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Styrene Polymerization by $TpTiCl_2(OR)$ Precatalysts

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Summary

The combination of $TpTiCl_2(OR)$ (Tp = Hydrotris(pyrazolyl)borate; R = Me, Et, *i*-Pr, *n*-Bu) precatalysts with methylaluminoxane (MAO) produced active catalysts for styrene polymerization. In general, these precatalysts showed higher activities than $TpTiCl_3$. The activity and syndiospecificity of $TpTiCl_2(OR)$ were affected by alkoxyl ligands. The syndiotacticity of the polystyrenes (s-PS) obtained was in the range of 47-70 %.

Introduction

Since Ishihara and co-workers reported that $CpTiCl_3$ activated with MAO produced very active and syndiospecific catalysts for styrene polymerization [1], the half-sandwich metallocenic complexes of group 4 have been studied extensively [2-11]. Alkoxide derivatives like $CpTi(OR)_3$ [12-14], $Cp^{R'}Ti(OR)_3$ [15] and $CpTiCl_2(OR)$ [16-17] activated with MAO have been found very active for syndiotactic styrene polymerization. The catalytic activity as well as the syndiospecificity of these complexes decreased in the order: $CpTiCl_2(OR) >> CpTi(OR)_3 > Cp^{R'}Ti(OR)_3 > CpTiCl_3$. These studies showed that both electronic and steric properties of the alkoxyl and cyclopentadienyl ligands play a major role over the catalytic and syndiospecific responses of the catalysts. Also, the activity and syndiospecificity of cyclopentadienyl titanium derivatives are affected by polymerization conditions such as temperature, [Al]/[Ti] molar ratio, monomer concentration and solvent used.

The alkoxide derivatives $CpTiCl_2(OR)$ type with alkyl chain such as R = Me, Et, *i*-Pr [16-17], R = Cyclohexyl, CH_2Ph, C_6H_4-*t*-Bu-4, *n*-Bu, *i*-Bu, $CH_2CH{=}CH_2$ [18] and R = $(CH_2)_2OCH_3$, $(CH_2)_3OCH_3$, $CH(CH_3)CH_2OCH_3$, C_6H_4-OCH_3-2, Tetrahydrofurfuryl [19] have been used to polymerize styrene. The tendencies found in these studies showed that the substitution of chlorine by an alkoxyl ligand in $CpTiCl_3$ increases the catalytic activity. Catalysts containing a second alkoxyl ligand seem to be more active than those with one alkoxyl ligand. When R has an aryl group, the catalyst is less active than its aliphatic analogues. More sterically hindered R groups yield more syndiospecific catalysts.

Moreover, indenyl titanium chloride complexes such as $IndTiCl_3$ and $IndTiCl_2(OR)$ (R = Me, Et, *i*-Pr, Cyclohexyl) [20-21], have been found to mainly produce syndiotactic polystyrene (s-PS in the range of 95.9 to 99.6 %). As in the case of $CpTiCl_2(OR)$, the catalytic and syndiospecific responses of the $IndTiCl_2(OR)$ complexes are mainly affected by the electronic and steric properties of the alkoxyl and indenyl ligands. Alkoxide derivatives showed higher activities than $IndTiCl_3$. The indenyl systems seem to be less sensitive to polymerization conditions than cyclopentadienyl systems.

For the half-sandwich metallocenic titanium complexes, the following syndiospecific and catalytic order can be established $IndTiCl_2(OR) > IndTiCl_3 > CpTiCl_2(OR) > CpTiCl_3$. Like indenyl ligand, tris(pyrazolyl)borates are isoelectronic to cyclopentadienyl ligands. The tris(pyrazolyl)borates differ from cyclopentadienyl and indenyl ligands since they bind in a σ rather than a π fashion to the metal center as well as in their electronic donating properties. The donor ability of hydrotris(pyrazolyl)borate (Tp) is closer to pentamethylcyclopentadienyl (Cp*) than to cyclopentadienyl while the hydrotris(3,5-dimethylpyrazolyl)borate (Tp*) is similar to indenyl, but less electron donating than cyclopentadienyl (Cp > Ind ≈ Tp*) [22].

Nakazawa and co-workers reported that $TpMCl_3$ (M = Ti, Zr) exhibits higher catalytic activity in ethylene polymerization than the corresponding $CpMCl_3$ analogues (M = Ti, Zr). In addition, they found that Tp^RMCl_3 (R = H, Me; M = Ti, Zr) can be activated with modified methylaluminoxane (MMAO) to produce mainly atactic polystyrene (a-PS) [23]. In this kinds of complexes, Tp ligand in combination with titanium center ($TpTiCl_3$) are more suitable to improve polystyrene yield than Tp^*TiCl_3 or Tp^RZrCl_3 (R = H, Me) complexes.

Continuing with our interest to find out homogeneous catalytic applications of poly(pyrazolyl)borates complexes, herein we report the use of $TpTiCl_2(OR)$ (R = Me, Et, *i*-Pr, *n*-Bu) precatalysts activated with methylaluminoxane in the syndiotactic styrene polymerization.

Experimental

Material

All reactions and manipulations of air and / or moisture-sensitive compounds were carried out under nitrogen, using standard Schlenk line techniques or a glovebox. Styrene and toluene were purified and dried according to procedures reported in the literature [24]. The $TpTiCl_3$ and $TpTiCl_2(OR)$ (R = Me, Et, *i*-Pr, *n*-Bu) precatalysts were prepared according to the published procedure [25-26]. MAO (13.1 wt % Al, Akzo Nobel, USA) was used as cocatalyst.

Polymerization

The polymerization reactions were performed in a Schlenk containing a magnetic bar. The Schlenk was charged with an aluminoxane toluene solution (20 mL) and styrene

(12 mL). Subsequently, the Schlenk was introduced into a thermostated jacket at the polymerization temperature required (25-60 °C). 15 minutes later, the polymerization was started by injection of a toluene solution (10 mL) of the precatalyst (5 mg) and the mixture was stirred for the reaction time (1-24 h.). Once the reaction was quenched by addition of 1 % HCl solution in methanol, the polymer was filtered and washed with distilled water. After stirring the polymer in distilled water overnight, it was filtered and vacuum dried to constant weight.

Characterization

The melting temperature (T_m) of the polystyrenes was determinated in a METTLER TOLEDO, DSC822^e calorimeter, calibrated with Indium. Samples of polystyrene (5 to 10 mg) were sealed in an aluminum pan and subjected to the following steps: heating at 10 ºC/min from 25 °C to 300 ºC and, after 3 minutes at 300 ºC isothermally, cooling at 5 ºC/min from this temperature to 25 ºC, and finally, heating it at 5 ºC/min from 25 ºC to 300 ºC to obtain the melting peak temperature (T_m). The polymers were characterized by ^{13}C NMR using a JEOL 270 Spectrometer. The polymer samples were prepared in chloroform-d at 50 ºC using a 5 mm NMR tube.

Results and Discussion

Figure 1 shows $TpTiCl_2(OR)$ (R = Me, Et, *i*-Pr, *n*-Bu) and $TpTiCl_3$ complexes tested in the polystyrene polymerization.

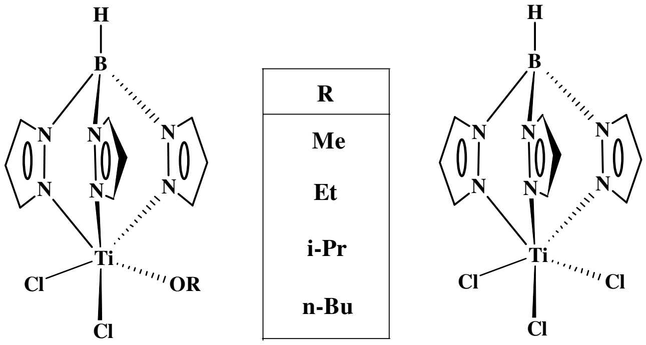

Figure 1. $TpTiCl_2(OR)$ and $TpTiCl_3$ precatalysts.

Optimization of polymerization conditions

In order to find the best conditions to produce the maximum conversion of polystyrene from $TpTiCl_2(OR)$ precatalysts the temperature, Al/Ti molar ratio and time of polymerization were optimized using $TpTiCl_2(OMe)$ as catalyst. The results are summarized in Table 1. The activation $TpTiCl_2(OMe)$ with MAO using Al/Ti molar ration between 1000-2000 (entry 1 vs 2) increases the conversion up to 2.2 %. When the temperature was changed between 25-60°C (entries 2-4), the best conversion was obtained at 25°C. Finally, the variation of time polymerization (entries 2, 5-6) showed that at 16 h the conversion raises the maximum (16.1%).

Table 1. Optimization of polymerization conditions using $TpTiCl_2(OMe)$/MAO

Entry	T (°C)	Al/Ti	Time (h)	Yield Polymer (g)	Conversion^{a,b} (%)	Activity ^{a} (g.PS/molTi.molSt.h) [A x 10^{-4}]
1	25	1000	1	0.17	1.6	11.7
2	25	2000	1	0.24	2.2	16.6
3	40	2000	1	0.18	1.6	12.4
4	60	2000	1	0.23	2.1	15.9
5	25	2000	16	1.75	16.1	7.6
6	25	2000	24	1.72	15.8	4.9

Conditions: Toluene (30 ml); P-MAO ; m_{cat}= 5 mg. ; $V_{styrene}$= 12 ml. a = Average of two run polymerization. b = (gPS.Obtained/gPS.Theoric)*100

Styrene polymerization by $TpTiCl_2(OR)$

Under the previously determinated optimization conditions the $TpTiCl_2(OR)$ (R = Me, Et, *i*-Pr, *n*-Bu) and $TpTiCl_3$ precatalysts activated with MAO were evaluated in the styrene polymerization. As seen in the Table 2, when a chlorine ligand is substituted by a methoxy group, the conversion slightly increases (entry 7 vs 8) while the ethoxy group showed the maximum conversion (entry 9). For more sterically hindered alkoxide derivatives such as *i*-propoxy and *n*-buthoxy the conversion decreases with respect to $TpTiCl_2(OEt)$ (entry 9 vs 10, 11), but still higher than $TpTiCl_3$ (entry 7 vs 10, 11). We previously determinate that $TpTiCl_2(OR)$ complexes have almost the same electronic environment around the titanium center (459.1- 460.2 eV for Ti $2p^{3/2}$) [28]. These suggest that over $TpTiCl_2(OEt)$ the alkyl chain size can be controlling the catalytic behavior, thus $TpTiCl_2(On\text{-}Bu)$ and $TpTiCl_2(Oi\text{-}Pr)$ decrease their activities because the coordination and insertion of the styrene to the metal center can be more sterically impeded than in $TpTiCl_2(OEt)$. In general, all alkoxide derivatives showed higher conversion than $TpTiCl_3$ (entry 7 vs 8-11).

Table 2. Styrene polymerization by $TpTiCl_2(OR)$/ MAO

Entry	Precatalyts	Yield Polymer (g)	Conversion $^{a,\ b}$ (%)	Activity ^{a} (g.PS/molTi.molSt.h) [A x 10^{-4}]
7	$TpTiCl_3$	1.20	11	5.2
8	$TpTiCl_2(OMe)$	1.85	17	8.0
9	$TpTiCl_2(OEt)$	2.60	24	11.2
10	$TpTiCl_2(Oi\text{-}Pr)$	2.30	21	9.9
11	$TpTiCl_2(On\text{-}Bu)$	1.75	16	7.6

Conditions: Toluene: 30 ml; P-MAO; Al/Ti= 2000; m_{cat}= 5 mg.; $V_{styrene}$= 12 ml.; T= 25 °C; t = 16 h. a = Average of two run polymerization. b = (gPS.Obtained/gPS.Theoric)*100

The polystyrene conversion of the $TpTiCl_2(OR)$ precatalysts decreases in the order: $TpTiCl_2(OEt) > TpTiCl_2(Oi\text{-}Pr) > TpTiCl_2(On\text{-}Bu) \approx TpTiCl_2(OMe) > TpTiCl_3$.

These results show that the electronic and steric effects of the alkoxyl ligands play an important role in the catalytic behavior of the $TpTiCl_2(OR)$ precatalysts. This general tendency has been found in the syndiospecific polymerization of styrene by $IndTiCl_2(OR)$/MAO (R = Me, Et, *i*-Pr, cyclohexyl) [20-21] and $CpTiCl_2(OR)$/MAO (R = Me, Et, *i*-Pr) [16-17]. The improvement of conversion by the incorporation of alkoxyl ligand in these complexes could explain why the π donation from the oxygen atom to the titanium center promotes the formation and stabilization of the active species [19]. Considering that the indenyl (Ind) and cyclopentadienyl ligands are isolectronic to tris(pyrazolyl)borates ligands [22] we can assume a similar explanation for the activity behavior of $TpTiCl_2(OR)$ precatalysts. However, the catalytic and stereospecific behavior are different. Thus, the decreasing tendencies can be established: $IndTiCl_2(OR)$ (R= Me, Et, *i*-Pr, *n*-Bu) > $IndTiCl_3$ [20-21]) > $CpTiCl_2(OR)$ (R= Me, Et, *i*-Pr, *n*-Bu) > $CpTiCl_3$ [20-21] > $TpTiCl_2(OR)$ > $TpTiCl_3$.

Polystyrene characterization

In order to determinate the stereospecificity of the polystyrenes synthesized from $TpTiCl_2(OR)$ (R = Me, Et, *i*-Pr, *n*-Bu) and $TpTiCl_3$, the polymers were characterized by ^{13}C NMR in chloroform-d at 50 °C. The polymers showed poorly solubility at the temperature used but the polymers swelled up in the solvent after a while, which permitted the characterization. In the Table 3 is summarized the percentages of isotactic, atactic and syndiotactic configurations of all polymers. Figure 2 shows the spectrum of the polystyrene produced by $TpTiCl_2(OEt)$ which is representative of those spectrums obtained from all polystyrenes. The resonance of the quaternary carbons C_1 (145.6-146.6 ppm) consist of partially resolved multiplet with a predominant peak at 145.3 ppm which can be assigned to syndiotactic configuration. The relative peak area in the range 145.6-146.6 ppm indicates that the configurations are present as following: syndiotactic 70 %, isotactic 11 % and atactic 19 %. The aliphatic region shows only two sharp peaks at 44.0 and 40.7 ppm which can be assigned to methine C_5 and methylene in a highly stereoregular environment, confirming that syndiotactic configuration prevails in the polystyrene synthesized [9].

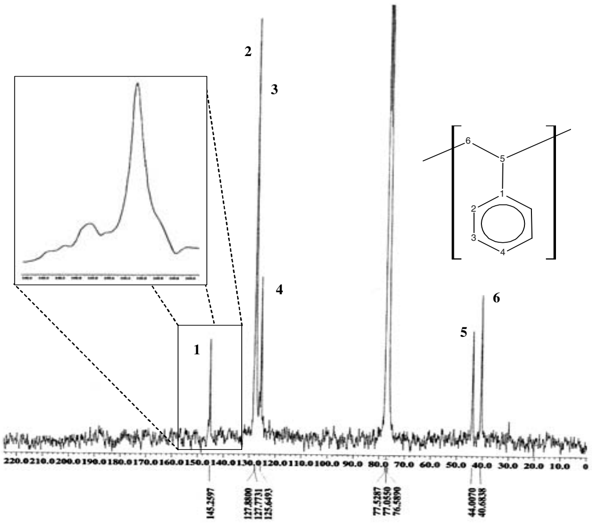

Figure 2. ^{13}C NMR of polystyrene produce by $TpTiCl_2(OEt)$.

Table 3. Tacticity of Polystyrenes synthesized from $TpTiCl_2(OR)$ and $TpTiCl_3$

Entry	Catalysts	Isotactic mm (%)	Atactic mr (%)	Syndiotactic rr (%)	T_m (°C)
12	$TpTiCl_3$	16	30	54	264.6
13	$TpTiCl_2(OMe)$	18	25	57	268.3
14	$TpTiCl_2(OEt)$	11	19	70	267.3
15	$TpTiCl_2(Oi\text{-}Pr)$	20	33	47	267.2
16	$TpTiCl_2(On\text{-}Bu)$	12	19	69	265.5

As can be seen in the Table 3, all the $TpTiCl_2(OR)$ and $TpTiCl_3$ precatalysts produce a tacticities mixture of polystyrenes where the syndiotactic configuration prevails (47-70 %). The atactic is the second configuration with 19-30 % while the isotactic with 12-20 % is the last one. The incorporation of an alkoxyl ligand to $TpTiCl_3$ enhances the syndiotacticity from 54 % up to 70 %. It seems plausible to attribute the stereospecificity differences of the precatalysts to the alkoxy groups that might sterically affect the styrene insertion. The melting temperature of the polymers obtained is characteristic of syndiotactic polystyrene.

In conclusion, this study shows that $TpTiCl_2(OR)$ derivatives with more electron donating and less steric alkoxyl ligand are more active and stereospecific for styrene polymerization than $TpTiCl_3$, and in comparison to cyclopentadienyl and indenyl derivatives the tris(pyrazolyl)borate derivatives are less active and less syndiospecific.

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