Synthesis of new substituted cyclopentadienyl titanium monomethoxydifluorides with $BF_3 \cdot OEt_2$ as fluorinating reagent and their use in syndiotactic polymerization of styrene

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Abstract

Five substituted cyclopentadienyl titanium trimethoxide complexes, $RCpTi(OMe)_3$ (R = Me (**2b**), ^{i}Pr (**2c**), Me_3Si (**2d**), allyl (**2e**), $PhCH_2$ (**2f**)), were prepared. By reacting $RCpTi(OMe)_3$ with BF_3OMe_2, six $RCpTiF_2(OMe)$ (R = H (**3a**), Me (**3b**), ^{i}Pr (**3c**), Me_3Si (**3d**), allyl (**3e**), $PhCH_2$ (**3f**)) were obtained. When activated with methylaluminoxane (MAO), the activities of $RCpTiF_2(OMe)$ system were less than those of $RCpTi(OMe)_3$ system in solution polymerization of styrene, but the polymers made by $RCpTiF_2(OMe)$ exhibited higher Mw and melting point than those by $RCpTi(OMe)_3$. Both systems produced polymers with similar syndiotacticities in the range 92.4–97.6%. Introduction of a substituent group into the Cp-ligand enhanced the melting points of the polymers, and meanwhile decreased the catalytic activities of $RCpTi(OMe)_3$/MAO and $RCpTiF_2(OMe)$/MAO systems, where the order of activity was $RCp = Cp > MeCp > {}^iPrCp > Me_3SiCp > CH_2=CHCH_2Cp > PhCH_2Cp$. Complexes **2a** ($CpTi(OMe)_3$) and **3a** showed the highest activities respectively for both systems, and are three to four times more active than $CpTiCl_3$. In bulk polymerization, the difference of activities between $RCpTi(OMe)_3$/MAO and $RCpTiF_2(OMe)$/MAO systems became small, where complexes **2e** and **3e** exhibited remarkably higher activities compared with their solution polymerization activities. The maximum polymerization activities were found at the polymerization temperature of 50 °C for most of the complexes. The influence of the polymerization time (t_P), polymerization temperature (T_P) and Al/Ti ratio on the activities of complexes **2b** and **3b** were investigated. It was observed that the initial rate of propagation of complex **2b** was higher than that of complex **3b** and the highest activities of both catalysts were reached at the relatively low Al/Ti ratio of 150 and decrease for larger ratios.
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1. Introduction

In 1986, Ishihara et al. [1,2] first discovered syndiotactic polystyrene (s-PS) by using homogeneous titanium compounds and methylaluminoxane (MAO). s-PS is a crystalline polymeric material with a melting temperature of about 270 °C, and has a high crystallization rate, a high modulus of elasticity and an excellent resistance to heat and chemical agents, which make s-PS suitable for a large number of applications in industries.

In order to obtain an efficient catalyst system, which should have a high polymerization activity, increase the

tacticity, the melting point and the molecular weight of s-PS, and meanwhile decrease the amount of MAO, a wide variety of new catalysts based on titanium, zirconium or other transition metal compounds have been developing [3–5]. Among them, half-sandwich titanocenes of types $Cp'TiX_3$ and $Ind'TiX_3$ (where Cp' is (un)substituted cyclopentadienyl, Ind' is (un)substituted indenyl, and X is Cl, F, Alkyl or alkoxyl, etc.) have been demonstrated to be the most effective syndiotactic catalyst precursors for styrene polymerization.

The polymerization mechanism and the structure of the active site were investigated [6–13]. Many observations have been made viz.: (1) Replacing Cp ligand by Cp^* ligand dramatically increased the molecular weight of s-PS (Mw > 600 000), and the corresponding melting

point of polymer also rised [14,15]. (2) Replacing Cp ligand by Ind ligand enhanced the catalyst activity, the syndiotacticity and the melting point of the polymer. This catalyst was relatively insensitive to polymerization conditions compared with $CpTiCl_3$ [16,17]. (3) Partial or full replacement of chlorine atoms by alkyl or alkoxyl groups often raised catalytic activity [14,15,18–24]. (4) Full replacement of chlorine atoms by fluorine atoms showed a large increase in the catalyst activity, especially for Cp^*TiF_3 and $Ind'TiF_3$, and reduced the amount of excess MAO to an Al:Ti ratio of 300 [25,26].

To investigate the catalytic activities and properties of polymers produced by a new half-sandwich titanocene system in which one chlorine atom is substituted by an alkoxyl group and the other two by fluorine atoms is the basis of this report.

The first fluorinated half-sandwich titanocene ($CpTiF_3$) was prepared through the reaction of $CpTi(OEt)_3$ with CH_3COF by Nesmeyanov in 1968. He further obtained $CpTiF_2(OEt)$ and $CpTiF(OEt)_2$ by the exchange reaction of $CpTiF_3$ with $CpTi(OEt)_3$ [27]. In recent years, Roesky [28–30] used AsF_3 and especially Me_3SnF as fluorinated reagents, and succeeded in preparing a large range of fluorinated half-sandwich titanocenes and other organometallic fluorides.

In this work, we begin by using an easily available, inexpensive and less toxic boron trifluoride diethyl etherate ($BF_3 \cdot OEt_2$) as fluorinating reagent to synthesize six substituted cyclopentadienyl titanium mono-methoxydifluoride complexes of general formula $RCpTiF_2(OMe)$ (R = H, Me, ^iPr, Me_3Si, Allyl, $PhCH_2$) by the reaction of $RCpTi(OMe)_3$ with the $BF_3 \cdot OEt_2$ and detailed compare their catalytic behavior with $RCpTi(OMe)_3$ and $CpTiCl_3$ in the syndiotactic polymerization of styrene.

2. Results and discussion

2.1. Catalyst synthesis

Direct reaction of $CpTiCl_3$ with $BF_3 \cdot OEt_2$ did not result in halide exchange even at reflux temperature in

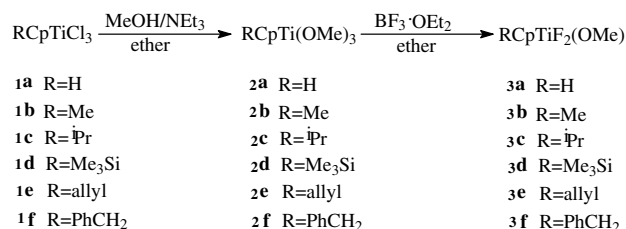toluene for 24 h, although the exchange reaction of $(RCp)_2TiCl_2$ with $BF_3 \cdot OEt_2$ easily took place [31]. Instead, we found that $RCpTi(OMe)_3$ reacts in a molar ratio of 3:2 with $BF_3 \cdot OEt_2$ in diethyl ether to give target compounds in 40–80% yield, which are purified by sublimation under vacuum and found to be elementally pure (Scheme 1). Synthetic details and spectral data for these compounds are given in the experimental section.

It was found that the fluorine atoms in complexes 3a to 3f shown two peaks in ^{19}F NMR spectrum at room temperature (Table 1). There existed a broad peak in 100–150 ppm and a sharp peak in 160–190 ppm. The area ratio of two peaks depended on the substituted group in Cp. It indicated that the chemical environment of the fluorine atoms is different. When the temperature increased to 50 °C, the two peaks turned to one peak.

2.2. Polymerization results

Table 2 summarizes the results on the syndiotactic polymerization of styrene in solution with $RCpTi(OMe)_3$/MAO and $RCpTiF_2(OMe)$/MAO systems. The $RCpTiF_2(OMe)$/MAO system is less active than the corresponding $RCpTi(OMe)_3$/MAO system at 50 °C. The polymers produced by both systems have similar syndiotacticities.

The active catalytic site for sPS polymerization, illustrated in Scheme 2, is thought to be $(RCp\text{-}TiMe)^+(MAO \cdot X_2)^-$, where X is methoxy group or fluoride. The methoxy group and fluoride are stripped during the formation of active species. They could still surround the active species and stabilize active species

$$RCpTiCl_3 \xrightarrow[\text{ether}]{MeOH/NEt_3} RCpTi(OMe)_3 \xrightarrow[\text{ether}]{BF_3 \cdot OEt_2} RCpTiF_2(OMe)$$

1a R=H	2a R=H	3a R=H
1b R=Me	2b R=Me	3b R=Me
1c R=^iPr	2c R=^iPr	3c R=^iPr
1d R=Me_3Si	2d R=Me_3Si	3d R=Me_3Si
1e R=allyl	2e R=allyl	3e R=allyl
1f R=$PhCH_2$	2f R=$PhCH_2$	3f R=$PhCH_2$

Scheme 1.

Table 1
^{19}F NMR spectrum of complexes 3a to 3f

| Complex	27 °C			50 °C
	Peak A (δ ppm)	Peak B (δ ppm)	Area ratio (A/B) δ ppm	
(3a) $CpTiF_2(OMe)$[a]	134 (br. s)	184 (s)	3.6	135 (s)
(3b) $MeCpTiF_2(OMe)$[b]	114 (br. s)	161 (s)	1.9	
(3c) $^iPrCpTiF(OMe)$[b]	106 (br. s)	160 (s)	3.6	
(3d) $Me_3SiCpTiF_2(OMe)$[a]	136 (br. s)	183 (s)	31	
(3e) $CH_2=CHCH_2CpTiF_2(OMe)$[b]	109 (br. s)	163 (s)	1.6	
(3f) $PhCH_2CpTiF_2(OMe)$[a]	129 (br. s)	179 (s)	1.8	135 (s)

[a] Solvent: C_6D_6.
[b] Solvent: $CDCl_3$.

Table 2
Syndiotactic polymerization of styrene in solution catalyzed by RCpTi(OMe)$_3$/MAO and RCpTiF$_2$(OMe)/MAO systems[a]

Catalyst	Yield (g)	Conversion (%)	Activity[b] (10^6)	s-PS[c] (%)	T_m[d] (°C)	Mw	MWD
(2a) CpTi(OMe)$_3$	1.5847	87.2	18.16	92.7	258.3	48 000	2.16
(2b) MeCpTi(OMe)$_3$	1.4403	79.2	16.50	97.0		76 500	2.12
(2c) ^{i}PrCpTi(OMe)$_3$	1.4108	77.6	16.16	96.7	266.8		
(2d) Me$_3$SiCpTi(OMe)$_3$	1.1263	62.0	12.91	97.6	266.4		
(2e) CH$_2$=CHCH$_2$CpTi(OMe)$_3$	0.6508	35.8	7.46	96.2			
(2f) PhCH$_2$CpTi(OMe)$_3$	0.3285	18.1	3.76	93.3			
(3a) CpTiF$_2$(OMe)	1.3630	75.0	15.62	93.9	258.9	54 800	1.94
(3b) MeCpTiF$_2$(OMe)	1.2143	66.8	13.91	97.2	266.1	96 400	1.96
(3c) ^{i}PrCpTiF$_2$(OMe)	1.0329	56.8	11.84	97.3	269.4		
(3d) Me$_3$SiCpTiF$_2$(OMe)	0.6550	36.0	7.50	94.2	269.8		
(3e) CH$_2$=CHCH$_2$CpTiF$_2$ (OMe)	0.4566	25.1	5.23	95.8	267.4		
(3f) PhCH$_2$CpTiF$_2$(OMe)	0.2169	11.9	2.49	92.4	264.5		
CpTiCl$_3$	0.3328	18.3	3.81	92.5	257.9		

[a] Polymerization conditions: [Ti] = 0.42 mM, Al/Ti = 300, 50 °C for 1 h, styrene = 2 ml, V_{total} = 12 ml.
[b] g bulk polymer/(mol Ti · mol S · h).
[c] g of 2-butanone insoluble polymer/g of bulk polymer.
[d] Melting temperature of s-PS.
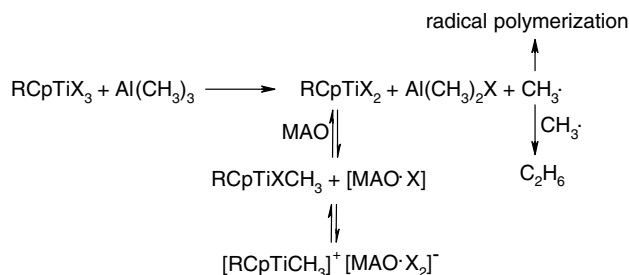
Scheme 2. Formation of initiating species by RcpTiX$_3$ MAO system.

[32]. The methoxy group is better π-donor than fluoride ligand [33], which might lead to generating more active sites in RCpTi(OMe)$_3$/MAO system than in RCpTiF$_2$(OMe)/MAO systems. Therefore, the RCpTi(OMe)$_3$ shows more active than RCpTiF$_2$(OMe).

Compared with CpTiCl$_3$, complexes **2a** and **3a** show much higher catalytic activities. It indicates that they could generate more active sites and enhance the catalytic activity. Similar phenomena have been described in the literature [25,26].

Introduction of substituent group into Cp-ligand decreases the catalytic activities for RCpTi(OMe)$_3$/MAO and RCpTiF$_2$(OMe)/MAO systems, where the order of activity is RCp = Cp > MeCp > ^{i}PrCp > Me$_3$SiCp > CH$_2$=CHCH$_2$Cp > PhCH$_2$Cp. Generally, the stronger electron-donating and less bulky substituent groups are beneficial to the polymerization by increasing the rate of propagation. Compared with complexes **2a** and **3a**, complexes **2f** and **3f** have only a fifth of the activity. Besides the steric bulk of the benzyl group, it was able to coordinate to the titanium [34]. This coordination was so strong that it interfered with coordination and insertion of styrene. So complexes **2f** and **3f** show the lowest activities in both systems. Similar

observation was shown in [(PhCH$_2$CH$_2$)Me$_4$C$_5$]-Ti(OMe)$_3$/MAO system by Newman [35]. The allyl group is sterically less bulky than the isopropyl and trimethylsilyl groups, but complexes **2e** and **3e** exhibit lower activities. This indicates that the electron-donor ability of the allyl group is less than that of the isopropyl and trimethylsilyl groups. Moreover, the C=C bond of allyl group might coordinate to the active center, as suggested in the literature [36]. In addition, introduction of substituent group into Cp-ligand increases the melting points of the polymers. On average, the melting points of the polymers are 6–11 °C higher than those of the polymers obtained with complexes **2a** and **3a**. When R = ^{i}Pr and Me$_3$Si, the melting points of the polymers made with RCpTiF$_2$(OMe) are 2–3 °C higher than those with RCpTi(OMe)$_3$. This shows that the substituent groups not only have an influence on the activity due to steric and electronic effects but also have an effect on the syndiotacticities and the melting points of the polymers.

Compared with complexes **2a** and **3a**, the polymers made by complexes **2b** and **3b** exhibit higher molecular weight. The molecular weight is controlled by the relative rates of two competing processes, the β-hydride elimination and the styrene insertion. This means the introduction of fluoride ligand into the coordination sphere of the metal compound can reduce the β-hydride elimination.

Taking complexes **2b** and **3b** as representatives of each corresponding system, we further investigated the influence of polymerization time (t_P), polymerization temperature (T_P) and Al/Ti ratio on their activities. The dependence of the polymerization activity on the polymerization time with the two complexes is as shown in Fig. 1. The highest activities can be observed after 5 min for both complexes and thereafter decreased. However, the activity of the trimethoxy-substituted complex (**2b**) is
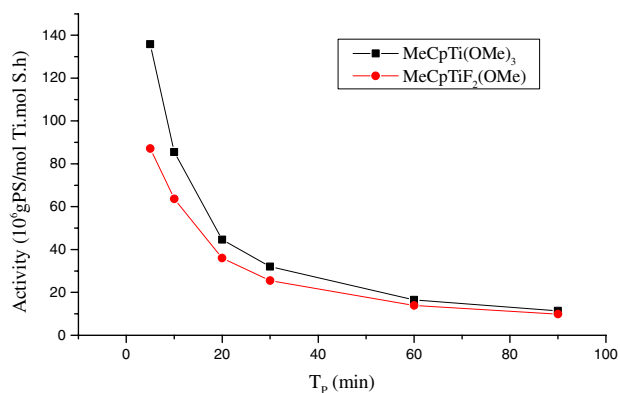
Fig. 1. Dependence of the polymerization activity on the polymerization time with MeCpTi(OMe)$_3$ and MeCpTiF$_2$(OMe). Polymerization conditions: [Ti] = 0.42 mM, Al/Ti = 300, 50 °C, styrene = 2 ml, V_{total} = 12 ml.

higher than that of the difluoromethoxy substituted complex (**3b**) at the initial stages of polymerization. With the passage of time, the difference of their activities becomes smaller. The activity of complex **2b** decreases much faster than that of complex **3b** after 10 min. The decrease may be attributed to the deactivation of the active centers and to the occlusion of part of the catalyst in the precipitating polymer [2]. This indicates again that the fluorinated complex **3b** is more stable than complex **2b**, although complex **2b** has a faster propagation rate than complex **3b** at the beginning of polymerization due to more active sites. A time dependence of activity was observed in CpTiF$_3$, MeCpTiF$_3$ and MeIndTiF$_3$ [25,26].

Table 3 summarizes the comparison of polymerization results at different T_P and Al/Ti ratio. In the range 25–90 °C, the activity of complex **3b** is slightly less than that of complex **2b**, and the syndiotacticities of obtained polymers are similar. The highest activity is reached at

50 °C for both catalysts. At 90 °C, the syndiotacticity decreases sharply, because syndio-directing active sites are destroyed into atactic sites [20]. In addition, Table 3 shows that the activity is affected by Al/Ti ratio. The highest activities for both catalysts are reached at the relatively low Al/Ti ratio of 150 and decrease for larger ratios. This is contrary to the CpTiCl$_3$ system where activity is maximum at Al/Ti ratio of 1500 under identical condition.

When the polymerization is carried in bulk (Table 4), polymer yield is higher, and the possibility for the occlusion of active centers in the precipitated polymer is aggravated as a consequence of the restricted mobility. The difference of the activities for RCpTi(OMe)$_3$/MAO and RCpTiF$_2$(OMe)/MAO systems becomes small, compared with that in solution polymerization (Table 2). With the exception of complexes **2f** and **3f**, all other complexes maintain high levels of syndiotacticity at the high monomer concentration used. For both systems, the unsubstituted-Cp complexes afford the highest polymer yields and hence activities, while the benzyl-Cp complexes yield the least activities. Similar results were observed in 2-PhCH$_2$IndTiCl$_3$ system [16]. A remarkable change is observed in the complexes **2e** and **3e** systems, whereby in bulk polymerization, they show much higher activities than in solution polymerization. The variation of the monomer concentration probably causes the difference of a dynamic interaction between the allyl group and titanium. Because of the unusual behavior of alkenyl groups, a more detailed research about their influence on catalytic activity is in progress.

As shown in Table 4, maximum polymerization activities are obtained at 50 °C for most of the complexes. Higher temperature (T_P = 90 °C) led to the decrease of the activities of catalysts and syndiotacticities of polymers.

Table 3
Comparison of the activities of MeCpTi(OMe)$_3$ and MeCpTiF$_2$(OMe) at different T_P and Al/Ti ratio[a]

Catalyst	Al/Ti (mol/mol)	T_P (°C)	Yield (g)	Conversion (%)	Activity[b] (10^6)	s-PS[c]
MeCpTi(OMe)$_3$	300	25	0.9785	53.8	11.21	98.6
	300	50	1.4403	79.2	16.50	97.0
	300	70	1.2880	70.8	14.76	92.6
	300	90	1.0687	58.8	12.25	77.3
	150	50	1.5001	82.5	17.19	96.8
	500	50	1.2781	70.3	14.64	97.2
MeCpTiF$_2$(OMe)	300	25	0.9157	50.4	10.49	98.9
	300	50	1.2143	66.8	13.91	97.2
	300	70	1.1680	64.2	13.38	92.6
	300	90	0.9552	52.5	10.94	74.6
	150	50	1.3468	74.1	15.43	96.0
	500	50	0.9328	51.3	10.69	93.8

[a] Polymerization conditions: [Ti] = 0.42 mM, 1 h, styrene = 2 ml, V_{total} = 12 ml.
[b] g of bulk polymer/(mol Ti · mol S · h).
[c] g of 2-butanone insoluble polymer/g of bulk polymer (%).

Table 4
Syndiotactic polymerization of styrene in bulk catalyzed by $RCpTi(OMe)_3$/MAO and $RCpTiF_2(OMe)$/MAO systems[a]

Catalyst	T_P (°C)	Yield (g)	Conversion (%)	Activity[b] (10^6)	s-PS[c] (%)
(2a) $CpTi(OMe)_3$	30	1.4859	14.9	6.14	95.0
	50	4.6228	46.2	19.11	92.0
	70	4.2580	42.6	17.60	92.2
	90	2.9735	29.7	12.29	85.3
(2b) $MeCpTi(OMe)_3$	30	1.3656	13.7	5.64	92.4
	50	4.4201	44.2	18.27	94.9
	70	3.6181	36.2	14.95	93.7
	90	2.4962	25.0	10.32	86.1
(2c) $^iPrCpTi(OMe)_3$	30	1.4204	14.2	5.87	92.1
	50	3.5475	35.5	14.66	95.6
	70	2.8341	28.3	11.71	95.9
	90	2.5767	25.8	10.65	91.0
(2d) $Me_3SiCpTi(OMe)_3$	30	2.6009	26.0	11.00	93.5
	50	3.3117	33.1	13.69	95.0
	70	2.9776	29.8	12.31	93.3
	90	2.5812	25.8	10.67	88.6
(2e) $CH_2{=}CHCH_2CpTi(OMe)_3$	50	4.3329	43.3	17.91	92.0
(2f) $PhCH_2CpTi(OMe)_3$	30	0.6823	6.8	2.82	89.3
	50	0.8882	8.9	3.67	87.4
	70	0.9840	9.8	4.07	84.9
	90	0.9338	9.3	3.86	71.2
(3a) $CpTiF_2(OMe)$	30	1.8829	18.8	7.78	96.0
	50	4.1231	41.2	17.04	93.4
	70	4.0215	40.2	16.62	92.0
	90	2.9899	29.9	12.36	88.8
(3b) $MeCpTiF_2(OMe)$	30	1.9508	19.5	8.06	95.8
	50	3.9404	39.4	16.29	95.0
	70	3.2235	32.2	13.32	94.6
	90	2.4788	24.8	10.25	91.6
(3c) $^iPrCpTiF_2(OMe)$	30	1.0690	10.7	4.42	82.8
	50	3.4948	35.0	14.45	90.6
	70	2.5920	25.9	10.71	93.8
	90	2.1011	21.0	8.68	85.4
(3d) $Me_3SiCpTiF_2(OMe)$	30	2.4330	24.3	10.06	93.2
	50	2.9177	29.2	12.06	93.2
	70	3.2470	32.5	13.42	92.1
	90	2.9650	29.7	12.25	89.0
(3e) $CH_2{=}CHCH_2CpTiF_2(OMe)$	50	3.9339	39.3	16.26	92.3
(3f) $PhCH_2CpTiF_2(OMe)$	30	0.7482	7.5	3.09	91.5
	50	0.8632	8.6	3.56	88.4
	70	0.9810	9.8	4.05	73.0
	90	0.9207	9.2	3.81	68.8
$CpTiCl_3$	50	0.8056	8.1	3.33	82.3

[a] Polymerization conditions: [Ti] = 0.21 mM, Al/Ti = 300, t_P = 1 h, styrene = 11 ml.
[b] g of bulk polymer/(mol Ti · mol S · h).
[c] g of 2-butanone insoluble polymer/g of bulk polymer.

3. Experimental

All manipulations were carried out under a dry argon atmosphere using standard Schlenk techniques. Solvents were purified by distillation over sodium benzophenone (diethyl ether, THF, toluene and n-hexane) and CaH_2 (dichloromethane).

MAO was produced by Witco GmbH. Styrene was dried over anhydrous $CaCl_2$, vacuum distilled from CaH_2 and stored at −25 °C in the dark. $BF_3 \cdot OEt_2$ was

distilled from CaH_2 at reduced pressure before use. $CpTi(OMe)_3$ [37], $^iPrCpTiCl_3$ [38], $Me_3SiCpTiCl_3$ [39], $CH_2=CHCH_2CpTiCl_3$ [40], and $PhCH_2CpTiCl_3$ [41] were synthesized by using published methods. The general procedure for the preparation of $RCpTi(OMe)_3$ was carried out as in the literature [41].

Mass spectra were measured on a HP5989A spectrometer. IR spectra were recorded on Nicolet FTIR 5SXC spectrometer. ^1H NMR and ^{19}F NMR were measured on an ADVANCE-500 spectrometer using tetramethylsilane (TMS) and CF_3COOH as internal standards, respectively. Elemental analyses were performed by Shanghai Institute of Organic Chemistry.

3.1. $MeCpTi(OMe)_3$ (2b)

To an Et_2O solution (120 ml) of $MeCpTiCl_3$ (4.2 g, 18.0 mmol) was added dropwise an Et_2O solution (30 ml) of MeOH (2.2 ml, 54.0 mmol) and NEt_3 (7.5 ml, 54.0 mmol) at room temperature, and stirred overnight. The reaction mixture was filtered, and the residue was washed with diethyl ether (2 × 25 ml). All filtrates were combined and concentrated under vacuum to remove the solvent. The residual oil was distilled at 57–59 °C/0.04 mmHg to give 3.3 g (83%) of a pale yellow oil. ^1H NMR (CDCl$_3$): δ 2.26 (s, 3H, CH$_3$), 4.11 (s, 9H, OCH$_3$), 6.12 (t, J = 2.6 Hz, 2H, Cp), 6.21 (t, J = 2.6 Hz, 2H, Cp). IR (KBr): v 3085w, 2909m, 2887m, 2806s, 1498m, 1439m, 1375w, 1353w, 1241w, 1127s, 1052m, 1036m, 935w, 855s, 796s, 628m, 530s. EI MS: 220 (M$^+$, 29), 189 (M$^+$–OCH$_3$, 39), 188 (M$^+$–HOCH$_3$, 67), 158 (M$^+$–2OCH$_3$, 57), 141 (M$^+$–CH$_3$Cp, 100), 127 (M$^+$–3OCH$_3$, 14). Anal. Calc. for C$_9$H$_{16}$O$_3$Ti: C, 49.12; H, 7.33. Found: C, 49.12; H, 6.98%.

3.2. $^iPrCpTi(OMe)_3$ (2c)

The operation was the same as that described for **2b**. $^iPrCpTiCl_3$ (3.9 g, 12.8 mmol), MeOH (1.6 ml, 38.5 mmol) and NEt_3 (5.4 ml, 38.5 mmol) were used to give to give 2.6 g (82%) of a pale yellow oil (72–75 °C/0.1 mmHg). ^1H NMR (CDCl$_3$): δ 1.28 (d, J = 6.9 Hz, 6H, CH$_3$), 2.96–3.01 (m, 1H, CH), 4.11 (s, 9H, OCH$_3$), 6.20 (s, 4H, Cp). IR (KBr): v 3091w, 2959s, 2910m, 2872m, 2808m, 1731w, 1489m, 1462m, 1456m, 1422w, 1380w, 1362m, 1317m, 1247w, 1154s, 1130s, 1037m, 932m, 847s, 793s, 683s, 622s, 542s. EI MS: 248 (M$^+$, 3), 217 (M$^+$–OCH$_3$, 79), 186 (M$^+$–2OCH$_3$, 45), 155 (M$^+$–3OCH$_3$, 10), 141 (M$^+$–^iPrCp, 60). Anal. Calc. for C$_{11}$H$_{20}$O$_3$Ti: C, 53.24; H, 8.12. Found: C, 53.28; H, 8.20%.

3.3. $Me_3SiCpTi(OMe)_3$ (2d)

The operation was the same as that described for **2b**. $Me_3SiCpTiCl_3$ (7.4 g, 25.4 mmol), MeOH (3.1 ml, 76.2

mmol), and NEt_3 (10.7 ml, 76.2 mmol) were used to get 5.7 g (80%) of a pale yellow oil (74–76 °C/0.05 mmHg). ^1H NMR (CDCl$_3$): δ 0.28 (s, 9H, SiMe$_3$), 4.09 (s, 9H, OCH$_3$), 6.46 (t, J = 2.6 Hz, 2H, Cp), 6.56 (t, J = 2.6 Hz, 2H, Cp). IR (KBr): v 3078w, 2952m, 2910m, 2809m, 1440w, 1406w, 1367m, 1314w, 1247s, 1182m, 1122m, 1047s, 908m, 840s, 797s, 733m, 650m, 628m, 562s. EI MS: 278 (M$^+$, 6), 263 (M$^+$–CH$_3$, 100), 247 (M$^+$–OCH$_3$, 23), 232 (M$^+$–CH$_3$–OCH$_3$, 12), 216 (M$^+$ – 2OCH$_3$, 13). Anal. Calc. for C$_{11}$H$_{22}$O$_3$SiTi: C, 47.48; H, 7.97. Found: C, 47.49; H, 7.96%.

3.4. $CH_2=CHCH_2CpTi(OMe)_3$ (2e)

The operation was the same as that described for **2b**. $CH_2=CHCH_2CpTiCl_3$ (3.1 g, 12.1 mmol), MeOH (1.5 ml, 36.3 mmol), and NEt_3 (5.1 ml, 36.3 mmol) were used to produce 2.5 g (83%) of a bright yellow oil (80–82 °C/0.2 mmHg). ^1H NMR (CDCl$_3$): δ 3.38 (d, J = 6.7 Hz, 2H, CH$_2$), 4.10 (s, 9H, OCH$_3$), 5.09–5.16 (m, 2H, CH$_2$=), 5.95–6.03 (m, 1H, CH=), 6.17 (t, J = 2.7 Hz, 2H, Cp), 6.25 (t, J = 2.7 Hz, 2H, Cp). IR (KBr): v 3077w, 2977w, 2910m, 2808m, 1638m, 1491w, 1429m, 1288w, 1114s, 1038m, 995m, 912m, 855s, 799s, 630m, 530s. EI MS: 246 (M$^+$, 9), 215 (M$^+$–OCH$_3$, 18), 184 (M$^+$–2OCH$_3$, 100), 141 (M$^+$–C$_3$H$_5$Cp, 63), 105 (C$_3$H$_5$Cp$^+$, 46), 79 (TiOMe$^+$, 31). Anal. Calc. for C$_{11}$H$_{18}$O$_3$Ti: C, 53.68; H, 7.37. Found: C, 53.35; H, 7.18%.

3.5. $PhCH_2CpTi(OMe)_3$ (2f)

The operation was the same as that described for **2b**. $PhCH_2CpTiCl_3$ (5.4 g, 17.6 mmol), MeOH (2.1 ml, 52.8 mmol), and NEt_3 (7.5 ml, 52.8 mmol) were used to produce 3.5 g (68%) of a pale yellow oil (128–130 °C/0.05 mmHg). ^1H NMR (CDCl$_3$): δ 3.95 (s, 2H, CH$_2$), 4.10 (s, 9H OCH$_3$), 6.12 (t, J = 2.7 Hz, 2H, Cp), 6.23 (t, J = 2.7 Hz, 2H, Cp), 7.19–7.33 (m, 5H, Ph). IR (KBr): v 3060w, 3026w, 2910m, 2808m, 1602w, 1494m, 1453m, 1437w, 1109m, 1036m, 938w, 796s, 704s, 623m, 546s. EI MS: 296 (M$^+$, 1), 265 (M$^+$–OCH$_3$, 25), 264 (M$^+$–HOCH$_3$, 44), 234 (M$^+$–2OCH$_3$, 100), 203 (M$^+$–3OCH$_3$, 27). Anal. Calc. for C$_{15}$H$_{20}$O$_3$Ti: C, 60.83; H, 6.81. Found: C, 60.79; H, 6.74%.

3.6. $CpTiF_2(OMe)$ (3a)

To an Et_2O solution (20 ml) of $CpTi(OMe)_3$ (0.55 g, 2.7 mmol) was added dropwise an Et_2O solution (10 ml) of $BF_3 \cdot OEt_2$ (0.25 ml, 2.0 mmol) at −30 °C, whereupon a solid immediately began to form. The reaction mixture was allowed to warm to room temperature, and stirred overnight. The solvent was removed under vacuum, and the residue sublimed at 110 °C/0.1 mmHg to yield 0.37 g (76%) of a yellow solid. m.p. = 130–132 °C. ^1H NMR

(CDCl$_3$): δ 4.11 (br.s, 3H, OCH$_3$), 6.71 (s, 5H, Cp). IR (KBr): ν 3098m, 2932w, 2892w, 2826w, 1804w, 1656w, 1445m, 1361w, 1038s, 1018m, 863m, 828s, 618s, 591s, 543s. EI MS: 182 (M$^+$, 80), 163 (M$^+$–F, 49), 151 (M$^+$–OCH$_3$, 68), 132 (M$^+$–F–OCH$_3$, 98), 117 (M$^+$–Cp, 60), 86 (TiF$_2^+$, 38). Anal. Calc. for C$_6$H$_8$F$_2$OTi: C, 39.60; H, 4.43. Found: C, 39.52; H, 4.40%.

3.7. MeCpTiF$_2$(OMe) (3b)

The same procedure as described for **3a** was used. MeCpTi(OMe)$_3$ (0.76 g, 3.4 mmol) and BF$_3$·OEt$_2$ (0.32 ml, 2.5 mmol) were used to give 0.47 g (70%) of a bright yellow solid. m.p. = 107–109 °C. ^{1}H NMR (CDCl$_3$): δ 2.38 (s, 3H, CH$_3$), 4.05 (br.s, 3H, OCH$_3$), 6.39 (s, 2H, Cp), 6.59 (s, 2H, Cp). IR (KBr): ν 3114w, 3084w, 2943w, 2833w, 1497m, 1459w, 1378w, 1247w, 1042m, 1006m, 937w, 895m, 844s, 615s, 581s, 542s. EI MS: 196 (M$^+$, 17), 177 (M$^+$–F, 9), 165 (M$^+$–OCH$_3$, 20), 146 (M$^+$–F–OCH$_3$, 28), 86 (TiF$_2^+$, 14), 79 (MeCp$^+$, 56). Anal. Calc. for C$_7$H$_{10}$F$_2$OTi: C, 42.89; H, 5.14. Found: C, 42.77; H, 5.01%.

3.8. ^{i}PrCpTiF$_2$(OMe) (3c)

The same procedure as the described for **3a** was used. ^{i}PrCpTi(OMe)$_3$ (0.82 g, 3.3 mmol) and BF$_3$·OEt$_2$ (0.30 ml, 2.4 mmol) were used to give 0.36 g (48%) of a yellow solid. m.p. = 78–80 °C. ^{1}H NMR (CDCl$_3$): δ 1.30 (d, J = 6.9 Hz, 6H, CH$_3$), 3.07–3.15 (m, 1H, CH), 4.12 (br.s, 3H, OCH$_3$), 6.46 (s, 2H, Cp), 6.56 (s, 2H, Cp). IR (KBr): 3106w, 2961s, 2928m, 2872m, 1735w, 1637w, 1491m, 1462m, 1424w, 1382w, 1364w, 1318w, 1152w, 1105w, 1082w, 1041m, 931m, 804s, 732m, 681m, 628s, 583s, 503m. EI MS: 224 (M$^+$, 3), 205 (M$^+$–F, 18), 193 (M$^+$–OCH$_3$, 20), 174 (M$^+$–F–OCH$_3$, 10), 107 (^{i}PrCp$^+$, 24). Anal. Calc. for C$_9$H$_{14}$F$_2$OTi: C, 48.24; H, 6.30. Found: C, 47.98; H, 6.19%.

3.9. Me$_3$SiCpTiF$_2$(OMe) (3d)

To an Et$_2$O solution (20 ml) of Me$_3$SiCpTi(OMe)$_3$ (0.74 g, 2.7 mmol) was added dropwise an Et$_2$O solution (10 ml) of BF$_3$·OEt$_2$ (0.25 ml, 2.0 mmol) at −30 °C. The reaction mixture was allowed to warm to room temperature, and stirred overnight. The solvent was removed under vacuum. The residue was washed with cold n-hexane, and dried under vacuum. The solid was kept at 50 °C/0.05 mmHg to removed orange-red oil, and then sublimed at 80 °C/0.05 mmHg to yield 0.25 g (37%) of a yellow solid. m.p. = 73–75 °C. ^{1}H NMR (CDCl$_3$): δ 0.33 (s, 9H, SiMe$_3$), 4.17 (br.s, 9H, OCH$_3$), 6.79 (s, 2H, Cp), 7.26 (s, 2H, Cp). IR (KBr): 3103w, 2955m, 2897w, 1606w, 1448w, 1410m, 1369w, 1317w, 1250s, 1178m, 1119w, 1050m, 907m, 840s, 759m, 729m, 696w, 627s, 591m, 544m, 516m. EI MS: 254 (M$^+$, 1), 239

(M$^+$–CH$_3$, 33), 238 (M$^+$–CH$_4$, 100), 235 (M$^+$–F, 5), 223 (M$^+$–OCH$_3$, 68), 208 (M$^+$–CH$_3$–OCH$_3$, 48), 117 (M$^+$–Me$_3$SiCp, 6). Anal. Calc. for C$_9$H$_{16}$F$_2$OSiTi: C, 42.53; H, 6.34. Found: C, 42.41; H, 6.45%.

3.10. CH$_2$=CHCH$_2$CpTiF$_2$(OMe) (3e)

The same procedure as the described for **3a** was used. CH$_2$=CHCH$_2$CpTi(OMe)$_3$ (1.5 g, 6.1 mmol) and BF$_3$·OEt$_2$ (0.57 ml, 4.5 mmol) were used to yield 0.90 g (66%) of an orange solid. m.p. = 82–84 °C. ^{1}H NMR (CDCl$_3$): δ 3.49 (d, J = 6.6 Hz, 2H, CH$_2$), 4.04 (br.s, 3H, OCH$_3$), 5.13–5.19 (m, 2H, CH$_2$=), 5.93–6.06 (m, 1H, CH=), 6.41 (s, 2H, Cp), 6.59 (s, 2H, Cp). IR (KBr): ν 3111w, 3080w, 2978w, 2913w, 1639m, 1490m, 1429m, 1290w, 1045m, 996m, 913m, 851s, 810s, 733m, 631s, 580s, 510s. EI MS: 222 (M$^+$, 3), 203 (M$^+$–F, 45), 184 (M$^+$–2F, 19), 172 (M$^+$–F–OCH$_3$, 61), 105 (C$_3$H$_5$Cp$^+$, 66), 79 (TiOCH$_3^+$, 100). Anal. Calc. for C$_9$H$_{12}$F$_2$OTi: C, 48.68; H, 5.45. Found: C, 48.60; H, 5.50%.

3.11. PhCH$_2$CpTiF$_2$(OMe) (3f)

To an Et$_2$O solution (20 ml) of PhCH$_2$CpTi(OMe)$_3$ (0.75 g, 2.5 mmol) was added dropwise an Et$_2$O solution (10 ml) of BF$_3$·OEt$_2$ (0.23 ml, 1.9 mmol) at −30 °C. The reaction mixture was allowed to warm to room temperature, and stirred overnight. The solvent was removed under vacuum. The residue was washed with n-hexane, and dried under vacuum. The solid was recrystallized with CH$_2$Cl$_2$/n-hexane at −25 °C to obtain 0.42 g (61%) of a orange crystal. m.p. = 122–124 °C. ^{1}H NMR (CDCl$_3$): δ 4.04 (br.s, 3H, OCH$_3$), 4.07 (s, 2H, CH$_2$), 4.00 (br.s, 3H, OCH$_3$), 6.36 (s, 2H, Cp), 6.56 (s, 2H, Cp), 7.23–7.34 (m, 5H, Ph). IR (KBr): ν 3095m, 3025w, 2923w, 2826w, 1723w, 1600w, 1491m, 1450m, 1425m, 1366w, 1233w, 1041m, 854s, 836m, 769w, 732m, 704m, 620s, 593m, 544s. EI MS: 253 (M$^+$–F, 6), 252 (M$^+$–HF, 18), 241 (M$^+$–OCH$_3$, 12), 240 (M$^+$–HOCH$_3$, 98), 222 (M$^+$–F–OCH$_3$, 56), 155 (PhCH$_2$Cp$^+$, 53), 86 (TiF$_2^+$, 16), 77 (Ph$^+$, 44). Anal. Calc. for C$_{13}$H$_{14}$F$_2$OTi: C, 57.38; H, 5.19. Found: C, 56.95; H, 5.11%.

3.12. Polymerization procedure

Polymerization was conducted in small ampoules baked under vacuum and flushed with argon several times. Styrene, toluene, MAO was sequentially injected. After the catalyst precursor in toluene was added, the bottle was placed in an oil bath at the desired polymerization temperature at once. After 1 h, the polymerization was quenched with 10% HCl in ethanol, filtered, washed with ethanol and dried under vacuum at 80 °C for 24 h to a constant weight. The melting temperature of the polymers was recorded on DSC Universal V2.3C TA Instrument.

Acknowledgements

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