Styrene polymerization with half-sandwiched titanocene trichloride catalysts combined with alkylaluminum-Ph$_3$CB(C$_6$F$_5$)$_4$ cocatalyst systems

Naofumi Naga [*]

*Department of Applied Chemistry, Materials Science Course, College of Engineering, Shibaura Institute of Technology,
3-7-5 Toyosu, Kohtoh-ku, Tokyo 135-8548, Japan*

Abstract

Half-sandwiched titanocene trichloride (Cp′TiCl$_3$; Cp′ = cyclopentadienyl, Cp; pentamethylcyclopentadienyl, Cp*; indenyl, Ind) combined with an alkylaluminum (triisobutylaluminum, diisobutylaluminum hydride, or trioctylaluminum)/Ph$_3$CB(C$_6$F$_5$)$_4$ cocatalyst system has been examined for polymerization of styrene. Syndiospecific polymerization of styrene proceeded under limited polymerization conditions. The maximum productivity of syndiotactic polystyrene was attained under the following conditions: Al/Ti molar ratio = 20 (mol/mol), polymerization temperature = 40–50 °C. The nature of alkylaluminum compounds and the ligand structure of the catalysts affected the range of the polymerization temperature in which proceeds the syndiospecific polymerization of styrene.
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Keywords: Styrene; Syndiospecific polymerization; Half-sandwiched titanocene trichloride; Alkylaluminum; Borate compound

1. Introduction

Half-sandwiched titanocene catalyst, such as Cp′TiR$_3$ (Cp′ = substituted cyclopentadienyl, R = halogen, alkoxyl, or alkyl), is one of the most effective catalysts for syndiospecific polymerization of styrene combined with methylaluminoxane (MAO) as a cocatalyst [1]. Modification of Cp′ ligand or R substituent has been made to develop the catalyst efficiency in the polymerization [2–21]. MAO has been mainly used as a cocatalyst in the styrene polymerization with the half-sandwiched titanocene catalysts. The cocatalyst system of trialkylaluminum/borane compound, which is effective for ethylene or propylene polymerization with zirconocene catalysts [22,23], also has been applied to the syndiospecific polymerization of styrene with the half-sandwiched titanium trimethyl catalysts, such as Cp*Ti(CH$_3$)$_3$ (Cp* = pentamethylcyclopentadienyl) catalyst. Chien and co-workers [24] investigated syndiospecific polymerization of styrene with Cp*Ti(CH$_3$)$_3$ combined with Ph$_3$CB(C$_6$F$_5$)$_4$ at 50 °C. They also reported that addition of

20 times equivalents of triisobutylaluminum (AliBu$_3$) caused the increase of polymerization activity. Idemitsu Kosan has developed the syndiospecific polymerization of styrene with various catalyst systems composed of Cp′TiR$_3$ (R = CH$_3$, OCH$_3$, benzyl)-AliBu$_3$/borane compound [25–33]. These results have been reviewed by Po' and Cardi [34]. The syndiospecific polymerization of styrene with Cp*Ti(CH$_3$)$_3$ combined with some borate or boron compounds has been investigated from various scientific points of view [35–41]. However, few results of the polymerization half-sandwiched titanocene trichloride catalysts systems using cocatalysts of trialkylaluminum/borane compound have been reported. The author applied the alkylaluminum/borane compound system to the polymerization of styrene with some conventional half-sandwiched titanium trichloride catalysts [Cp′TiCl$_3$: Cp′ = cyclopentadienyl (Cp), pentamethylcyclopentadienyl (Cp*), indenyl (Ind)], and found out the limited polymerization conditions which achieve syndiospecific polymerization of styrene. This paper reports the effect of alkylaluminum and polymerization conditions on the productivity of syndiotactic-polystyrene (SPS) using Cp′TiCl$_3$; (Cp′ = Cp, Cp*, Ind) catalysts combined with alkylaluminum [AliBu$_3$, diisobutylaluminum hydride (AliBu$_2$H), trioctylaluminum(AlOct$_3$)]/Ph$_3$CB(C$_6$F$_5$)$_4$ cocatalyst systems.

[*] Tel.: +81 3 5859 8152; fax: +81 3 5859 8101.
E-mail address: nnaga@sic.shibaura-it.ac.jp.

2. Experimental

2.1. Materials

CpTiCl$_3$ and Cp*TiCl$_3$ were commercially obtained from Aldrich, and used without further purification. IndTiCl$_3$ was synthesized according to the literature [5]. A toluene solution of AliBu$_3$ was commercially obtained from Wako Pure Chemical Industries, and used without further purification. A toluene solution of AliBu$_2$H and a hexane solution of AlOct$_3$ were commercially obtained from Aldrich, and used as received. Ph$_3$CB(C$_6$F$_5$)$_4$ was purchased from Albemarle, and used without further purification. Styrene (Wako Pure Chemical Industries) was dried with CaH$_2$ and distilled before use under nitrogen atmosphere.

2.2. Polymerization

Polymerization of styrene was carried out in a 100 mL glass reactor equipped with a magnetic stirrer. Toluene and styrene were added to the reactor under nitrogen atmosphere. The reactor was heated and kept at the desired polymerization temperature. Polymerization was started by introducing the toluene solution of a catalyst, an alkylaluminum, and Ph$_3$CB(C$_6$F$_5$)$_4$ into the reactor. The polymerization was terminated by adding a small amount of methanol to the reaction medium. The resulting polymer was precipitated in a large excess of methanol including HCl and recovered by filtration and washed several times with methanol. The polymer obtained was extracted with acetone to separate into atactic-polystyrene (APS) (soluble fraction) and SPS (insoluble fraction). The acetone solution of extracted polymer was concentrated by evaporation and precipitated in a large excess of methanol. The precipitated polymer was recovered by filtration and dried in vacuo at 60 °C for 6 h. Syndiotacticity of the resulting SPS was high, and [rrrr] values determined by ^{13}C

NMR spectroscopy were higher than 95%. Stereoregularity of APS was statistically atactic. The melting points of resulting SPSs were about 270 °C.

2.3. Analytical procedures

Molecular weight and molecular weight distribution of the polymer were measured at 140 °C by means of gel permeation chromatography (Waters 150CV) using ODCB as a solvent and calibrated with standard polystyrene samples.

3. Results and discussion

3.1. Polymerization with CpTiCl$_3$

Polymerization of styrene was conducted with CpTiCl$_3$–AliBu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$ at 40 °C (runs 1–6) or 50 °C (runs 7–13). The results are summarized in Table 1. When the polymerization was conducted with less than the Al/Ti molar ratio = 20, only APS was produced. SPS was obtained with more than the Al/Ti molar ratio = 20 of AliBu$_3$. Relationship between the Al/Ti molar ratio and the activity for SPS production is illustrated in Fig. 1. In the polymerization at 40 and 50 °C, the highest productivity of SPS was attained at molar ratio of Al/Ti = 20. The activity for SPS decreased with increasing molar ratio of Al/Ti. Active sites for syndiospecific polymerization of styrene have been considered Ti(III) complex. The most likely explanation is that reduction of Ti(IV) complex to Ti(III) did not proceed in the polymerization with a small amount of AliBu$_3$, less than Al/Ti = 20, On the other hand, in the polymerization with the Al/Ti molar ratio of AliBu$_3$ higher than 25, the further reduction from Ti(III) complex to Ti(II) should proceed with an increasing of Al/Ti ratio. Another explanation for the result that the reactions with insufficient or excess of AliBu$_3$ would be given in terms of dormant complexes, as proposed in Scheme 1, which

Table 1
Results of styrene polymerization with CpTiCl$_3$–AliBu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$[a]

Run	T_p[b] (°C)	Al/Ti (mol/mol)	Polymerization time (min)	SPS			
				Yield (g)	Activity (kg/mol Ti h)	M_n[c] ($\times 10^{-3}$)	M_w/M_n[c]
1	40	10	120	0	0		
2	40	20	14	1.15	490	15.6	2.1
3	40	25	20	1.02	310		
4	40	30	20	0.72	220		
5	40	50	36	0.67	110		
6	40	75	120	0.15	7.6		
7	50	10	120	0	0		
8	50	15	120	0	0		
9	50	20	20	2.42	730	8.2	1.9
10	50	25	25	2.12	510		
11	50	30	20	1.23	370		
12	50	50	30	1.22	240	6.5	1.6
13	50	75	60	1.01	100		
14	23	20	120	Trace	Trace		
15	60	20	120	Trace	Trace		

[a] Polymerization conditions: CpTiCl$_3$ = Ph$_3$CB(C$_6$F$_5$)$_4$ = 10.0 μmol, toluene + AliBu$_3$ = 45 mL, styrene = 5 mL.
[b] Polymerization temperature.
[c] Determined by GPC using polystyrene standard samples.

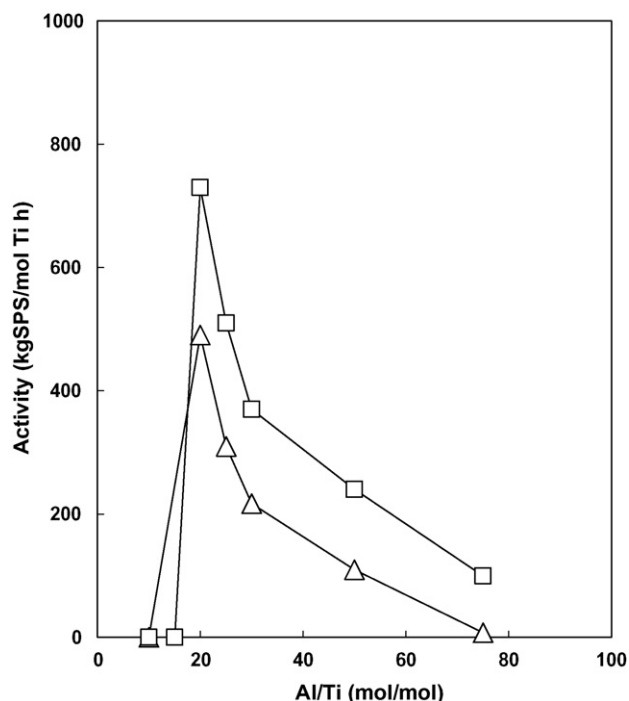Fig. 1. Relationship between the Al/Ti ratio and polymerization activity in the syndiospecific styrene polymerization with $CpTiCl_3$–$AliBu_3$/$Ph_3CB(C_6F_5)_4$: $T_p = 40\,°C$ ($\triangle$), $T_p = 50\,°C$ ($\square$).

refers to the reactions in ethylene polymerization with the zirconocene dichloride-trialkylaluminum/$Ph_3CB(C_6F_5)_4$ catalyst system [42]. Assuming that the free ion or solvent-separated ion pair 1 is the active specie for the syndiospecific polymerization of styrene, the author can suggest that two kinds of dormant sites form in the polymerization with the catalyst system. In the polymerization with a small amount of $AliBu_3$, a reaction of two alkylated $Cp'TiCl_3$ complexes ($Cp'TiR_3$) with one $Ph_3CB(C_6F_5)_4$ would yield a dormant complex of 2. On the other hand, a reaction with excess of $AliBu_3$ would lead to the formation of a dormant complex of 3 containing an aluminum compound.

Number-average molecular weight (M_n) of SPS decreased with increasing polymerization temperature (runs 2 and 9) and the Al/Ti ratio (runs 9 and 12) due to the increase in frequency of chain transfer reactions.
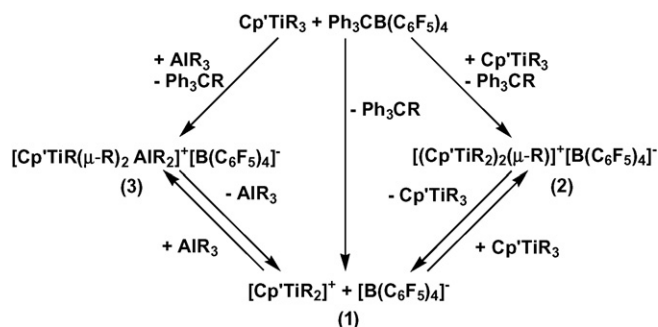
Scheme 1. Proposed reaction mechanism in the formation of active species with $Cp'TiCl_3$—the AlR_3/$Ph_3CB(C_6F_5)_4$ catalyst system.

Table 2
Results of styrene polymerization with $CpTiCl_3$–$AliBu_3$/$Ph_3CB(C_6F_5)_4$, effect of contact time of $CpTiCl_3$ and $AliBu_3$[a]

Run	Aging[b] (min)	Polymerization time (min)	SPS	
			Yield (g)	Activity (kg/mol Ti h)
16	40	18	2.25	750
17	40	25	1.60	380
18	40	30	1.49	300

[a] Polymerization conditions: $CpTiCl_3 = Ph_3CB(C_6F_5)_4 = 10.0\,\mu mol$, $AliBu_3 = 0.2\,mmol$, toluene + $AliBu_3 = 45\,mL$, styrene = 5 mL, polymerization temperature = 50 °C.
[b] Aging of $CpTiCl_3$ and $AliBu_3$ was conducted at 50 °C.

Effect of polymerization temperature on the productivity of SPS has been investigated at the molar ratio of Al/Ti = 20 (mol/mol) and the results are also included in Table 1 (runs 14, 2, 9, and 15). The polymerization at room temperature (23 °C) or 60 °C mainly yielded APS with a small quantity of SPS. The most likely explanation for the result obtained at high temperature polymerization (at 60 °C) may be the dismutation of the titanium species such as $2Ti(III) \rightarrow Ti(II) + Ti(IV)$. The effective syndiospecific polymerization proceeded under the limited polymerization temperatures ranging from 40 to 50 °C.

Effect of contact time of $CpTiCl_3$ and $AliBu_3$ on the polymerization activity has been studied. The results are summarized in Table 2. The activity of SPS production decreased with increasing contact time. This tendency should be derived from the reduction of titanium oxidation states, and indicates that preceded contact of half-sandwiched titanium catalyst with $AliBu_3$ would change the nature of active species as time passes.

The polymerization has been also investigated with $CpTiCl_3$ using $AliBu_2H$ or $AlOct_3$ and the results are summarized in Tables 3 and 4, respectively. The maximum activity of SPS production was attained at the ratio of

Table 3
Results of styrene polymerization with $CpTiCl_3$–$AliBu_2H$/$Ph_3CB(C_6F_5)_4$[a]

Run	T_p[b] (°C)	Al/Ti (mol/mol)	Polymerization time (min)	SPS, activity (kg/mol Ti h)
19	23	20	120	0
20	40	20	120	0
21	50	10	120	0
22	50	15	120	0
23	50	20	60	120
24	50	25	120	Trace
25	50	30	120	Trace
26	60	20	70	150
27	60	25	120	35
28	60	30	120	24
29	70	20	120	93
30	70	25	120	Trace
31	70	30	120	Trace
32	80	20	120	0

[a] Polymerization conditions: $CpTiCl_3 = Ph_3CB(C_6F_5)_4 = 10.0\,\mu mol$ (runs 27–32; 5.0 μmol), toluene + $AliBu_2H = 45\,mL$ (runs 27–32; 22.5 mL), styrene = 5 mL (runs 27–32; 2.5 mL).
[b] Polymerization temperature.

Table 4
Results of styrene polymerization with $CpTiCl_3$–$AlOct_3$/$Ph_3CB(C_6F_5)_4$[a]

Run	T_p[b] (°C)	Al/Ti (mol/mol)	Polymerization time (min)	SPS, activity (kg/mol Ti h)
33	23	20	120	17
34	40	20	120	27
35	50	10	120	0
36	50	20	120	32
37	50	30	120	23
38	50	50	120	12
39	60	20	120	0
40	70	20	120	0

[a] Polymerization conditions: $CpTiCl_3$ = $Ph_3CB(C_6F_5)_4$ = 5.0 μmol, toluene + $AlOct_3$ = 22.5 mL, styrene = 2.5 mL.
[b] Polymerization temperature.

Table 5
Results of styrene polymerization with $IndTiCl_3$–$AliBu_3$/$Ph_3CB(C_6F_5)_4$[a]

Run	T_p[b] (°C)	Al/Ti (mol/mol)	Polymerization time (min)	SPS, activity (kg/mol Ti h)
41	23	20	120	3.7
42	40	20	30	120
43	50	10	120	0
44	50	20	90	56
45	50	30	120	21
46	50	50	120	4.2
47	60	20	120	0

[a] Polymerization conditions: $IndTiCl_3$ = $Ph_3CB(C_6F_5)_4$ = 5.0 μmol, toluene + $AliBu_3$ = 22.5 mL, styrene = 2.5 mL.
[b] Polymerization temperature.

Al/Ti = 20 (mol/mol), as observed in the polymerization using $AliBu_3$. The activity of SPS was strongly affected by the nature of alkylalminum used and decreased in the following order: $AliBu_3$ > $AliBu_2H$ > $AlOct_3$. Relationship between the polymerization temperature and the activity of SPS is illustrated in Fig. 2. In the polymerization using $AliBu_2H$, SPS was obtained at higher polymerization temperatures, from 50 to 70 °C, than those for the polymerization with $AliBu_3$. The difference in the polymerization activity and temperature range would be derived from the difference in alkylation ability between $AliBu_3$ and $AliBu_2H$. In the polymerization using $AlOct_3$, SPS was obtained in the wide range of the polymerization temperatures, from room temperature (23 °C) to 50 °C. One possibility is that the varieties of polymerization behavior would be derived

from the difference in reduction ability and/or alkylation ability between $AliBu_3$ and $AlOct_3$. Another possibility is that the difference in stability of the dormant sites, as proposed in Scheme 1, would affect the polymerization activity and/or the range of the polymerization temperature that cause the effective syndiospecific polymerization.

3.2. Polymerization with $IndTiCl_3$

The styrene polymerization has also been investigated with $IndTiCl_3$ combined with $AliBu_3$/$Ph_3CB(C_6F_5)_4$ as a cocatalyst system. The results are summarized in Table 5. Effect of the Al/Ti ratio on the productivity of SPS was examined at 50 °C. The catalyst system showed the highest activity in the polymerization at the ratio of Al/Ti = 20 (mol/mol), as observed in the polymerization with $CpTiCl_3$. Effect of polymerization temperature on the activity of SPS was examined at the ratio of Al/Ti = 20 (mol/mol), and the results are illustrated in Fig. 3. SPS was obtained at the polymerization temperature from room temperature to 50 °C. The maximum activity was attained at 40 °C. The temperature at which attained the highest activity was lower than that observed in the polymerization with $CpTiCl_3$ catalyst (50 °C).

3.3. Polymerization with Cp^*TiCl_3

The styrene polymerization has also been investigated with Cp^*TiCl_3 combined with $AliBu_3$/$Ph_3CB(C_6F_5)_4$ as a cocatalyst system. The results are summarized in Table 6. Effect of Al/Ti ratio on the activity of SPS was examined at 50 °C. The catalyst system showed the highest activity in the polymerization at the ratio of Al/Ti = 20 (mol/mol), as observed in the polymerization with the other catalysts. Effect of polymerization temperature on the activity of SPS was examined at the ratio of Al/Ti = 20 (mol/mol), and the results are illustrated in Fig. 3. SPS was obtained at the polymerization temperature from room temperature to 50 °C. The maximum activity was attained at 50 °C.

The substituents on Cp′ affected the activity and the suitable temperature of the syndiospepcific polymerization of styrene with the catalyst systems. In the styrene polymerization with the half-sandwiched titanocene catalysts, the active sites are
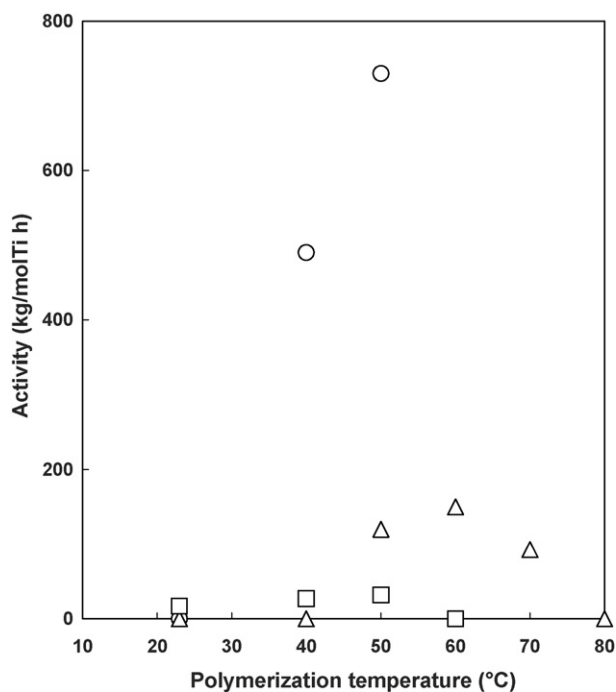

Fig. 2. Relationship between the polymerization temperature and polymerization activity in the syndiospecific styrene polymerization with $CpTiCl_3$–alkylalumium/$Ph_3CB(C_6F_5)_4$: (○) $AliBu_3$, (△) $AliBu_2H$ and (□) $AlOct_3$ [Al]/[Ti] = 20 (mol/mol).
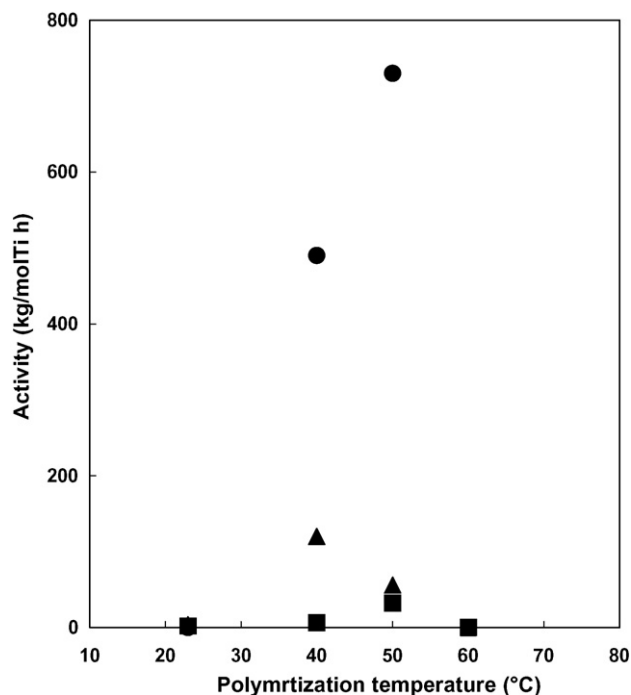
Fig. 3. Relationship between the polymerization temperature and polymerization activity in the syndiospecific styrene polymerization with half-sandwich titanium (IV) catalysts—AliBu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$: (●) CpTiCl$_3$, (▲) IndTiCl$_3$ and (■) Cp*TiCl$_3$ [Al]/[Ti] = 20 (mol/mol).

4. Conclusions

Polymerization of styrene has been investigated by half-sandwiched titanium trichloride catalysts, CpTiCl$_3$, Cp*TiCl$_3$ and IndTiCl$_3$, combined with the alkylaluminum (AliBu$_3$, AliBu$_2$H, AlOct$_3$)/Ph$_3$CB(C$_6$F$_5$)$_4$ cocatalyst systems under various polymerization temperatures and Al/Ti molar ratios. The polymerization carried out at Al/Ti molar ratio = 20 (mol/mol) in the temperature range from 40 to 50 °C produced SPS in good yield. The range of the polymerization temperature and the Al/Ti molar ratio which admits of syndiospecific polymerization of styrene was affected by the nature of alkylaluminum compounds and the ligand structure of the catalysts.

Various factors, substituents of the Cp$'$ ligand or R in the Cp$'$TiR$_3$ catalysts, the nature of alkylaluminum, as mentioned before, affected the activity and suitable temperature for the syndiospecific polymerization of styrene with the half-sandwiched titanocene catalysts combined with the alkylaluminum/Ph$_3$CB(C$_6$F$_5$)$_4$ cocatalyst system. The cation forming reagents, such as tetrakis(pentafluorophenyl) borate compounds, also strongly affected the polymerization, as previously reported [34]. Research on this polymerization with the catalyst systems, however, often fails to grasp the total explanation. Electron spin resonance study of the catalyst system should be useful for elucidating the subject, and will be reported elsewhere.

widely opened and the substituents of the Cp$'$ ligand should not sterically hider the insertion of styrene. From these view points, it is reasonable to consider that the differences in the polymerization behavior should not be due to the difference in bulkiness of Cp$'$ ligands but due to a difference in the electronic nature of the Cp$'$ ligands. In the previous reports, Cp*Ti(CH$_3$)$_3$ or Cp*Ti(OCH$_3$)$_3$ catalyst combined with the same cocatalyst system showed high activity in the conditions of a higher Al/Ti molar ratio (30–150 mol/mol) and/or a higher polymerization temperature (at 70 °C) [25–34]. Not only the substituents on the Cp$'$ ligand but also the R substituents of the Cp$'$TiR$_3$ catalyst strongly affected the behavior of the syndiospecific polymerization of styrene.

Table 6
Results of styrene polymerization with Cp*TiCl$_3$–AliBu$_3$/Ph$_3$CB(C$_6$F$_5$)$_4$[a]

Run	T_p[b] (°C)	Al/Ti (mol/mol)	Polymerization time (min)	SPS, activity (kg/mol Ti h)
48	23	20	120	1.9
49	40	20	120	6.3
50	50	10	120	0
51	50	20	65	32
52	50	30	90	11
53	50	50	120	2.4
54	60	20	120	0

[a] Polymerization conditions: Cp*TiCl$_3$ = Ph$_3$CB(C$_6$F$_5$)$_4$ = 5.0 μmol, toluene + AliBu$_3$ = 22.5 mL, styrene = 2.5 mL.
[b] Polymerization temperature.

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