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Syndiospecific polymerization of styrene with half-titanocene catalysts containing fluorinated phenoxy ligands†

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Novel half-titanocene catalysts containing fluorinated phenoxy ligands were synthesized and used for the syndiotactic polymerization of styrene in the presence of low methylaluminoxane (MAO) and triisobutylaluminum (TIBA) as cocatalysts. The influences of polymerization conditions, including temperature and Al/Ti ratio, on polymerization behaviour and the molecular weight of the resultant polymer were studied. The fluorinated half-titanocene catalysts displayed higher catalytic activity and produced syndiotactic polystyrene (sPS) with a higher molecular weight as a result of the electron-withdrawing conjugation effect of fluorinated phenoxy ligands. This effect stabilizes Ti(III) active centers and/or enhances propagation while reducing the chain transfer rate constant.

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Introduction

In 1985, Ishihara and co-workers^{1–6} used half-titanocene complexes, CpTiL₃ (Cp = η⁵-cyclopentadienyl)/methylaluminoxane (MAO), to efficiently synthesize syndiotactic polystyrene (sPS). Due to its high melting point (*T*_m = 270 °C), low density, and low dielectric constant, sPS has been widely used in automotive materials, electronic appliances, and precision instruments.^{6–8} Since then, syndiospecific styrene polymerization catalyzed by half-titanocene/MAO catalysts has drawn significant attention from both the academia and industry.^{9,10}

After nearly four decades of exploration, researchers found that the catalytic activity of CpTiL₃ activated by MAO, as well as the molecular weight (*M*_w) of sPS, increases with the electron-donating ability and steric hindrance of the ligands.^{11–16} For example, among Cp rings, Flu > Ind > Cp*(C₅Me₅) > Cp,^{17,18} and for ancillary ligand (L), F > OⁱPr ≈ OMe > OPh > Cl.^{19,20} The structure and composition of the cocatalyst MAO directly affect the formation, structure, and performance of the active center, including the oxidation state and distribution of Ti.^{17–20} Only Ti(III) active centers are effective for syndiospecific styrene polymerization.^{13,21}

Furthermore, the structure and composition of MAO significantly impact the catalytic performance of half-titanocene complexes. MAO has been revealed to exist as a two-dimensional sheet cluster.²² MAO with an Al/C ratio near 1/1.41 exhibits higher activity, indicating that a minimum Al_{MAO}/Ti ratio is required to maximize the number of active centers as [Ti]. In addition, MAO is always one of the most important economic factors in syndiospecific styrene polymerization under common industrial conditions.^{7,8,17} The cost of MAO often exceeds that of the main half-titanocene complex catalyst. Therefore, developing a catalytic system that requires less MAO as a cocatalyst remains a challenging topic with significant economic implications.

Based on these findings, this work designed and synthesised two fluorinated phenoxy half-titanocene catalysts, Cp*Ti(OC₆F₅)₃ and Cp*Ti(-O-2,6-C₆H₃F₂)₃, for syndiospecific styrene polymerization under MAO activation. Compared with Cp*TiCl₃ and Cp*Ti(OMe)₃, they showed higher catalytic activity and produced sPS with higher MW under economical production conditions (Al_{MAO}/Ti = 100). Furthermore, this study primarily explored the relationship between the structure of the phenoxy half-titanocene catalysts and the syndiospecific styrene polymerization as well as the MW of sPS.

Experimental

Materials

All experiments were carried out under a nitrogen atmosphere using the standard Schlenk techniques. All chemicals were used as received unless otherwise specified. Toluene (Analytical Reagent, Guangzhou Brand) was distilled in the presence of potassium and benzophenone under a nitrogen atmosphere,

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and then stored over the activated molecular sieves (3 Å). Superdry dichloromethane, and *n*-hexane (99.9%, extra dry, with molecular sieves, water \leq 50 ppm (by K. F.)) were purchased from Energy Chemical. Styrene was purchased from Amethyst. Methylaluminoxane solution (MAO, 4.7 wt% Al in toluene) was purchased from Botai. Triisobutylaluminum solution (TIBA, 1.0 M solution of toluene) was purchased from Rhawn. Trichloro(pentamethylcyclopentadienyl) titanium(IV) was purchased from Sigma-Aldrich. Trimethoxy(pentamethylcyclopentadienyl) titanium(IV) was purchased from Laajoo. Pentafluorophenol and 2,6-difluorophenol were purchased from Aladdin.

^1H , ^{13}C and ^{19}F NMR spectra of catalysts were recorded at ambient temperature using a Bruker AVANCE III-600 MHz spectrometer using standard parameters. ^{13}C NMR spectra of sPS were recorded at 125 °C. The chemical shifts were referenced to the peaks of residual CDCl_3 ($\delta = 7.26$ in ^1H NMR). Elemental analyses were performed using a Vario Elementar (EA).

Synthesis of $\text{Cp}^*\text{Ti}(\text{OC}_6\text{F}_5)_3$

A dichloromethane solution of $\text{Cp}^*\text{Ti}(\text{OMe})_3$ (4.65 g, 16.8 mmol) was added dropwise at -78 °C to a solution of pentafluorophenol (9.57 g, 52.0 mmol) in 300 mL of dichloromethane. The reaction mixture was gradually warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was washed with 90 mL of *n*-hexane for 3 times. The desired product $\text{Cp}^*\text{Ti}(\text{OC}_6\text{F}_5)_3$ was isolated as orange crystals after recrystallization from the dichloromethane/*n*-hexane solution at 4 °C in a refrigerator overnight (10.66 g, 87%).

^1H NMR (CDCl_3 , 600 MHz): $\delta = 2.08$ (s, 15H, C_5Me_5).

^{19}F NMR (CDCl_3 , 600 MHz): $\delta = -169.92$ (t, 1F, $J = 23.0$ and 23.8 Hz), -165.55 (t, 2F, $J = 22.8$ and 20.4 Hz), 160.60 (d, 2F, $J = 20.2$ Hz).

Anal. calc. for $\text{C}_{28}\text{H}_{15}\text{F}_{15}\text{O}_3\text{Ti}$: C, 45.93; H, 2.06. Found: C, 45.82, H, 3.41.

Synthesis of $\text{Cp}^*\text{Ti}(\text{O}-2,6-\text{C}_6\text{H}_3\text{F}_2)_3$

A dichloromethane solution of $\text{Cp}^*\text{Ti}(\text{OMe})_3$ (0.46 g, 1.68 mmol) was added dropwise at -78 °C to a solution of 2,6-difluorophenol (0.68 g, 5.20 mmol) in 30 mL of dichloromethane. The reaction mixture was warmed to room temperature and stirred for 12 h. The residue, obtained by removing the solvent under vacuum, was washed 3 times with 10 mL of *n*-hexane. The desired product $\text{Cp}^*\text{Ti}(\text{O}-2,6-\text{C}_6\text{H}_3\text{F}_2)_3$ was isolated as dark orange crystals after recrystallization from the dichloromethane/*n*-hexane solution at 4 °C in a refrigerator overnight (0.86 g, 90%).

^1H NMR (CDCl_3 , 600 MHz) $\delta = 6.70$ (d, 6H, O-2,6- $\text{C}_6\text{H}_3\text{F}_2$), 6.57 (t, 3H, O-2,6- $\text{C}_6\text{H}_3\text{F}_2$), 2.07 (s, 15H, C_5Me_5).

^{19}F NMR (CDCl_3 , 600 MHz): $\delta = -129.32$ (s, 2F).

Anal. calc. for $\text{C}_{28}\text{H}_{25}\text{F}_6\text{O}_3\text{Ti}$: C, 58.86; H, 4.10. Found: C, 57.99, H, 4.73.

Bulk syndiospecific polymerization of styrene

Bulk syndiospecific polymerization of styrene with homogeneous half-titanocene catalysts was carried out in a 200 mL glass reactor equipped with a magnetic stirring bar under a nitrogen atmosphere. The calculated amounts of styrene were charged into the reactor and heated to the predetermined temperature in an oil bath. The polymerization reaction started after TIBA solution, MAO solution and the catalyst with toluene solution were injected in sequence. After the needed polymerization time, the reaction was terminated by adding 5.0 mL of methyl alcohol. The obtained solid or gel polymer was washed with 100 mL acidified ethanol (ethanol/HCl = 20/1) for 12 h and dried in vacuum at 60 °C. Approximately 0.5 g of polymer per sample was extracted in boiling butanone for 16 h in order to remove atactic polystyrene. The solid polymer was dried in vacuum at 60 °C for 12 h to obtain sPS.

Characterization of sPS

The melting temperature of polymer was determined using a DSC 204 F-1 (Netzsch, GER). Approximately 3.0 mg of polymer sample was heated from 30 °C to 300 °C at a heating rate of 10 °C min^{-1} under a nitrogen atmosphere to remove the thermal history. After maintaining the temperature for 5 min, the sample was cooled down at a rate of 10 °C min^{-1} to 30 °C, and the temperature was again maintained for 5 min. Then, the sample was heated to 300 °C at a heating rate of 10 °C min^{-1} . Finally, the second heating curve was recorded.

The molecular weight was determined by gel permeation chromatography (GPC) using a 1260 infinity II (Agilent, USA) at 150 °C with 1,2,4-trichlorobenzene (with 0.0125 wt% butylated hydroxytoluene, BHT) as the eluent. Sample concentration: 1.0 mg mL^{-1} .

A ^{13}C NMR experiment for the typical polymer sample was performed using a Bruker AVANCE III-600 MHz spectrometer with d_2 -1,1,2,2-tetrachloroethane as the solvent at 125 °C. ^{13}C NMR: (d_2 -1,1,2,2-tetrachloroethane, 600 MHz, 125 °C) $\delta = 40.92$, 44.15, 125.25, 127.58, 145.16.

Results and discussion

A half-titanocene complex $\text{Cp}^*\text{Ti}(\text{OC}_6\text{F}_5)_3$ (**c1**) was synthesized according to the methods previously described in the literature.^{23,24} The ^1H NMR spectra of **c1** are shown in Fig. 1. Another half-titanocene complex $\text{Cp}^*\text{Ti}(\text{O}-2,6-\text{C}_6\text{H}_3\text{F}_2)_3$ (**c2**) was synthesized in an identical manner for comparison with **c1**. The ^1H NMR spectra of **c2** are shown in the ESI.† The ^{13}C NMR spectra of the polymer after extraction are shown in Fig. 2(a), which was obtained insoluble during boiling 2-butanone from Run 14. The accurate spectrum indicated that the obtained polymer was syndiotactic polystyrene. Besides, the typical DSC curve of syndiotactic polystyrene gained from Run 14 is shown in Fig. 2(b), which noted that the melting point was about 271 °C.

For catalyst **c1**, Run 1–5 showed that the trend of polymerization activity first increased and then slowly decreased with the increase in the polymerization temperature. The results indicated that catalyst **c1** could form a more thermodynamically



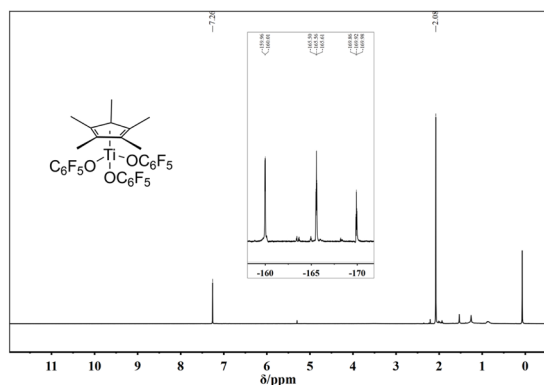


Fig. 1 ^1H and ^{19}F NMR spectra of $\text{Cp}^*\text{Ti}(\text{OC}_6\text{F}_5)_3$.

stable $\text{Ti}(\text{III})$ active center than other half-titanocene complexes.^{13,24–26} The MW of the resulting sPS decreased with the increase in the polymerization temperature. This difference might be caused by high temperatures, which increased the rate of chain transfer. Appropriately increasing the reaction temperature could improve the activity of the catalyst **c1**, but the high temperature would also increase the rate of chain transfer and reduce the MW of sPS.¹³

In Run 6–12, the results showed that 80 °C was thought to be a preferable reaction temperature to 70 °C. When a low content of MAO ($\text{Al}_{\text{MAO}}/\text{Ti} = 100$) was involved in the polymerization, a higher temperature could receive higher monomer conversion and higher catalytic activity in 3 h (Table 1). Besides, compared with Run 6–12, MAO was a more important factor than TIBA, which affected the catalytic activity and MW of the resulting sPS to a greater extent. When $\text{Al}_{\text{MAO}}/\text{Ti} = 50$, excessively sparse MAO might not provide enough active centers for half-titanocene complexes **c1** to form a $\text{Ti}(\text{III})$ catalytic active center. From the application viewpoint, it was acceptable to use cheap TIBA in place of expensive MAO where sPS with a MW more than 10^5 g mol^{-1} could be obtained and used for industrial production.

At 80 °C, $\text{Al}_{\text{MAO}}/\text{Ti} = 100$, as the amount of TIBA increased, the catalytic activity first increased and then slowly decreased. Meanwhile, the MW of sPS decreased with the increase in TIBA, which confirmed that TIBA acted as a chain transfer agent and

increased the number of active centers in polymerization. In the catalytic system, Ti existed multiple valence states, including $\text{Ti}(\text{IV})$, $\text{Ti}(\text{III})$, and $\text{Ti}(\text{II})$, but only $\text{Ti}(\text{III})$ could explain the high stereoselectivity of syndiospecific styrene polymerization.^{13–21} While excessive TIBA would increase the content of $\text{Ti}(\text{II})$ in the system and reduce the amount of catalytic $\text{Ti}(\text{III})$ active center, it was specifically manifested as the MW and the yield decreased.

The polymerization reaction conditions for Run 14: 80 °C, 3 h, $\text{Al}_{\text{MAO}}/\text{Ti} = 100$, $\text{Al}_{\text{TIBA}}/\text{Ti} = 500$, would be preferable to obtain sPS products with a MW of approximately 150 000 g mol^{-1} and a D value of approximately 2. Besides, we discussed that the volume of additional toluene affects the polymerization, and the results are shown in the ESI.^{†27} In Table 2, Run 17–25, we supplemented the polymerization behavior of catalysts **a**, **b** and **c2** under different conditions.

When $\text{Al}_{\text{MAO}}/\text{Ti} = 100$ and $\text{Al}_{\text{TIBA}}/\text{Ti} = 300$, the order of catalytic activity from high to low was **c1** > **c2** > **b** > **a**, and even when $\text{Al}_{\text{TIBA}}/\text{Ti}$ increased from 300 to 500, the order remained the same. The order showed that fluorinated phenoxy half-titanocene complexes **c1** and **c2** had a higher catalytic activity than that of **a** or **b**, which was surprisingly different from the order, OMe > OPh > Cl, discovered in previous studies.^{18,28} By modifying the phenoxy group with the electron-withdrawing fluorine atom, more electrons remained in the phenoxy conjugated system, and the electron-withdrawing effect of the fluorinated phenoxy ligand was enhanced, which is beneficial for high catalytic activity.^{29–31} This results were the same as Shen's study about syndiospecific styrene polymerization with various *para*-substituted phenoxy ligands. The enhancement of electron-releasing ability in *para*-substitution resulted in an increase in the catalytic activity.²⁹ With the same main ligands, the ancillary ligands with stronger electron-releasing ability possessed greater catalytic activity. For the formation of the $\text{Ti}(\text{III})$ activity center, alkylation was a key step.^{6,32,33} From the perspective of the electronic effect of substitution reactions, ancillary ligands with stronger electron-withdrawing ability were easier to alkylate.³² The fast formation of $\text{Ti}(\text{III})$ active center was a reason why the fluorinated half-titanocene complex CpTiF_3 has the highest catalytic activity.³ Therefore, the half-titanocene complexes with stronger electron-withdrawing ligands had a faster alkylation rate, the $\text{Ti}(\text{III})$

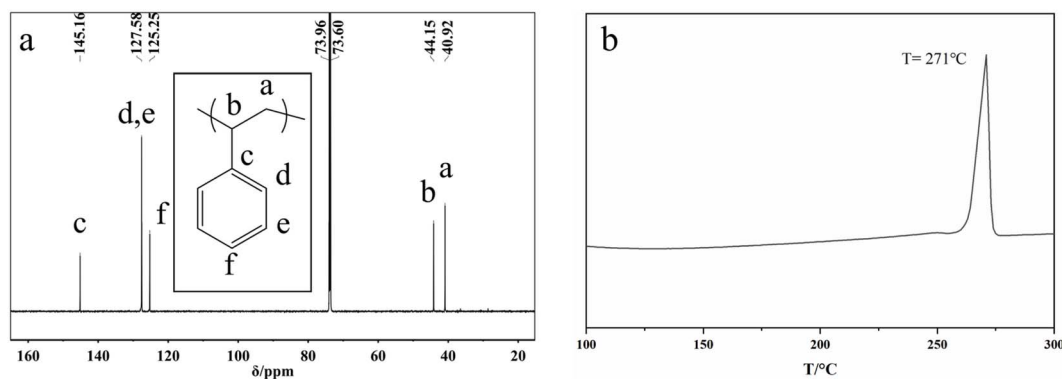


Fig. 2 (a) ^{13}C NMR spectrum of sPS (Run 14). (b) Typical DSC curve of sPS (Run 14).



Table 1 Syndiospecific styrene polymerization with half-titanocene complexes **c1** depending on temperature, Al_{MAO}/Ti, and Al_{TIBA}/Ti^a

Run	Cat.	T (°C)	Al _{MAO} /Ti	Al _{TIBA} /Ti	Yield ^b (g)	Conversion ^b %	Syndiotactic index ^b (%)	Activity ^c	M _w ^d (10 ⁻⁵ g mol ⁻¹)	D ^d	T _m ^e (°C)
1	c1	50	300	200	6.87	37.77	96	0.57	8.21	2.20	271
2	c1	60	300	200	9.35	51.40	96	0.77	4.19	1.92	271
3	c1	70	300	200	15.26	83.89	98	1.27	1.44	3.00	271
4	c1	80	300	200	14.92	82.02	98	1.24	1.02	2.49	270
5	c1	90	300	200	13.80	75.87	98	1.15	0.80	2.35	270
6	c1	70	200	200	14.35	78.89	96	1.19	3.11	2.70	270
7	c1	70	100	200	6.61	36.34	97	0.55	4.32	1.84	270
8	c1	70	50	200	2.77	15.23	97	0.15	6.07	1.73	269
9	c1	70	100	300	7.10	39.03	93	0.39	3.67	1.81	270
10	c1	80	150	350	14.10	77.52	97	0.78	1.23	2.26	271
11	c1	80	100	400	12.73	69.98	96	0.70	1.47	2.09	271
12	c1	80	50	450	5.01	27.54	94	0.27	2.58	1.95	270
13	c1	80	100	300	9.52	52.34	96	0.52	2.17	1.92	271
14	c1	80	100	500	13.33	73.28	99	0.74	1.31	2.20	271
15	c1	80	100	600	10.79	59.32	96	0.59	1.19	1.81	271

^a Polymerization conditions: catalyst, 6.0 μmol in 2.0 mL toluene; styrene, 20 mL. Run 1–7, 2 h, Run 8–15, 3 h. ^b Estimated by the extraction experiment. ^c Activity in 10³ kg sPS per mol cat per h. ^d GPC data. ^e DSC data.

Table 2 Syndiospecific styrene polymerization with different half-titanocene in the presence of MAO and TIBA^a

Run	Cat.	T (°C)	Al _{MAO} /Ti	Al _{TIBA} /Ti	Yield ^b (g)	Conversion ^b %	Syndiotactic index ^b (%)	Activity ^c	M _w ^d (10 ⁵ g mol ⁻¹)	D ^d	T _m ^e (°C)
17	a	80	100	300	4.01	22.05	98	0.22	1.31	1.87	270
18	a	80	100	500	4.49	24.68	98	0.24	0.92	1.81	271
19	a	90	100	500	5.63	30.95	97	0.31	0.71	1.78	270
20	b	80	100	300	7.30	40.13	97	0.40	5.10	1.93	271
21	b	80	100	500	10.64	58.49	95	0.59	1.76	1.94	269
22	b	90	100	500	9.28	51.02	95	0.51	1.22	2.06	271
23	c2	70	300	200	14.56	80.04	96	1.21	1.96	1.86	271
24	c2	80	100	300	10.54	57.94	96	0.46	2.10	2.06	270
25	c2	80	100	500	11.43	62.84	96	0.63	1.68	2.72	270

^a Polymerization conditions: catalyst 6.0 μmol with 2.0 mL toluene; styrene 20 mL. Reaction time, 3 h, Run 23, 2 h. ^b Estimated by the extraction experiment. ^c Activity in 10³ kg sPS per mol cat per h. ^d GPC data. ^e DSC data.

active center are formed more quickly, the proportion of Ti(III) active centers in the catalytic system increased, and the catalytic activity was higher.

The results presented in Fig. 3 showed that when Al_{MAO}/Ti = 100 and Al_{TIBA}/Ti = 300, the order of the MW of sPS was **b** > **c1** > **c2** > **a**. However, when Al_{TIBA}/Ti increased to 500, the order of the MW changed to **c2** > **c1** > **b** > **a**. The differences in the MW of sPS were related to the polymerization rate and chain transfer rate in the syndiospecific styrene polymerization.³⁴

The currently recognized mechanism A, in Scheme 1, held that the ancillary ligand was replaced by alkyl after alkylation and did not participate in the subsequent chain propagation, including styrene coordination and insertion reactions.^{20,35,36} However, it was difficult to explain why different trisubstituted half-titanocene complexes could obtain sPS with various MW values under the same conditions. According to the mechanism A, they should be the same. Moreover, the half-titanocene complex CpTiF₃ could obtain an ultra-high MW of sPS.³ This result could be attributed to the fact that the fluoride ion had a strong interaction with the Ti(III) active center cation formed

by Ti(III) and MAO, and that it had a large rate of styrene insertion.³⁴ After the latest discoveries revealing the structure of MAO and the way MAO combined with the active center, the above explanation became less reliable.^{21,37–39}

Meanwhile, mechanism B held that an ancillary ligand should remain after alkylation and play a role in subsequent reactions, thus influencing the MW of sPS.^{37,38} In the studies by Yi and Nomara *et al.*,^{21,39} it was found that the half-titanocene complexes Cp*TiCl₂(O-2,6-*i*-Pr₂C₆H₃) retained one phenoxy ancillary ligand after treatment with MAO. In addition, they theoretically verified that the neutral Ti(III) active center with ancillary ligands was also one of the active species for catalytic polymerization.²¹ In our studies, on comparison between Run 13–14 and 17–25, we found that the MW of sPS catalysed by **c2** was higher than that of **c1**, although the results in Run 13 and Run 14 were very close.

Besides, it could be concluded from Fig. 2 that the catalytic activity of each half-titanocene complex and the influence of TIBA on MW were different. When the content of TIBA was increased, the catalytic activity of a slightly increased, and the



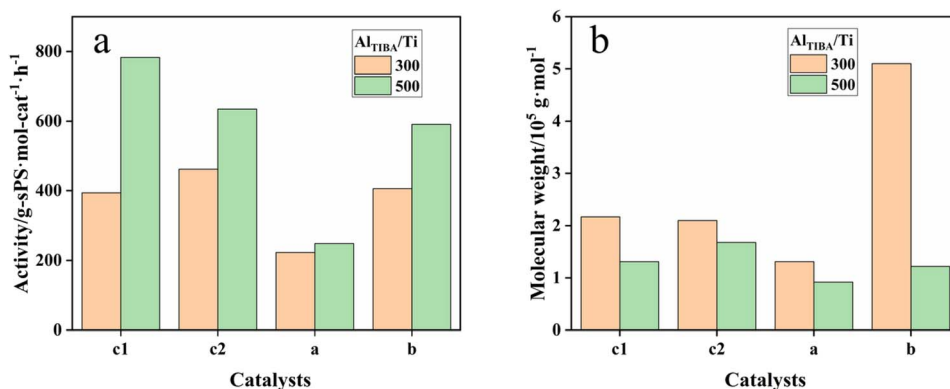
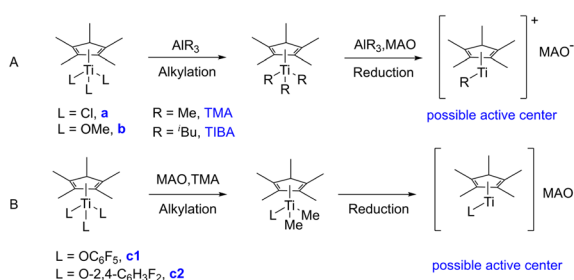


Fig. 3 Influence of Al_{TIBA}/Ti on syndiospecific styrene polymerization with different half-titanocene catalysts at 80 °C and $Al_{MAO}/Ti = 100$: (a) activity and (b) molecular weight.



Scheme 1 Formation of two possible Ti(III) active centers. (A) Cationic active center, (B) neutral active center.

decrease in MW was also small. However, the catalytic activity of **b** increased significantly, and the decrease in MW was also large. The fluorinated half-titanocene complexes **c1** and **c2** had the advantages of both **a** and **b**. Increasing the content of TIBA can greatly improve their catalytic activity (which was better than that of **b**), and they could obtain sPS with a stable MW over 10^5 g mol⁻¹. This unique property should be related to the large benzene ring ligand and the fluorine atoms. The phenoxy group with large steric hindrance and fluorine atoms, with strong electron-withdrawing ability, hindered the chain transfer from the Ti(III) active center to TIBA.^{13,25}

Conclusions

In this work, two novel half-titanocene complexes containing fluorinated phenoxy ligands, Cp*Ti(OC₆F₅)₃ (**c1**) and Cp*Ti(O-2,6-C₆H₃F₂)₃ (**c2**), were synthesized in high yields. In the presence of MAO as a cocatalyst, the two resulting half-titanocene complexes were compared with their precursor complex of Cp*Ti(OMe)₃ under optimized polymerization conditions ([Ti] = 0.30 mmol L⁻¹, Al_{MAO}/Ti = 100, Al_{TIBA}/Ti = 500, styrene = 20 mL, 80 °C for 3 h) displaying ~2-fold higher catalytic activity as a result of electron-withdrawing conjugation effect of the fluorinated phenoxy ligand to promote the formation rate of Ti(III) active centers. Furthermore, it was noteworthy that the external addition of TIBA to the catalyst system led to a reduction of MAO dosage and an enhancement for catalytic activity, while

the syndiotacticity and MW of the polymerization product were hardly influenced as a result of the higher stability of the Ti(III) active center with fluorinated phenoxy ligands.

Data availability

The data supporting this article have been included as part of the ESI.†

Conflicts of interest

There are no conflicts to declare.

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