Syndiospecific polymerization of styrene catalyzed in situ by alkoxyl substituted half-sandwich titanocene and BF₃·Et₂O

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Abstract

A series of alkoxyl substituted half-sandwich titanocenes [CpTiCl₂(OR), CpTi(OR)₃ and IndTiCl₂(OR)] were treated with BF₃·Et₂O, which were employed in situ as catalyst precursors for the syndiospecific polymerization of styrene. When activated with methylaluminoxane (MAO), the catalyst precursors obtained in situ from the reaction of methoxyl substituted complexes [CpTiCl₂(OMe), CpTi(OMe)₃] and BF₃·Et₂O exhibited increased activities by factors of 2–4 compared with the corresponding original complexes, and provide improved syndiotacticity and higher activity up to a temperature of 70 °C. The catalyst precursor may consist of [CpTiClF₂ and/or CpTiCl₂F] and [CpTiF₂(OMe)·BF₃ and/or CpTiF(OMe)₂·2BF₃], through conversion from BF₃-coordinated intermediates to fluorinated complexes, respectively, which has properties in polymerization similar to that of CpTiF₃. But in the case of IndTiCl₂(OR) and alkoxyl substituted half-sandwich titanocene with bulky OR groups, the activity considerably decrease probably due to the bulky group retarding the conversion from BF₃-coordinated intermediates to fluorinated complexes, which can stabilize catalytic precursor and inhibit reduction from Ti(IV) to Ti(III).
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1. Introduction

Polystyrene is an indispensable commodity plastic similar to polyolefins. The monomer is easily available, in principle, polystyrene may be produced with isotactic, atactic or syndiotactic configurations. In most cases, isotactic polymers are obtained, and syndiotactic polymers are rare. In contrast to the long known isotactic polystyrene, which shows a slow crystallization rate and is therefore useless for most industrial applications, the syndiotactic material shows a fast crystallization rate and a higher melting point of 275 °C. This contrasts with 240 and 100 °C for the isotactic and atactic polymers, respectively. These new properties, which are similar to those of some expensive engineering plastics, are the reasons for the interest in syndiotactic polystyrene [1].

But, syndiotactic polystyrene was unknown until Ishihara showed how to produce it by using titanium/MAO catalysts. From then on, a great number of patents and papers for technical applications have been published [2–14], and research found that the highest activities are achieved with half-sandwich

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titanocenes of the type $CpTiCl_3$, Cp^*TiCl_3, $IndTiCl_3$, and substituted $IndTiCl_3$ with methylaluminoxane (MAO) as co-catalyst. $B(C_6F_5)_3$ and other borates can be used as precursors instead of MAO. The polymerization mechanism [13,15,16] and the structure of the active site [7,8,17–22] have also been investigated. Now, more efforts are devoted to the synthesis of new kinds of half-sandwich titanocenes and the elucidation of the relationship between the precursor structure and its catalytic behavior [23–28]. The electron-donating ability of the π-donor ligand (e.g. cyclopentadienyl and indenyl), basicity, steric effects, and chirality of the ligands attached to the group 4 metal centers strongly influence the polymerization.

Kaminsky et al. [1] compared the above-mentioned catalysts ($CpTiCl_3$, and Cp^*TiCl_3), and their fluorinated counterparts under similar conditions. Experiments show that fluorinated catalysts not only have much higher activities and produce polymers with higher molecular weights but also allow the reduction of the titanium/MAO molar ratio. Xu and Ruckenstein [23] believe that the higher activity and syndiospecificity of the fluorinated catalysts is attributable to a greater number of more stable Ti(III) active sites and/or a higher propagation rate constant. The fluorinated complexes been employed were obtained via the halide redistribution reaction between chloride complexes and Me_3SnF_3, a convenient but toxic fluoridate method.

In our laboratory, a series of monoalkoxy substituted cyclopentadienyl titanium chlorides [$CpTiCl_2(OR)$] [29–32] and indenyl titanium chlorides [$IndTiCl_2(OR)$] [33–35] were synthesized and investigated for syndiospecific styrene polymerization. Experiment demonstrated that the structure and nature of the R group have a great effect on the catalyst activity. Unsaturated groups and the conjugation of unsaturated group with oxygen result in the drop of activity, while a more hindered R group decreases activity. In order to investigate the influence of $BF_3·Et_2O$ to the catalyst activity of $CpTiCl_2(OR)$, $CpTi(OR)_3$ and $IndTiCl_2(OR)$, we treated these complexes with $BF_3·Et_2O$ in situ as catalyst precursor along with MAO in syndiotactic polymerization of styrene. Some catalyst precursors performed similar to the fluorinated complexes mentioned above, while others show a considerable decrease in activity.

2. Experimental

2.1. General procedures

Experiments were performed under an argon atmosphere using standard Schlenk techniques unless otherwise noted. Methylene chloride was distilled under argon from P_2O_5. Styrene was purified by washing several times with dilute NaOH solution and dried over anhydrous $CaCl_2$, vacuum distilled from CaH_2 and stored at −20 °C in the dark. Toluene and other solvents were distilled from sodium and biphenyl ketone under argon prior to use. ^{1}H NMR and ^{19}F NMR spectra were recorded on a Varian GERMINI-300 spectrometer. The melting point of polystyrene was recorded on DSC 2910 Modulated DSC Universal V1.10B TA Instruments. MAO was purchased from Wittco.

$CpTiCl_3$, $CpTiCl_2(OMe)$, $CpTiCl_2(O^iPr)$, $CpTiCl_2$-$(O-C_6H_4-^tBu)$, $CpTi(OMe)_3$, $CpTi(O-cyclopentyl)_3$, $IndTiCl_3$, $IndTiCl_2(OMe)$, $IndTiCl_2(OEt)$, $IndTiCl_2$-(O^iPr) and $IndTiCl_2(O-cyclohexyl)$ were prepared according to the literature [29–32,34,36–39].

2.2. Polymerization

Polymerization was conducted in small ampoules baked under vacuum and flushed with argon several times. Styrene (2 ml), an appropriate amount of MAO in 10 ml toluene, and titanium compounds in toluene were sequentially injected. The parallel experimental procedures were similar except that titanium compounds were treated with 4 eq. $BF_3·Et_2O$ prior to the injection. The contents of the ampoule were kept at a desired temperature and polymerized for a selected time, then quenched with 100 ml 10% HCl in EtOH, filtered, and dried under vacuum at 50 °C to constant weight. The polymer was then extracted with 2-butanone for 2 h to remove any actactic component. The syndiotactic polymer was determined as the amount of 2-butanone insoluble component.

3. Results and discussions

The influences of temperature on the catalytic behaviors of $CpTiCl_2(OMe)$, $CpTi(OMe)_3$ and their $BF_3·Et_2O$-treated counterparts are shown in Table 1.

Table 1
Polymerization of styrene by $CpTiCl_2(OR)/MAO$, $CpTi(OR)_3/MAO$ and their $BF_3 \cdot Et_2O$-treated counterparts under different temperature conditions

Run	Catalysts	Al/Ti (10^3)	Time (h)	Temperature (°C)	Yield (g)	A^a (10^6)	s-PS[b] (%)	T_m (°C)
1	$CpTiCl_2(OMe)$	2.0	1	30	0.3260	3.25	92.0	261
2	$CpTiCl_2(OMe)$	2.0	1	50	0.4788	5.50	92.6	–
3	$CpTiCl_2(OMe)$	2.0	1	70	0.4162	4.79	75.7	252
4	$CpTiCl_2(OMe) + BF_3 \cdot Et_2O$	2.0	1	30	0.2429	2.79	89.7	261
5	$CpTiCl_2(OMe) + BF_3 \cdot Et_2O$	2.0	1	50	0.5527	6.35	91.7	–
6	$CpTiCl_2(OMe) + BF_3 \cdot Et_2O$	2.0	1	70	0.7321	8.42	82.9	250
7	$CpTi(OMe)_3$	2.0	1	30	0.1494	1.72	75.6	–
8	$CpTi(OMe)_3$	2.0	1	50	0.4057	4.66	87.2	–
9	$CpTi(OMe)_3$	2.0	1	70	0.2003	2.34	80.7	247
10	$CpTi(OMe)_3 + BF_3 \cdot Et_2O$	2.0	1	30	0.2108	2.42	84.0	–
11	$CpTi(OMe)_3 + BF_3 \cdot Et_2O$	2.0	1	50	0.6174	7.10	91.6	–
12	$CpTi(OMe)_3 + BF_3 \cdot Et_2O$	2.0	1	70	0.6960	8.00	83.7	248
13	$CpTiCl_2(O^iPr)$	2.0	1	50	0.2708	3.10	90.7	–
14	$CpTiCl_2(O^iPr) + BF_3 \cdot Et_2O$	2.0	1	50	0.3248	3.27	93.5	–
15	$CpTiCl_2(O\text{-}C_6H_4\text{-}^tBu)$	2.0	1	50	0.3045	3.49	89.9	–
16	$CpTiCl_2(O\text{-}C_6H_4\text{-}^tBu) + BF_3 \cdot Et_2O$	2.0	1	50	0.2724	3.12	93.6	–
17	$CpTi(O\text{-cyclopentyl})_3$	2.0	1	50	1.4170	16.3	95.7	256
18	$CpTi(O\text{-cyclopentyl})_3 + BF_3 \cdot Et_2O$	2.0	1	50	0.4945	5.68	92.0	256
19	$CpTiCl_3$	2.0	1	50	0.2199	2.52	92.3	–
20	$CpTiCl_3 + BF_3 \cdot Et_2O$	2.0	1	50	0.2152	2.46	89.7	–

Polymerization conditions: styrene, 2 ml; toluene, 9 ml as solvent; [Ti] = 0.42 mM.

 [a] A (activity): bulk polymer (g)/[Ti (mol) × monomer (mol) × time (h)].

 [b] s-PS (%): [2-butanone insoluble polymer (g)/bulk polymer (g)] × 100.

Similar to our previous works [29–32], the most favorable temperature for $CpTiCl_2(OMe)$ and $CpTi(OMe)_3$ polymerization of styrene is 50 °C, and the syndiotacticity of the polystyrene has no direct relationship with temperature. These two catalyst precursors are less stable, as can be seen by the decrease of the average activity at 70 °C. After been treated with $BF_3 \cdot Et_2O$, both catalyst precursors reach their highest activity at 70 °C, which is analogous to the behavior of $CpTiF_3$ [1]. In the case of $CpTiCl_2(OMe)$, the $BF_3 \cdot Et_2O$-treated catalyst precursors are more active than its chlorinated counterpart at 50 and 70 °C. While at all the temperatures, the activities of the $BF_3 \cdot Et_2O$-treated catalyst precursors are superior to that of the $CpTi(OMe)_3$ counterpart. These findings indicate that the $BF_3 \cdot Et_2O$-treated catalyst precursors are more stable than the original catalyst precursors even at high polymerization temperatures. The activity of $CpTiCl_2(OMe)$ is higher at all temperature levels than those of $CpTi(OMe)_3$, but their activities are almost equal at all the temperatures after treatment with $BF_3 \cdot Et_2O$. We can see the slight increase in activity at $CpTiCl_2(O^iPr)$ after the introduction of $BF_3 \cdot Et_2O$

compared to that without $BF_3 \cdot Et_2O$ at 50 °C. In contrast, the activity of $CpTiCl_2(O\text{-}C_6H_4\text{-}^tBu)$ decreased after been treated with $BF_3 \cdot Et_2O$ from (3.49 to 3.12) × 10^6 gPS/molTi molS h, while $CpTiCl_3$ has little change in activity at the same temperature. The syndiospecificity of polystyrene obtained by all catalyst precursors increase more or less than their counterparts expect for $CpTiCl_3$. We can also see the sharp decrease in activity in $CpTi(O\text{-cyclopentyl})_3$ from (16.3 to 5.68) × 10^6 gPS/molTi molS h, the same trend is obvious in Table 2 (runs 27 and 28) and both cases involve a cyclo-alkyl substituent.

Table 2 summarize the polymerization results of $IndTiCl_2(OR)$ and that of treatment with $BF_3 \cdot Et_2O$. All of the $IndTiCl_2(OR)$ exhibit lower activity as well as syndiospecificity after treatment in situ with $BF_3 \cdot Et_2O$, especially $IndTiCl_2(O\text{-cyclohexyl})$, the activity of which decrease dramatically from (12.56 to 2.98) × 10^6 gPS/molTi molS h. The activity of $IndTiCl_3$ is similar that of $CpTiCl_3$ with little changes.

From these observations, we can summarize the data of the two tables as follows: the activity of methoxyl substituted half-sandwich titanocene [$CpTiCl_2(OMe)$

Table 2
Polymerization of styrene by IndTiCl$_2$(OR)/MAO and their BF$_3$·Et$_2$O-treated counterparts

Run	Catalysts	Al/Ti (10^3)	Time (h)	Temperature (°C)	Yield (g)	A^a (10^6)	s-PS^b (%)
21	IndTiCl$_2$(OMe)	2.0	1	50	0.1972	2.27	86.1
22	IndTiCl$_2$(OMe) + BF$_3$·Et$_2$O	2.0	1	50	0.1513	1.74	86.1
23	IndTiCl$_2$(OEt)	2.0	1	50	0.2423	2.79	92.7
24	IndTiCl$_2$(OEt) + BF$_3$·Et$_2$O	2.0	1	50	0.1913	2.20	87.6
25	IndTiCl$_2$(O^{i}Pr)	2.0	1	50	0.7767	8.65	96.8
26	IndTiCl$_2$(O^{i}Pr) + BF$_3$·Et$_2$O	2.0	1	50	0.1378	1.59	85.2
27	IndTiCl$_2$(O-cyclohexyl)	2.0	1	50	1.1269	12.56	97.0
28	IndTiCl$_2$(O-cyclohexyl) + BF$_3$·Et$_2$O	2.0	1	50	0.2596	2.98	84.5
29	IndTiCl$_3$	2.0	1	50	0.1643	1.63	86.4
30	IndTiCl$_3$ + BF$_3$·Et$_2$O	2.0	1	50	0.1784	1.71	83.4

Polymerization conditions: styrene, 2 ml; toluene, 9 ml as solvent; [Ti] = 0.42 mM.

[a] A (activity): bulk polymer (g)/[Ti (mol) × monomer (mol) × time (h)].

[b] s-PS (%): [2-butanone insoluble polymer (g)/bulk polymer (g)] × 100.

and CpTi(OMe)$_3$] for syndiospecific polymerization of polystyrene will increase after treatment in situ with BF$_3$·Et$_2$O as catalyst precursors. But the activity of BF$_3$·Et$_2$O-treated precursors will decrease with the increasing steric effect of alkoxyl substituent or the replacement of Cp ring with an indenyl ring. The activity of trichloride half-sandwich titanocenes changes little under the same conditions. In other words, BF$_3$·Et$_2$O can influence the catalytic behaviors of alkoxyl substituted half-sandwich titanocenes probably through a kind of reaction, and obvious evidence is that the color of catalyst solution changes with the addition of BF$_3$·Et$_2$O.

The NMR spectra analyses were employed to further investigate the function of BF$_3$·Et$_2$O in this process. Fig. 1c is the ^{1}H NMR spectrum of the reaction mixture of CpTi(OMe)$_3$ and BF$_3$·Et$_2$O in CDCl$_3$ solution. Compared to the ^{1}H NMR spectrum of CpTi(OMe)$_3$ (Fig. 1a), two different singlet peaks of protons on Cp ring shifted downfields (from δ 6.38 to 6.86 and 6.65 ppm) and two signal of OMe group shifted upfields (from δ 4.11 to 3.69 and 3.52 ppm), these phenomena indicate that a kind of reaction must be occurring between CpTi(OMe)$_3$ and BF$_3$·Et$_2$O. BF$_3$ is a very strong Lewis acid, which easily forms coordination complexes with molecules having at least a lone pair of electrons. Taking these factors into account, there exist the possibility of BF$_3$ coordinating with OR group to form a complex.

The shape of two singlet peaks of OMe (Fig. 1c) is similar to that of CpTiF$_2$(OMe) (Fig. 1b), but there

is no signal found in the range of 0–150 ppm in ^{19}F NMR, where the signal of Ti–F bond located, such as Cp′TiF$_3$ (δ 100–140 ppm) [23] and CpTiF$_2$(OMe) (δ 15.6 ppm), while the new strong signals of F appeared at −160 to −165 ppm (Fig. 2a) and the peak of BF$_3$·Et$_2$O (δ −152 to −155 ppm) decreased compare to Fig. 2b. These facts support our hypothesis that the BF$_3$ coordinates with OR group, the peak at ca. −160 ppm probably is the signal of BF$_3$ coordination in the complexes.

We mixed one equivalent of CpTi(OMe)$_3$ and four equivalents of BF$_3$·Et$_2$O in toluene, the mixture keep at 70 °C for 1 h (the optimum polymerization condition), after removal of solvent, the residue shows two peak at δ 27.5 and 28.1 ppm (Fig. 3), which may be the signal of Ti–F bonds belonging to CpTiF$_2$(OMe) and CpTiF(OMe)$_2$, respectively, and another two peaks at −171.9 and −172.5 ppm which belong to the BF$_3$ still coordinating with the OMe group. In addition, The pure CpTi(OMe)F$_2$ compound has been obtained via the reaction of three equivalents of CpTi(OMe)$_3$ and two equivalents of BF$_3$·Et$_2$O under the optimal conditions. These facts indicates that under the optimal polymerization condition, excess of BF$_3$·Et$_2$O can react with CpTi(OMe)$_3$ to produce the BF$_3$-coordinated fluorinated products [CpTiF$_2$(OMe)·BF$_3$ and/or CpTiF(OMe)$_2$·2BF$_3$], although may form the BF$_3$-coordinated intermediate products without the formation of Ti–F bond at the beginning of the mixture. All of the BF$_3$-coordinated fluorine complexes
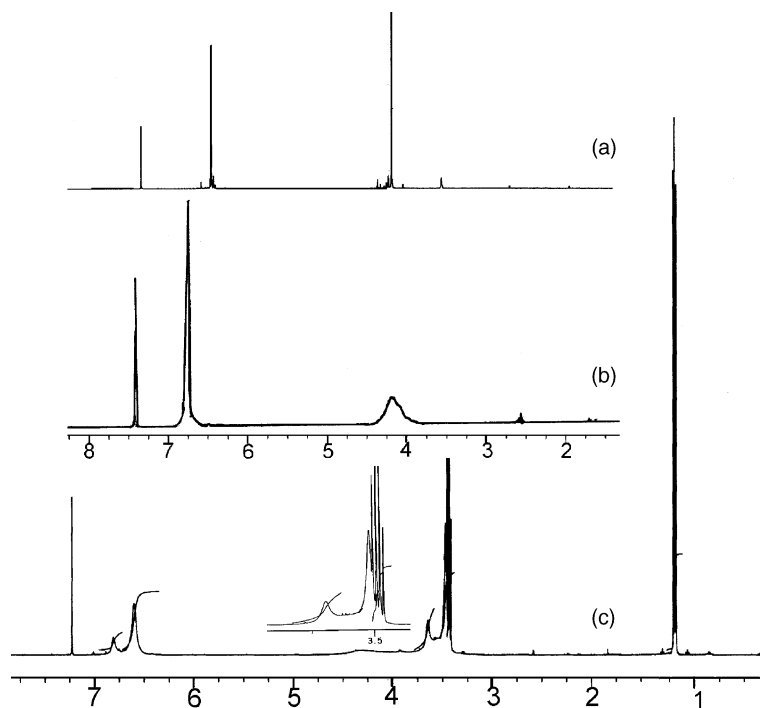
Fig. 1. ^{1}H NMR spectra of (a) CpTi(OMe)$_3$, (b) CpTiF$_2$(OMe) and (c) the mixture obtained in situ by mixing CpTi(OMe)$_3$ with BF$_3$·Et$_2$O.

[CpTiF(OMe)$_2$·2BF$_3$, CpTiF$_2$(OMe)·BF$_3$] generate a greater number of more stable Ti(III) active sites, reflected in the higher activity and syndiospecificity.

In order to investigate the reaction of CpTiCl$_2$(OMe) with BF$_3$·Et$_2$O, we treated it with four equivalents of BF$_3$·Et$_2$O. A green–yellow product was obtained upon recrystallization from toluene/CH$_2$Cl$_2$. In the

Fig. 2. ^{19}F NMR spectra of (a) the mixture obtained in situ by mixing CpTi(OMe)$_3$ with BF$_3$·Et$_2$O and (b) BF$_3$·Et$_2$O.

^{1}H NMR spectrum (Fig. 4c), we observe that the OMe group signal (δ 4.52 ppm in Fig. 4b) has disappeared and two singlet peaks of protons on Cp ring with different chemical shift (δ 6.91 and 6.83 ppm) appeared between the peaks of CpTiCl$_2$(OMe) (δ 6.74 ppm) and CpTiCl$_3$ (δ 7.05 ppm in Fig. 4a), probably belonging to CpTiCl$_2$F and CpTiClF$_2$, respectively.

The relative signal is also found in the ^{19}F NMR spectra at δ 77.47 and 77.64 ppm. In addition, the fragments of CpTiFCl and CpTiF$_2$ were found in the mass spectra of the product. These facts put together demonstrate that not only the alkoxyl group (OMe) but also the chloride ion was replaced by the fluoride ion (Scheme 1).

Attempts to separate the two complexes by recrystallization or sublimation were unsuccessful due to the similarity in chemical properties. Thus, catalyst precursor obtained in situ by treating CpTiCl$_2$(OMe) with BF$_3$·Et$_2$O contains both CpTiCl$_2$F and CpTiClF$_2$, which exhibit higher polymerization catalytic activity than CpTiCl$_2$(OMe). This result indicates that BF$_3$·Et$_2$O fluorinated CpTiCl$_2$(OMe) easier than
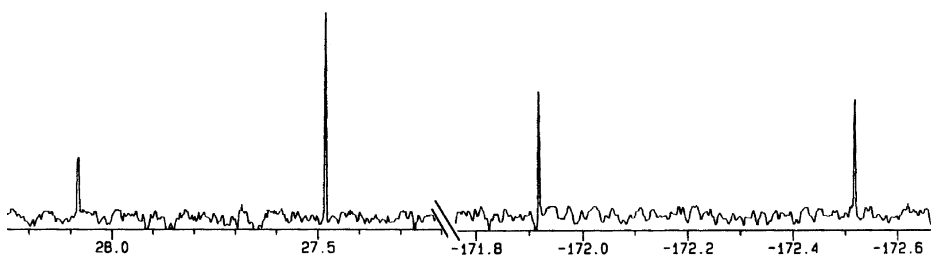
Fig. 3. ^{19}F NMR spectra of residue from the reaction $CpTi(OMe)_3$ with $BF_3 \cdot Et_2O$ under the selected polymerization condition.

$CpTi(OMe)_3$ with a more unstable BF_3-coordination intermediate or even without this step.

Kaminsky et al. [1] report that fluorinated half-sandwich complexes of titanium, such as $CpTiF_3$, show an increase in activity of up to a factor of 50 compared to chlorinated compounds. Xu and Ruckenstein [23] believe that the Ti–F bond which is more polarized than the Ti–Cl bond in the half-sandwich titanocenes, allows the formation of more active and stable active sites of Ti(III) complexes needed for the syndiospecific polymerization of styrene.
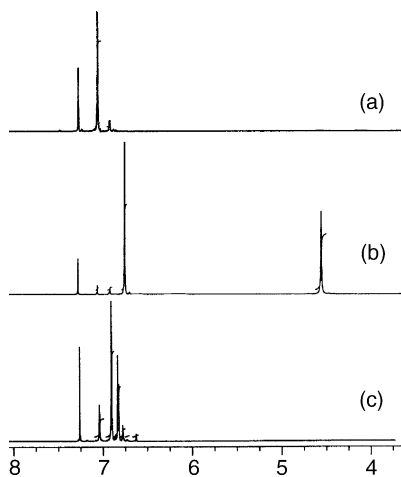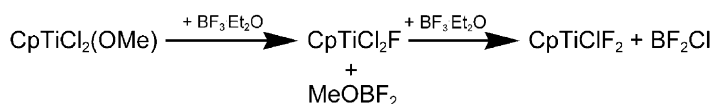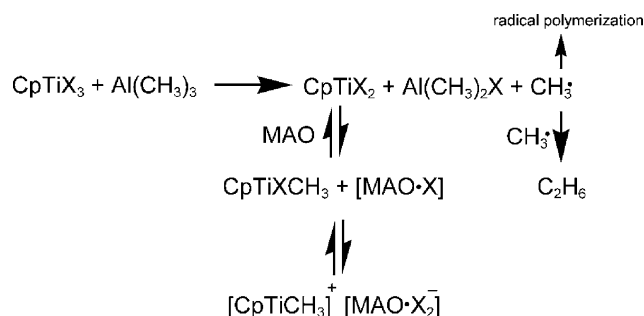

Fig. 4. ^1H NMR spectra of (a) $CpTiCl_3$, (b) $CpTiCl_2(OMe)$ and (c) the mixture of $CpTiCl_2F$ and $CpTiClF_2$.

This explanation may be employed to elucidate the increased catalytic activity of catalyst system containing $CpTiCl_2F$ and $CpTiClF_2$ compared to that of $CpTiCl_3$. $CpTiCl_2(OMe)$ precursor treated in situ with $BF_3 \cdot Et_2O$ exhibits higher catalytic activity than that without this treatment due to the production of the mixed fluorinated complexes of $CpTiCl_2F$ and $CpTiClF_2$, which generates more active sites that enhance the catalytic activity. In addition, according to Scheme 2 [4], the formation of $[CpTiMe_3]^+[MAO \cdot X_2]^-$ involves methylation, alkoxyl groups and halide ligands abstraction by MAO, a bulky alkoxyl group could present a barrier for these processes. As we can see, the activity of run 5 not only is higher than that of run 2, but also higher than those of runs 19 and 20. A similar explanation can account for the observed behavior of $CpTiCl_2(O^iPr)$ (runs 13 and 14). But the same result can not be found in the case of $CpTiCl_2(O-C_6H_4-{}^tBu)$ probably due to the steric effect of the bulky $O-C_6H_4-{}^tBu$ group, which would interfere with the conversion from BF_3-coordinated intermediate to fluorinated compound under the selected conditions. The BF_3-coordinated intermediate exert more steric effects that may help to stabilize the catalyst precursor against reduction from Ti(IV) to Ti(III), which is the key step to generating the active species $[CpTiMe]^+$. This is reflected in the lowering of catalyst polymerization activity after treatment with $BF_3 \cdot Et_2O$ (runs 15 and 16).

$$CpTiCl_2(OMe) \xrightarrow{+ BF_3 Et_2O} CpTiCl_2F \xrightarrow{+ BF_3 Et_2O} CpTiClF_2 + BF_2Cl$$
$$+$$
$$MeOBF_2$$

Scheme 1.

radical polymerization

$$CpTiX_3 + Al(CH_3)_3 \longrightarrow CpTiX_2 + Al(CH_3)_2X + CH_3^\cdot$$

MAO ↕   CH_3^\cdot ↓

$$CpTiXCH_3 + [MAO \cdot X] \qquad C_2H_6$$

↕

$$[CpTiCH_3]^+ [MAO \cdot X_2^-]$$

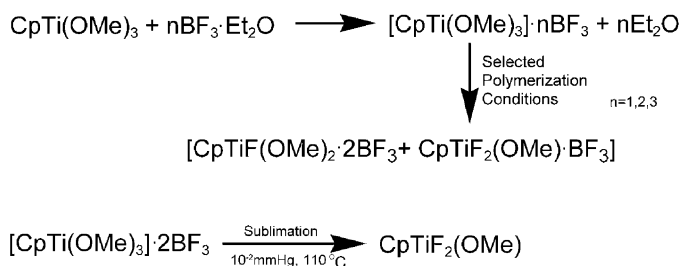Scheme 2. Formation of initiating species by $CpTiX_3$/MAO catalytic systems.

In the case of $CpTi(OMe)_3$, which we treated in situ with $BF_3 \cdot Et_2O$, the catalyst system contains BF_3-coordinated fluoride complexes [$CpTiF_2(OMe) \cdot BF_3$ and/or $CpTiF(OMe)_2 \cdot 2BF_3$], the replacement of OMe group with F ligand increases the likelihood of formation active species. This is because, the electronegativity of fluorine in the fluorinated compound is much stronger than that of chlorine in chloride complexes, this stronger polarity of the Ti–F bond facilitates the replacement of the F ligand by MAO at the electrophilic Ti metal, thus generating more active site and enhancing the catalytic activity. In addition, the size of the fluoride ion is much smaller than those of methoxyl and chloride ions, which is also beneficial to the methylation, alkoxyl group and halide abstraction during the formation of $[CpTiMe_3]^+[MAO \cdot X_2]^-$ species. Our previous works [29–35] showed that monoalkoxyl-group-substituted $CpTiCl_2(OR)$, $IndTiCl_2(OR)$ and $1-(Me)IndTiCl_2(OR)$ complexes showed higher catalytic activity for the syndiospecific polymerization of styrene than their trichloride counterparts, because the alkoxyl ligand stripped during the formation of active species could still surround the active species and stabilize them. The same comparison can be made between BF_3-coordinated fluorinated complexes [$CpTiF_2(OMe) \cdot BF_3$ and/or $CpTiF(OMe)_2 \cdot 2BF_3$] and $CpTiCl_3$. On the other hand, the influence of BF_3-coordinated methoxyl is limited because the methoxyl group is smaller than other bulky alkoxyl groups, which explains why BF_3-coordinated methoxyl substituted complexes have higher activity than other BF_3-coordinated bulky alkoxyl substituted complexes, and why the other BF_3-coordinated bulky alkoxyl substituted complexes show activities

lower than the corresponding original complexes. These results demonstrate that both electron-donating and steric effects have influence on the catalytic activity.

Indene ring has greater electron-donating ability relative to a Cp ring [12,38,41], and exerts more hindrance than Cp ring in half-sandwich titanium metallocenes. These factors may account for the difficulty in conversion from a BF_3-coordinated intermediate to a fluorinated compound even in the case of a methoxyl substituted complex [$IndTiCl_2(OMe)$].

The catalytic activity of $IndTiCl_3$ and $CpTiCl_3$ only has a slight difference compared to their $BF_3 \cdot Et_2O$-treated counterparts due to the absence of lone pair electrons with which BF_3 can coordinate to. According to the investigation [40] for the thermodynamics and kinetics of the redistribution reaction, $CpTiCl_3$ can not react with $BF_3 \cdot Et_2O$ to prepare $CpTiCl_2F$ or $CpTiClF_2$ under the selected condition. We presume that the addition of $BF_3 \cdot Et_2O$ in $IndTiCl_3$ and $CpTiCl_3$ will be beneficial to the formation of active species because both MAO and BF_3 are Lewis acids. Also, BF_3 is a polymerization catalyst for unsaturated molecules via a carbocationic polymerization processes [8,42]. But, no evidence to support this hypothesis. Baird believes that styrene polymerization catalyzed by carbocation initiator give atactic polystyrene, which may account for the decrease of syndiotacticity after addition of $BF_3 \cdot Et_2O$ in some cases.

From the above discussion, we propose the possible mechanism for the mixture of alkoxyl substituted half-sandwich titanocene and $BF_3 \cdot Et_2O$ for the polymerization of styrene as in Scheme 3.

$$CpTi(OMe)_3 + nBF_3 \cdot Et_2O \longrightarrow [CpTi(OMe)_3] \cdot nBF_3 + nEt_2O$$

$$\Big\downarrow \text{Selected Polymerization Conditions} \quad n=1,2,3$$

$$[CpTiF(OMe)_2 \cdot 2BF_3 + CpTiF_2(OMe) \cdot BF_3]$$

$$[CpTi(OMe)_3] \cdot 2BF_3 \xrightarrow[10^{-2}\text{mmHg, }110\,^\circ\text{C}]{\text{Sublimation}} CpTiF_2(OMe)$$

Scheme 3. Formation of $CpTiF_2(OMe) \cdot BF_3$, $CpTiF(OMe)_2 \cdot 2BF_3$ and $CpTiF_2(OMe)$.

At the beginning of the treatment with $BF_3 \cdot Et_2O$, BF_3 coordinates with the alkoxyl group to form the intermediate $CpTi(OMe)_3 \cdot BF_3$. The BF_3-coordinated intermediate would inhibit the catalyst to produce active species. Then the intermediate will transform into a BF_3-coordinated fluorinated product, which then generates more active species under the optimal conditions, but this process may be influenced by the steric effect of catalyst molecular structure (runs 15–18, and 27 and 28) and the polymerization temperature (runs 1 and 4). This process is slightly different from that of Cp^*TiCl_3 and AsF_3 [43], the compound Cp^*TiCl_3 reacts with an excess of AsF_3 to form complex $[Cp^*TiF_3]_2 \cdot 2AsF_3$, and the AsF_3 was removed in vacuum to give Cp^*TiF_3, although $CpTiF_2(OMe) \cdot BF_3$ changes into $CpTiF_2(OMe)$ by sublimation at $110\,^\circ C/10^{-2}$ mmHg.

Work is in progress to attempt to obtain the BF_3-coordinated intermediates and to prepare the fluorinated alkoxyl substituted half-sandwich titanocene, then further investigate their catalytic behaviors for styrene polymerization activated with MAO in the absence of $BF_3 \cdot Et_2O$.

4. Conclusions

Treatment of methoxyl substituted half-sandwich titanocenes $[CpTiCl_2(OMe), CpTi(OMe)_3]$ with $BF_3 \cdot Et_2O$ in situ result in the formation of the mixed fluorinated complexes, $[CpTiClF_2$ and/or $CpTiCl_2F]$, $[CpTiF_2(OMe) \cdot BF_3$ and/or $CpTiF(OMe)_2 \cdot 2BF_3]$, respectively. These are better catalytic processors for styrene polymerization than their original counterparts activated with MAO even at temperatures as high as $70\,^\circ C$. At the beginning of the treatment with

$BF_3 \cdot Et_2O$, the BF_3 will coordinate with the alkoxyl group to form intermediates, and the intermediates will then convert to the fluorinated products that generate more active species for styrene polymerization under the selected conditions. But the conversion is sensitive to steric effects of half-sandwich titanocene and polymerization temperature. The substituted half-sandwich titanocene with bulky alkoxyl group $[CpTiCl_2(OR)$ or $CpTi(OR)_3]$ or indene ring $[IndTiCl_2(OR)]$ can not be fluorinated by $BF_3 \cdot Et_2O$ under the selected condition, but still coordinates with the BF_3, this coordination then enhances the steric effect that stabilizes the precursor and hinders the reduction of the Ti(IV) to the Ti(III) species, reflected in the decrease in polymerization activity.

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