Articles

Oxidation States of Active Species for Syndiotactic-Specific Polymerization of Styrene

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Five η^5-L-TiCl$_3$ catalyst precursors, where L is Cp, substituted Cp, Ind, or substituted Ind, having differing resistance to reduction, have been activated by methylaluminoxane (MAO) under identical conditions. Their activities for syndiotactic-specific styrene polymerization and the concentrations of Ti(III) species under polymerization conditions as determined by electron paramagnetic resonance (EPR) have been measured and compared. A linear but inverse relationship was obtained for log(activity) vs log[(%Ti = Ti(III))], with the precursor most resistant to reduction having the highest activity. The results indicate that both η^5-L-Ti$^+$(IV)L′P and η^5-L-Ti$^+$(III)P intermediates, where P is the propagating chain and L′ is Cl or CH$_3$, catalyze styrene polymerization, with the former being 10−20 times more active than the latter.

Introduction

Syndiotactic-specific polymerization of styrene was accomplished only recently.[1,2] The active Ziegler−Natta catalyst precursors found for it include a variety of Ti compounds of +4, +3,[1−3] and +2 oxidation states,[2−4] containing benzyl, phenyl, alkoxy, acac, halide, and especially monocyclopentadienyl (Cp) ligands. Zirconium compounds were also investigated,[5] epecially as a model to elucidate the insertion mechanism.[6] They are generally lower in syndiospecificity and catalytic activity than the titanium compounds. CpTi(OBu)$_3$ is a precursor with appreciable hydrolytic stability and solubility, and MAO activation converts it quantitatively to catalysts exhibiting very high activity and syndiotactic specificity.[7] An electron paramagnetic resonance (EPR) spectrum of this catalyst *under polymerization conditions* of [Ti] and [MAO] exhibits signals at g = 1.989 and 1.995, which were assigned to a syndiospecific and an aspecific Ti^{3+} species, respectively.[8] CpTiCl$_3$ and even CpZrCl$_3$ were shown to be reduced to paramagnetic products in the +3 oxidation state by MAO.[9] Consequently, Zambelli et al. proposed a multihapto-ligated Ti$^+$(III) structure for the catalytic species.[10−12] The metal ligand bonding schemes are assumed to be the same as in the X-ray molecular structures of benzyl Zr$^+$(IV) model compounds.[6,11,13−16]

However, there are catalyst systems in which a Ti$^+$(IV) complex is likely to be the active species, at least in the initial stage: Cp*TiBz$_3$/B(C$_6$F$_5$)$_3$,[17] Cp*TiMe$_3$/B(C$_6$F$_5$)$_3$,[17,18] TiBz$_4$/B(C$_6$F$_5$)$_3$,[17] and Cp*TiMe$_3$/(C$_6$H$_5$)$_3$C$^+$B$^-$(C$_6$F$_5$)$_4$.[19] Grassi, Zambelli, and co-workers studied the reductive decomposition of Cp*Ti$^+$Bz$_2$[20] and Cp*Ti$^+$Me$_2$[21] and concluded[11] that a pseudotetrahedral chiral CpTi$^+$(III) or CpZr$^+$(III) cation is the active species for

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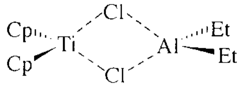
syndiotactic-specific polymerization of styrene. It should be pointed out, however, that in these instances reduction of $Ti^+(IV)$ to $Ti^+(III)$ for EPR measurements was performed on mixtures having concentrations of Ti compounds 100 or more times greater than those employed for polymerization. This could greatly accelerate the bimolecular reductive decomposition.[22] Other investigators[23,24] also have expressed preference for $Ti^+(III)$ as the active species, even when the observed catalytic activities for both $Cp^*Ti(OMe)_3$/MAO and $Cp^*Ti(OMe)_2$/MAO are very similar.

We have recently been engaged in the synthesis of η^5-L-$TiCl_3$ compounds where η^5-L's are Cp and substituted Cp,[25] indenyl (Ind) and substituted Ind,[26−28] and substituted benz[*e*]indenyl,[29] with the objectives of developing more stable and thus more productive syndiotactic-specific catalysts for styrene polymerization. It occurred to us that this series of compounds could offer a way to investigate the relationship between the titanium oxidation state and catalyst performance. The study has led to the results reported here.

Results and Discussion

The first Cp_2TiCl_2/AlR_2Cl ethylene polymerization catalyst invented by Breslow and Newburg[30] was observed to decay rapidly to an inactive trivalent complex. This deactivation process is second order in [Ti−R],[31] but the actual mechanism is complicated. Sinn and Patat[32] showed that ethane was rapidly produced, followed by the elimination of ethylene. They proposed the initial formation of a metal−CH_2−CH_2−metal intermediate. In this regard, the product of Cp_2TiCl_2 reaction with $AlEt_3$[33] was isolated, and an X-ray structural determination showed it to be



This Ti(III) complex is inactive toward ethylene polymerization.

The situation is far more complicated for the syndiotactic-specific styrene polymerization catalyst because precursors of all three common oxidation states are active for both homoleptic hydrocarbyl and mono-η^5-Cp titanium complexes. Furthermore, redox processes can transform a complex of one oxidation state into another. The present study is based on the finding that different η^5-L-$TiCl_3$ precursors exhibit different polymerization activities when compared under identical conditions. This result may be due to either differing stereoelectronic effects of the η^5 ligand or their differences in the relative rates of reduction.

Table 1. Amount of Ti(III) as Measured by EPR

η^5-L-$TiCl_3$	%Ti = Ti(III) at reaction time: 10 min	30 min	fractional increase of Ti(III)
2-(Me)$IndTiCl_3$	0.62	0.82	0.32
1-(Me)$IndTiCl_3$	1.65	2.23	0.35
$IndTiCl_3$	5.05	6.31	0.25
$H_4IndTiCl_3$a	15.6	20.4	0.31
$CpTiCl_3$	22.0	29.1	0.32

[a] $H_4IndTiCl_3$ is η^5-(4,5,6,7-tetrahydroindenyl)trichlorotitanium.

In this study, the styrene polymerization activities and EPR intensities for Ti(III) species are all measured under the *same concentrations*. The [Ti] chosen is 50 μM, at which concentration even if all the Ti(IV) precursors were reduced, there is no appreciable dipolar broadening to interfere with quantitative EPR determination. Other studies[20,21] used 200 times higher concentration of the precursors. When a concentrated toluene solution of $CpTi(OBu)_3$ (29 mM) was activated with MAO, the EPR intensity corresponds to only <43% of Ti(III) and the spectra indicate the presence of several paramagnetic species. Changes of $CpTi(OBu)_3$ concentration were also observed to markedly affect the polymerization activity.[7,8] For instance, the styrene polymerization activity at 60 °C increases from 3.84×10^6 to 32×10^6 g PS $[(\text{mol Ti})(\text{mol styrene})(\text{h})]^{-1}$ at $[CpTi(OBu)_3]$ of 1.0 mM and 100 μM, respectively. Therefore, a relationship of catalytic activity and distribution of oxidation states of Ti is meaningful only when they are determined under exactly the same conditions of [Ti], [Al], T_p, time, medium, etc.

In general the rate of polymeriztion is

$$\frac{R_p}{[\text{styrene}]} = \sum_1^n k_{p,n}(\text{IV})[\text{Ti}_n(\text{IV})] + \sum_1^n k_{p,m}(\text{III})[\text{Ti}_m(\text{III})] + \sum_1^r k_{p,r}(\text{II})[\text{Ti}_r(\text{II})]$$

where *n*, *m*, and *r* are the number of Ti(IV), Ti(III), and Ti(II) species in either the neutral or ionic state with the corresponding rate constant of propagation k_p. To a first approximation, the last term involving Ti(II) species may be neglected. The activity of $Ti(Ph)_2$/MAO is only about one-eighth of $CpTiCl_3$/MAO.[3] The activity of arene Ti(II) complex has an activity so low that a large amount of it ([Ti] = 0.27 M) was used to polymerize styrene at 30 °C.[4] The obtained activity is only about 4×10^4 g PS $[(\text{mol Ti})(\text{mol styrene})(\text{h})]^{-1}$, which is about 6300 times smaller than 2-(Me)$IndTiCl_3$/MAO, a catalyst that is composed predominantly of Ti(IV) species, and is about 400 times smaller than $CpTi(OBu)_3$/MAO, a catalyst that is composed of mostly Ti(III) species.[7]

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[22] It is well established that reduction of the catalysts occurs via a bimolecular mechanism (i.e., two Ti centers). For metallocene/aluminum alkyl catalyst systems see: (a) Chien, J. C. W. *J. Am. Chem. Soc.* **1959**, *81*, 86. (b) Olive, H. J.; Olive, S. *Angew. Chem., Int. Ed. Eng.* **1967**, *6*, 790. (c) Olive, H. J.; Olive, S. *J. Polym. Sci.; Part C* **1969**, *22*, 965. For metallocene/MAO catalyst systems see: (d) Kaminsky, W.; Steiger, R. *Polyhedron* **1988**, *7*, 2375. For $Cp^*Ti(CH_2C_6H_5)_3/B(C_6F_5)_3$ system see: ref 20. Hence, at high precursor concentrations, both the rate of reduction and the concentration of Ti(III) species should increase.

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Table 2. Styrene Polymerization Activity[a]

	activity × 10^{-7} = g PS/[(mol Ti)(mol styrene)(h)]	
η^5-L-TiCl$_3$	with preactivation	without preactivation
2-(Me)IndTiCl$_3$	24.9	16.6
1-(Me)IndTiCl$_3$	17.2	5.1
IndTiCl$_3$	15.1	3.7
H$_4$IndTiCl$_3$[b]	8.8	2.7
CpTiCl$_3$	5.46	1.4

[a] Polymerization procedures have been previously reported.[27] [b] H$_4$IndTiCl$_3$ is η^5-(4,5,6,7-tetrahydroindenyl)trichlorotitanium.

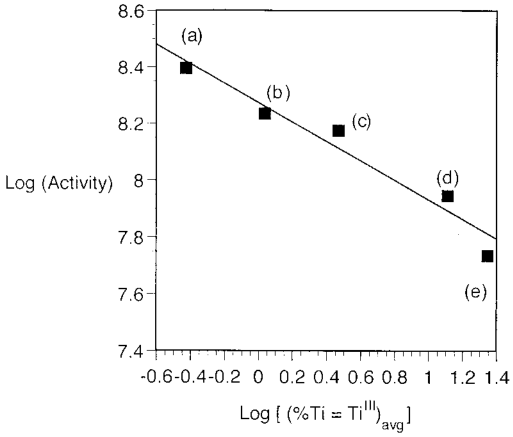

Figure 1. Plot of log(preactivated activity) vs log[(%Ti = Ti^{III})$_{av}$] for η^5-L-TiCl$_3$ catalysts. ESR samples aged for 10 min: (a) 2-(Me)IndTiCl$_3$, (b) 1-(Me)IndTiCl$_3$, (c) IndTiCl$_3$, (d) H$_4$IndTiCl$_3$, (e) CpTiCl$_3$. $f(x) = -0.343x + 8.274$; $R = 0.949$.

Table 1 summarizes the percent of Ti(III) for five η^5-L-TiCl$_3$ compounds activated by MAO, which are the average of three runs. The reaction conditions are [Ti] = 50 μM, Al/Ti = 4000, temp = 25 °C. Column 2 lists the results of 10 min of activation, while column 3 gives the amount of Ti(III) after 30 min of reaction. There is only 25%−40% more reduction of the precursor between 30 and 10 min of reaction with MAO. Since polymerizations were run between 10 and 30 min, the results indicate that further reduction of the Ti precursor after aging, which may occur during the course of a polymerization, would be less than 40%.

Table 2 summarizes the activity of the various MAO-activated precursors in styrene polymerization catalysis. Column 2 gives the activity with preactivated catalyst for 10 min of polymerization. Column 3 gives the activity with catalyst not preactivated for 30 min of polymerization.

Figure 1 is a plot of log(polymerization activity) using preactivated catalyst vs log [(%Ti = Ti(III)] after 10 min of reaction.

Figure 2 plots log(polymerization activity) of catalyst without preactivation against log [(%Ti = Ti(III)] after 10 min of stirring.

The results suggest at a first approximation that both the Ti(IV) and Ti(III) η^5-L-Ti$^+$ complexes are catalytically active and that the former may be about 10−20 times more active than the latter. This is consistent with electrophilicity of the active species[10−12] as shown by I$^+$ substituents on styrene that enhance the monomer reactivity.[34,35] Other factors such as steric and electronic effects also need to be taken into consideration. Certainly, the X-ray crystal structures of Cp*Zr$^+$(η^7-Bz)(η^3-Bz),[15] of Cp*Zr$^+$(η^1:η^6-CH$_2$CHMeCH$_2$Ph)(Bz),[16] and of (CpZr$^+$Bz$_2$)(η^5-PhCH$_2$B$^-$(C$_6$F$_5$)$_3$)[14] indicate the steric viability of η^5-L-Ti$^+$(IV)L′P active species.

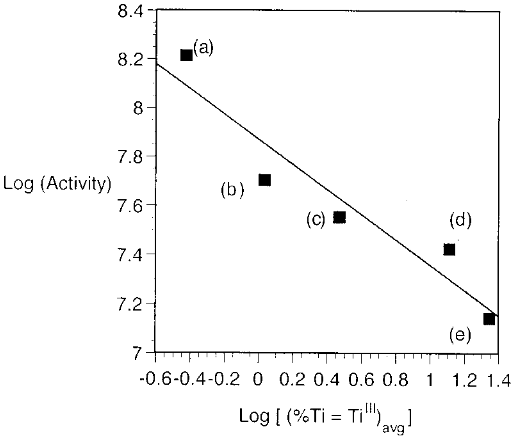

Figure 2. Plot of log(non-preactivated activity) vs log[(%Ti = Ti^{III})$_{av}$] for η^5-L-TiCl$_3$ catalysts. ESR samples aged for 10 min: (a) 2-(Me)IndTiCl$_3$, (b) 1-(Me)IndTiCl$_3$, (c) IndTiCl$_3$, (d) H$_4$IndTiCl$_3$, (e) CpTiCl$_3$. $f(x) = -0.513x + 7.871$; $R = 0.905$.

There is no strong evidence against a neutral trivalent η^5-L-Ti(III)L′P active species which is isolobal to the cationic η^5-L-Ti$^+$(IV)L′P. Even if the former is present, it is expected to be less active than the cationic species on the basis of its lower electrophilicity compared to η^5-L-Ti$^+$(III)P.[36]

There seems to be a natural preference among some Ziegler−Natta scientists to favor the single-site model for a homogeneous catalyst. This conclusion seems open to question in the cases of homoleptic hydrocarbyls and half-metallocene group IV complexes as the polydispersities of the s-PS produced from these systems[37] are quite variable and often exhibit values ≫ 2.0. Prior EPR studies[38] on activated half-metallocenes have shown the presence of s-PS active Ti(IV), s-PS active Ti(III), and s-PS inactive Ti(III) species depending on the system conditions and the investigators. The results

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(36) We submit that the formation of η^5-L-Ti(III)P and η^5-L-Ti$^+$(III)P are both possible and might both be s-PS active. However, there is experimental evidence for the formation of both s-PS active and s-PS inactive Ti(III) species.[8,21] The present EPR experiments cannot identify which Ti(III) species are formed or differentiate between s-PS active or s-PS inactive species.

(37) A single-site catalyst, an idealized situation where one active species is present, is usually indicated by a polydispersity (MWD = M_w/M_n) = 2.0. This is a necessary condition, but not a sufficient condition, for the single-site postulate. There can be a situation where there is more than one active site which have the same k_p/k_{tr} (k_p = rate of polymerization, k_{tr} = rate of chain transfer). The MWD for this case will still have a narrow polydispersity. On the other hand, if MWD > 2.5, the system must be considered multisite. Whereas, there is a preponderance of narrow polydispersities (M_w/M_n = 2.0) using half-metallocene precursors with a variety of cocatalysts,[2,12,18,20,23,39−45] there are also many instances where broad polydispersities (M_w/M_n > 2.5) were reported including CpTiCl$_3$/MAO,[3] CpTi(OBu)$_3$/MAO,[7,8] Cp*TiCl$_3$/MAO,[12,39,40] Cp*Ti(CH$_2$Si(CH$_3$)$_3$)$_3$/B(C$_6$F$_5$)$_3$/TiBA,[41] and Cp*Ti(CH$_3$)$_3$/B(C$_6$F$_5$)$_3$.[46] In addition, virtually all non-Cp-containing catalyst systems activated with MAO produced s-PS with very broad polydispersities.[3,4,12,35,47−49]

of the present study are consistent with the hypothesis of multisite catalysts.

Experimental Section

Synthesis of the catalyst precursors ($CpTiCl_3$, $H_4IndTiCl_3$, $IndTiCl_3$, 1-(Me)$IndTiCl_3$, and 2-(Me)$IndTiCl_3$) as well as their respective catalytic activities for the polymerization of styrene was described previously.[26,27] MAO was obtained from Akzo Chemicals (PMAO: S1, 9.6 wt % Al, 3.13 M in Al).

The catalyst EPR samples were prepared in 250 mL crown-capped pressure bottles sealed under inert atmosphere by injecting 47 mL of toluene, followed with 3.2 mL of MAO solution (3.1 M in toluene) and stirring for 10 min at 25 °C to scavenge impurities. The catalyst precursor (0.5 mL of 5 mM toluene solution of the Ti complex) was injected into the vessel. The resulting solution, [Ti] = 50 μM and Al/Ti = 4000, was allowed to react at 25 °C for 10 or 30 min. Afterward, 2 mL of the activated catalyst solution was transferred to a quartz Schlenk tube for recording of EPR spectra at ambient temperature.

An IBM ESP 330 spectrometer was used for this work. The spectrometer was calibrated using a series of freshly prepared α,α'-diphenyl picrylhydrazyl solutions in toluene of 200, 150, 100, 75, 50, and 25 μM concentration to a calibration curve. These solutions docompose after a few hours. The same instrument settings for cavity resonance frequency, modulation amplitude, and sensitivity were used to record the DPPH and the catalyst solutions. Double integration of the EPR signal intensity of the catalyst solution afforded, according to the calibration curve, the quantitative determination of the paramagnetic Ti(III) species. The same calibration curve was used for all measurements made on that day. A new calibration curve was constructed for measurements made on different days. The % Ti = Ti(III) observable by EPR was calculated as {[EPR intensity of Ti(III)]/[EPR intensity of 50 μM DPPH]} × 100. All the spectra are the same as previously described,[8,9] $g = 1.990$, $H_a = 7.4$ G, $Ti_a = 8.0$ G for Ti(III)−H intermediate.

Two procedures were employed for styrene polymerization.[27] It is often observed that activation of a catalyst precursor by MAO at room temperature does not occur immediately upon mixing. To eliminate any possible differences in this induction period for the various precursors and obtain a better comparison of the relative activities of the catalyst precursors, the catalyst mixture was "aged" first (or "preactivated") before exposure to styrene. Polymerization was also performed without preactivation of the catalyst. Both procedures have been described previously.[27]

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(38) Kucht et al.[19] detected no paramagnetic species present at all for the $Cp^*Ti(CH_3)_3/[(C_6H_5)_3C]^+B(C_6F_5)_4]^-$ system, a system that is highly active and syndiotactic specific for polystyrene. Ewart, Baird, and co-workers[50] found the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ system EPR silent for propylene polymerizations. Conversely, Grassi et al.[21] monitored the reduction in the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ system over a period of hours and have identified s-PS active Ti(III) and s-PS inactive Ti(III) species. Likewise, $CpTi(OBu)_3$/MAO was shown to form both s-PS active and s-PS inactive Ti(III) species,[8] while the present study suggests that at least in the early stages of the polymerization using half-metallocene/MAO systems (when significant amounts of s-PS are produced) diamagnetic Ti(IV) is also s-PS active. Taking all of these studies into consideration, one can conclude that both borane/borate-activated catalysts as well as MAO-activated catalysts are capable of being multisite depending on the specific precursor used, the amount of precursor aging, and the duration of the polymerization.

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