Half-Titanocene-Based Catalysts in the Syndiospecific Polymerization of Styrenes: Possible Oxidation States of the Titanium Species and Geometries of the Active Sites

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ABSTRACT: Half-titanocenes ($CpCH_2CH_2O)TiCl_2$ (**1**) and ($CpCH_2CH_2OCH_3)TiCl_3$ (**2**), (Cp = cyclopentadienyl), activated by methylaluminoxane (MAO), have been tested in the polymerization of styrene, *p*-methylstyrene, and *p*-chlorostyrene. Both catalysts produce syndiotactic polystyrene and poly-*p*-methylstyrene in the whole range of explored temperatures and concentrations. In the polymerization of *p*-chlorostyrene, however, catalyst **1** affords a syndiotactic polymer only at the low temperature and the high monomer concentrations; and catalyst **2** gives only an atactic product. The results have been compared to those obtained in the presence of the catalytic system $CpTiCl_3$ (**3**)/MAO and have been discussed considering the possible oxidation states of the titanium species and the geometries of the active sites.

Introduction

The development of homogeneous Ziegler–Natta catalysts for the polymerization of hydrocarbon monomers has provided an efficient, selective means for producing a wide variety of new polymeric materials.

Among these new materials, syndiotactic polystyrene has attracted much attention because of its high melting point (~270 °C), fast crystallization rate, low density, high modulus of elasticity and excellent resistance to heat and chemicals.[1,2]

Since the first report on its preparation by Ishihara,[3] a very large number of soluble titanium compounds in different oxidation states and a few zirconium derivatives were reported to be effective precursors for the homogeneous catalytic syndiospecific polymerization of styrene.[4−6] The most active catalysts are based upon monocyclopentadienyl-titanium compounds such as $LTiX_3$, $LTiX_2$ (where L = cyclopentadienyl, pentamethylcyclopentadienyl, or substituted cyclopentadienyl, and X = halide, alkoxide, alkyl, aryl, etc.). Moreover, cyclopentadienyl-free compounds as tetrabenzyltitanium, tetra(alkoxy)-titanium, and titanium triacetylacetonate also represent suitable precatalysts.[4a−c]

Several studies have been carried out in order to clarify the reaction mechanism and the nature of the true active species. The experimental investigations previously developed have revealed valuable information on the polymerization mechanism. In particular, it was shown that (i) the syndiospecific polymerization of styrene is a polyinsertion reaction in metal–carbon bonds,[4b,7] (ii) the regiochemistry of styrene insertion is secondary, being the growing chain bonded to the metal atom of the catalytic complex through a methine carbon,[4b,8] (iii) the addition to the monomer double bond is cis,[9] and (iv) the stereoselectivity of the insertion step is controlled by the chirality of the growing chain-end.[4a,10] These features[4,7−10] of the polymerization mechanism were corroborated by theoretical studies.[11] On the contrary, in spite of the intensive research, the nature of the real active species is still debated. In the case of catalysts based on half-titanocene precatalysts, Zambelli and Grassi,[4c,10,12a−d] by NMR and ESR experiments, proposed that the active species could be Ti(III); while Waymouth, by well-designed experiments, established that Ti(III) complexes are active precursors for syndiospecific polymerization of styrene.[12e] Detailed studies carried out by Baird and co-workers showed that a mixture of Ti(IV), Ti(III), and Ti(II) complexes is present in the polymerization medium, and all these species could be active in the syndiospecific polymerization of styrene.[13]

It is also known that even a fine-tuning of the electronic and steric properties of the monocyclopentadienyl ligand can result in a remarkable change in such catalytic properties, as activity and stereospecificity. Now, we are going to describe the catalytic behavior of two half-titanocenes ($CpCH_2CH_2O)TiCl_2$ (**1**) and ($CpCH_2CH_2OCH_3)TiCl_3$ (**2**) (Cp = cyclopentadienyl), activated by methylaluminoxane (MAO), in the polymerization of styrene and substituted styrenes. These monocyclopentadienyltitanium complexes are characterized by a dianionic bidentate ligand and a monoanionic bidentate ligand, respectively. The catalytic properties of **1** and **2** are compared with those of the classical half-titanocene $CpTiCl_3$ (**3**), where, as well-known, Cp is a monoanionic monodentate ligand.

The influence of the ligand on the catalytic behavior of these complexes in relation to the most reliable oxidation states of the active titanium species is also discussed. It is worth underlining that compounds **1** and **2**, activated by methylaluminoxane (MAO), have already been tested in both ethene–cyclopentene copolymerization[14] and butadiene homopolymerization,[15] and show a different behavior. Moreover, concerning the polymerization of styrene, **1** has not been investigated yet, while **2** has only been superficially studied.[16]

Experimental Section

General Procedure. All operations were performed under a nitrogen atmosphere by using conventional Schlenk-line techniques. Styrene and substitued styrenes were purchased from Aldrich and distilled over calcium hydride under reduced pressure and stored at −20 °C. Toluene was refluxed over sodium diphenylketyl for 48 h and distilled before use. Methylalumoxane was purchased from Witco and used as a solid after solvent distillation. Half-titanocenes ($CpCH_2CH_2O)TiCl_2$ (**1**) and ($CpCH_2CH_2OCH_3)TiCl_3$ (**2**) were synthesized according to the literature. ^1H and ^{13}C NMR analysis and elemental analysis were in agreement with data reported.[15,16a,17] $CpTiCl_3$ (**3**) was purchased from Aldrich and used as received.

Styrene and Substituted Styrenes Homopolymerization. Polymerizations of styrene and substituted styrenes were carried out following a standard procedure. A 100 mL round-bottom flask, equipped with a magnetic stirrer, was charged with MAO (based on Al) = 6.8×10^{-3} mol and the proper amount of monomer and

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Table 1. Polymerizations of Styrene (S) in the Presence of 1−3 Based Catalysts

entry[a]	complex	[S][b] (mol/L)	*T* (°C)	time (h)	yields (g)	relative activities[c]	[r][d] (%)	M_w[e] (×10^5)	M_w/M_n[e]
1	**1**	0.83	80	9.25	0.06	19.5	97.7	0.42	2.0
1′[f]	**1**	0.83	80	11	0.07	19.1	97.6	0.42	2.0
2	**2**	0.83	80	19	0.15	23.7	98.9	0.35	2.4
2′[f]	**2**	0.83	80	20	0.03	4.5	98.8	0.33	2.3
3	**3**	0.83	80	0.33	0.17	1548	94.8	0.10	1.4
4	**1**	0.83	50	19	0.28	43.1	98.5	1.62	2.3
5	**2**	0.83	50	4	0.06	43.7	98.4	0.78	2.5
6	**3**	0.83	50	0.33	1.10	10016	98.4	0.29	1.7
7	**1**	1.66	50	1.1	0.06	83.2	>99	2.27	2.0
8	**2**	1.66	50	3	0.15	75.1	>99	1.98	2.0
9	**3**	1.66	50	0.17	1.60	15851	98.3	0.62	1.4
11	**1**	0.83	25	19	0.17	27.7	99.2	3.30	2.5
12	**2**	0.83	25	19	0.09	14.2	>99	3.20	2.4
13	**3**	0.83	25	0.25	0.25	3005	98.4	0.82	1.9
14	**1**	0.83	−20	180	0.06	1	>99	6.00	1.8
15	**2**	0.83	−20	180	traces	−	−	−	−
16	**3**	0.83	−20	102	0.57	16.8	98	5.30	1.7

[a] Polymerization conditions: solvent = toluene; Ti complex = 1.36 × 10^{-5} mol; MAO (based on Al) = 6.8 × 10^{-3} mol; total volume= 20 mL. [b] Styrene concentration in the feed. [c] Activities (g of polymer/[monomer]·mol of catalyst·h) are referred to that of styrene in the polymerization conditions of entry 14, arbitrarily defined to be equal to 1. [d] Percent content of syndiotactic diads in the polymer, determined by ^{13}C NMR analysis. [e] Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard. [f] These runs were performed in the dark.

Table 2. Polymerizations of *p*-Methylstyrene (PMS) in the Presence of 1−3 Based Catalysts

entry[a]	complex	[PMS][b] (mol/L)	*T* (°C)	time (h)	yields (g)	relative activities[c]	[r][d] (%)	M_w[e] (×10^5)	M_w/M_n[e]
17	**1**	0.83	80	0.5	0.21	1222	>99	0.40	1.6
18	**2**	0.83	80	1.17	0.20	524	99.0	0.32	1.7
19	**3**	0.83	80	0.33	0.62	5636	96.0	0.11	1.4
20	**1**	0.83	50	1	0.60	1803	>99	0.66	1.8
21	**2**	0.83	50	1	0.23	691	>99	0.53	1.9
22	**3**	0.83	50	0.17	1.04	18826	>99	0.38	1.7
23	**1**	0.83	25	1	0.20	599	>99	1.10	1.5
24	**2**	0.83	25	1	0.08	249	>99	1.30	1.9
25	**3**	0.83	25	0.38	0.95	7432	99.0	0.78	1.7

[a] Polymerization conditions: solvent = toluene; Ti complex = 1.36 × 10^{-5} mol; MAO (based on Al) = 6.8 × 10^{-3} mol; total volume= 20 mL. [b] *p*-Methylstyrene concentration in the feed. [c] Activities (g of polymer/[monomer]·mol of catalyst·h) are referred to that of styrene in the polymerization conditions of entry 14 in Table 1, arbitrarily defined equal to 1. [d] Percent content of syndiotactic diads in the polymer, determined by ^{13}C NMR analysis. [e] Molecular weight and polydispersity index (M_w/M_n) determined by gel permeation chromatography versus polystyrene standard.

Table 3. Polymerizations of *p*-Chlorostyrene (PCS) in the Presence of 1−3 Based Catalysts

entry[a]	complex	[PCS][b] (mol/L)	*T* (°C)	time (h)	yields (g)	relative activities[c]	[r][d] (%)	M_w[e] (×10^4)	M_w/M_n[e]
25	**1**	0.83	80	26.2	0.28	32.1	−	4.6	2.1
26	**2**	0.83	80	19	0.19	29.9	−	0.8	1.4
27	**3**	0.83	80	6.9	0.17	74.8	−	0.7	1.6
28	**1**	1.66	80	25.5	0.91	54.9	−	11.0	2.0
29	**2**	1.66	80	25.5	0.81	47.4	−	12.7	1.4
30	**3**	1.66	80	7.8	0.85	149.6	−	1.8	2.0
31	**1**	1.66	50	24	0.09	55.1	−	20.6	1.6
32	**2**	1.66	50	24	0.43	26.9	−	20.3	1.6
33	**3**	1.66	50	24	0.54	33.8	−	1.2	1.6
34	**1**	1.66	25	38	0.05	1.8	−	20.6	2.0
35	**2**	1.66	25	38	0.09	3.7	−	21.9	2.0
36	**3**	1.66	25	38	0.13	5.1	97.7	1.1	1.8
37	**1**	3.33	25	119	0.20	1.2	−	20.2	1.8
38	**2**	3.33	25	119	0.31	1.9	−	22.5	2.1
39	**3**	3.33	25	26	0.22	6.3	98.8	1.6	1.9
40	**1**	6.66	25	18	0.10	2.1	81.9	22.2	1.9
41	**2**	6.66	25	9	0.18	7.7	−	26.3	2.4
42	**3**	6.66	25	9	0.45	18.7	98.7	2.5	2.0

[a] Polymerization conditions: solvent = toluene; Ti complex = 1.36 × 10^{-5} mol; MAO (based on Al) = 6.8 × 10^{-3} mol; total volume= 20 mL. [b] *p*-chlorostyrene concentration in the feed. [c] Activities (g of polymer/[monomer]·mol of catalyst·h) are referred to that of styrene in the polymerization conditions of entry 14 in Table 1, arbitrarily defined equal to 1. [d] Percent content of syndiotactic diads in acetone insoluble fractions, determined by ^{13}C NMR analysis. [e] Molecular weight and polydispersity index (M_w/M_n) of unfractionated polymers determined by gel permeation chromatography versus polystyrene standard.

toluene (see Table 1−3). The flask was thermostatted at the reaction temperature, and the run was started by introducing 1.3 × 10^{-5} mol of the appropriate half-titanocene complex dissolved in 2 mL of toluene. The temperatures of the reactions were monitored and kept constant during all the runs, as specified in Tables 1−3. Polymerizations were stopped by introducing a few milliliters of methanol, then the mixture was poured into acidified ethanol. The polymer was recovered by filtration, washed with fresh ethanol and dried in vacuum at 60 °C.

Fractionations. Styrene and substituted styrene polymers were fractionated by sequential exhaustive extractions with boiling acetone and with boiling 2-butanone in a Kumagawa extractor.

Measurements. *^{13}C NMR Analysis.* ^{13}C NMR spectra were recorded on an AV 300 Bruker spectrometer operating at 75 MHz,

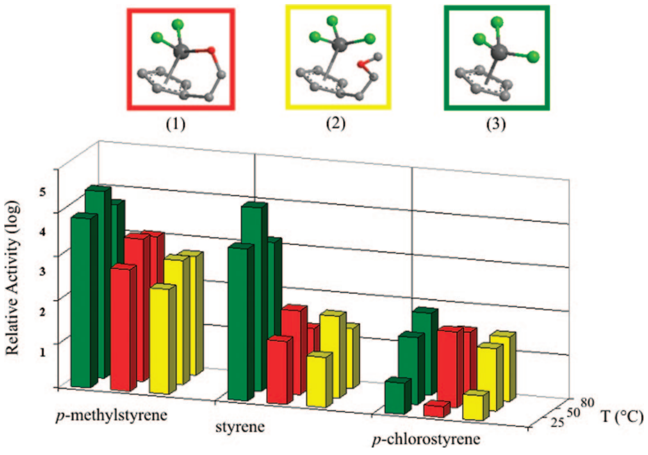


Figure 1. Polymerizations of styrene, *p*-methylstyrene and *p*-chlorostyrene with **1**−**3**/MAO catalytic systems at different temperatures. Conditions: $c_{\mathrm{monomer}} = 0.83$ mol/L; toluene = 20 mL; Ti = 1.36×10^{-5} mol; MAO (based on Al) = 6.8×10^{-3} mol.

using an inverse-gated-decoupling mode in order to eliminate the nuclear Overhauser effect (NOE) and, therefore, to assume that the areas of the resonances of the ^{13}C NMR spectra were proportional to the amounts of the different carbons. The following ^{13}C NMR acquisition parameters were used: acquisition time AQ = 1.2 s, pulse delay D1 = 4 s and pulse angle P1 = 8.25 μs (90°). The samples were prepared by dissolving a polymer sample (40 mg) into tetrachloro-dideuterio-ethane (0,5 mL). The spectra were recorded at 100 °C using hexamethyldisiloxane (HMDS) as an internal chemical shift reference. The resonances were assigned according to the data reported in the literature.[4a,10] The concentration of *r* diads in the polymers were calculated by the following equation:

$$[r] = \{[rrr] + [mrm] + [rrm]\}/\{[rrr] + [mrm] + [rrm] + [mmm] + [mmr] + [rmr]\}$$

Gel Permeation Chromatography (GPC) Analysis. The analysis of the samples were performed at 135 °C by Waters instrument GPCV 2000 equipped with refractive index and viscosimeter detectors, using a set consisting of four PSS columns: 10^5, 10^4, 10^3, 10^2 Å (pore size) with 10 μm (particle size). *o*-dichlorobenzene was the carrier solvent used with a flow rate of 1.0 mL/min. The calibration curve was established with polystyrene standards.

Results and Discussion

After activation by MAO, half-titanocene complexes **1**−**3** were used in polymerization tests with styrene, *p*-methylstyrene and *p*-chlorostyrene.

The effect of the temperature, ranging from −20 to +80 °C, on the catalytic activity of complexes **1**−**3** was investigated, and the results are reported in Table 1. Due to low conversion the yields are roughly proportional to the polymerization rates, so the activities appear to decrease in the order **3** > **1** ≥ **2**, and they significantly depend on the polymerization temperature, as shown in Figure 1.

All catalysts disclose their highest activity at 50 °C, while at 80 °C they are less effective, perhaps because of the decomposition processes of the active species. **1**−**3** are different with **3** being more active than both **1** and **2** by 2 orders of magnitude at 80 °C. At 50 °C, **3** becomes more active than both **1** and **2** by 3 orders of magnitude (see Figure 1) whereas at −20 °C **3** differs from **1** by 1 order of magnitude while **2** is practically inactive. These findings suggest that, at 50 °C, **3** gives a higher amount of active species than at −20 °C, while the effect of temperature is less important for **1**. More significantly, at −20 °C, the activation reaction of **2** with MAO is actually unproductive. As mentioned above, the true active species derived from half-titanocene precatalysts was proposed to be the Ti(III) [Cp′TiR]$^+$ cationic complex (Cp′ = any η^5 ligand), derived from Cp′TiX$_n$ precursor through non-Cp ligand removal and reduction by MAO.[12] According to this proposal, it seems reasonable to think that MAO, at −20 °C, is able to give alkylation and cationization of the half-titanocenes **1**−**3** but it is not able to accomplish a reduction reaction. While activation of **1** for the polymerization reaction can occur only by alkylation and cationization reactions, activation of **2** and **3** probably needs also a reduction of the metal. This means that, at low temperatures (e.g., −20 °C), a minor amount of catalytic species is formed because the reduction of the metal could not likely take place. The difference of reactivity between **1** and **3** becomes less considerable while the catalyst based on **2** results is practically inactive.

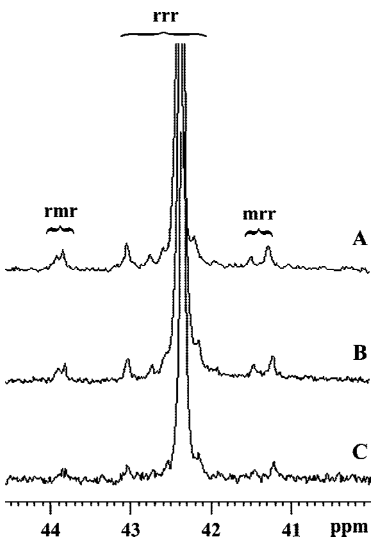


Figure 2. Methylene region of ^{13}C NMR spectra of polystyrene samples, obtained at 80 °C with the following: (A) **2**/MAO (entry 2 of Table 1); (B) **1**/MAO (entry 1 of Table 1); (C) **3**/MAO (entry 3 of Table 1). δ is given in ppm from hexamethyldisiloxane.

All the polymers are insoluble in both boiling acetone and boiling 2-butanone, and they have a highly syndiotactic microstructure as determined by the ^{13}C NMR analysis. The aliphatic region of spectra of polymers with **1**, **2**, and **3** (see Figure 2) presents intense resonances in the range of chemical shift from 43.4 to 42.2 ppm due to methylene carbon atom, attributable to *rrr* tetrads.

A careful check of the methylene region of ^{13}C NMR spectra of different samples obtained by **1**−**3**/MAO catalysts do not show signals attributable to *mmm* or *mmr* stereochemical tetrads, but only resonances due to *rrr*, *rmr*, and *rrm* tetrads (see Figure 2). This fact is in agreement with chain-end stereocontrol, and the areas of the resonances show that the statistical model of the syndiospecific propagation is always first order Markovian, no matter what catalyst is used.[4a,10]

As reported in the Experimental Section, the syndiotacticity of polystyrenes was determined by estimating the area of tetrads. At 80 °C the catalytic system based on CpTiCl$_3$ discloses the lowest stereospecificity (compare entries 1−3). When the polymerization is carried out at 50 °C, the stereoregularity of polymers obtained by **1**−**3** is about 98% (entries 4−6). Moreover, increasing the concentration of the styrene in the feed from 0.83 mol/L to 1.66 mol/L (entries 7−9), the polymers obtained by **1** and **2** do not present stereoerrors, being the concentration of [*rrr*] syndiotactic tetrad higher than 99%.

Gel permeation chromatography traces of polystyrenes are all monomodal with moderately narrow-molecular weight distributions, consistent with single-site catalysts. The molecular weight of the polymers increases with the increase of the monomer concentration in the feed. Complex **1** produces higher molecular weights than **2** and **3** under the same experimental conditions (entries 1−3). As expected, higher polymerization temperatures induce a decrease of M_w values.

Half-titanocenes **1**−**3**, combined with MAO, were also used in the polymerization tests with substituted styrenes at different temperatures (25, 50 and 80 °C).

The results of polymerizations of *p*-methylstyrene (PMS) are summarized in Table 2. All the catalytic systems produce highly stereoregular polymers insoluble in both boiling acetone and 2-butanone with a fraction of [*r*] diads, evaluated by ^{13}C NMR analysis, ≥99%. A slight decrease of stereoregularity is detected for the polymer obtained in the presence of **3** at 80 °C. A comparison between data of Table 1 and Table 2 indicates that, under identical reaction conditions, the catalytic activities of **1**−**3** in the polymerization of *p*-methylstyrene exceed those of styrene homopolymerization and are in the order **3** > **1** > **2** (see Figure 1).

The gel permeation chromatography analysis of all poly(PMS) samples shows monomodal molecular weight distributions with polydispersity indexes lower than two, consistent with a possible single-site nature of the catalysts.

Table 3 reports the results of *p*-chlorostyrene (PCS) polymerizations. The relative activities of **1**−**3** were very similar, the difference being lower than 1 order of magnitude; moreover, they seem scarcely affected by polymerization temperature (as depicted in Figure 1). By comparing the relative activities of **1**−**3** (reported in Tables 1−3), it is apparent that the PCS has a lower reactivity than PMS and S. The ^{13}C NMR spectra of poly(PCS) samples show poor stereoregular microstructures; in a few cases, hexaustive extraction of crude polymers by boiling acetone and by boiling 2-butanone allows the isolation of an insoluble stereoregular fraction (entries 36, 39, 40 and 42).

From data reported in Table 3, one can observe that:

- Only at 25 °C and at a high concentration of monomer (entry 40), the catalytic system based on **1** gives rise to a polymer with a 20% of boiling-acetone insoluble fraction having 82% of [*r*] diads.
- In all the tested conditions, catalytic precursor **2** produces a polymer substantially atactic and soluble in boiling acetone (entries 26, 29, 32, 35, 38 and 41).
- Only at 25 °C, both at high and at low PCS concentrations, precatalyst **3** gives rise to polymers with a considerable boiling acetone insoluble fraction (around 70%). These fractions are highly stereoregular with a concentration of [*r*] diads >97% (e.g., see entries 36, 39, 42).

In Figure 3 methylene regions of samples obtained at 25 °C are reported.

The molecular weights of the polymers increase while decreasing the polymerization temperature, whereas, they are minimally influenced by monomer concentration (e.g., compare entries 34−36 with 40−42). Additionally, the GPC traces show unimodal molecular weight distributions (close to 2) consistent with single-site catalysts.

Judging from the polymerization results described so far, one can infer that: i) half-titanocene compounds **1**−**3** produce single site catalysts able to polymerize PMS, S and PCS; ii) the polymers obtained with **1**−**3** show a different stereoregularity. Moreover, under comparable conditions, poly(PMS) are more syndiotactic than poly(S), while poly(PCS) are prevailingly stereoirregular.

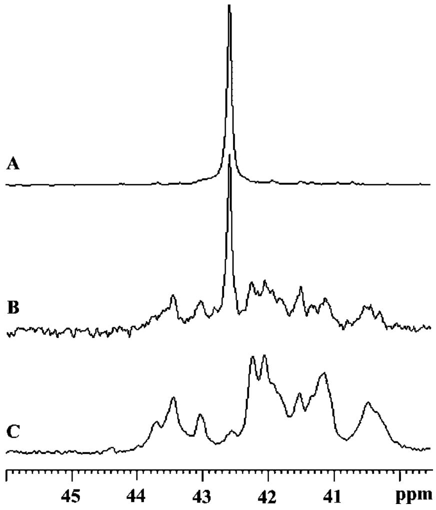
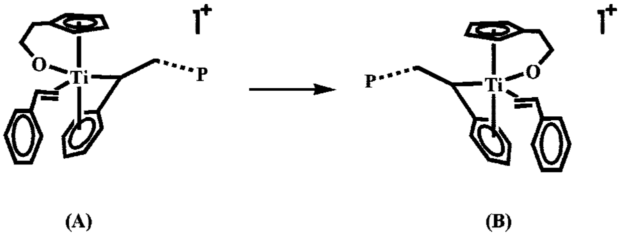


Figure 3. Methylene region of ^{13}C NMR spectra of poly(*p*-chlorostyrene) samples, obtained at 25 °C with the following: (A) **3**/MAO (entry 42 of Table 3), (B) **1**/MAO (entry 40 of Table 3), and (C) **2** /MAO (entry 41 of Table 3). *δ* is given in ppm from hexamethyldisiloxane.

Scheme 1. Incorporation of the Coordinated Monomer and Stereospecific Coordination of a New Styrene Molecule Give Rise to a Mirror Related Active Species



In order to reach a better understanding of the behavior shown by a catalytic system based on **1**−**3**, it is worth recalling that the syndiospecific polymerization mechanism of styrene and substituted styrenes was reported to occur as a sequence of the following events:[10,11]

(i) η^2-coordination of a monomeric unit to the metal bearing the ancillary ligand and the growing chain. The latter is bonded to the metal by methine carbon and by the coordination of the aromatic ring of the last enchained unit.

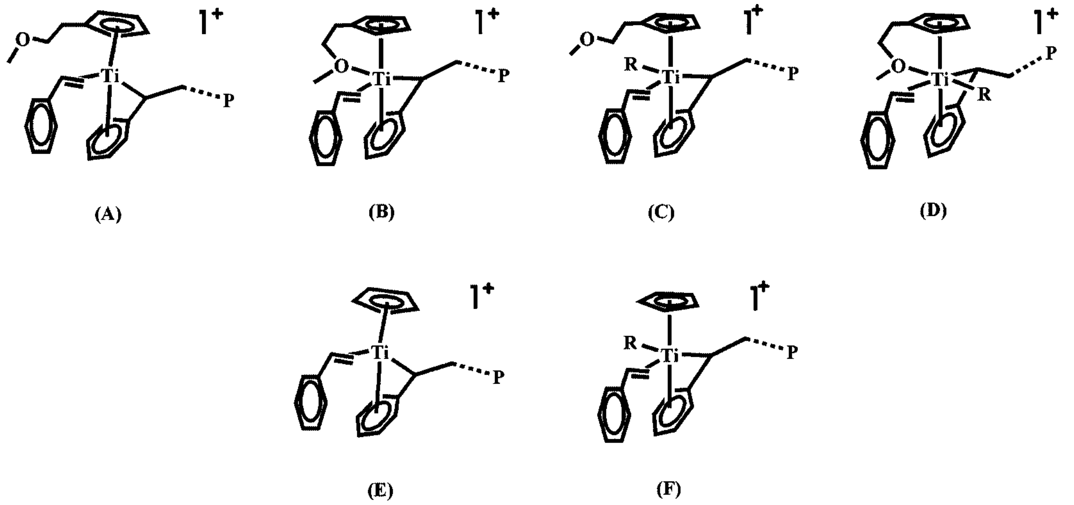
(ii) Nucleophilic substitution of arene coordinated.

(iii) Insertion of incoming monomer.

Thus, the different reactivity of monomers (PMS is more reactive than S, which is more reactive than PCS) could be rationalized considering that the electronic density on the vinyl double bond of the monomer decreases, turning from an electron-releasing methyl to an electron-withdrawing chlorine substituent of the aromatic ring. A similar trend was previously observed both for the syndiotactic[10,18] and isotactic polymerization of styrene.[19]

Syndiotactic propagation occurs according to a first-order Markovian statistical model, and with regard to stereoregularity of polymers, we can consider that the formation of a syndiotactic diad deriving from a chain-end stereocontrol always requires the η^n interaction ($n \geq 2$) of the aromatic group of the last enchained unit with the metal. In this framework, the insertion of the incoming monomer and the following nucleophilic substitution of the arene coordinate, produces an inversion of the absolute configuration of the metal atom, resulting in the coordination of a new monomeric unit with opposite face in respect to the last inserted unit.[10,11b] Since occasional configuration inversions to the metal atom can derive from a lacking of a coordinated aromatic ring in the last inserted monomer unit of the growing chain, the configuration of the titanium will be retained as the electronic density of the aromatic ring increases, resulting in a superior stereoregularity of poly(PMS) in respect

Scheme 2. Possible Active Species Based on Compound 2 (A−D) and 3 (E, F) Considering Different Oxidation States of Titanium



(A) (B) (C) (D) (E) (F)

to poly(S) and poly(PCS). Moreover, insertion of a monomer coordinated by its wrong enantioface would leave the configuration of both Ti and the growing chain end unchanged, giving rise to isolated *m* diads in the polymer chain.[4a,10]

According to this stereochemical reaction mechanism, a very strong influence on the stereospecificity is operated by the size of the η^5 anionic ligand of the metal. In fact, (indenyl)$TiCl_3$, η^5-(methylcyclopentadienyl)$TiCl_3$, and (pentamethylcyclopentadienyl)$TiCl_3$[10] are more stereospecific than $CpTiCl_3$ because they experience severe nonbonded interactions among the incoming monomer and ligand. Therefore, the substituent on the cyclopentadienyl ring for both **1** and **2**, gives rise to catalysts more stereospecific than that obtained with the **3**-based catalyst (e.g., see entries 1−3).

Further considerations on the oxidation state of metal and on different geometries of the catalytic site are indispensable. In fact, as a consequence of the nature of the ligands and of possible oxidation states of the titanium, the active species of **1**−**3** could present different geometries.

Compound **1**, which has a dianionic bidentate ancillary ligand, in combination with MAO, should be alkylated and cationized. This has often been reported as the activation reaction for group 4 metallocenes in the olefin polymerization.[20−22] Hence, if the syndiospecific polymerization of styrenes in the presence of the **1**-based catalyst occurs by the previously reported sequence of events, the preinsertion species will be a pentacoordinate complex of Ti(IV). The hypothesis that the oxidation state of the metal in the active species is IV, is supported by polymerization experiments performed in the dark, with identical results to those performed in light (compare entry 1 with entry 1′ of Table 1). Assuming η^n coordination of the aromatic ring of the last inserted monomeric unit ($n \leq 6$), the cationic complex could reach even 18 electrons (see Scheme 1A).

The incorporation of the monomer would occur by cis-migratory insertion and by a nucleophilic substitution of the phenyl of the last unit of the growing chain by the aromatic ring of the newly incorporated unit. The subsequent enantioselective coordination of a new styrene unit leads to the mirror related co-ordination complex with configuration inversion at Ti, at the methine bonded to the metal and, of course, at the enantioface of the new coordinated monomer (see Scheme 1).[10,11]

More intricate is the situation relative to compound **2**, having a monoanionic bidentate ancillary ligand. In this case, the reaction of MAO with **2** could also give rise to the reduction of the metal together with alkylation and cationization, and, the resulting metal cation, both in the oxidation state +3 and +4, would possess the metal−carbon bond necessary for the insertion reaction. Titanium(III) and titanium(IV) species, depending on the possible coordination of pendant oxygen of the cyclopentadienyl−ethene−methoxy ligand, should have different geometries. The preinsertion species of Ti(III) is tetracoordinate when the ligand ($CpCH_2CH_2OCH_3$) is coordinated only by cyclopentadienyl, and its behavior should be similar to the active species derived from $CpTiCl_3$ (compare scheme 2A and scheme 2E).[10]

Obviously, the oxygen of the $CpCH_2CH_2OCH_3$ ligand can compete with the phenyl group of the last-inserted monomeric unit for the coordination to titanium. This competition could be unfavorable when the aromatic group of the last unit of the growing chain end has a high electronic density and, according to the proposed mechanism, could imply the production of stereoregular polymers from S and PMS. Instead, when styrenes with aromatic rings having electron-withdrawing substituents (e.g., PCS) are involved, the stereocontrol mechanism could be perturbed by the competition between the oxygen of the $CpCH_2CH_2OCH_3$ ligand and the phenyl group of the last inserted unit of the growing chain. This competition would hamper the expected stereochemical outcome of the polymerization reaction, making ineffective the nucleophilic substitution of the coordinate aromatic ring which controls the absolute configuration of the metal. As a consequence, the polyPCS obtained with this catalytic system is essentially stereoirregular.

When $CpCH_2CH_2OCH_3$ acts as a bidentate ligand through the cyclopentadienyl ring and the methoxy group, the preinsertion species of Ti(III) becomes pentacoordinate and its behavior should be similar to the species derived from compound **1** (compare Scheme 2B and Scheme 1A).

It is also reasonable to consider the catalytic species of Ti(IV), as more electrophilic than that of Ti(III) and, therefore, more active. Obviously, regarding the oxidation state for species derived from compound **2** as III, and that of compound **1** as IV, the latter should be more electrophilic and, therefore, it would be more active. In the preinsertion step, if compound **2** is only alkylated and cationized by MAO, it should gives a penta-coordinate species when the oxygen is not coordinate to the metal (see Scheme 2 C) and consequently a behavior similar to **1**, whereas, when the oxygen is coordinate to the metal it gives an octahedral species (see Scheme 2 D). The latter could not be active, because at low temperature the fluxionality of the ether group of the $CpCH_2CH_2OCH_3$ ligand is not favorable so a stable coordination of oxygen to the metal could be achieved. This coordinatively and electronically saturated species is not able to polymerize styrene (see entry 15 in Table 1). On the other hand the hypothesis that the reduction of the metal is necessary in order to obtain a catalytically active species is supported by the polymerization experiments performed in the dark which had different results than those of runs performed in the light (compare entry 2 with entry 2′ of Table 1).

Compound **3** reacting with MAO is likely alkylated and cationized; moreover, as already reported, it should at least partially give a Ti(III) species responsible for styrene polymerization.[12] In addition, the hypothesis of a Ti(IV) species catalytically active cannot be ruled out.[13] According to these observations, in preinsertion step the Ti(III) species should be tetracoordinate (see Scheme 2E), whereas the Ti(IV) species should be pentacoordinate (see Scheme 2F).

Conclusions

Half-titanocenes $\mathrm{(CpCH_2CH_2O)TiCl_2}$ (**1**) and $\mathrm{(CpCH_2CH_2OCH_3)TiCl_3}$ (**2**), activated by MAO, are able to polymerize both styrene and substituted styrenes. Polymerization results have been compared to those obtained in the presence of half-titanocene $\mathrm{CpTiCl_3}$ (**3**). All the systems produce highly syndiospecific single site catalysts for the styrene and *p*-methylstyrene polymerization. On the contrary, in the polymerization of *p*-chlorostyrene, catalysts **1** and **3** are stereospecific, at least at a low temperature (25 °C) and at high monomer concentrations, whereas catalyst **2** produces only atactic polymer.

The obtained results, unfortunately, do not provide any unimpeachable evidence concerning the oxidation state of the titanium species competent for syndiotactic-specific polymerization of styrene, but they add supplementary elements to better understand the nature of the true active species.

Thus, according to Baird,[13c] the role of titanium(III) is in doubt. Perhaps different oxidation states of active titanium species can produce syndiotactic polystyrene, depending on coordinated ancillary ligands. Considering that compound **1** has a dianionic bidentate ancillary ligand, it could polymerize only if its oxidation state is +4. Moreover, as the stereoregularity of the polymers is influenced by the electronic properties of examined styrenes and the statistical model of propagation is always first order Markovian, we suggest that (i) the preinsertion complex should be pentacoordinate, and (ii) syndiotactic propagation would occur according to the proposed mechanism for styrene polymerization in the presence of monocyclopentadienyl titanium complexes (e.g., $\mathrm{CpTiCl_3}$).[12]

The stereospecificity of the catalytic system based on **1** would arise from the nonbonded interactions between the Cp ligand and the η^2-bonded styrene, and from the fact that syndiotactic insertion would produce a configuration inversion at the cation through nucleophilic substitution of the η^n coordinated arene ($2 \le n \le 6$) of the last inserted unit of the growing chain. Compound **2**, which bears a monoanionic bidentate ligand, can provide active species either in the oxidation state +3 or +4. Evidently, the coordination geometries for these species are strongly conditioned by the fluxionality of the ether moiety of the $\mathrm{CpCH_2CH_2OCH_3}$ ligand: (i) in the oxidation state +3, the catalytic species would be tetracoordinate when the oxygen is not bonded to the metal, and pentacoordinate when the oxygen is bonded to the metal; (ii) in the oxidation state +4, the catalytic species would be pentacoordinate when the oxygen is not bonded to the metal and hexacoordinate when the oxygen is bonded to the metal. The latter species is catalytically inactive. Compound **3** presenting a monoanionic monodentate ligand can give active species both in the oxidation state +3 and +4, with consequent titanium coordination numbers 4 and 5, respectively.[13]

Since each of the catalysts produce polystyrenes with a molecular weight distribution close to 2, we can conclude that by the reaction of **1**−**3** with MAO only one active species is able to promote the polymerization of styrene and substituted styrenes. Accordingly, we can assume that Ti(IV) is the active species when the catalytic precursor is compound **1**, whereas both Ti(III) and Ti(IV) active species can be produced by activation of **2** and **3** with MAO. Nevertheless, as compound **2** is inactive at −20 °C and compound **3** shows an activity close to **1**, most likely in these cases, as reported by Zambelli and Waymouth, the oxidation state of the active species could be Ti(III).

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