

# Comparison of the Regiochemical Behavior of Zirconium and Hafnium in the Polyinsertion of Styrenes

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The hafnocene-based catalyst ethylenebis(1-indenyl)hafnium dichloride/methylalumoxane, as well as its zirconium analogue, is able to oligomerize styrene, *p*-methylstyrene, and *p-tert*-butylstyrene in the presence of hydrogen to produce hydrooligomers. The composition of the product mixture compared to that obtained using zirconium-based catalysts indicates that the primary insertion occurs with greater frequency. This difference in regioselectivity is likely to be related to the electronic differences between the two metal centers. Previous experimental and theoretical evidence suggests that increasing the electron density at the incoming metal–carbon bond decreases the preference for the secondary insertion; so by exploiting the contribution from the electron-releasing substituent of the monomer and changing the metal center, from zirconium to hafnium, the regiochemistry of insertion is engraved into the structure of ethylene–styrene copolymers. Some relevant differences can be observed by comparing the <sup>13</sup>C NMR spectra of copolymer obtained with zirconium- and hafnium-based catalysts. In fact the structure of the chains obtained with hafnium, compared to zirconium, shows higher styrene uptake and the presence of styrene homosequences and of regioirregularly arranged units.

## 1. Introduction

The catalysts promoting styrene insertion into the metal– carbon and metal–hydrogen bond are many, with different regiochemical behavior.<sup>1</sup>

In addition to being interested in enlightening the relationship between the features of the catalytic site and the styrene insertion regiochemistry, it is worth noting that the preferential formation of a metal—methylene rather than a metal methyne bond can be crucial when the catalysis aims at promoting the synthesis of low molecular weight products. This is the case in the recently reported<sup>2</sup> asymmetric C–C bond formation resulting from styrene polyinsertion in the presence of molecular hydrogen (so-called hydrooligomerization). It was shown that it is possible to obtain

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the chiral 1,3-diphenylbutane by using styrene hydrooligomerization promoted by the optically active ethylenebis-(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (R,R-EBTHIZrCl<sub>2</sub>) activated by methylalumoxane (MAO). Both the turnover and the enantiomeric excess are interesting, but a drawback of this reaction lies in the regiochemistry of the styrene insertion, preferentially yielding 1,4-diphenylbutane (head-to-head insertion) rather than the desired regioregular asymmetric hydrodimer (Scheme 1).

While the encumbrance at the catalytic site clearly plays a role in regulating the regiochemistry of the monomer insertion,<sup>1f</sup> experimental evidence for the relationship between the electronic features of the site and its regioselectivity has been more difficult to collect. In particular, this can be obtained by comparing systems in which there is a clear-cut separation between steric and electronic factors, a prerequisite fulfilled in the author's recent kinetic study comparing the tendencies of styrene and two substituted styrenes, *p*-chlorostyrene and *p*-methylstyrene,<sup>3</sup> to give primary and secondary insertion into the Zr-C bond. The results led to a discussion of the possible effect that electron-withdrawing and electron-releasing substituents of the monomer aromatic ring may have on the relative rate of insertion with the two possible regio-orientations. With the additional support of computational modeling, it was concluded that, generally speaking, increasing the electron density at the incoming metal-carbon bond increases the tendency toward primary insertion.

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<sup>(3)</sup> Correa, A.; Galdi, N.; Izzo, L.; Cavallo, L.; Oliva, L. Organometallics **2008**, *27*, 1028–1029.

# Scheme 1. Regiochemistry of Styrene Insertion into the Zr-Hydrogen and Zr-Carbon Bond



Evidence supporting this idea was put forward by Scott et al., who reported how an electron-releasing substituent in ethylene-styrene copolymerization can reactivate a catalyst by shifting the vinylaromatic monomer insertion from secondary to primary.<sup>4</sup>

In addition to these kinetic aspects, the regiochemistry of styrene insertion in ethylene–styrene copolymerization could determine the microstructure of the macromolecules and consequently also the material properties. In fact, blockwise copolymerizations<sup>5</sup> have been reported when the styrene insertion is primary, while, more in general, secondary insertion produces alternating ethylene–styrene copolymers.<sup>6</sup>

#### 2. Results and Discussion

2.1. Hydrooligomerizations. In light of the evidence on the influence of the electron density of the incoming metalcarbon bond on the regiochemistry of styrene insertion with zirconium-based catalysts, we devised to extend the investigation to a hafnium-based catalyst. In the present work we report the comparison of the behavior of the dichloride complexes of hafnium and zirconium bearing the ethylenebis(1-indenyl) ancillary ligand, so that the effect of the electronic features of the metallic center on the regiochemistry of insertion could be explored. As a matter of fact the literature reports that these two ansa metallocenes have substantially identical geometry<sup>7</sup> and in particular indicates that the metal-ring centroid distance in the rac-ethylenebis-(1-indenyl)hafnium dichloride (rac-EBIHfCl<sub>2</sub>) is only 0.002 Å shorter than in the rac-ethylenebis(1-indenyl)zirconium dichloride (rac-EBIZrCl<sub>2</sub>) due to the contraction of the 4f lanthanide. Consequently, it can be assumed that the pockets for the incoming substrate have a very similar shape.

The regiochemistry can be studied by keeping in mind that the styrene polyinsertion can be regulated by feeding the reaction mixture with  $H_2$ . The molecular hydrogen breaks the metal-carbon bond, inducing the production of oligomers, thus giving also a picture of the regiochemistry of insertion. We showed that, in the presence of zirconocenes, increasing the ratio between hydrogen and styrene in the feed increases the ratio between the 1,3-dimer and 1,4-dimer in the product mixture.<sup>2</sup> This observation is a strong clue of primary insertion into the Zr–H bond followed by primary



**Figure 1.** Plot of [1,3-dim.]/[1,4-dim.] ratio versus feed composition: (A) styrene-[(*rac*-EBIZrCl<sub>2</sub>)/MAO]; (B) styrene-[(*rac*-EBIHIZrCl<sub>2</sub>)/MAO] (from ref 2); (C) styrene-[(*rac*-EBIHfCl<sub>2</sub>)/MAO]; (D) *p*-tert-butylstyrene-[(*rac*-EBIHfCl<sub>2</sub>)/MAO]; (E) *p*-methylstyrene-[(*rac*-EBIHfCl<sub>2</sub>)/MAO].

or secondary insertion into the Zr-C bond, the secondary one giving an intermediate more prone to attack by hydrogen rather than further styrene insertion.

Figure 1 proposes the comparison among the experimental results obtained with several hafnium- and zirconiumbased catalysts. In agreement with the reasoning above,<sup>2,3</sup> the ratio between primary and secondary insertion is quite accurately represented by the ratio between the 1,3-dimer and 1,4-dimer extrapolated at a hydrogen pressure high enough to inhibit the production of trimers and heavier oligomers. So lines A and C show for both Zr and Hf a prevailing secondary styrene insertion into the metal-carbon bond, this preference being less relevant for the hafnium. A deeper insight into the influence of the electronic factors on the regiochemistry is given by the comparison with the behavior of styrenic monomers with increased electron density at the vinyl double bond. The results of the *p*-methylstyrene hydrooligomerization are represented by line E in Figure 1, which shows that the 1,3/1,4-dimer ratio reaches and plateaus at a value greater than 1. The behavior of *p-tert*-butylstyrene seems to be similar (line D). This monomer was recently scrutinized by Scott et al.,<sup>4</sup> who observed that the tert-butyl substituent had a powerful ability to shift the insertion from secondary to primary. The picture proposed by the results of Figure 1 is that the preference for the secondary styrene insertion into the metal-carbon bond decreases on passing from Zr to Hf, as well as decreases by introducing electron-releasing substituents into the monomer aromatic ring. By combining these two observations it is possible to obtain a prevailing primary insertion into the metal-carbon bond when the metal is hafnium and the monomer is an alkyl-substituted styrene.

An analogous difference in the regiochemistry has been observed in the couple of complexes methylenebis(1-indenyl)zirconium dichloride and methylenebis(1-indenyl)hafnium

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Figure 2. Ionic pair generated by reaction of the rac-EBIMMe<sub>2</sub> complex (M = Zr or Hf) with tris(pentafluorophenyl)borane.

Scheme 2. (1) Metal Methylation; (2) Methyl Abstraction



dichloride activated by MAO. These catalytic systems produce the hydrodimers with a ratio 1,3/1,4 respectively of 0.05 and 1, supporting the conclusion that hafnium-based catalysts are more prone to give primary styrene insertion into the carbonmetal bond (see Experimental Section).

**2.2.** NMR Evidence from the Ion Pair. Experimental evidence for the difference in the acidity of the two catalytic centers can be obtained by synthesis and NMR analysis of the cationic species in a well-characterized form. In fact, the catalytic site in the systems described above is produced by methylalumoxane following metal methylation and methyl abstraction (see Scheme 2).<sup>8</sup> But the features of this ion pair are difficult to study because of the complicated and variable composition of MAO.

However, a useful model of the catalytic center can be obtained by reacting the dimethyl derivatives rac-EBIZrMe<sub>2</sub> and rac-EBIHfMe<sub>2</sub> with the stoichiometric abstractor tris(pentafluorophenyl)borane.<sup>9</sup> Consequently, the same cationic complex active in the catalysis is generated, but in this case it is paired with a well-defined counterion, methyltris-(pentafluorophenyl)borate.

Many studies show that this kind of ion pair is not separated, as some interaction between the positively charged center and the negatively charged one persists (Figure 2).

According to Brintzinger et al., the <sup>1</sup>H NMR chemical shift of a Me-B(C<sub>6</sub>F<sub>5)3</sub><sup>-</sup> anion can be regarded as a measure of its "freedom", with a limit value of  $\delta = 0.8$  ppm being found for the methyl group of a loose ion pair.<sup>10</sup> Table 1 reports the chemical shifts observed in the ionic pair obtained from the zirconium and hafnium complexes. Their comparison seems to support the idea that the hafnium cationic

Table 1. <sup>1</sup>H NMR Data for  $L_2M(Me)_2 + B(C_6F_5)_3$  in  $C_6D_6$ at 25 °C

complex	$\delta \operatorname{CH}_3-\operatorname{B}(\operatorname{C}_6\operatorname{F}_5)_3^-$ (ppm)	δ CH <sub>3</sub> -M <sup>+</sup> (ppm)	$\delta$ CH <sub>3</sub> -M (neutral)
<i>rac</i> -EBIZrMe <sub>2</sub>	-0.61	-0.44 -0.66	-0.97
<i>rac</i> -EBIHfMe <sub>2</sub>	-0.35		-1.16

 Table 2. Polymerization Conditions and Composition of Copolymers

precatalyst <sup>a</sup>	$T(^{\circ}\mathrm{C})$	$f_{\rm E}{}^b$	% styrene $(mol)^c$	$M_{\rm w}$	$M_{\rm w}/M_{\rm n}$
rac-EBIHfCl <sub>2</sub>	20	0.045	44	24900	1.3
rac-EBIHfCl <sub>2</sub>	50	0.029	32	16700	1.5
rac-EBIZrCl <sub>2</sub>	20	0.045	21	44750	1.8
rac-EBIZrCl <sub>2</sub>	50	0.029	14.5	30 000	1.6

<sup>*a*</sup> All of the runs were carried out in the presence of metallocene (5 mg), MAO (Al/M = 1000), styrene (12 mL), toluene (8 mL), and ethylene pressure suited to producing the desired monomer feed composition. The catalyst activity is respectively 6.8, 6.5, 15, 181 kg/mol·h. <sup>*b*</sup> Mole ratio of ethylene to styrene in the feed. <sup>*c*</sup> Content of styrene units in the copolymer determined from the <sup>13</sup>C NMR spectra.



**Reaction Coordinate** 

Figure 3. Qualitative schematic energy profiles for insertion of monomer into catalyst.

center is less acidic than the corresponding zirconium center, being less attracted toward the counteranion.

However this conclusion should be handled with caution because, while it is in accordance with the statements by Ewen et al.,<sup>7a</sup> by Cardin et al.,<sup>11a</sup> and by Felten et al.,<sup>11b</sup> it disagrees with the findings of Luo and Marks<sup>12</sup> in their calorimetric study. These authors, for a series of metallorganic compounds of Zr and Hf, observed that the detachment of the methide by  $B(C_6F_5)_3$  from the zirconium compounds is generally more exothermic than from the hafnium compounds.

**2.3. Ethylene**—**Styrene Copolymerization.** The development of the homogeneous polyinsertion catalysis made it

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Figure 4. Aliphatic region of the <sup>13</sup>C NMR spectrum of the ethylene–styrene copolymer obtained at 20 °C using *rac*-EBIHfCl<sub>2</sub>-based catalyst.

possible to synthesize previously unknown polymer materials. Of these, the ethylene–styrene (E–S) copolymers<sup>13</sup> are of particular interest, as, depending on their composition, they exhibit<sup>13e</sup> either elastomeric or thermoplastic behavior. The ansa zirconocenes are also known to promote this copolymerization, so the catalytic properties of the two ansa metallocenes EBIZrCl<sub>2</sub> and EBIHfCl<sub>2</sub>, after activation using MAO, could be compared in ethylene–styrene copolymerization in order to observe how regiochemical features affect the catalytic behavior and the properties of the material.

The results of the E-S copolymerizations in the presence of metallocenes are summarized in Table 2, and it can be observed that the hafnocene also is able to copolymerize these monomers but with lower activity.

The narrow polydipersity indicates a single-site catalyst produces these macromolecules and allows us to discuss the relationship between catalyst feature and macromolecule microstructure.

The styrene content in the copolymer increases remarkably when the reaction temperature is decreased, showing a decrease of the ethylene–styrene reactivity ratio. The same trend is well known for the ansa zirconocenes and justified by assuming different pathways for ethylene and styrene insertions.<sup>6</sup> While the coordination of ethylene should be the ratedetermining step, the following insertion having a lower energy barrier, the coordination of the styrene, should be an equilibrium step forming a barrier to the insertions (Figure 3).

A similar picture was produced also by DFT calculations on the mechanism of E-S copolymerization when constrained geometry catalysts were used.<sup>14</sup>

Since the styrene coordination is stronger than that of ethylene, the availability of the catalytic site for ethylene coordination decreases with decreasing temperature. The result is that reactivity toward the less reactive monomer increases as the temperature decreases.

Unfortunately, the Hf-based catalyst is practically inactive at 0  $^{\circ}$ C and at temperatures lower than 0  $^{\circ}$ C. This fact

contrasts sharply with what is observed with the Zr complex, whose relevant activity at -20 °C gives isotactic alternating ethylene–styrene copolymer,<sup>6,15</sup> but it is not surprising because of the reported low ability of MAO to activate the hafnocenes at low temperature.<sup>16</sup>

Moreover, the copolymers obtained with Hf show a significant presence of regioirregularities (the peaks around 35 ppm in Figure 4) as a result of several primary inserted styrene units in addition to the secondary ones.

Due to the two possible regiochemical orientations, it is worth noting that the kinetic picture of the ethylene-styrene copolymerization in the presence of the hafnium-based catalyst is more complex than that in the presence of the zirconium-based catalyst; thus the copolymerization should be treated as terpolymerization.<sup>17</sup> Furthermore, the NMR spectrum reveals a peak around 41 ppm assigned to the styrene homosequences in the copolymer chains that could be related to the occasional primary polyinsertion.<sup>5</sup>

### 3. Conclusion

The styrene insertion into the metal—carbon bond with hafnocene-based catalysts is scarcely regioregular, showing to a similar degree 1,2- and 2,1-insertion. In this respect the analogous zirconium-based catalysts show higher tendency toward secondary insertion. It is unlikely that this different behavior could be ascribed to geometric differences of the catalytic site; more probably differences in the electronic features of the metallic center must be invoked.

The different regiochemistry is also recorded by the microstructure of the ethylene-styrene copolymers, with the presence of styrene homosequences and of a relevant amount of regioirregularly enchained units in the macromolecules obtained with the hafnium-based catalyst. On the contrary,

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with the analogous zirconocene catalyst, the prevailingly secondary insertion substantially prevents the formation of styrene sequences and is the key factor for the alternating stereoselective copolymerization.

# 4. Experimental Section

**4.1. General Considerations.** All the moisture-sensitive operations were carried out in an atmosphere of nitrogen using standard Schlenk techniques. Dry solvents were freshly distilled before use. The toluene was kept under reflux in the presence of sodium for 48 h and then distilled in an atmosphere of nitrogen. Styrene (99% GC, Aldrich) and 4-methylstyrene (96%, Aldrich) were purified by stirring 1 h over calcium hydride before distillation under nitrogen at reduced pressure. Methylalumoxane (MAO) was supplied by Witco as 30 wt % solution in toluene, then dried by removing *in vacuo* solvent and traces of trimethylaluminum.

1,2-Bis(3-indenyl)ethane was purchased from Aldrich, while *rac*-ethylenebis(4,5,6,7-tetrahydro-1-indenyl)zirconium dichloride (*rac*-EBTHIZrCl<sub>2</sub>) was purchased from MCAT.

*rac*-Ethylenebis(1-indenyl)zirconium dimethyl (*rac*-EBIZrMe<sub>2</sub>) and *rac*-methylenebis(1-indenyl)hafnium dichloride were prepared by using the procedures described in the literature.<sup>18,19</sup>

Other materials and reagents available from commercial suppliers were generally used without further purification.

4.2. Synthesis of rac-EBIHfMe2. A 2.33 g sample of 1,2-bis-(indenyl)ethane (98.4% GC, 9.02 mmol) was dissolved at room temperature in 40 mL of Et<sub>2</sub>O contained in a 250 mL Schlenk flask. Then 22.5 mL of 1.6 M MeLi in Et<sub>2</sub>O (36.1 mmol) was added dropwise with stirring over 10 min. The mixture was stirred for a further 3 h at room temperature under a nitrogen atmosphere to obtain a thick yellow suspension. HfCl<sub>4</sub> (2.91 g, 9.02 mmol) in 20 mL of hexane was added to this suspension. The reaction mixture was stirred at room temperature for 1 h to give a dark gray suspension. The Et<sub>2</sub>O was removed under reduced pressure, and the resulting dark gray solid was extracted using  $2 \times 100$  mL of toluene at 40 °C. Finally, the toluene solution was filtered and the solvent was evaporated under reduced pressure to give 1.9 g of a yellow solid (45.3% yield). After crystallization using toluene, spectroscopically pure *rac*-EBIHfMe<sub>2</sub> was obtained as demonstrated by <sup>1</sup>H NMR analysis.

<sup>1</sup>H NMR (400 MHz,  $\delta$ , ppm, C<sub>6</sub>D<sub>6</sub>): -1.16 (s, HfCH<sub>3</sub>, 6H), 2.86-2.89 (m, CH<sub>2</sub> bridge, 4H), 5.53 (d, Cp H, 2H, J = 3.43 Hz), 6.32 (d, Cp H, 2H, J = 3.43 Hz), 6.71-7.34 (m, Ar, 8H).

**4.3. Reaction of** *rac***-EBIHfMe<sub>2</sub> with**  $B(C_6F_5)_3$ **.** A 12 mg (0.025 mmol) sample of *rac*-EBIHfMe<sub>2</sub> and 13 mg (0.025 mmol) of  $B(C_6F_5)_3$  were dissolved in deuterated benzene contained in an NMR tube.

<sup>1</sup>H NMR (400 MHz,  $\delta$ , ppm, C<sub>6</sub>D<sub>6</sub>): -0.66 (s, HfCH<sub>3</sub>, 3H), -0.35 (bs, CH<sub>3</sub>B(C<sub>6</sub>F<sub>5</sub>)<sub>3</sub>, 3H), 2.49–2.74 (m, CH<sub>2</sub> bridge, 4H), 4.97 (d, Cp H, 1H), 5.58 (d, Cp H, 1H), 5.72 (d, Cp H, 1H), 6.19 (d, Cp H, 1H), 6.20–7.32 (m, Ar, 8H).

**4.4. Oligomerization Procedure.** Styrene, 4-methylstyrene, and 4-*tert*-butylstyrene were hydrooligomerized in a 250 mL steel autoclave, which was evacuated and then charged with a mixture of monomer, MAO, and *rac*-dichloride complexes of hafnium and zirconium (Al/M in mol = 1000) and, when necessary, toluene. The autoclave was thermostated at 50 °C, fed with hydrogen at constant pressure (5, 8, 20, or 40 atm), and mechanically stirred.

Hydrooligomerizations at atmospheric pressure of hydrogen were performed at 50  $^{\circ}$ C in a 100 mL glass flask. The reactions

were stopped after 9 h by quenching the reaction mixture in acidified ethanol. The organic phase was separated and recovered by shaking with water and *n*-pentane ( $3 \times$ ). After desiccation of the solution with Na<sub>2</sub>SO<sub>4</sub>, the *n*-pentane was removed under reduced pressure. The composition of the mixture obtained was determined by GC-MS analysis, which showed the complete consumption of the monomer in all cases.

A further distillation under reduced pressure affords a fraction of hydrogenated monomer, a second fraction containing the mixture of hydrodimers, and a third containing the hydrotrimer.

The percentage of monomers converted into dimers ranges from 31% to 4%, except for the run in the presence of *rac*-methylenebis(1-indenyl)hafnium dichloride, where the amount of dimer is around 1%.

**4.5.** Oligomer Analyses. The NMR spectra were recorded on Bruker DRX 400 spectrometers at room temperature. The sample was prepared by dissolving 30 mg of sample in 0.5 mL of chloroform-*d*. The solvent peak ( ${}^{13}CDCl_3$ :  $\delta = 77.23$  ppm) was used as the reference for the chemical shift, in  $\delta$  units (ppm).

GC-MS measurements of the mixture of hydrooligomers were recorded on a GC Trace 2000 Series connected to a Finnigan Thermoquest GLQ Plus 2000 spectrometer with an ion trap detector.



 $R = -H, -CH_{3} - C(CH_{3})_{3}$ 

Styrene. 1,3,6-Triphenylhexane. <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 29.5 (C-5), 34.0 (C-1), 36.1 (C-6), 36.8 (C-4), 38.7 (C-2), 45.6 (C-3), the aromatic C atoms resonate between 125.8 and 145.5 ppm. MS: 314 (M<sup>+</sup>).

**1,4-Diphenylbutane.** <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 31.3 (C-2), 36.0 (C-1), the aromatic C atoms resonate between 125.8 and 145.5 ppm. MS: 210 (M<sup>+</sup>).

**1,3-Diphenylbutane.** <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 22.7 (C-4), 34.1 (C-1), 39.7 (C-3), 40.2 (C-2), the aromatic C atoms resonated between 125.8 and 147.5 ppm. MS: 210 (M<sup>+</sup>).

**Ethylbenzene.** <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 15.8 (C-2), 29.1 (C-1), the aromatic C atoms resonated between 125.8 and 147.5 ppm. MS: 106 (M<sup>+</sup>).

*p*-Methylstyrene. 1,3,6-Tri-*p*-tolylhexane. <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 21.2 (CH<sub>3</sub>-Ph), 29.7 (C-5), 33.5 (C-1), 35.7 (C-6), 36.9 (C-4), 38.9 (C-2), 45.2 (C-3), the aromatic C atoms resonate between 127.9 and 147.8 ppm. MS: 356 (M<sup>+</sup>).

**1,4-Di-***p***-tolylbutane.** <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 21.2 (CH<sub>3</sub>-Ph), 31.5 (C-2), 35.6 (C-1), the aromatic C atoms resonate between 126.2 and 147.8 ppm. MS: 238 (M<sup>+</sup>).

**1,3-Di**-*p*-tolylbutane. <sup>13</sup>C NMR (400 MHz, δ, ppm, CDCl<sub>3</sub>): 21.2 (CH<sub>3</sub>-Ph), 22.9 (C-4), 33.7 (C-1), 39.2 (C-3), 40.3 (C-2), the

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aromatic C atoms resonated between 126.2 and 147.8 ppm. MS: 238 ( $M^+$ ).

**4-Ethyltoluene.** <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 16.0 (C-2), 21.7 (CH<sub>3</sub>-Ph), 28.6 (C-1), the aromatic C atoms resonate between 126.2 and 147.8 ppm. MS: 120 (M<sup>+</sup>).

*p-tert*-Butylstyrene. **1,3,6-Tris**(4-*tert*-butylphenyl)hexane. <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 29.6 (C-5), 31.7 (*C*H<sub>3</sub>-CPh), 33.5 (C-1), 34.5 (CH<sub>3</sub>-*C*-Ph), 35.7 (C-6), 37.0 (C-4), 38.7 (C-2), 45.2 (C-3), the aromatic C atoms resonate between 125.3 and 148.6 ppm. MS: 482 (M<sup>+</sup>).

**1,4-Bis**(4-*tert*-butylphenyl)butane. <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 31.4 (C-2), 31.7 (*C*H<sub>3</sub>-CPh), 34.5 (CH<sub>3</sub>-*C*-Ph), 35.5 (C-1), the aromatic C atoms resonate between 125.3 and 148.6 ppm. MS: 322 (M<sup>+</sup>).

**1,3-Bis**(4-*tert*-butylphenyl)butane. <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 22.7 (C-4), 31.7 (CH<sub>3</sub>-CPh), 33.6 (C-1), 34.5 (CH<sub>3</sub>-C-Ph), 39.2 (C-3), 40.2 (C-2), the aromatic C atoms resonated between 125.3 and 148.6 ppm. MS: 322 (M<sup>+</sup>).

**1-tert-Butyl-4-ethylbenzene.** <sup>13</sup>C NMR (400 MHz,  $\delta$ , ppm, CDCl<sub>3</sub>): 15.8 (C-2), 28.5 (C-1), 31.7 (CH<sub>3</sub>-CPh), 34.5 (CH<sub>3</sub>-C-Ph), the aromatic C atoms resonate between 125.3 and 148.6 ppm. MS: 162 (M<sup>+</sup>).

**4.6. Ethylene**—Styrene Copolymerizations. The copolymerizations were carried out in a 100 mL glass flask provided with a magnetic stirrer and thermostated at the required temperature. The reactor was sequentially charged under a nitrogen atmosphere with toluene (8 mL), styrene (12 mL), MAO, and *rac*-dichloride complexes of hafnium or zirconium (Al/M in mol = 1000). The inert atmosphere was removed and the reaction mixture was saturated with ethylene. The flask was continuously fed with gaseous monomer at atmospheric pressure to keep the monomer concentration constant. The copolymerizations were stopped after 2 h, and the mixture was poured into 100 mL of

acidified ethanol. The polymers were recovered by filtration and dried *in vacuo*. The raw polymers were washed with boiling acetone in a Kumagawa-type extractor in order to remove traces of atactic polystyrene. The products were fully soluble in CHCl<sub>3</sub>.

The copolymer yield is about 130 mg in the presence of the Hfbased catalyst, whereas in the presence of Zr it is 4.5 g at 50  $^{\circ}$ C and 360 mg at 20  $^{\circ}$ C.

The ethylene concentration in the liquid phase was determined by using the fugacity function chart of ethylene reported in the literature.<sup>20</sup>

**4.7.** <sup>13</sup>C NMR Analysis. The spectra were recorded at room temperature on an AM 250 Bruker spectrometer operating at 62.89 MHz in the Fourier transform mode. The samples were prepared by dissolving 30 mg of polymer into 0.5 mL of chloroform-*d*. The solvent peak of CDCl<sub>3</sub> was used as internal reference at  $\delta = 77.23$  ppm for the chemical shifts.

The content of the styrene units was evaluated from the area of methylene resonances by applying the equation

$$\begin{split} \chi_{s} = & \\ \frac{\{A(S_{\alpha\gamma+}) + A(S_{\alpha\beta}) + A(S_{\alpha\alpha})\}}{\{A(S_{\gamma+\gamma+}) + A(S_{\beta\beta}) + A(S_{\beta\gamma+}) + 1.5A(S_{\alpha\gamma+}) + 1.5A(S_{\alpha\beta}) + A(S_{\alpha\alpha})\}} \end{split}$$

**4.8. GPC Analysis.** Molecular weight and molar weight distribution of the polymers were determined by gel permeation chromatography (GPC) analysis carried out at 30 °C using THF as solvent and narrow MWD polystyrene standards as reference. The measurements were taken on a Waters 1525 binary system equipped with a Waters 2414 RI detector using four columns (range 1000–1000 000 Å).

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