upon the addition of AlMe$_3$ when the Cp* analogues (**4′**, **7**) were used as the catalyst precursors and were somewhat analogous to those reported by Tomotsu for styrene polymerization by Cp*Ti(OMe)$_3$,[23,27] the M_w value re-

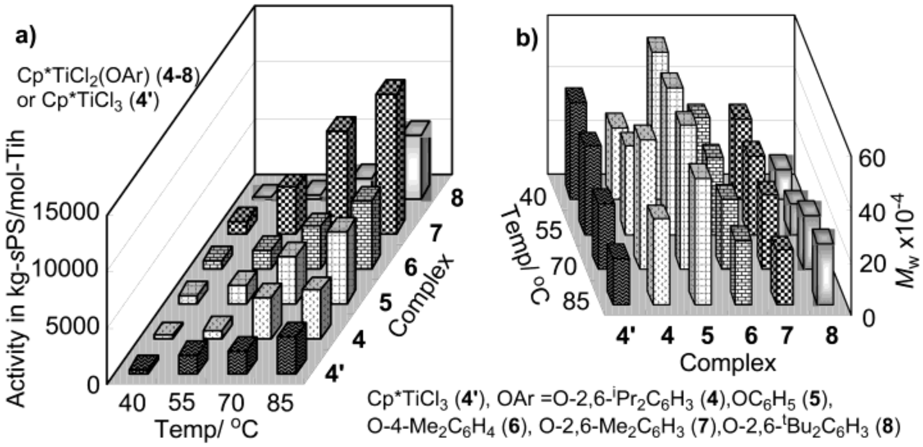


Figure 3. Temperature dependence in syndiospecific styrene polymerization by Cp*TiCl$_3$ (**4′**) or Cp*Ti(OAr)−MAO catalyst systems. Plots of (a) catalytic activity and (b) molecular weight for SPS. OAr = O-2,6-^{i}Pr$_2$C$_6$H$_3$ (**4**), OPh (**5**), O-4-MeC$_6$H$_4$ (**6**), O-2,6-Me$_2$C$_6$H$_3$ (**7**), O-2,6-^{t}Bu$_2$C$_6$H$_3$ (**8**). Conditions: complex 2.0 μmol, styrene/toluene = 10/20 mL, MAO 3.0 mmol (Al/Ti = 1500, molar ratio), 10 min.

Table 3. Effect of Al/Ti Molar Ratio for Styrene Polymerization by Cp′TiCl$_2$(X)−MAO Catalyst[a]

complex	Al/Ti[b]	activity[c]	M_w[d] × 10^{-4}	M_w/M_n[d]
Cp*TiCl$_3$ (**4′**)	500	1280	36.0	2.6
Cp*TiCl$_3$ (**4′**)	1000	1990	28.1	2.3
Cp*TiCl$_3$ (**4′**)	1500	1970	24.8	2.5
Cp*TiCl$_3$ (**4′**)	2000	2230	23.2	2.3
Cp*TiCl$_3$ (**4′**)	4000	2560	18.7	2.2
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	500	4030	41.1	2.4
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	1000	7830	34.6	2.1
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	1500	9200	28.0	2.1
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	2000	8680	27.2	2.2
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	4000	7210	20.7	2.1
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	500	1650	5.5	2.0
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	1000	6970	5.1	2.0
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	1500	15300	4.0	2.5
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	2000	14400	5.0	2.0
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	4000	16200	4.1	2.0
CpTiCl$_3$ (**1′**)	500	4900	3.9	2.1
CpTiCl$_3$ (**1′**)	1000	13600	3.6	2.1
CpTiCl$_3$ (**1′**)	1500	15300	3.3	2.4
CpTiCl^3 (**1′**)	2000	15700	3.4	2.0
CpTiCl$_3$ (**1′**)	4000	14300	3.3	2.1

[a] Conditions: catalyst 2.0 μmol styrene/toluene = 10/20 mL, MAO white solid, 70 °C, 10 min. [b] Molar ratio of Al/Ti. [c] Activity in kg of SPS/(mol of Ti h). [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

mained unchanged in the presence of AlMe$_3$ when the Cp analogues (**1**, **1′**) were used as the catalyst precursors. Taking the above results into account, it is clear that the major pathway for the chain transfer reaction was strongly affected by the nature of cyclopentadienyl fragment.

Since the degree of chain transfer pathway (chain transfer to Al) could be controlled at low temperature when the Cp* analogues were used as the catalyst precursors, time-course plots for polymerization of styrene with the **7**−MAO catalyst system, especially at low temperature, were explored (Table 5). As suggested from the result at 40 °C, the activity decreased at lower temperatures of 0 and 23 °C. On the other hand, the decrease in the activity was not observed even after 18 h at 0 °C. The M_w value for resultant polystyrene increased for longer reaction hours, and SPS with M_w of 177.7 × 10^4 was thus obtained under these reaction conditions (at 0 °C after 18 h). This clearly shows that degree of chain transfer reaction could thus be suppressed at lower temperature, and the M_w value increased upon the consumption of styrene monomer. Although the molecular weight distribution was somewhat broad (M_w/M_n = 3.5) probably due to the insolubility of resultant polymer in the reaction mixture at 0 °C because of its high molecular weight, this is one of the highest molecular weight SPS prepared by the Ti complex catalyst.

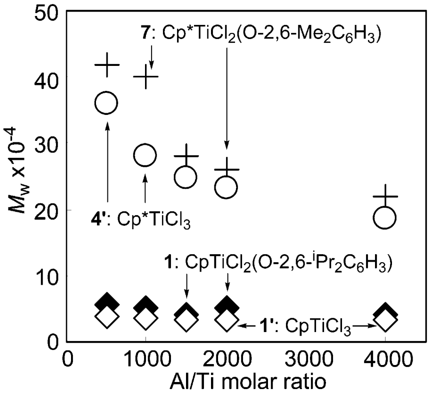


Figure 4. Effect of Al/Ti molar ratios in syndiospecific styrene polymerization by CpTiCl$_3$ (**1′**, ◇), CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$)−MAO (**1**, ◆), Cp*TiCl$_3$−MAO (4′, ○), and Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$)−MAO (**7**, +) catalyst systems. Conditions: complex 2.0 μmol styrene/toluene = 10/20 mL, 70 °C, 10 min.

Table 4. Effect of AlMe$_3$ Addition for Styrene Polymerization by Cp′TiCl$_2$(X)−MAO Catalyst[a]

complex	Al/Ti[b] MAO	Al/Ti[b] AlMe$_3$	activity[c]	M_w[d] × 10^{-4}	M_w/M_n[d]
Cp*TiCl$_3$ (**4′**)	1000		1230	11.5	1.8
Cp*TiCl$_3$ (**4′**)	1000	1000	239	2.2	2.3
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	1000		1490	11.5	2.0
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	1000	250	1100	5.9	1.9
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	1000	500	610	3.7	2.1
Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)	1000	1000	220	2.1	2.2
CpTiCl$_3$ (**1′**)	1000		1190	8.3	2.3
CpTiCl$_3$ (**1′**)	1000	1000	459	7.8	2.3
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	1000		1290	7.4	2.2
CpTiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**1**)	1000	1000	554	7.9	2.2

[a] Conditions: catalyst 2.0 μmol styrene/toluene = 2/28 mL, MAO white solid (Al/Ti = 1000, molar ratio), AlMe$_3$ (1.0 M in *n*-hexane), 85 °C, 10 min. [b] Molar ratio of Al/Ti. [c] Activity in kg of SPS/(mol of Ti h). [d] GPC data in *o*-dichlorobenzene vs polystyrene standards.

1.3. Styrene Polymerization by (1,3-Me$_2$C$_5$H$_3$)-TiCl$_2$(L)−MAO Catalyst Systems.

Since it is clear that both the catalytic activity and the M_w values for

Table 5. Styrene Polymerization by $Cp^*TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ (7)−MAO Catalyst[a]

temp/ °C	time	polymer yield/mg	activity[b]	TON	M_w[c] × 10^{-4}	M_w/M_n[c]
23	10 min	21.5	64.5	103	36.5	2.2
23	2 h	278.8	69.7	1340	70.6	2.3
0	2 h	11.4	2.9	55	62.4	2.5
0	6 h	51.2	4.3	246	80.5	2.7
0	10 h	98.2	4.9	471	96.0	3.0
0	18 h	171.2	4.8	822	177.7	3.5

[a] Conditions: catalyst 2.0 μmol styrene/toluene = 10/20 mL, MAO white solid (Al/Ti = 500, molar ratio). [b] Activity in kg of SPS/(mol of Ti h). [c] GPC data in *o*-dichlorobenzene vs polystyrene standards.

Table 6. Effect of Anionic Ancillary Donor Ligand in Styrene Polymerization by $(1,3\text{-}Me_2C_5H_3)TiCl_2(X)$−MAO Catalysts[a]

X	temp/ °C	activity[b]	M_w[c] × 10^{-4}	M_w/M_n[c]
Cl (**2′**)	40	6110	34.3	2.2
Cl (**2′**)	55	9510	17.6	2.0
Cl (**2′**)	70	7270	10.3	2.1
Cl (**2′**)	85	6950	6.3	2.1
$O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**2**)	40	8460	35.2	2.3
$O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**2**)	55	11500	18.2	2.0
$O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**2**)	70	13700	8.6	1.9
$O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**2**)	85	13200	5.5	2.6
NMeCy (**9**)	40	2270	13.2	1.9
NMeCy (**9**)	55	6480	11.2	2.0
NMeCy (**9**)	70	6530	8.2	2.1
NMeCy (**9**)	85	5680	5.1	2.2
$N(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (**10**)	40	154	41.7	5.7[d]
$N(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (**10**)	55	642	17.3	3.9[d]
$N(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (**10**)	70	1830	9.5	2.6[d]
$N(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (**10**)	85	4890	6.1	2.8[d]

[a] Conditions: catalyst 2.0 μmol, styrene/toluene = 10/20 mL, MAO white solid Al/Ti = 1500, 10 min. [b] Activity based on SPS. [c] GPC data in *o*-dichlorobenzene vs polystyrene standards. [d] Bimodal molecular weight distributions.

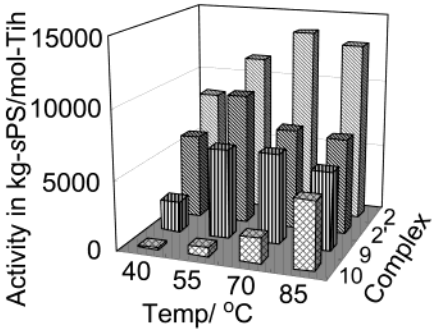


Figure 5. Temperature dependence toward the catalytic activity in syndiospecific styrene polymerization by $(1,3\text{-}Me_2C_5H_3)TiCl_2(L)$ (**2,2′,9−10**)−MAO catalyst systems. L = $O\text{-}2,6\text{-}{}^iPr_2C_6H_3$ (**2**), Cl (**2′**), NMeCy (**9**), $N(2,6\text{-}Me_2C_6H_3)(SiMe_3)$ (**10**). Conditions: catalyst 2.0 μmol, styrene/toluene = 10/20 mL, MAO 3.0 mmol (Al/Ti = 1500), 10 min.

resultant SPS are strongly influenced by the nature of not only the cyclopentadienyl but also the aryloxo ligand employed, the effect of the anionic ancillary ligand for styrene polymerization by $(1,3\text{-}Me_2C_5H_3)TiCl_2(L)$ [L = Cl (**2′**), aryloxo (**2**), amide (**9**), anilide (**10**)]−MAO catalyst systems was thus explored (Table 6). As shown in Figure 5, the catalytic activity was strongly dependent upon the anionic donor ligand employed, and the activity at 55 °C increased in the order L = OAr (**2**) ≫ Cl (**2′**) > NMeCy (**9**) ≫ $N(2,6\text{-}Me_2C_6H_3)(SiMe_3)$. Use of aryloxo lignd was found to be effective in exhibiting high catalytic activity, and the molecular weight distribution for SPS prepared by **10** was bimodal probably due to several catalytically active species being present in the reaction mixture. Since, as shown above, both the catalytic activity and the M_w value for resultant SPS as well as the temperature dependence were strongly affected by the anionic donor ligand employed, it is thus suggested that the role of anionic ancillary ligand is present in this catalytic polymerization.

Taking these results into account, it is clear that the substituent not only on cyclopentadienyl but also on anionic ancillary donor ligand (aryloxo, amide, anilide) plays an essential role for exhibiting high catalytic activity as well as for affording high molecular weight syndiotactic polymer with unimodal molecular weight distribution.

2. Syndiospecific Polymerization of Styrene with (Aryloxo)(cyclopentadienyl)titanium Complex−Borate Catalyst Systems. We have recently reported in a preliminary communication that $({}^tBuC_5H_4)TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**11**) exhibited a relatively high catalytic activity for syndiospecific styrene polymerization in the presence of $[PhMe_2NH]B(C_6F_5)_4$ and a mixture of $Al^iBu_3/Al(n\text{-}C_8H_{17})_3$.[22] As summarized in Table 7, not only the choice of both borate and alkylaluminum compounds but also the optimization of molar ratios of the catalyst component are key for an efficient syndiospecific polymerization. This is because that $Ph_3CB(C_6F_5)_4$ explosively produces atactic polymer (APS) probably in a cationic manner (run 9), and $[PhMe_2NH]B(C_6F_5)_4$ and alkylaluminum compounds also afforded APS under similar polymerization conditions (runs 8, 10, 11). This may be related to the fact that the ratio of SPS/APS in the styrene polymerization by $Cp^*TiMe_2(\mu\text{-}Me)B(C_6F_5)_3$, prepared from the reaction of Cp^*TiMe_3 with $B(C_6F_5)_3$ in hexane/toluene mixed solvent[28] depended on the polymerization conditions[29] because not only a carbocationic but also a coordination mechanism could be involved in this catalysis.[28−30]

Time-course plots for the styrene polymerization under the optimized conditions are summarized in Table 8. As is also shown in Figure 6, a decrease in the catalytic activity was not observed under these conditions, and the rate of SPS formation was found to be much higher than that for APS. No linear relationships between the polymer yields and the M_n values were observed, and the M_n values for resultant SPS were constant ($M_n = (4.4{-}5.0) \times 10^3$, runs 5, 12, and 13) over the time course. The observed fact is an interesting contrast to the syndiospecific living polymerization resulting from the catalyst system composed of $Cp^*TiMe_3/B(C_6F_5)_3/Al(n\text{-}C_8H_{17})_3$[3c,d] because the present result clearly indicates that some extents of chain transfer reactions took place in these polymerizations. On the basis of these results in addition to the results by the Cp analogues (**1** and **1′**)−MAO catalysts systems especially shown in Tables 4 and 5, the dominant chain transfer pathway should be the β-hydrogen elimination for the present polymerization. The fact is also interesting because efficient living 1-hexene polymerization affording high molecular weight poly(1-hexene) with narrow molecular weight distribution [e.g., $M_n = 186.5 \times 10^4$, $M_w/M_n = 1.27$] was reported in the presence of the $Cp^*TiMe_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)/Al^iBu_3/Ph_3CB(C_6F_5)_4$− catalyst system.[31]

Table 9 summarizes results concerning styrene concentration dependence toward catalytic activity.[32] A linear first-order relationship between the catalytic

Table 7. Effect of Cocatalyst for Styrene Polymerization by $({}^tBuC_5H_4)TiCl_2((O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (11)−$[PhMe_2NH]B(C_6F_5)_4$ Catalyst System[a]

		MEK insoluble[c]					
run no.	Al(i-Bu)$_3$/ Al(n-C_8H_{17})$_3$[b]	yield/mg (content[e])	activity[f]	TON[g]	M_n[h] × 10^{-3}	M_w/M_n[h]	MEK-soluble[d] yield/mg
1	100/−	33 (40.0)	33	160	8.9	2.10	50
2[i]	100/−	65 (11.0)	131	629	27.7	1.59	530
3	500/−	12 (14.0)	12	57	5.5	1.45	73
4	2/498	11 (26.7)	11	53	3.1	1.20	30
5	2/98	341 (85.0)	341	1640	4.4	1.66	60
6[i]	2/98	166 (16.5)	332	1600	bimodal		840
7	2/48	411 (93.0)	411	1980	6.2	1.78	31
8[j]	−/−	− (−)	- - -	- - -	- - -	- - -	69
9[k]	−/−		high exotherm[l]				
10[m]	200 μmol/−	− (−)	- - -	- - -	- - -	- - -	61
11[m]	−/200 μmol	− (−)	- - -	- - -	- - -	- - -	53

[a] Reaction conditions: styrene 5 mL, **11** 2.0 μmol (2.0 μmol/mL of toluene), $[PhMe_2NH]B(C_6F_5)_4$ 6.0 μmol [6.0 μmol /mL of toluene, molar ratio of $[PhMe_2NH]B(C_6F_5)_4$ to Ti = 3.0], styrene + toluene = total 7.0 mL, 25 °C, 30 min. [b] Molar ratio of Al/Ti. [c] Syndiotactic polystyrene (SPS). [d] Atactic polystyrene (APS). [e] Content (wt %) in whole polymer. [f] Activity in kg of SPS/(mol of Ti h). [g] TON = molar amount of styrene consumed (for SPS)/mol of Ti. [h] By GPC data in THF vs polystyrene standard. [i] $Ph_3CB(C_6F_5)_4$ was used in place of $[PhMe_2NH]B(C_6F_5)_4$. [j] Polymerizations were performed with $[PhMe_2NH]B(C_6F_5)_4$ (6.0 μmol). [k] Polymerization was performed with $Ph_3CB(C_6F_5)_4$ (3.0 μmol). [l] Explosive exotherm was observed and the reaction was terminated within 1 min (APS was obtained). [m] Polymerization was performed with Al compounds (200 μmol).

Table 8. Styrene Polymerization by $({}^tBuC_5H_4)TiCl_2((O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (11)−$[PhMe_2NH]B(C_6F_5)_4$−$Al{}^iBu_3$/Al(n-C_8H_{17})$_3$ Catalyst System

			MEK-insoluble[b]						
run no.	toluene/mL	time/min	yield/mg	content[c]/wt %	activity[d]	TON[e]	M_n[f] × 10^{-3}	M_w/M_n[f]	MEK-soluble[g] yield/mg
12	2.0	10	95	83.0	284	455	4.8	1.48	19
13	2.0	20	262	85.0	393	1260	5.0	1.67	46
5	2.0	30	341	85.0	341	1640	4.4	1.66	60
14	3.0	10	46	68.0	137	219	4.5	1.42	21
15	3.0	20	82	80.0	124	396	3.9	1.45	21
16	3.0	30	126	98.0	126	608	3.4	1.38	31

[a] Reaction conditions: styrene 5 mL, **11** 2.0 μmol (2.0 μmol/mL of toluene), $[PhMe_2NH]B(C_6F_5)_4$ 6.0 μmol [6.0 μmol/mL of toluene, molar ratio of $[PhMe_2NH]B(C_6F_5)_4$ to Ti = 3.0], 25 °C, $Al{}^iBu_3$/Al(n-C_8H_{17})$_3$/Ti = 2/98/1. [b] Syndiotactic polystyrene (SPS). [c] Content (wt %) in whole polymer. [d] Activity in kg of SPS/(mol of Ti h). [e] TON = molar amount of styrene consumed (for SPS)/mol of Ti. [f] By GPC data in THF vs polystyrene standard. [g] Atactic polystyrene (APS).

Table 9. Effect of Monomer Concentration in Styrene Polymerization by $({}^tBuC_5H_4)TiCl_2((O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (11)−$[PhMe_2NH]B(C_6F_5)_4$−$Al{}^iBu_3$/Al(n-C_8H_{17})$_3$ Catalyst System[a]

			MEK-insoluble[c]						
run no.	styrene/mL	styrene concn[b]/ mol/L	yield/mg	content[e]/wt %	activity[f]	TON[g]	M_n[h] × 10^{-3}	M_w/M_n[h]	MEK-soluble[d] yield/mg
17	3	2.62	41	71.1	41	195	3.6	1.31	16
18	5	4.36	157	83.0	157	754	3.6	1.37	32
19	8	6.98	258	84.0	258	1240	5.4	1.66	49

[a] Reaction conditions: **2** 2.0 μmol (2.0 μmol/mL of toluene), $[PhMe_2NH]B(C_6F_5)_4$ 6.0 μmol [6.0 μmol/mL of toluene, molar ratio of $[PhMe_2NH]B(C_6F_5)_4$ to Ti = 3.0], 25 °C, $Al{}^iBu_3$/Al(n-C_8H_{17})$_3$/Ti = 2/98/1, styrene + toluene total 10.0 mL, 30 min. [b] Initial styrene concentration in mol/L. [c] Syndiotactic polystyrene (SPS). [d] Atactic polystyrene (APS). [e] Content (wt %) in whole polymer. [f] Activity in kg of SPS/(mol of Ti h). [g] TON = molar amount of styrene consumed (for SPS)/mol of Ti. [h] By GPC data in THF vs polystyrene standards.

Table 10. Styrene Polymerization with $Cp'TiCl_2(OAr)$−$[PhMe_2NH]B(C_6F_5)_4$−$Al{}^iBu_3$/Al(n-C_8H_{17})$_3$ Catalyst Systems[a]

		MEK insoluble fraction[b]					
run no.	complexes Cp′, OAr (μmol)	yield/mg	content[c]/wt %	activity[d]	TON[e]	M_n[f] × 10^{-3}	M_w/M_n[f]
5	${}^tBuC_5H_4$, O-2,6-${}^iPr_2C_6H_3$ (**11**)	341	85.0	341	1640	4.4	1.66
20	1,3-$Me_2C_5H_3$, O-2,6-${}^iPr_2C_6H_3$ (**2**)	71	68.0	71	340	bimodal	
21	1,3-$Me_2C_5H_3$, O-2,6-$Me_2C_6H_3$	91	51.0	91	439	5.4	1.73
22	1,3-$Me_2C_5H_3$, O-3,5-$Me_2C_6H_3$	136	78.0	136	653	6.3	1.73
23	1,2,3-$Me_3C_5H_3$	42	44.0	42	203	8.9	2.14
24	Cp* (**1**)	25	19.0	25	118	15.5	1.98
25	$({}^tBuC_5H_4)TiCl_3$	9	26.5	9	43		

[a] Reaction conditions: styrene 5 mL, complex 2.0 μmol (2.0 μmol/mL of toluene), $[PhMe_2NH]B(C_6F_5)_4$ 6.0 μmol [6.0 μmol/mL of toluene, molar ratio of $[PhMe_2NH]B(C_6F_5)_4$ to Ti = 3.0], styrene + toluene total 7 mL, 25 °C, $Al{}^iBu_3$/Al(n-C_8H_{17})$_3$/Ti = 2/98/1, 30 min. [b] Syndiotactic polystyrene (SPS). [c] Content (wt %) in whole polymer. [d] Activity in kg of SPS/(mol of Ti h). [e] TON = molar amount of styrene consumed (for SPS)/mol of Ti. [f] By GPC data in THF vs polystyrene standards.

activity and monomer concentration was observed (Figure 7), and an attempt to control the chain transfer reaction (and then to develop the catalyst system for a living polymerization) was unsuccessful, although the M_w/M_n value became narrow under low styrene concentration conditions (M_w/M_n = 1.31−1.37).

Table 10 summarizes the polymerization results with a series of (aryloxo)(cyclopentadienyl)titanium com-

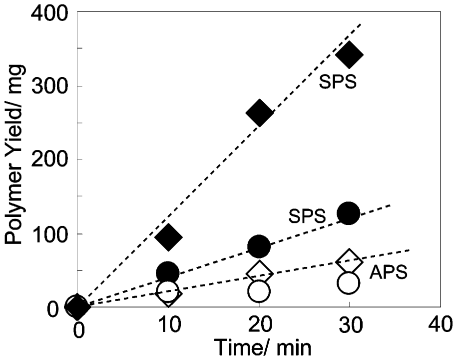


Figure 6. Time-course plots for styrene polymerization by (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**11**)−Al^{i}Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$−[PhMe$_2$NH]B(C$_6$F$_5$)$_4$ catalyst system at 25 °C. Conditions: **11** 2.0 μmol, 25 °C, Al^{i}Bu$_3$/Al(n-C$_8$H$_{17}$)$_3$/[PhMe$_2$NH]B(C$_6$F$_5$)$_4$/Ti = 2/98/3.0/1 molar ratio, styrene/toluene = 5.0/2.0 mL [toluene total 4.0 mL, ◆ (SPS) or ◇ (APS), runs 5, 12, and 13] or 5.0/3.0 mL [toluene total 5.0 mL, ● (SPS) or ○ (APS), runs 14−16]. Detailed experimental conditions are described in Table 8.

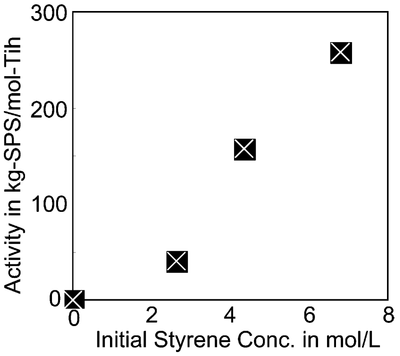


Figure 7. Plots of the catalytic activity (after 30 min, kg of SPS/(mol of Ti h)) vs monomer concentration based on results shown in Table 9.

plexes under the same conditions. Complex **11** containing a *tert*-butyl substituent on the Cp exhibited the highest catalytic activity among the series of complexes employed, affording SPS with unimodal molecular weight distribution. (^{t}BuC$_5$H$_4$)TiCl$_3$ showed extremely low catalytic activity under these conditions, and the polymerization stopped after 10 min, suggesting a role of aryloxide ligand being present. In contrast, **2** exhibited low catalytic activity, and the molecular weight distribution for the resultant SPS was bimodal. The catalytic activity could be improved by reducing the steric bulk on aryloxo ligand, and the activity increased in the order OAr = O-3,5-Me$_2$C$_6$H$_3$ > O-2,6-Me$_2$C$_6$H$_3$ > O-2,6-^{i}Pr$_2$C$_6$H$_3$. These results strongly indicate that a role of the aryloxide ligand is present for exhibiting high catalytic activity in the present syndiospecific styrene polymerization. The catalytic activity also depended on the steric bulk on the cyclopentadienyl group, and the activity increased in the order 1,3-Me$_2$C$_5$H$_3$ (**2**) > 1,2,3-Me$_3$C$_5$H$_2$ > C$_5$Me$_5$ (**4**). These results clearly suggest that the effect of the steric bulk around the titanium metal center appear to be key for exhibiting high catalytic activity. Therefore, both the aryloxide ligand and cyclopentadienyl fragment play essential roles for this syndiospecific styrene polymerization and for exhibiting high catalytic activity.

Concluding Remarks

We have explored the effect of substituents on both cyclopentadienyl and anionic ancillary ligands for syndiospecific styrene polymerization using various nonbridged half-titanocenes containing aryloxo, anilide, and amide ligands of the type Cp′TiCl$_2$(L) in the presence of MAO or borate cocatalyst. The results through this study can be summarized as follows.

1. The catalytic activities by half-titanocenes containing aryloxide ligands were higher than those by the trichloride analogues, Cp′TiCl$_3$, irrespective of the cocatalyst employed (MAO, borate), and the activity increased at higher temperature (MAO cocatalyst). The activity with Cp*TiCl$_2$(OAr) (OAr = aryloxo) and (1,3-Me$_2$C$_5$H$_3$)TiCl$_2$(L) (L = aryloxo, anilide, amide) was also dependent upon the anionic ancillary ligand (substituent on aryloxide and L) used. It is thus clear that the substituents on both the cyclopentadienyl and the anionic ancillary donor ligand *directly affect* the catalytic activity.

2. The molecular weight for the resultant polymer was also affected by substituents on both the cyclopentadienyl and the aryloxo ligand, and this was rather strongly influenced by the nature of cyclopentadienyl fragment used.

3. Synthesis of high molecular weight polymer in an efficient manner can be accomplished by using the Cp*TiCl$_2$(O-2,6-Me$_2$C$_6$H$_3$) (**7**)−MAO catalyst system, and the synthesis of extremely high molecular weight syndiotactic polystyrene (M_w = 177.7 × 10^4) can be attained by this system at 0 °C. The dominant chain transfer reaction was strongly influenced by the substitutent on cyclopentadienyl group, Cp, analogues, resulting in β-hydrogen elimination, whereas chain transfer to Al was dominant in the case of Cp* analogues.

4. Choice of both borate and aluminum cocatalyst is the key for syndiospecific styrene polymerization in the presence of borate catalyst. (^{t}BuC$_5$H$_4$)TiCl$_2$(O-2,6-^{i}Pr$_2$C$_6$H$_3$) (**11**) was effective for efficient polymerization, and the effect of steric bulk (for both cyclopentadienyl and aryloxo ligand) seems to be sensitive for exhibiting the high catalytic activity.

On the basis of the results presented in this paper, it is suggested that the aryloxide ligand plays an important role for exhibiting high catalytic activity regardless of the cocatalyst employed. Although it has been invoked that cationic Ti(III) plays an essential role for syndiospecific styrene polymerization, the role of anionic donor ligands toward both the activity and the molecular weight is also present. Although the origin for this effect might not be perfectly clear at this moment, this does not deny the possibility that a neutral Ti(III) or a cationic Ti(IV) species also plays a role for this polymerization with this unique catalyst system. We believe that the contents in this paper should be very important for understanding the reaction mechanism for both syndiospecific styrene polymerization and ethylene/styrene copolymerization and should also be important for designing efficient transition metal complexes catalysts for desired precise olefin polymerization.

Experimental Section

All experiments were carried out under a nitrogen atmosphere in a Vacuum Atmospheres drybox unless otherwise specified. Anhydrous grade of toluene (Kanto Kagaku Co. Ltd.) was transferred into a bottle containing molecular sieves (mixture of 3A and 4A 1/16 and 13X) in the drybox and was used without further purification. Styrene of polymerization grade (Idemitsu Petrochemicals Co.) was stored in a freezer after passing through alumina short column under nitrogen flow in the drybox, and the styrene was further purified by the same procedure in the drybox prior to use. Syntheses of $Cp'TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ [Cp' = Cp (**1**), 1,3-$Me_2C_5H_3$ (**2**), 1,2,4-$Me_3C_5H_2$ (**3**), C_5Me_5 (Cp*, **4**), ${}^tBuC_5H_4$ (**11**)], and $Cp^*TiCl_2(O\text{-}4\text{-}MeC_6H_4)$ were according to our previous report.[12a,14] (1,3-$Me_2C_5H_3)TiCl_2(NMeCy)$ (**9**, Cy = cyclohexyl)[17] and (1,3-$Me_2C_5H_3)TiCl_2[N(2,6\text{-}Me_2C_6H_3)(SiMe_3)]$ (**10**)[16] were also prepared according to our previous reports. Reagent grade $Ph_3CB(C_6F_5)_4$ and $[PhMe_2NH]B(C_6F_5)_4$ (Asahi Glass Co. Ltd.) were stored in the drybox and were used as received. Al^iBu_3 and $AlMe_3$ were purchased from Kanto Kagaku Co. Ltd. as the *n*-hexane solution (ca. 1.0 M), and $Al(n\text{-}C_8H_{17})_3$ was purchased from Tosoh Finechem Co. Toluene and $AlMe_3$ in the commercially available methylaluminoxane [PMAO-S, 9.5 wt % (Al) toluene solution, Tosoh Finechem Co.] were taken to dryness 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.

Molecular weights and the molecular weight distributions of the polystyrenes (prepared by borate coccatalyst systems) were measured by gel permeation chromatography (GPC). HPLC grade THF was used for GPC and were degassed prior to use. GPC were performed at 40 °C on a Shimazu SCL-10A using a RID-10A detector (Shimazu Co. Ltd.) in THF (containing 0.03 wt % 2,6-di-*tert*-butyl-*p*-cresol, flow rate 1.0 mL/min). GPC columns (ShimPAC GPC-806, 804, and 802, 30 cm × 8.0 mm diameter, spherical porous gel made of styrene/divinylbenzene copolymer, ranging from $<10^2$ to 2×10^7 MW) were calibrated vs polystyrene standard samples. Molecular weight and molecular weight distribution for polystyrenes (prepared by MAO cocatalyst systems) were measured by gel permeation chromatography (Tosoh HLC-8121GPC/HT) with a polystyrene gel column (TSK gel GMH_{HR}-H HT × 2, 30 cm × 7.8 mm i.d.), 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 solvent. The molecular weight was calculated by a standard procedure based on the calibration with standard polystyrene samples. Elemental analyses were performed by using PE2400II Series (Perkin-Elmer Co.).

Synthesis of $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^tBu_2C_6H_3)$ (8). LiO-2,6-${}^tBu_2C_6H_3$ (739 mg, 3.46 mmol) was added to a toluene solution (30 mL) of Cp^*TiCl_3 (1000 mg, 3.46 mmol) equipped with a sealed Schlenk tube in one portion at −30 °C. The reaction mixture was warmed slowly to room temperature and was then heated at 70 °C for 10 h. The mixture was then filtered through Celite pad, and the filter cake was washed with toluene. The combined filtrate and the wash were taken to dryness under reduced pressure to give a deep red solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled (−30 °C) solution gave red microcrystals (first crop), and the chilled concentrated mother liquor gave a second crop. Yield 1.24 g (78.4%). ${}^1H$ NMR (C_6D_6): 1.51 (s, 18H, $(CH_3)_3C-$), 1.88 (s, 15H, $C_5(CH_3)_5-$) 6.89 (t, 1H, C_6H_3) 7.21 (d, 2H, C_6H_3). ${}^{13}C$ NMR (C_6D_6): 13.8 [$C_5(CH_3)_5$], 32.1, 36.3, 121.8 [$C_5(CH_3)_5$], 125.3, 133.5, 139.9, 166.9 (C_6H_3). Anal. Calcd for $C_{24}H_{36}Cl_2OTi$: C, 62.76%; H, 7.90%. Found: C, 62.36%; H, 7.73%.

Synthesis of $Cp^*TiCl_2(OC_6H_5)$ (5). The synthetic procedure for **5** was the same as that for $Cp^*TiCl_2(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$ (**4**) described previously,[12a] except that $LiOC_6H_5$ was used instead of $Li(O\text{-}2,6\text{-}{}^iPr_2C_6H_3)$. Yield 78.3%. ${}^1H$ NMR (C_6D_6): 1.98 (s, 15H, $C_5(CH_3)_5-$) 6.88 (t, 1H, $J = 7.3$ Hz, C_6H_5) 7.02 (d, 2H, $J = 7.3$ Hz, C_6H_5), 7.09 (t, 2H, $J = 7.3$ Hz, C_6H_5). ${}^{13}C$ NMR (C_6D_6): 12.8 [$C_5(CH_3)_5$], 119.8 [$C_5(CH_3)_5$], 123.2, 129.6, 132.6, 165.3 (C_6H_5).

Synthesis of (1,3-$Me_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$. LiO-2,6-$Me_2C_6H_3$ (287 mg, 2.24 mmol) was added in one portion to a Et_2O solution (30 mL) containing (1,3-$Me_2C_5H_3)TiCl_3$ (555 mg, 2.24 mmol) at −30 °C. The reaction mixture was warmed slowly to room temperature and was stirred for 10 h. The mixture was then filtered through Celite, and the filter cake and was washed with Et_2O. The combined filtrate and the wash were taken to dryness under reduced pressure to give an orange solid. The solid was then dissolved in a minimum amount of CH_2Cl_2 layered by a small amount of *n*-hexane. The chilled (−30 °C) solution gave orange microcrystals (550 mg, first crop). The microcrystals were pure enough by ${}^1H$ and ${}^{13}C$ NMR and by elemental analysis. Yield 78%. The second crop would increase the yield. ${}^1H$ NMR ($CDCl_3$): δ 2.28 (s, 6H), 2.35 (s, 6H), 6.23 (d, 2H, $J = 2.4$ Hz, $Me_2C_5H_3$), 6.40 (t, 1H, $J = 2.4$ Hz, $Me_2C_5H_3$), 6.86 (t, 1H, $J = 7.6$ Hz, C_6H_3), 6.98 (d, 2H, $J = 7.8$ Hz, C_6H_3). ${}^{13}C$ NMR ($CDCl_3$): δ 16.7, 17.2, 120.6, 122.2, 123.6, 127.9, 128.4, 136.8, 165.2. Anal. Calcd for $C_{15}H_{18}Cl_2OTi$: C, 54.09; H, 5.80. Found (1): C, 54.14; H, 5.44; N, 0.03. Found (2): C, 54.13; H, 5.45; N, 0.03.

Synthesis of (1,3-$Me_2C_5H_3)TiCl_2(O\text{-}3,5\text{-}Me_2C_6H_3)$. The synthetic procedure was the same as that in (1,3-$Me_2C_5H_3)TiCl_2(O\text{-}2,6\text{-}Me_2C_6H_3)$ except LiO-3,5-$Me_2C_6H_3$ (304 mg, 2.37 mmol) and (1,3-$Me_2C_5H_3)TiCl_3$ (587 mg, 2.37 mmol) were used. Yield: 565 mg (first crop, 78%). ${}^1H$ NMR ($CDCl_3$): δ 2.28 (s, 6H), 2.35 (s, 6H), 6.38 (d, 2H, $J = 2.2$ Hz, $Me_2C_5H_3$), 6.40 (m, 1H, $Me_2C_5H_3$), 6.61 (s, 2H, C_6H_3), 6.72 (s, 1H, C_6H_3). ${}^{13}C$ NMR ($CDCl_3$): δ 16.6, 21.2, 116.2, 120.8, 122.3, 125.8, 136.4, 139.1, 167.3. Anal. Calcd for $C_{15}H_{18}Cl_2OTi$: C, 54.09; H, 5.80. Found: C, 53.90; H, 5.38; N, 0.01.

Polymerization of Styrene. A typical polymerization procedure (described in Table 1, complex **2** at 85 °C) is as follows: into a 100 mL scale stainless steel autoclave, MAO (3.0 mmol, 174 mg), a prescribed amount of toluene (19.0 mL), and then styrene (10.0 mL) were added in the drybox. A toluene solution containing titanium complex (2.0 μmol/ mL toluene, 1.0 mL) was added into the solution to start the polymerization at 85 °C, and the reaction mixture was stirred for 10 min. The polymerization was then terminated with the addition of ethanol containing HCl, and the resultant white solid was collected by filtration and was dried in vacuo (at 60 °C for 6 h). Polymer yield: 4436 mg. The resultant solid (1038.4 mg/4436 mg) was then separated into two fractions by washing with acetone as the extraction solvent and was dried in vacuo for 6 h at 60 °C. Yields: 10.3 mg (acetone-soluble, atactic PS) and 1028.1 mg (syndiotactic PS, total amount 4392 mg). Typical ${}^1H$ and ${}^{13}C$ NMR spectra for resultant polymer (acetone-insoluble fraction, SPS) were the same as those reported previously.[13]

Typical styrene polymerizations in the presence of borate cocatalyst (Table 7, run 7) are performed as follows. A prescribed amount of styrene (5.0 mL) was added into a round-bottom flask (25 mL) in the drybox, and the polymerization was started by addition of a mixture of $Al^iBu_3/Al(n\text{-}C_8H_{17})_3$ (4.0/96.0 μmol) soon after the addition of a certain amount of toluene solution containing **11** (2.0 μmol/mL of toluene, 1.0 mL) and $[PhMe_2NH]B(C_6F_5)_4$ (6.0 μmol/mL of toluene, 1.0 mL). The reaction mixture was stirred for a prescribed time (30 min), and the polymerization was terminated with the addition of EtOH. The white reaction product was collected by filtration (yield 442 mg), and the syndiotactic polymer was isolated as 2-butanone (MEK)-insoluble fraction according to our established procedure.[13] Atactic polymer was also obtained as 2-butanone-soluble fraction (31 mg). Resultant polymer was then dried in vacuo. Yields: 31.0 mg (acetone-soluble, atactic PS) and 411 mg (syndiotactic PS). ${}^1H$ and ${}^{13}C$ NMR spectra for resultant polymer (SPS) were the same as those reported previously.[13]

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(24) As described in ref 13, the reaction products were a mixture of syndiotactic polystyrene [SPS-, acetone-, or 2-butanone (MEK)-insoluble fraction] and atactic polystyrene [APS-, acetone-, or MEK-soluble fraction]. A small amount of APS was obtained especially at the initial stage, and the amount was smaller than that produced by MAO itself in all cases. On the basis of these results, we thus concluded that half-titanocene catalyst precursor employed this research affords SPS exclusively.

(25) Related to this fact, we reported (in the Supporting Information in ref 13) that the activity with a series of $(1,3\text{-}Me_2C_5H_3)TiCl_2(OAr)$−MAO catalyst systems (at 25 °C) increased in the order OAr = O-2, 6-$^iPr_2C_6H_3$ > O-2,6-$Me_2C_6H_3$ > O-3,5-$Me_2C_6H_3$. Although the M_w value was not affected by the aryloxide ligand employed, the molecular weight distribution became broad, especially when $(1,3\text{-}Me_2C_5H_3)TiCl_2(O\text{-}3,5\text{-}Me_2C_6H_3)$ was used as the catalyst precursor.[13]

(26) According to their DFT (B3LYP/3-21G*) calculation,[2m,n] the syndiospecific polymerization takes place exclusively, and the primary (1,2-insertion) insertion does not occur because the coordination of the monomer is not stable, and stereoirregular insertion is difficult to occur because of the steric hindrance of the Cp′ ligand, even if neutral Ti(III) species, Cp′Ti(L)(R)-(styrene) (L = anionic donor ligand, R = alkyl, polymer chain), plays a role as the catalytically active species for syndiospecific styrene polymerization. This is also because the polymerization took place with chain-end control manner, and inserted monomer *weakly* coordinates to the Ti metal center that would control the stereospecificity. In addition, Ti(III) is the preferable active site, and styrene coordinatesd

in both vinyl and phenyl group seems hard to activate mononer in case of cationic species [both Ti(III) and Ti(IV)].[2m,n]

(27) Tomotsu et al. reported that the catalytic activity decreased upon the addition of $AlMe_3$ for styrene polymerization by the $Cp^*Ti(OMe)_3$–MAO catalyst system.[4a–c] They also reported that the M_w value decreased upon the addition of alkylaluminum, especially the effect of $Al(i\text{-}Bu)_3$ addition toward the M_w value was explored,[4a] although the experimental details were not seen. These results also assume that dominant chain transfer in the styrene polymerization by the Cp* analogue would be the chain transfer to aluminum.

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(32) Styrene concentration dependence was explored under the same concentrations of **11**, Al^iBu_3, $Al(n\text{-}C_8H_{17})_3$, and $[PhMe_2NH]B(C_6F_5)_4$ because, as described in Table 7, these cocatalysts (alkylaluminum and borate compounds) affords atactic polystyrene independently, and the observed catalytic activity for syndiospecific styrene polymerization depended upon these concentrations.

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