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Syndiospecific Styrene Polymerization Promoted by Half-Titanocene Catalysts: A Kinetic Investigation Providing a Closer Insight to the Active Species[†]

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ABSTRACT: Syndiospecific styrene polymerization promoted by mixtures of Cp^*TiR_3 ($R = CH_3$, CH_2Ph) with MAO, $B(C_6F_5)_3$, and $CPh_3B(C_6F_5)_4$ has been investigated by means of conventional kinetic methods. A first-order kinetics of the monomer in the propagation rate has been determined at 25 °C. At polymerization temperatures higher than 50 °C, the β-H migration from the growing polymer chain to the metal of the active species appears to be the main termination reaction. The average molecular weights of the polymer products depend on the type and coordinating behavior of the counterions ($[MAOX]^-$, $[MeB(C_6F_5)_3]^-$, $[(PhCH_2)B(C_6F_5)_3]^-$). The trityl-activated catalysts produce sPS samples with the highest molecular weights. The comparison of the molar concentrations of the active species, determined by kinetic methods, with those of $Cp^*Ti^{III}R^+$ ($R = CH_3$, CH_2Ph) evaluated in the polymerization conditions by ESR measurements, confirms the involvement of these complexes in syndiospecific styrene polymerization.

Introduction

The discovery of syndiotactic polystyrene (sPS) by Ishihara at IDEMITSU Kodan Co.[1] opened a new field in stereospecific polymerization. The great interest on sPS arises in view of practical applications of this new thermoplastic polymer in different fields.[2] A wide variety of catalytic systems based on titanium and zirconium organometallic complexes, highly active in syndiospecific styrene polymerization, has been reported in the literature[3] among which cyclopentadienyl and substituted cyclopentadienyl derivatives of titanium, $Cp'TiR_3$ ($Cp' = C_5H_5$, C_5Me_5 and R = halide, alkyl, alkoxyl) appear the most interesting.[2b] Recent examples of these catalysts include (indenyl)$TiCl_3$[4] and substituted indenyl derivatives[5] activated with a large excess of methylaluminoxane (MAO). Electron-releasing substituents on the cyclopentadienyl ligand yield catalysts with higher polymerization activities.[2b,5] Replacement of alkyl or alkoxy for chloride ligands in the coordination sphere of titanium does not appreciably affect the productivity and the stereospecificities of these systems.[2,6]

A novel class of catalysts for the sPS production is represented by tris(hydrocarbyl)(pentamethylcyclopentadienyl) derivatives of titanium, Cp^*TiR_3, activated with 1 equiv of strong Lewis acids such as $B(C_6F_5)_3$[7] or $Ph_3CB(C_6F_5)_4$.[8] These catalysts, strongly related to $Cp'TiR_3$/MAO systems, show high productivity and stereospecificity in sPS polymerization. These simple systems attracted our attention in view of spectroscopic and kinetic investigations to obtain a closer insight into the structure and the polymerization behavior of the active species.

The reaction of Cp^*TiR_3 ($R = CH_3$, CH_2Ph) with 1 equiv of $B(C_6F_5)_3$ or $Ph_3CB(C_6F_5)_4$ results in alkyl abstraction from the titanium complex producing in a few seconds at room temperature the $Cp^*TiR_2^+$ cations with $[RB(C_6F_5)_3]^-$ [9] or $[B(C_6F_5)_3]^-$ [8] counterions, respectively. By ESR (electron spin resonance) spectroscopy investigation of this reaction, we discovered that $Cp^*TiR_2^+$ complexes decompose to Cp^*TiR^+ in the polymerization condition.[10] The molar concentration of the Ti(III) complex is roughly 1% of the total titanium but it increases to 10% after the addition of styrene.[11] The extent of the reduction depends on the concentration of the monomer. In the ESR spectrum of the ^{13}C-enriched methyl system ($Cp^*Ti(^{13}CH_3)_3/B(C_6F_5)_3$) we assigned to $Cp^*Ti(^{13}CH)_3^+$ a doublet due to the coupling of the Ti(III) unpaired electron with one ^{13}C nucleus (spin = $^1/_2$). After the addition of styrene this signal was replaced by a new one without any nuclear spin coupling. We attributed the latter signal to the polymerizing species produced through the insertion of the styrene unit into the $Ti-^{13}CH_3$ bond. These findings moved us to propose the Cp^*TiR^+ cation as the active species in syndiospecific styrene polymerization.[11]

To support these data, we carried out a kinetic investigation of these systems in order to have some more information on the concentration and polymerization behavior of the active species.

Results and Discussion

Kinetics of the Polymerization and Evaluation of the Molar Concentration of the Active Species. Several data in the literature support an Arlam−Cossee mechanism in syndiospecific styrene polymerization. The polymerization proceeds through a 2,1 polyinsertion reaction of the styrene units into the Ti−polymer bond.[3a,6,11,12] Preliminary GPC (gel permeation chromatography) investigation of sPS samples obtained with half-titanocene-based catalysts showed that the polydispersity of these polymers is about 2, indicating that

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a single polymerizing species is active in these systems.[3e] According to this picture, the kinetic equation for the propagation reaction rate *R* is the following:

$$R = kC^{*}[\mathrm{S}]^{\alpha} \tag{1}$$

where k, C^*, [S], and α are the specific kinetic constant of the propagation reaction, the molar concentration of the active sites, the styrene molar concentration and the reaction order of the monomer, respectively. Assuming that C^* is almost constant, the yields of the polymers produced at low conversion are proportional to the polymerization rate and the bilogarithmic plot of the yields (Y) versus styrene molar concentration ([S]) can provide the α value. We applied this analysis to the styrene polymerization at 25 °C in the presence of the following catalytic systems: $Cp^*Ti(CH_2Ph)_3/MAO$, $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$, $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$, and $Cp^*Ti(CH_3)_3/Ph_3C^+B(C_6F_5)_4^-$. In most of the polymerization runs performed without MAO, triisobutylaluminum (TIBA) was used (Al/Ti = 4:1) as scavenger of the monomer and solvent impurities. The addition of the aluminum organyl did not dramatically affect the productivity of the systems. We carried out kinetic measurements using a styrene molar concentration in the range 0.1−1 M and polymerization time equal to 10 min.

In all considered cases the plot of Y versus [S] is linear, suggesting a first-order kinetics with respect to the monomer (see Figure 1) and that C^* is roughly constant when polymerizations are run at 25 °C and for times as short as 10 min or less. Similarly, the bilogarithmic plot of Y versus [S] is linear and shows $\alpha = 1$ in all cases (Figure 2). In a previous paper, an α value greater than 1 was observed for the less active TiR_4−MAO catalytic systems (R= OC_4H_9, CH_2Ph). This finding was explained on the basis of a competition between the solvent and monomer for coordination to the metal of the active species.[13] The different behavior between TiR_4- and $Cp'TiR_3$-based catalysts suggests a different structure of the active species in these systems.[6] The polydispersity (M_w/M_n) of the polymers obtained with the title catalysts is about 2 (see Table 1) and appears too large compared with that expected for a "living polymerization",[14] but the number average molecular weights, M_n, of the sPS samples produced at 25 °C increase almost linearly with both polymerization time and monomer concentration (see Tables 1 and 2), especially in the case of the benzyl catalysts at low styrene concentration and at short polymerization time.

The ratio of the yields of polymers obtained at low conversion and at short polymerization time to M_n provides the upper limit of the concentration of the active species C^*.[15] The experimental values calculated according to this method obviously could be equal to or larger than the real ones as a consequence of termination and/or transfer reactions. The C^* calculated for the $Cp^*Ti(CH_2Ph)_3/MAO$ system is 1.3×10^{-5} mol (corresponding to about 30% of the total Ti) and is 8×10^{-6} mol (about 20% of the total Ti) for the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ system. A slightly lower value, namely 4×10^{-6} mol (corresponding to about 10% of the total titanium) has been calculated for the methyl system $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$. These concentrations of the active species appear close to the molar concentrations of Ti(III) complexes determined in the presence of styrene for the mentioned systems (see Introduction) by means of quantitative ESR spectroscopy. The greater value of C^* in the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ system is in the experimental error of the method. The larger C^* value observed in the MAO-activated catalyst could be related to the reducing properties of aluminum organyls such as MAO and it depends on its concentration in the polymerization conditions.

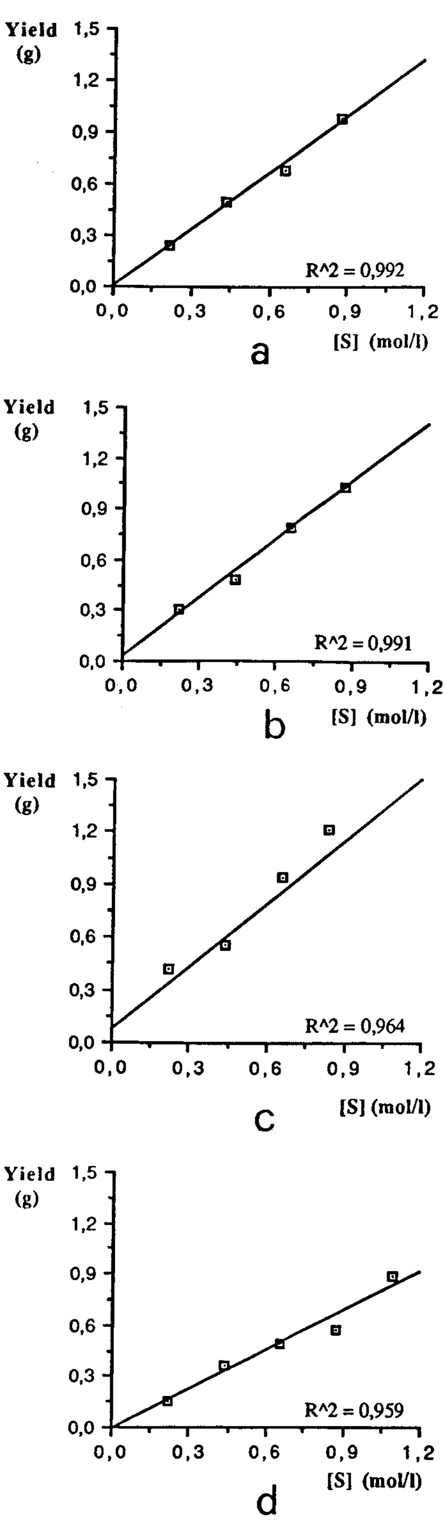

Figure 1. Plots of Y versus [S] for sPS polymerization in the presence of (a) $Cp^*Ti(CH_2Ph)_3/MAO$, (b) $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$, (c) $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$, and (d) $Cp^*Ti(CH_3)_3/Ph_3C^+B(C_6F_5)_4^-$.

In sPs polymerization promoted by the $Ti(CH_2Ph)_4/MAO$ system, the C^* value, determined by radiolabeling with tritiated methanol, was found to be of the same order of magnitude (about 10% of the total titanium).[16] The lower activity of this system suggests a smaller k_P value in the propagation reaction.

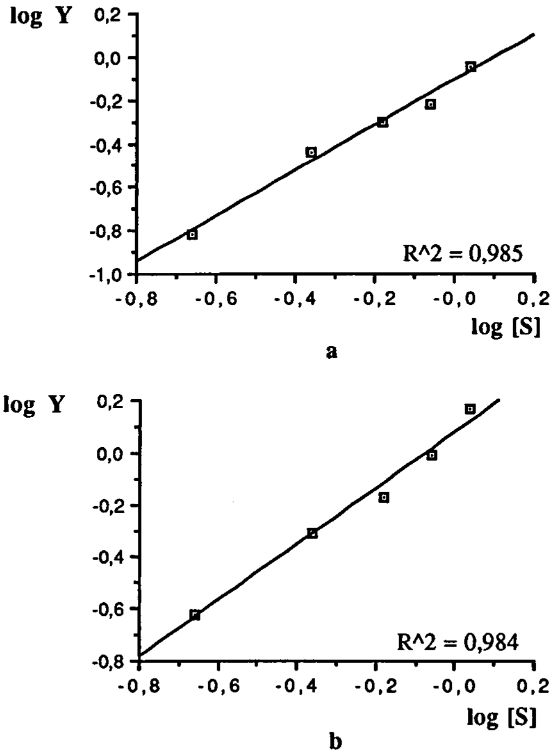

Figure 2. Plots of log *Y* versus log [S] for sPS polymerization at 25 °C (runs 1−11 of Table 1) in the presence of (a) Cp*Ti-$(CH_2Ph)_3$/MAO (α = 1.04) and (b) Cp*Ti$(CH_2Ph)_3$/$B(C_6F_5)_3$ (α = 1.06).

Transfer Mechanism Active at 50 °C. ^{13}C NMR spectra of the sPS samples produced with $M(CH_2Ph)_4$/MAO (M = Ti, Zr) at 50 °C or higher polymerization temperatures showed that β-H elimination is the main chain transfer reaction. As a matter of fact, in the ^{13}C spectrum were detected signals corresponding to PhCH=CHCH(Ph)CH_2− and −CH(Ph)CH_3 end groups, the former arising *via* β-H transfer from the polymer to the metal and the latter from secondary insertion of styrene onto M−H bond.[17] If β-H transfer is the dominant chain termination process, an increase in molecular weight approximately proportional to the monomer concentration is to be expected. Chain transfer with monomer would produce the same end groups, but the average molecular weights would not be affected by the concentration of the monomer. A quantitative evaluation of the relative weights of these two processes can be derived from a plot of the reciprocal degree of polymerization, $1/P_N$, versus the reciprocal of the monomer concentration, 1/[S]. The mean degree of polymerization, P_N, can be calculated according to the relationship $P_N = M_n$/(monomer molecular weight). We can also assume P_N is equal to the ratio of propagation with termination rate ($P_N = v_P/v_T$) where the rate of chain termination is the sum of the rates of β-H transfer from the polymer chain to the metal of the active site (v_{TM}) and to the styrene monomer (v_{TS}).

In conclusion the following equation can be derived:

$$v_T = v_{TM} + v_{TS} = C^*(k_{TM} + k_{TS}[S]) \qquad (2)$$

By combining eq 1 and 2 one can obtain

$$1/P_N = (k_{TM}/k_P)(1/[S]) + k_{TS}/k_P \qquad (3)$$

A plot of 1/*P* versus [1/S] provides the k_{TM}/k_P and k_{TS}/k_P ratios and, as a consequence, the ratio of the two chain transfer processes k_{TM}/k_{TS} can be also evaluated. We calculated $k_{TM}/k_P = 5.8 \times 10^{-3}$ and $k_{TS}/k_P = 1.3 \times 10^{-3}$ (see Table 3 and Figure 3) for styrene polymerizations carried out at 50 °C in the presence of the Cp*Ti-$(CH_2Ph)_3$/$B(C_6F_5)_3$ system. The ratio k_{TM}/k_{TS} is equal to about 5 indicating that β-H migration from the polymer chain to the metal of the active sites is the main termination process and that hydrogen transfer to the monomer is negligible, if any. In the ^{1}H spectrum of the low molecular weight samples, the intensity ratio of the ^{1}H signals of the monomer units in the polymer chain to the ^{1}H signals of the chain end groups provides M_n values in good agreement with M_n values determined by GPC analysis (see Experimental Section). The evaluation of the stereoirregular methylene tetrads observed in the ^{13}C NMR spectra of these samples confirms the Bernoullian statistical model for the stereospecific propagation (see Experimental Section). The sPS samples obtained at low styrene concentrations are still highly stereoregular.

Behavior of the Catalytic Systems with the Temperature. The polymerization activities of Cp*TiR_3/MAO systems (R = OCH_3, Cl) are strongly dependent on the temperature.[2a] The curves of the activities versus temperature reach a maximum at about 70 °C and then decrease at higher temperatures. In Table 4 the polymerization activities of the Cp*Ti$(CH_2Ph)_3$/$B(C_6F_5)_3$ system are compared with those of the corresponding MAO-activated systems. Inspection of this table suggests a similar temperature dependence of the polymerizing species active with both borane- and MAO-activated systems. When the polymerization runs were carried out at temperatures lower than 0 °C, only traces of polymer were obtained. It is worth noting that when the Cp*$TiCl_3$/MAO system was thermostated in toluene for 30 min at 70 °C, it produces sPS at −10 °C even if in small yields.[18] Then the low activities observed below 0 °C are mainly related to the low concentration of the active species in that condition. The partial deactivation of the systems at temperatures higher than 90 °C can be easily understood by assuming a thermal decomposition of the organometallic complexes active in styrene polymerization. Furthermore, the activities are only marginally affected by the ancillary ligands of titanium.

Campbell et al. reported that the average molecular weights of the sPS samples produced by Cp* derivatives of titanium decrease with increasing polymerization temperature.[2a] In our polymerization conditions we observed the same behavior with the borane-activated systems (see Table 4). As discussed in the previous section, the average molecular weights are mainly determined by the k_P/k_T ratio where k_T increases with temperature faster than k_P with the following decrease of M_w and M_n with increasing temperature. The M_w and M_n values of the sPS samples obtained with the different catalytic systems are discussed in more detail in the following section.

Role of the Counterion. Several experimental evidences support the ionic nature of the catalysts active in syndiospecific styrene polymerization. The active species seem to be highly coordinatively unsatured cationic complexes.[6,11] When the polymerization activities of the catalytic systems and the average molecular weights of the sPS products are discussed, the role of the counterion has been very often neglected. On the contrary, in homogeneous Ziegler−Natta olefin polymerization, where the active species has been clearly recognized as metallocenium cations, the influence of

Table 1. Polymerization Data[a] for the sPS Samples Obtained at Increasing Styrene Molar Concentration with the $Cp^*TiCH_2Ph)_3/MAO$, $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$, $Cp^*TiMe_3/B(C_6F_5)_3$, and $Cp^*TiMe_3/Ph_3C^+B(C_6F_5)_4^-$ Catalytic Systems

run no.	polymerization time (s)	[S] ($mol·L^{-1}$)	organometallic precursor	cocatalyst[b]	yields (g)	$10^{-3}M_n$[c]	η_{inh}[d] ($dL·g^{-1}$)	M_w/M_n[c]
1	600	0.218	$Cp^*Ti(CH_2Ph)_3$	MAO	0.150	12	0.12	1.9
2	600	0.437	$Cp^*Ti(CH_2Ph)_3$	MAO	0.360	19	0.19	2.0
3	600	0.656	$Cp^*Ti(CH_2Ph)_3$	MAO	0.495	38	0.30	1.9
4	600	0.874	$Cp^*Ti(CH_2Ph)_3$	MAO	0.575	48	0.36	1.8
5	600	1.093	$Cp^*Ti(CH_2Ph)_3$	MAO	0.890	106	0.60	1.7
6	600	2.183	$Cp^*Ti(CH_2Ph)_3$	MAO	1.500	90	0.61	2.0
7	600	0.218	$Cp^*Ti(CH_2Ph)_3$	$B(C_6F_5)_3$	0.240	29	0.27	2.0
8	600	0.437	$Cp^*Ti(CH_2Ph)_3$	$B(C_6F_5)_3$	0.496	53	0.38	1.8
9	600	0.656	$Cp^*Ti(CH_2Ph)_3$	$B(C_6F_5)_3$	0.680	72	0.47	1.7
10	600	0.874	$Cp^*Ti(CH_2Ph)_3$	$B(C_6F_5)_3$	0.980	n.d.[e]	n.d.[e]	n.d.[e]
11	600	1.093	$Cp^*Ti(CH_2Ph)_3$	$B(C_6F_5)_3$	1.480	72	0.50	1.9
12	300	0.218	Cp^*TiMe_3	$B(C_6F_5)_3$	0.370	106	0.62	2.0
13	300	0.437	Cp^*TiMe_3	$B(C_6F_5)_3$	0.580	132	0.80	2.3
14	300	0.656	Cp^*TiMe_3	$B(C_6F_5)_3$	0.790	103	0.73	2.6
15	300	0.874	Cp^*TiMe_3	$B(C_6F_5)_3$	1.034	n.d.[e]	n.d.[e]	n.d.[e]
16	300	1.093	Cp^*TiMe_3	$B(C_6F_5)_3$	1.000	n.d.[e]	n.d.[e]	n.d.[e]
17	300	0.218	Cp^*TiMe_3	$Ph_3CB(C_6F_5)_4$	0.425[f]	139	0.81	2.1[g]
18	300	0.437	Cp^*TiMe_3	$Ph_3CB(C_6F_5)_4$	0.560[f]	195	1.15	2.5[g]
19	300	0.656	Cp^*TiMe_3	$Ph_3CB(C_6F_5)_4$	0.940[f]	260	1.85	3.2[g]
20	300	0.874	Cp^*TiMe_3	$Ph_3CB(C_6F_5)_4$	1.220[f]	158	1.23	3.4[g]
21	300	1.093	Cp^*TiMe_3	$Ph_3CB(C_6F_5)_4$	1.020[f]	254	1.42	2.2[g]

[a] Polymerization conditions: 35 mL of toluene; 5 mL of styrene; $T_p = 25$ °C; amount of organometallic precursor = 4.38×10^{-5} mol. [b] Al/Ti = 500/1 molar ratio or Ti/B = 1/1 molar ratio. [c] Determined by GPC. [d] Inherent viscosity. [e] Not determined. [f] Mixture of sPS and aPS (see Experimental Section). [g] For the evaluation of these polydispersity data see the Experimental Section.

Table 2. Polymerization Data[a] for sPS Samples Obtained with $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ and $Cp^*TiMe_3/B(C_6F_5)_3$ Catalytic Systems at Increasing Polymerization Time

run no.	polymerization time (s)	organometallic precursor	yields (g)	$10^{-3}M_n$[b]	η_{inh}[c] ($dL·g^{-1}$)
22	150	$Cp^*Ti(CH_2Ph)_3$	0.240	27	0.44
23	300	$Cp^*Ti(CH_2Ph)_3$	0.546	31	0.48
24	450	$Cp^*Ti(CH_2Ph)_3$	0.998	41	0.52
25	600	$Cp^*Ti(CH_2Ph)_3$	1.472	56	0.59
26	150	Cp^*TiMe_3	0.317	129	0.95
27	300	Cp^*TiMe_3	0.620	113	1.14
28	450	Cp^*TiMe_3	0.910	254	1.51
29	600	Cp^*TiMe_3	1.190	271	1.68

[a] Polymerization conditions: 35 mL of toluene; 5 mL of styrene; $T_p = 25$ °C; amount of organometallic precursor = 4.38×10^{-5} mol; Ti/B = 1/1 molar ratio. [b] Determined by GPC. [c] Inherent viscosity.

Table 3. Polymerization Data[a] for sPS Samples Obtained with the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ Catalytic System at Increasing Styrene Molar Concentration and at 50 °C

run no.	[S] ($mol·L^{-1}$)	yield (g)	$10^{-3}M_n$[b]	η_{inh}[c] ($dL·g^{-1}$)	M_w/M_n[b]
30	0.218	0.120	4	0.05	2.1
31	0.437	0.920	6	0.08	2.3
32	0.656	1.355	13	0.14	2.4
33	0.874	1.700	12	0.14	2.4
34	1.093	2.426	19	0.20	2.5

[a] Polymerization conditions: 35 mL of toluene; 5 mL of styrene; polymerization time = 600 s; amount of $Cp^*Ti(CH_2Ph)_3$ = 4.38×10^{-5} mol; Ti/B = 1/1 molar ratio. [b] Determined by GPC. [c] Inherent viscosity.

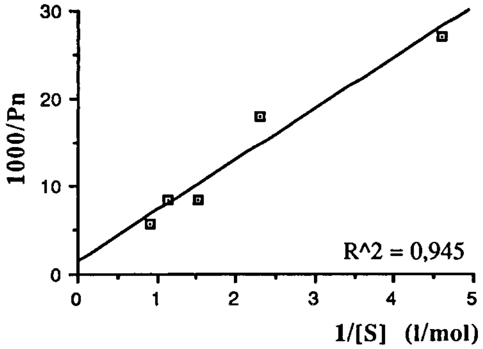

Figure 3. Plot of $1/P$ versus 1/[S] for sPS polymerization carried out with the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ catalytic system at 50 °C (runs 30–34 of Table 3).

Table 4. Polymeration Data[a] for sPS Samples Obtained with the $Cp^*Ti(CH_2Ph)_3/MAO$ and $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ Catalytic Systems at Increasing Polymerization Temperature

run no.	polymerization temp (°C)	cocatalyst[b]	yield (g)	$10^{-3}M_n$[c]	M_w/M_n[c]
35	0	MAO	traces	n.d.[d]	n.d.[d]
36	25	MAO	0.588	n.d.[d]	n.d.[d]
37	50	MAO	4.720	n.d.[d]	n.d.[d]
38	75	MAO	4.400	n.d.[d]	n.d.[d]
39	95	MAO	4.400	n.d.[d]	n.d.[d]
40	0	$B(C_6F_5)_3$	traces	n.d.[d]	n.d.[d]
41	25	$B(C_6F_5)_3$	0.875	175	1.5
42	50	$B(C_6F_5)_3$	2.200	80	1.8
43	65	$B(C_6F_5)_3$	2.650	n.d.[d]	n.d.[d]
44	75	$B(C_6F_5)_3$	1.416	34	1.6
45	95	$B(C_6F_5)_3$	1.329	28	1.5

[a] Polymerization conditions: 35 mL of toluene; 5 mL of styrene; polymerization time = 600 s; amount of $Cp^*Ti(CH_2Ph)_3$ = 4.38×10^{-5} mol. [b] Al/Ti = 500/1 molar ratio and Ti/B = 1/1 molar ratio. [c] Determined by GPC. [d] Not determined.

the counterion on the productivities and stereospecificities of the polymer products has been more deeply investigated.[19] Styrene homopolymerization performed with Cp^*TiCl_3/MAO systems produces sPS samples with greater polydispersity indexes (>3) than the corresponding hydrocarbyl derivatives.[20] In addition, inspection of Table 1 shows that sPS samples produced with $Cp^*Ti(Me)_3$-based systems exhibit a larger M_n and M_w than the polymers obtained with the corresponding benzyl systems, in the same experimental conditions. The carbenium-activated systems, in which the $[B(C_6F_5)_4]^-$ anion is poorly coordinating, produce sPS samples with the highest M_w (see runs 17–21 of Table1), while polymer products obtained with MAO-activated catalysts show the lowest M_w and M_n values (see runs 1–7 of Table 1). These findings can be explained by assuming that the coordinating behavior of the counterions can affect the k_P rate constant and the average molecular weights of the sPS products. The coordinating behavior of $[MeB(C_6F_5)_3]^-$ and $[(PhCH_2)B(C_6F_5)_3]^-$ anions is well documented in the literature. The NMR investigation of the solution structure of the ionic complex $Cp^*Ti(CH_3)_2^+(\mu\text{-}CH_3)B(C_6F_5)_3^-$ showed the presence of the μ-methyl-bridging boron and titanium.[9] The same structural feature was observed in the corresponding Ti(III) ionic complex by ESR spectroscopy.[11] The benzyl ligand of the borate anion strongly coordinates to highly electron deficient cationic complexes, producing stable arene complexes. Examples of these complexes include zwitterionic $(PhCH_2)_3Zr^+(\eta^6\text{-}PhCH_2)B(C_6F_5)_3^-$ [21] and $CpZr(CH_2Ph)_2^+(\eta^6\text{-}PhCH_2)B(C_6F_5)_3^-$ [22] complexes. Stable η^6-arene adducts of $Cp^*Ti(CH_3)_2^+$ with styrene or toluene were identified by low-temperature NMR experiments,[9] while the $Cp^*Hf(CH_3)_2^+$(toluene) structure was successfully elucidated by X-ray diffraction.[23] Unfortunately, ESR data concerning the same interaction of Ti(III) complexes with the benzyl borate anion are not available in the literature. When styrene polymerization was carried out with the $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ system in a more polar solvent such as chlorobenzene, the sPS samples exhibited higher M_w and M_n values than the polymer products obtained in toluene.[10] This finding confirms the effect of the counterion on the polymerization rate. As a matter of fact a polar solvent increases the extent of ion-pair dissociation, producing the "naked cation" with a higher polymerization rate.

MAO-activated systems show high concentrations of the active species, but the $RMAO^-$ anion could be more strongly coordinating than the borate anion yielding slightly lower polymerization activities and lower average molecular weights of the sPS products.

sPs samples obtained in runs 1–11 are highly syndiotactic, indicating that the coordinating properties of the anion do not affect the stereoregularity of the propagation reaction. Associated ion pairs, arising from the coordination of the counterion to the active species, most probably represent a resting state of the catalyst.

Conclusions

Half-titanocene complexes, activated with a large excess of MAO, promote the syndiospecific polymerization of styrene, either *cis* 1,4[24] or 1,2 syndiotactic polymerization[25] of conjugated alkadienes (depending on experimental conditions), random copolymerization of substituted styrene monomers[6] and styrene–alkadiene random copolymerizations.[26] 1-Olefins are polymerized to stereoirregular homopolymers.[27] When ethene and styrene were polymerized in the presence of the quoted catalyst, polymer mixtures comprising polyethylene, sPS, and *pseudorandom* styrene–ethylene copolymers have been obtained.[28] Related catalytic systems consisting of equimolar mixtures of $Cp^*Ti(CH_2Ph)_3$ and $B(C_6F_5)_3$ produce stereoirregular poly(1-olefins)[29] and sPS[7] in the homopolymerization runs of these monomers. Copolymerization of styrene and ethylene yields polyethylene, sPS, and alternating styrene–ethylene copolymer, independently from the feed composition.[30]

This picture shows that this apparently simple catalytic system consists of several species having a different behavior with respect to the mentioned monomers. One of these species appears active in syndiotactic styrene homopolymerization and styrene-*co*-alkadiene polymerizations, while polyolefins and *pseudorandom* styrene–ethylene copolymers are produced by different species. As a matter of fact, the styrene–ethylene copolymers do not exhibit syndiotactic styrene homosequences when copolymerizations were run at high styrene concentrations in the feed.

The kinetic investigation reported in the present article confirms that the active species promoting sPS polymerization in the catalytic system based on half-titanocenes are very similar, likely the same, in both $B(C_6F_5)_3$- or MAO-activated systems. The molar concentration of C^* in these systems is in agreement with that of Cp^*TiR^+ cationic complexes evaluated by ESR spectroscopy. This finding provides further experimental evidence that Cp^*TiR^+ complexes could be the active species in sPS polymerization promoted by half-titanocene catalysts.

Experimental Section

All manipulations of air- and moisture-sensitive materials were performed under a nitrogen atmosphere using either standard Schlenk-type techniques or a Braun drybox. Solvents (p.a. grade) were distilled in a nitrogen atmosphere over the appropriate drying agent (sodium benzophenone ketyl for ethyl ether and THF, sodium potassium alloy (1:1 w/w) for hydrocarbon solvents). Toluene was dethiophened by treatment with concentrated sulfhuric acid, neutralized by washing with saturated bicarbonate solution and distilled water in that order, and dried over calcium chloride. Finally, it was distilled over sodium before the use. MAO purchased from AZKO as 30% w/w toluene solution was dried in vacuo at 50 °C for 1 h in order to evaporate the solvent and free trimethylaluminum. The proper amount of MAO was added in the reactor as a white solid. Styrene (Carlo Erba) was distilled at reduced pressure over calcium hydride and stored in the refrigerator. $Cp^*Ti(CH_2Ph)_3$,[31] $Cp^*Ti(CH_3)_3$,[31] $B(C_6F_5)_3$,[32] and $Ph_3C^+B(C_6F_5)_4^-$ [33] were synthesized according to the procedures reported in the literature.

Polymerization Procedures. Polymerization runs were carried out by following this general procedure: toluene, styrene, and the proper aluminum compound (MAO or TIBA) were charged in a 100 mL glass reactor in the glovebox in that order. The reactor was sealed with a rubber septum, transferred out of the drybox, and thermostated for 10 min at the proper temperature. The polymerization runs were started in the MAO-activated system by injecting the organometallic precursor into the reactor. In the case of $B(C_6F_5)_3$- and $Ph_3C^+B(C_6F_5)_4^-$-activated systems the organometallic precursor and the proper cocatalyst were injected at the same time into the reactor by syringe. Polymerization was stopped with 2 mL of methanol and the polymer sample coagulated with acidified methanol. Polymer was recovered by filtration, washed several times with fresh methanol, and finally dried at 80 °C *in vacuo*.

In the polymerization runs carried out with the $Cp^*Ti(CH_3)_3/Ph_3C^+B(C_6F_5)_4^-$ system a slight excess of organometallic compound (5% mol) was used in order to prevent the carbocationic polymerization of styrene promoted by the carbenium salt. Despite this procedure, the polymer products always exhibit a fraction of atactic polymer (aPS) corresponding to 7–14% w/w of the raw polymer (depending on styrene concentration). To remove aPS, polymer samples were fractionated in a Kumagawa extractor with boiling 2-butanone. The polydispersity data reported in Table 1 for sPS samples obtained with this system were calculated on the basis of GPC curves corresponding to only the sPS fraction. Polydispersity values greater than 2 observed in runs 17–21 of Table 1 suggest that the presence of some aPS can affect the shape of GPC curves corresponding to sPS. Polymer samples produced by the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ system also contain traces of aPS, while the $Cp^*Ti(CH_2Ph)_3$-based catalysts produced pure sPS.

Evaluation of the C^* Values. The molar concentrations of the active species C^* reported in the text for the $Cp^*Ti(CH_3)_3/B(C_6F_5)_3$ and $Cp^*Ti(CH_2Ph)_3/B(C_6F_5)_3$ systems are the average values calculated on the basis of yields and M_n values reported in Table 2 (see runs 22–29). For the $Cp^*Ti(CH_2Ph)_3/$

MAO system the C^* values have been calculated using data of Table 1 (runs 1−6).

NMR Analysis of the sPS Samples. Nuclear magnetic resonance spectra were recorded on a Bruker AM250 spectrometer operating at 250 MHz for ^{1}H and 62.89 MHz for ^{13}C. Chemical shifts are reported in ppm downfield from hexamethyldisiloxane used as the internal reference. In the ^{1}H NMR spectra of the low molecular weight samples (see runs 30−32 of Table 3) the resonances observed at 0.92 (d, 3H) and 2.32 (m, 1H) ppm were assigned to $\mathrm{CH(Ph)C}H_3$ and $\mathrm{C}H\mathrm{(Ph)CH_3}$ protons of the saturated end groups and the resonances at 3.09 (m, 1H) and 6.01 (m, 2H) ppm assigned to $\mathrm{PhCH{=}CHC}H\mathrm{(Ph)\text{-}CH_2{-}}$ and $\mathrm{PhC}H\mathrm{{=}C}H\mathrm{CH(Ph)CH_2{-}}$ protons of the unsatured chain end groups, respectively. M_n values, calculated using the intensity ratios of the ^{1}H end group resonances and ^{1}H resonances of the monomer units inside the polymer chain, are in agreement with M_n values determined by GPC analysis. In the aliphatic region (50−30 ppm) of the ^{13}C NMR spectra of these low molecular weight samples, in addition to the resonances due to highly syndiotactic polymer and to saturated chain end groups, the presence of the resonances attributable to *rrm* and *rmr* stereoirregular tetrads and the absence of the *rmm* tetrad confirms that the stereochemical control during the polymerization arises from the chiral configuration of the methine of the last monomer unit in the growing polymer chain.

GPC Analysis of the sPS Samples. Gel permeation chromatography measurements were performed at 135 °C on a Waters 150-C equipped with Progel TSK columns using *o*-dichlorobenzene as the solvent. The calibration was based on standard polystyrene samples with narrow molecular weight distributions. The inherent viscosity of the samples was measured at 135 °C by using a 0.25 wt% solution of the polymer in tetralin (1,2,3,4-tetrahydronaphthalene).

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